
KINETICS OF ALKALINE HYDROLYSIS OF 3,4-THIOPHENE-DICARBOXYLIC ACID MONOMETHYL ESTER IN AQUEOUS-NONAQUEOUS MEDIA

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The kinetics of alkaline hydrolysis of 3,4-thiophenedicarboxylic acid monomethyl ester has been studied in mixed solvents water-methyl alcohol, water-tert-butyl alcohol, and water-dioxane. The specific effects causing different courses of these dependences have been evaluated. The greatest changes in the thermodynamic activation parameters have been observed in the medium of water-methyl alcohol.

The studies of alkaline hydrolysis of monoesters of dicarboxylic acids in mixed aqueous-nonaqueous solvents showed that the changes of reaction rates observed during transition from aqueous to mixed media are affected, beside the relative permittivity change, by further factors which are dominant in many cases. An addition of a nonaqueous component to the solvent can affect the solvation spheres of reactants and/or of the activated complex to such an extent that the dependence of the rate constant on the co-solvent concentration has a course opposite to that predicted by the simple electrostatic theory^{1,2}. The shape of this dependence is also determined by mutual positions of free carboxylic and ester groups in the compound investigated. If these groups are close to each other, then the activated complex can be stabilized by the intramolecular hydrogen bond in solvents of lower solvation ability than that of water³⁻⁵. In the reports^{6,7} it was shown that in mixed solvents with low relative permittivity $\epsilon_r < 30$ the reaction rate is substantially affected by formation of ion pairs of the ester ion and/or OH⁻ ion with the cation present.

The aim of this communication is an investigation of the effects of methyl and tert-butyl alcohols and dioxane on the rate and activation parameters of alkaline hydrolysis of 3,4-thiophenedicarboxylic acid monomethyl ester, and application of the kinetic data to evaluation of the above-mentioned effects in the reaction studied.

EXPERIMENTAL

3,4-Thiophenedicarboxylic acid monomethyl ester was synthesized in Department of Organic Chemistry, Comenius University by the procedure described in ref.⁸. For the titrations we used sodium hydroxide free of carbonate. The reaction rate was followed titrimetrically within two half-lives by the procedure described in ref.⁹. The reaction mixture was tempered in an ultra-thermostat with the accuracy of ± 0.2 K. The starting concentrations of reactants were the same, and the rate constant was calculated from the relation for the second order reaction, $kt = 1/(a-x) - 1/a$, where a and x are the concentrations of the reactants at the beginning and at the time t , respectively. The rate constant was determined at three temperature values with the accuracy of 5%. From the temperature dependence of the rate constants in the interval from 314.3 to 334.4 K we calculated the thermodynamic activation parameters ΔH^\ddagger and ΔS^\ddagger with the accuracy of 6% and 8%, respectively.

RESULTS AND DISCUSSION

Table I presents the dependence of the rate constant and activation parameters ΔH^\ddagger and ΔS^\ddagger on the concentration of the nonaqueous component of solvent. Increasing concentration of the nonaqueous component of solvent caused a monotonous decrease of the rate constant only in the mixture water-methyl alcohol. In this solvent the change of the reaction rate is mainly determined by the change in relative permittivity of the medium. On the basis of the previous results^{5,10} it can be presumed that methyl alcohol can replace water in the solvation sphere of the reactants and/or activated complex. In the other two solvents we observed minima in the dependences $k = f(x_2)$ (where x_2 means the concentration of the nonaqueous component expressed by its molar fraction). Although the minimum in the dependence $k = f(x_2)$ lies at nearly the same x_2 value for both dioxane and tert-butyl alcohol, we suppose it to be due to two different effects. In Fig. 1 it can be seen that the minimum was observed in the water-dioxane mixture at lower relative permittivity than in the mixture water-tert-butyl alcohol. The increase of the rate constant in the water-dioxane mixture at $\epsilon_r < 35$ is presumably connected with formation of ion pairs ($\text{ester}^{(-)}\text{-Na}^{(+)}$) and ($\text{OH}^{(-)}\text{-Na}^{(+)}$)^{6,7} which decreases the repulsive electrostatic forces between the reactants carrying the same charges. From ref.¹⁰ known are the rate constants and thermodynamic activation parameters of the hydrolysis of the ester studied in 70% by vol. dioxane. These values are in accordance with the results obtained in this present work. A similar course of the dependence $\log k = f(1/\epsilon_r)$ was observed in the water-dioxane mixture also in the case of alkaline hydrolysis of 1,4-benzenedicarboxylic acid monomethyl ester⁷. For this ester no minimum was observed at the dependences $k = f(x_2)$ and $k = f(1/\epsilon_r)$ in the water-tert-butyl alcohol mixture.

