

Kinetic study of the reaction between sodium chloroacetate and potassium ethylxanthogenate

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Abstract: The reaction kinetics of the synthesis of sodium ethyl xanthogeneacetate from potassium ethylxanthogenate and sodium chloroacetate in distilled water as the reaction medium at 25, 30, 35 and 40 °C, were investigated. The obtained reaction mixture was a complex system which demanded the use of two methods for the kinetic measurements. The reaction was followed using the conductometric and UV/Vis spectrophotometric method with equimolar initial concentrations of the reactants and under pseudo-first order conditions with respect to one of the reactants. The rate constants of the pseudo-first order and second order reactions were calculated from the data. On the basis of the reaction constants, the activation parameters were calculated and are discussed.

Keywords: kinetic rate, rate constant, sodium ethyl xanthogeneacetate, thermodynamic parameters.

INTRODUCTION

Sodium ethyl xanthogeneacetate (NaEtXAc) is a precursor in the synthesis of thiocarbamates.^{1–4} Since such compounds generally have fungicidal properties,⁵ a detailed study of the NaEtXAc synthesis should provide valuable information for its production.

Thiocarbamates are known as surfactants for the preconcentration of trace and major amounts of Ag and Hg.^{6,7} Their solution properties were investigated by potentiometric titrations, UV and Fourier transform IR (FTIR) in view of their usage as flotation collectors.^{8–10} Furthermore, surface enhanced 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

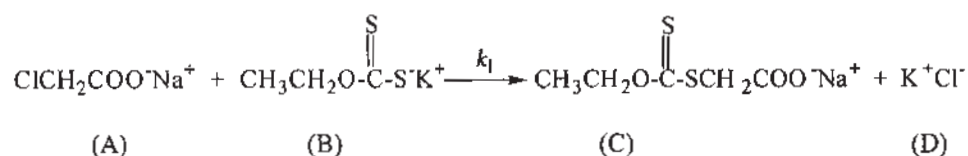
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processes. This interaction involves a charge transfer process in which the sulfur atom in the organic species becomes bonded to a metal atom while the hydrogen is replaced from the nitrogen atom.^{11–15} Moreover, the reactivity and mechanism of the aminolysis of aryl *N*-ethyl thionocarbamates were also studied.¹⁶ However, hitherto there are no available data in the literature on the synthesis of NaEtXAc and a corresponding kinetics study.

The synthesis of NaEtXAc and a kinetic study of the corresponding reaction were performed as presented in Scheme 1.



Scheme 1. Reaction between sodium chloroacetate (A) and potassium ethylxanthogenate (B).

The synthesis of NaEtXAc, as the first objective of this work, was accomplished starting from the reactants: NaClAc – sodium chloroacetate and KEtX – potassium ethylxanthogenate, whereby NaEtXAc and potassium chloride were the reaction products.

The obtained results were used for a discussion of the kinetics of the investigated reaction based on the data of spectrophotometric and conductometric measurements.

EXPERIMENTAL

Synthesis of NaClAc

Chloroacetic acid (95.0 g, 1.0 mol) was slowly added to a reaction flask containing 200 cm³ of water. The mixture was gently mixed. During the dissolution of chloroacetic acid, the temperature decreased from 14 to 5 °C. Once the chloroacetic acid had completely dissolved, 53.0 g (0.5 mol) sodium carbonate was added, under continuous stirring of the reactants. Carbon dioxide was evolved during the reaction. The solution was mixed until the appearance of crystals, and the volume was reduced to 1/3 of the initial solution. The mixture was cooled, the product isolated by filtration and dried to constant weight.

Synthesis of sodium ethyl xanthogeneacetate

To a solution of potassium ethylxanthogenate (16.03 g, 0.1 mol) in 40 ml of water in a three necked flask equipped with an addition funnel, condenser and thermometer, a solution of chloroacetic acid (9.5 g, 0.1 mol) in 25 ml of water was added *via* the addition funnel during 10 min, and the reaction mixture was left for a further 50 min at room temperature. After completion of the reaction, an appropriate volume of 0.1 mol/dm³ HCl, at a constant temperature (10 °C), was added to the reaction mixture until a pH ≈ 6 was attained. Ether was added to the reaction mixture under strong stirring to extract the ethyl xanthogeneacetic acid. After separation of the water layer, the organic layer was washed three times with distilled water following by evaporation of the ether. The reaction yield was 80 %. The purity of the waxy product was determined potentiometrically (97.5 %). The structure of the final compound was confirmed by FTIR, ¹H- and ¹³C-NMR spectroscopy. The ¹H- and ¹³C-NMR spectra were recorded in CDCl₃ solution, with tetramethylsilane (TMS) as the internal reference standard, using a Varian-Gemini 200 spectrophotometer. The NMR spectra were recorded at ambient temperature.

Preparation of NaEtXAc for kinetic experiments was performed by neutralization of the ethyl xanthogeneacetic acid with an appropriate volume of 0.1 mol/dm^3 sodium hydroxide. After evaporation of the solvent, the white salt was dissolved in the minimum amount of absolute ethanol and the solution was diluted with absolute ether until the appearance of turbidity. The fine white crystals which appeared after cooling were filtered and stored in a desiccator.

Kinetic measurements

Kinetic measurements were performed using an Iskra MA5964 conductometer, and HEK1213 Pt100 electrode and a Shimadzu 160 UV-spectrophotometer at 25, 30, 35 and 40 °C. In order to develop the kinetic measurement method, the absorbance of the system KEtX and NaClAc in the range of 200–800 nm was investigated. It was established that the absorption of the system at $\lambda = 340 \text{ nm}$ (corresponding to NaEtXAc production) increased. This wavelength was used for the determination of the reaction order. Also the absorption of the system at $\lambda = 374 \text{ nm}$ (corresponding to the KEtX concentration) decreased. This wavelength was used for monitoring the pseudo-first order reactions. The linear dependence of the conductance with respect to the concentration of the appropriate reactants and products were confirmed previously.

Conductometric measurements of the second order reaction of KEtX and NaClAc with equimolar initial concentrations

To a sealed thermostated glass flask, 29.4 cm^3 of an aqueous NaClAc solution was added, the conductometric electrode was inserted and the initial conductance was recorded after 15 min. Then 0.6 cm^3 of a freshly prepared KEtX solution was added and the conductance was monitored over the next 30 min. The initial concentrations of the reactants were $c_{0\text{KEtX}} = c_{0\text{NaClAc}} = 0.02 \text{ mol/dm}^3$.

Conductometric measurements of the hydrolysis of KEtX under pseudo-first order reaction conditions

To a thermostated sealed glass reaction flask, 25 cm^3 of a freshly prepared aqueous solution of KEtX, with an initial concentration $c_{0\text{KEtX}} = 0.02 \text{ mol/dm}^3$, was added and the conductance monitored for the next 5 h.

Conductometric measurements of the reaction between KOH and NaClAc, as a pseudo-first order reaction with respect to KOH

To a thermostated sealed glass reaction flask, 29.4 cm^3 of an aqueous solution of NaClAc (initial concentration $c_{0\text{NaClAc}} = 0.04 \text{ mol/dm}^3$) was added. After 15 min the initial conductance was recorded and then 0.6 cm^3 of a KOH solution, initial concentration $c_{0\text{KOH}} = 0.002 \text{ mol/dm}^3$, was quickly added and the conductance was monitored during the following 30 min.

Spectrophotometric measurements of the reaction between KEtX and NaClAc with equimolar initial concentrations

The solutions were thermostated to the determined temperatures for at least 30 min prior to the measurements. Solutions of NaClAc and KEtX, both 5 cm^3 , were mixed and a part was poured into adequate measuring cell and placed in the UV-spectrophotometer with a thermostate. The initial concentrations were $c_{0\text{KEtX}} = c_{0\text{NaClAc}} = 0.02 \text{ mol/dm}^3$. The absorbance ($\lambda = 340 \text{ nm}$) was monitored during the following 30 min.