In the aqueous-nonaqueous mixture mentioned the minima in the dependences $k = f(x_2)$ were observed in the cases of alkaline hydrolyses of monomethyl esters of 1,2-benzenedicarboxylic¹¹, 1,1-biphenyldicarboxylic⁵, and succinic¹² acids. Increasing concentration of tert-butyl alcohol causes desolvation of carboxylic

group whereby favourable conditions are created for formation of an intramolecular hydrogen bond in the activated complex. This bond stabilizes the OH group at the ester carbon atom. The alkaline hydrolysis of these esters goes by the $B_{Ac}2$ mechanism whose rate-limiting steps can be expressed as follows¹³:

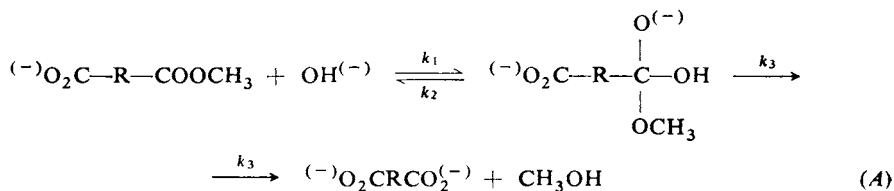
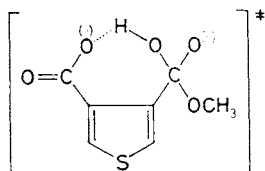


TABLE I

The dependence of the rate constant and of the thermodynamic activation parameters ΔH^\ddagger and ΔS^\ddagger of alkaline hydrolysis of 3,4-thiophenedicarboxylic acid monomethyl ester on concentration of the mixed solvents. $c(\text{ester}) = c(\text{NaOH}) = 0.01 \text{ mol dm}^{-3}$

x_2	$k \cdot 10^2, \text{ mol}^{-1} \text{ s}^{-1} \text{ dm}^3$			ΔH^\ddagger kJ mol ⁻¹	$-\Delta S^\ddagger$ J mol ⁻¹ K ⁻¹
	314.3 K	323.2 K	334.4 K		
0	1.05	1.92	3.86	53.2	114
Methyl alcohol					
0.047	0.982	1.79	3.41	52.1	118
0.100	0.658	1.20	2.65	57.7	103
0.159	0.550	0.956	1.98	54.5	115
0.228	0.383	0.660	1.12	44.2	151
0.400	0.233	0.360	0.607	39.9	169
Tert-butyl alcohol					
0.021	1.12	1.81	3.08	45.0	139
0.046	0.942	1.59	2.88	46.5	136
0.076	0.875	1.38	2.48	43.2	147
0.113	1.07	1.79	3.16	45.1	140
0.223	1.31	2.33	3.85	45.5	137
Dioxane					
0.023	0.95	1.62	3.05	48.9	128
0.050	0.925	1.56	3.00	49.5	127
0.083	0.725	1.28	2.65	54.1	114
0.123	0.817	1.47	2.90	54.3	113
0.241	1.28	2.28	4.68	54.8	107