Spectrophotometric determination of the reaction order with respect to KEtX and NaClAc

The procedures were the same as for spectrophotometric measurement of the reaction with equimolar initial concentrations. In the first case, the initial concentration of KEtX was varied ($c_{0\text{KEtX}} = 0.0001, 0.0003, 0.0005, 0.001$ and 0.002 mol/dm^3) and the initial concentration of NaClAc was $c_{0\text{NaClAc}} = 0.01 \text{ mol/dm}^3$.

In the second case, the initial concentration of NaClAc was varied ($c_{0\text{NaClAc}} = 0.2, 0.4, 0.6, 0.8$ and 1 mol/dm^3), and the initial concentration of KEtX was $c_{0\text{KEtX}} = 0.02 \text{ mol/dm}^3$. Measurements were performed at 25 °C ($\lambda = 340 \text{ nm}$).

Spectrophotometric recording of the reaction between NaClAc and KEtX at different temperatures

The procedure was the same as the previous. The initial concentration of KEtX was $c_{0\text{KEtX}} = 0.02 \text{ mol/dm}^3$ and the initial concentration of NaClAc was $c_{0\text{NaClAc}} = 0.4 \text{ mol/dm}^3$. Measurements of the absorbance ($\lambda = 374 \text{ nm}$) were performed at 25, 30, 35 and 40 °C.

RESULTS AND DISCUSSION

Based on the Scheme 1, it was assumed that the reaction would follow the second-order kinetic law. In order to check this assumption, the reaction order with respects to both reactants was determined.

Determination of reaction orders with respect to the reactants

The kinetic rate for determination of reaction order with respect to reactants was followed by UV/Vis spectrophotometry at 340 nm and at $t_{\text{const}} = 25 \pm 0.2 \text{ °C}$, with sodium chloroacetate in a great excess. The absorption as a function of time for the reaction mixture of NaClAc and KEtX is shown in Fig. 1.

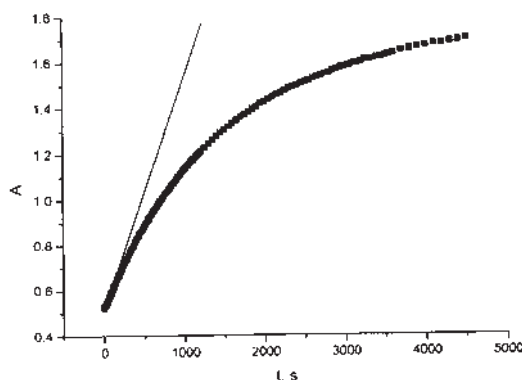


Fig. 1. Example of the absorbance change in the reaction of KEtX ($c_{0\text{KEtX}} = 0.02 \text{ mol/dm}^3$) and NaClAc ($c_{0\text{NaClAc}} = 0.6 \text{ mol/dm}^3$) at 25 °C.

On the basis of the kinetic data, the reaction order was calculated using the differential method, by determining the initial reaction rates ($\Delta A/\Delta t$) from the first two measurements points.^{17,18} In order to determine the partial orders of the reaction with respect to the reactants, the logarithms of the initial reaction rates ($\log(\Delta A/\Delta t)$) versus the logarithm of the initial concentration of one of the reactants, $\log c_{0\text{KEtX}}$ or $\log c_{0\text{NaClAc}}$, were plotted (the concentrations are given in experimental part). It was found that the reaction is the first order with respect to KEtX, as was confirmed by the linear correlation of $\log(\Delta A/\Delta t)$ versus $c_{0\text{KEtX}}$ ($b = 0.95 \approx 1 \pm 0.2$, $R = 0.94$). Value of linear correlation of $\log(\Delta A/\Delta t)$ versus $c_{0\text{KEtX}}$ ($b = -0.11 \pm 0.04$, $R = 0.94$) is not a negligible variation from the zero value, thus indicating that the reaction is not zero order with respect to NaClAc, which it should be in the case of the pseudo-first order reaction system with NaClAc in great excess.

Variation from the assumed second order kinetics of the reaction was also confirmed using a UV/Vis spectrophotometric method, by following the change of absorbance in the investigated reaction system with equimolar initial concentrations of the reactants. The equation for second-order reactions was applied.^{10,11}

$$\frac{1}{c_t} - \frac{1}{c_0} = k_2 t \quad (1)$$

Or using the equation as a function of the measured physical property:

$$\frac{A - A_0}{A_\infty - A} = ktc_0 \quad (2)$$

Plotting the value of $\frac{A - A_0}{A_\infty - A}$ versus time t should give a linear plot of kc_0 , if

the reaction is second order. However, for the reaction system with equimolar initial concentrations of reactants ($c_{0\text{KEtX}} = c_{0\text{NaClAc}} = 0.02 \text{ mol/dm}^3$), a non-linear curve was obtained (least-square method – linear curve fitting used for the calculation).

The variation from a linear dependence indicates non-conformity of the reaction with the second order reaction kinetic law. For further confirmation of the non-compliance of the reaction system with the second-order kinetic law, the conductometric method was also applied to monitor the change of conductivity (κ , mS/cm) of the reaction mixture with equimolar initial concentrations of reactants ($c_{0\text{KEtX}} = c_{0\text{NaClAc}} = 0.02 \text{ mol/dm}^3$). It was not feasible to measure correctly the infinite value of conductivity (κ , mS/cm) in order to apply the second order law:

$$\frac{\kappa - \kappa_0}{\kappa_\infty - \kappa} = ktc_0 \quad (3)$$

Therefore, the Kezdy–Swinbourne method was used for the determination of the second-order kinetic rate constants:¹⁸

$$\kappa_t = kc_0t(\kappa_\infty - \kappa_t) + \kappa_0 \quad (4)$$

where κ_t is the conductance in time t .

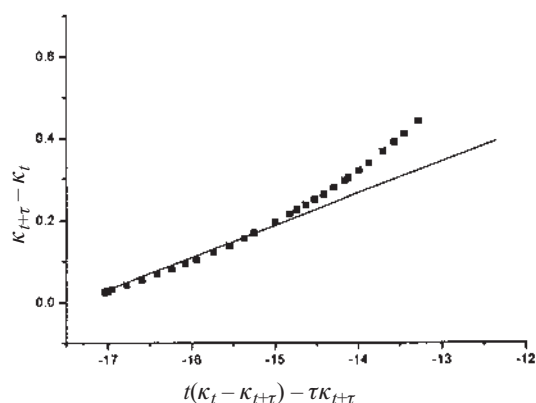


Fig. 2. Processing of the experimental data from conductivity change in the reaction of KEtX and NaClAc at 25 °C with equimolar initial concentrations of reactants ($c_{0\text{KEtX}} = c_{0\text{NaClAc}} = 0.02 \text{ mol/dm}^3$) using second-order kinetic law and the Kezdy–Swinbourne method.

Based on processing the data by Kezdy–Swinbourne method (Fig. 2), significant variation from a linear dependence was observed after a certain time, confirm-

(energy of activation E_a , entropy of activation ΔS^\ddagger , Gibbs energy of activation ΔG^\ddagger and enthalpy of activation ΔH^\ddagger) of the investigated elementary reaction given in Table II.

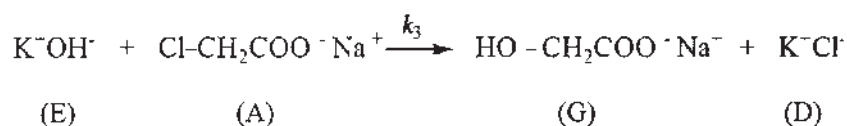
TABLE II. Activation parameters of the investigated reactions

Reaction	$\Delta E_a/\text{kJmol}^{-1}$	$\Delta H^\ddagger_{25}/\text{kJmol}^{-1}$	$\Delta S^\ddagger_{25}/\text{J mol}^{-1} \text{K}^{-1}$	$\Delta G^\ddagger_{25}/\text{kJmol}^{-1}$
1	32.53 ± 4.8	30.1	-193.4	87.7
2	31.18 ± 1.6	28.7	-217.6	93.6
3	52.30 ± 5.3	49.8	-122.9	86.5

Determination of the reaction rate for the alkaline hydrolysis of sodium chloroacetate

According to the above postulated reaction system, it can be supposed that a third reaction is possible, *i.e.*, the alkaline hydrolysis of sodium chloroacetate producing sodium glycolate (NaOHAc), presented in Scheme 3. In this way, the reaction system is even more complex.