The observed rate constant k_{obs} can be expressed by the relation $k_{\text{obs}} = k_1 k_3 / (k_2 + k_3)$. The stabilization of OH group in the activated complex decreases the decomposition probability of the complex to the starting compounds whereby the k_2 value decreases, which makes itself felt in the overall increase of the observed rate constant. Similar stabilization is also possible with 3,4-thiophenedicarboxylic acid monomethyl ester (I), but it is improbable with 1,4-benzenedicarboxylic acid



I

monomethyl ester. Beside the effect mentioned, a smaller decrease and increase of the rate constant in the water-*tert*-butyl alcohol and water-dioxane mixtures, respectively, as compared with the water-methyl alcohol medium, can also be affected by greater destabilization of the OH⁻ ion in the former two solvents. According to ref.¹ the alkaline hydrolysis of esters involves a desolvated OH⁻ ion, and the extent of desolvation (destabilization) represents – in some cases – the main factor affecting the reaction rate. The transfer functions of OH⁻ ion $\delta_m \mu_{\text{OH}^-}$ ($\delta_m \mu_{\text{OH}^-} = \mu_{(\text{OH}^-, x_2)} - \mu_{(\text{OH}^-, \text{H}_2\text{O})}$) represent a measure of its destabilization or stabilization on going from water to the medium considered, and for the same x_2

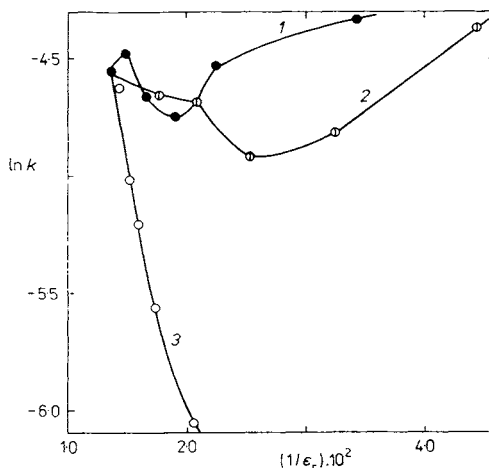


FIG. 1

The dependence of logarithm of the rate constant on the reciprocal value of relative permittivity of the mixed solvent. 1 Water-*tert*-butyl alcohol, 2 water-dioxane, 3 water-methyl alcohol. $T = 314.3 \text{ K}$

they stand in the following order: methyl alcohol (ref.¹⁴) < tert-butyl alcohol (ref.¹⁵) < dioxane (ref.¹⁶).

The greatest change in the thermodynamic activation parameters ΔH^\ddagger and ΔS^\ddagger was observed in the water–methyl alcohol mixture as it was the case with malonic acid monomethyl ester, too¹⁷. With the other monomethyl esters in this solvent mixture the changes of ΔH^\ddagger and ΔS^\ddagger were smaller^{7,12,18} or exhibited an opposite trend⁵. In the other two mixtures the thermodynamic activation parameters showed relatively small changes with respect to the accuracy of measurements. From the ΔS^\ddagger change connected with the transition from water to the mixed medium it can be concluded that the activated complex is better solvated in the water–methyl alcohol mixture as compared with the other two solvents.

In conclusion it can be stated that – similar to the earlier results – the reaction rate of alkaline hydrolysis of 3,4-thiophenedicarboxylic acid monomethyl ester is affected by several factors operating to different extents depending on the cosolvent used and its concentration. In the water–methyl alcohol mixture the change in the reaction rate is mainly determined by the change in the relative permittivity of the solvent. In the water–tert-butyl alcohol mixture the main factors are the desolvation of carboxylic group and stabilization of the activated complex by intramolecular hydrogen bond. In the water–dioxane mixture the relative permittivity decreases with increasing dioxane concentration to such an extent that suitable conditions are created for formation of ion pairs between negatively charged reactants and sodium ion at $x_2 \approx 0.08$ already, the ion pairs being more reactive.

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