The value of the reaction rate constant of this reaction depends on the sodium chloroacetate concentration and on the concentration of potassium hydroxide released during the hydrolytic decomposition of potassium ethylxanthogenate. The bimolecular substitution reaction (Scheme 3) obeys the second order kinetic law and can easily be solved when the reaction is observed independently of the previous two reactions. The determination of the reaction rate constant for the third reaction (Scheme 3) at the investigated temperatures is necessary for modeling the whole reaction mechanism.



Scheme 3. Alkaline hydrolysis of sodium chloroacetate (A).

The reaction was monitored by conductometry, with the initial concentration of potassium hydroxide $c_{0\text{KOH}} = 0.002 \text{ mol/dm}^3$ and of sodium chloroacetate $c_{0\text{NaClAc}} = 0.04 \text{ mol/dm}^3$, thus providing pseudo-first order reaction conditions. The initial reaction conditions were evaluated based on the results from the previous experiments, in which the concentration of KOH in the system did not exceed 10 % of the initial value of the potassium ethylxanthogenate concentration.

Based on the kinetic data of the conductance change in the investigated reaction, the values of the reaction rate constants were determined using the integral method (Table I).

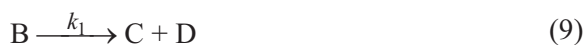
In addition, the activation parameters for the investigated elementary reactions between KOH and NaClAc were calculated and are given in Table II.

Rate determination for the reaction of potassium ethylxanthogenate and sodium chloroacetate

According to the postulated complex reaction system, and assuming side reactions, the investigated system can be presented as follows (Schemes 1, 2 and 3):



The system can be simplified by adjusting the starting concentration of the reactants by using a large excess of sodium chloroacetate (A in Schemes 1 and 3) with respect to the concentration of potassium ethylxanthogenate (B in Schemes 1 and 2) ($[A] \gg [B]$, *i.e.*, $[A]=[A_0] \approx \text{const.}$), thus giving the following system:



The differentiation of above equations, assuming integral kinetic laws for expressing the rates of individual reactions, gives the final expression:

$$[B] = [B_0] e^{-k_{\text{exp}}t} - [B_0] e^{-(k_1[A] + k_2)t} \quad (12)$$

Using the dependence of concentration change of B, it is possible to solve the time dependence of the concentration change of E (KOH, Schemes 2 and 3, Eqs. (10) and (11)):

$$[E] = \frac{k_2}{k_3' - k_{\text{exp}}} [B_0] (e^{(k_3' - k_{\text{exp}})t} - 1) e^{-k_3't} \quad (13)$$

The final expression of the time dependence of concentration change of E:

$$[E] = \frac{k_2}{[A_0](k_3 - k_1) - k_2} [B_0] (e^{-(k_1[A_0] + k_2)t} - e^{-k_3[A_0]t}) \quad (14)$$

Potassium hydroxide as a product from reaction 2 (Scheme 2) participates as a reactant in reaction 3 (Scheme 3) producing sodium hydroxyacetate (NaOHAc, sodium salt of glycolic acid). Differential form of equation which describes the increase of the amount of the product G (Scheme 3, Eq. (11)) has a form:

$$\frac{d[G]}{dt} = k_3'[E] \quad (15)$$

Solving this expression one obtains:

$$\frac{d[G]}{dt} = k_3' \frac{k_2}{k_3 - k_{\text{exp}}} [B_0] (e^{-k_{\text{exp}}t} - e^{-k_3't}) \quad (16)$$

Finally, the time dependence of the concentration increase of sodium glycolate is:

$$[G] = [A_0][B_0] \frac{k_2 k_3}{[A_0](k_3 - k_1) - k_2} \left[\frac{1}{k_3[A_0]} (e^{-k_3[A_0]t} - 1) - \frac{1}{k_1[A_0] + k_2} (e^{-(k_1[A_0] + k_2)t} - 1) \right] \quad (17)$$

In order to determine the value of k_{exp} (Eqs. (13) and (16)), the initial concentrations of NaClAc have to be in great excess with respect to KEtX, thus obtaining $[A] = const.$ Hence, the first and second reactions can be observed as pseudo-first order reactions. UV-spectrophotometric measurements were used (by following the concentration change of KEtX) to investigate the kinetics of the system with initial concentration of sodium chloroacetate $c_{0NaClAc} = 0.4 \text{ mol/dm}^3$ and potassium ethylxanthogenate $c_{0KEtX} = 0.02 \text{ mol/dm}^3$.

Since the monitoring of the kinetics of the system demanded a long time for an, even not sufficiently precise, determination of value of $[A_\infty]$, the value $[A_\infty]$ for the monitored reaction was determined by the Kezdy–Swinbourne method.¹⁸

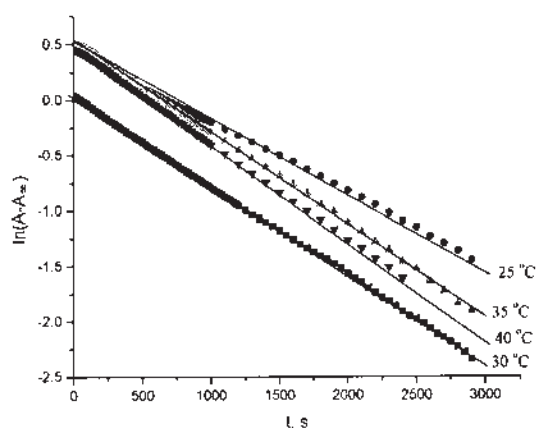


Fig. 3. Integrated form of the pseudo-first order reaction between KEtX and NaClAc at the investigated temperatures.

By using the integral method for the pseudo-first order reaction and the determined values of $[A_\infty]$, values of k_{exp} were determined from the slope (Fig. 3) at 25, 30, 35 and 40 °C, and the values are given in Table I.

Using the calculated values of k_{exp} and the equation $k_{exp} = k_1 c_{0NaClAc} + k_2$, the values of k_1 were calculated using Eq. (18) and are given in Table I (since $c_{0NaClAc} \gg c_{0KEtX}$, i.e., $c_{NaClAc} = c_{0NaClAc} \approx const.$).

$$k_1 = \frac{k_{exp} - k_2}{c_{0NaClAc}} \quad (18)$$

Based on the rate constants given in Table I, the activation parameters for the investigated reaction were calculated (Table II) using Eqs. (9) to (12). Of course, the determined values do not represent the exact thermodynamic characteristics of the complex system.

It can be seen from Table II that the values of the change of the entropy of activation for the hydrolysis reaction are negative (the activated complex has a significantly higher degree of order), and the energy of activation is relatively low, which is characteristic for catalyzed reactions and reactions of neutral reagents,¹⁹ thus confirming the assumed mechanism, being typical for similar compounds. The value of the entropy of activation for the alkaline hydrolysis is small (but approximately inside the limits given in literature references for bimolecular reactions²⁰) as a consequence of the significantly more arranged state of activated complex and solvent effects. The values of the Gibbs energy of activation are, as expected, in accordance with reaction rate constants.

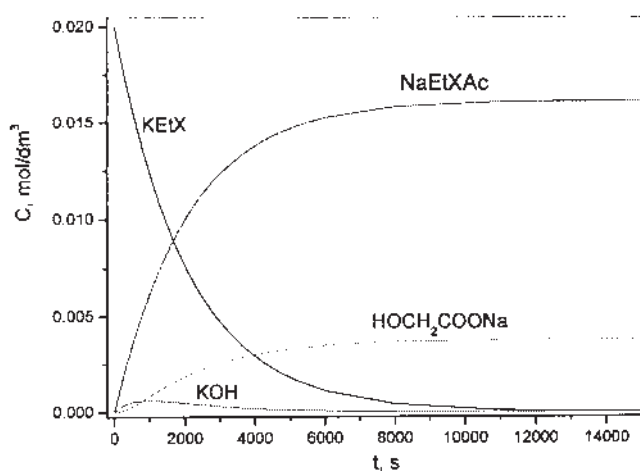


Fig. 4. Simulated curves for the chosen compounds of investigated reaction system at 25 °C.

The simulation of the changes of the reactant and product concentrations with time according to the solved integral kinetic equations and the determined rate constants for all three reactions is presented in Fig. 4 (reaction at 25 °C).

It is obvious that the validity of the system can be confirmed by following the change of concentration of sodium glycolate, since the expression for the time dependence of the glycolate concentration contains all three reaction rate constants (Eq. (17)) and, because of the more regular concentration increase, it can be monitored more precisely than KOH (E, Schemes 2 and 3) in the investigated reaction system.

As can be seen from Fig. 4, in the initial period of time ($t \approx 10$ min), the KEtX concentration decreased rapidly. In this initial period, there is an appropriate amount of non-reacted KEtX, not consumed in the first reaction, which is hydrolytically decomposed according to the second reaction. In this time period, an increase of the concentration of hydroxide ions was observed, achieving a maximum, which was followed by slow decrease as it was consumed in the third reaction.

Since the reaction rate constant of the second reaction is significantly lower than the substitution reaction rate constant (Scheme 3), in the period of time after the hydroxide ion maximum has been attained, the decrease of the KEtX concentration also caused a decrease of the hydroxide ion concentration which was con-

sumed at a higher rate in the third reaction. As the concentration of KEtX decreased during the reaction, the hydroxide ion decreased to a low value, after $t \approx 1$ h, causing the concentration of sodium glycolate to be almost constant (Scheme 2). The hydrolytic reaction becomes negligible causing a further decrease of hydroxide ion concentration in the reaction mixture.

Validation of this study was attempted by monitoring the concentration changes of the sodium glycolate during the course of time.²¹ This was not completely successful as some interference with the other component of the system exists. For an exact determination of sodium glycolate the complete removal of the impurity causing inaccuracies in the obtained results is necessary. In the initial period, the determined concentrations were significantly lower than the calculated values. As the reaction proceeded to the end, the results were more consistent being about 50 % of those calculated by the mathematical model. All of these results indicate a very complex reaction system in the spontaneously obtained conditions for the kinetic study, implying that, in the sense of simplification and suppression of the second and third reactions, reaction conditions under controlled pH values should be performed in further investigations.

CONCLUSION

The reaction kinetics of the synthesis of sodium ethyl xanthogeneacetate from potassium ethylxanthogenate and sodium chloroacetate in distilled water as the reaction medium at 25, 30, 35 and 40 °C, were investigated. The reaction was followed using conductometric and UV/Vis spectrophotometric methods with an equimolar initial concentration of the reactants and as pseudo-first order reactions with respect to one of the reactants.

Based on the determination of the reaction order, a complex mechanism is assumed. The rate constants of the pseudo-first order and second order reactions were calculated from the kinetic data. On the basis of the reaction constants for the three investigated reactions at 25, 30, 35 and 40 °C, the activation parameters were calculated.

The complex reaction system was elucidated by monitoring the individual reactions, and the determined rate constants were used for a mathematic simulation of this complex reaction system.

ИЗВОД

КИНЕТИЧКА ИСПИТИВАЊА РЕАКЦИЈЕ ИЗМЕЂУ
НАТРИЈУМ-ХЛОРАЦЕТАТА И КАЛИЈУМ-ЕТИЛ-КСАНТАТАМИЛУТИН МИЛОСАВЉЕВИЋ¹, АЛЕКСАНДАР МАРИНКОВИЋ¹, БОБАН ЦЕКОВИЋ² и
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Испитивана је кинетика реакције синтезе натријум-етил-ксантоген-ацетата из калијум-етил-ксантогената и натријум-хлорацетата у дестилованој води као реакционом медијуму и температурама 25, 30, 35 и 40 °С. Реакциона смеша је комплексан систем који је захтевао коришћење две методе за кинетичка мерења. Реакције су праћене коришћењем спектрофотометријске и кондуктометријске методе при еквимоларним почетним концентрацијама реактаната као и при условима реакција псеудо-првог реда у односу на један од реактаната. Реакционе константе псеудо-првог реда и другог реда израчунате су на основу кинетичких података. На основу реакционих константи израчунати су и дискутовани такође и активациони параметри.

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