

# Effect of solvents on reactions of oxidation with aliphatic peroxyacids

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**Abstract** – Organic solvents effect on the reactions of oxidation involving aliphatic peroxyacids was studied. It was found the kinetic and activation parameters of the oxidation of aniline. It is shown that the reaction medium has a significant effect on the rate of the process. The epoxidation reaction of  $\alpha$ -pinene and  $\Delta^3$ -karen by peroxydecanoic acid was studied. It was obtain the equation of correlation that connecting speed reaction with the basic physicochemical properties of solvents.

Key words – aniline, peroxyacid, oxidation, epoxidation,  $\alpha$ -pinene,  $\Delta^3$ -karene, influence of the reaction medium.

## I. Introduction

Oxidation of nitrogencontaining organic compounds and monoterpene hydrocarbons has attracted much attention due to their ability to obtain different products of oxidation. These reactions are typical electrophilic processes.

Oxidation of aniline (An) has been studied by many scientists, where by it was shown that the reaction mechanism occurs through a series of sequential steps [1 – 3].

Effect of solvent on studied processes was poorly studied, and the results that are presented in the literature are often incomplete and inconsistent.

Epoxidation reaction of monoterpene hydrocarbons is similar process. Therefore, study of the reaction medium on the rate of oxidation of aniline as well as monoterpene hydrocarbons –  $\alpha$ -pinene and  $\Delta^3$ -karen by peroxyacids can provide useful information to the best of these processes.

## II. Results and discussion

The process of oxidation by peroxydecanoic acid (PDA) satisfactorily described using the first-order kinetic equation of velocity. Kinetic curves of An oxidation by PDA in acetone are shown in Fig. 1.

Effective rate constants studied process in the coordinates  $\ln(C_0/C_\tau) - \tau$  which were calculated after the tangent of bent angle obtained dependences are shown in (Table 1).

Oxidation of An fastest occurs in propanol, whereas reaction rate in dioxane is the lowest. Oxidation reactions of An by PDA in other solvents does not carrying out change the kinetic order reaction, however, affect the total rate constant.

Estimated total energy of activation obtained slope of the temperature dependence of rate constants (k) in Arrhenius coordinates (Table 1).

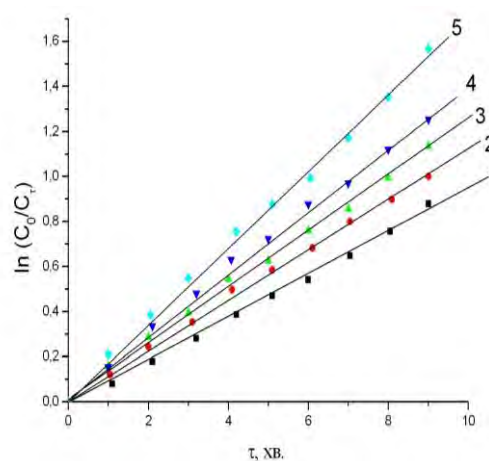


Fig. 1. Kinetic curves of oxidation process of An by PDA in acetone. Temperature, K: 1- 303K; 2-308 K; 3-313 K; 4-318 K; 5-323K

The reaction medium has a significant effect on the energy of activation. The numerical values of the energy of activation for process of An oxidation by PDA close to the values that appear in the literature for processes involving electrophilic oxidation with peroxyacids [1,3,4].

TABLE 1

EFFECTIVE RATE CONSTANT OF PSEUDO FIRST-STAGE OXIDATION OF ANILINE (AN) BY PEROXYDECAOIC ACID (PDA).

Solvent	$k \cdot 10^3 \text{ c}^{-1}$	$E_{act}$ , kJ/mol
	303K	
Acetic acid	1,40	63,3
Carbon tetrachloride	1,83	19,7
Propanol-2	4,39	42,1
Toluene	1,47	47,9
Acetone	1,61	21,3
Benzene	1,46	32,5
Chloroform	3,78	15,2
Dioxane	1,23	36,2
Hexane	1,31	40,1
Ethyl acetate	1,58	30,0
Butyl acetate	1,43	43,4
Methyl ethyl ketone	2,68	24,4
Dimethylformamide	1,48	43,0

The parameters of transition state for study process based on experimental results was calculated ( $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ ,  $\Delta G^\ddagger$ ) (Table 2). The numerical values of  $\Delta S^\ddagger$  – negative, that indicating a more orderly transition state compared to the original. Between the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  parameters is a linear relationship, which indicates on the presence of countervailing effect in a series of our experiments. This shows the complexity of the effects of solvents on the study process.

The results indicate that the resulting effective rate constant of oxidation and activation parameters correspond to the first stage oxidation of aniline. As is well known products that are formed on the first stage can react with peroxyacids giving those compounds [5].

TABLE 2

PARAMETERS OF TRANSITION STATE FOR OXIDATION OF ANILINE (AN) BY PEROXYDECANOIC ACID (PDA)

Solvent	$\Delta H^\ddagger$ , kJ/mol	$-\Delta S^\ddagger$ , J/mol K	$\Delta G^\ddagger$ , kJ/mol
Acetic acid	60,6	91,7	90,2
Carbon tetrachloride	16,9	233,2	92,3
Propanol-2	39,4	152,1	88,5
Toluene	45,2	142,8	91,3
Acetone	18,6	228,5	92,4
Benzene	29,8	192,4	91,9
Chloroform	12,5	241,7	90,6
Dioxane	33,5	181,6	92,2
Hexane	37,4	168,5	91,8
Ethyl acetate	27,3	199,2	91,6
Butyl acetate	40,7	157,2	91,5
Methyl ethyl ketone	21,7	214,7	91,1
Dimethyl-formamide	40,3	157,9	91,3

The heat of formation of the reactants and reaction products of the first stage oxidation using the semi-empirical quantum-chemical methods: AM1, PM3, PM5, PM6, RM1 was calculated. Quantum-chemical calculations performed using the program Mopac 2009 using graphic interface Winmostar 3.75. The heat of formation for this reaction ( $\Delta H_{ex}$ ) was calculated according to Hess's law. Found that the values calculated by  $\Delta H_{ex}$  thermochemical data close to the numerical values  $\Delta H_{ex}$ , obtained by quantum-chemical methods by AM1 and PM6.

Processes of epoxidation  $\alpha$ -pinene and  $\Delta^3$ -karene are similar. On the first stage rapidly formed intermediates. In the second stage, which determines the overall speed of the process, the intermediate compound decomposes to form the corresponding carboxylic acid and epoxy compound. The stage of destruction intermediate compound can be describe the "true" rate constant decomposition. The solvent that is used for reactions of epoxidation affect on the first and the second stage of the process. According to the experimental data rate of epoxidation  $\Delta^3$ -karene slightly higher than  $\alpha$ -pinene. The numerical values of  $E_{ac}$  for epoxidation reaction  $\Delta^3$ -karene somewhat lower than the corresponding parameters for the reaction of  $\alpha$ -pinene epoxidation (Table 3). The above fact indicates that the  $\Delta^3$ -karene epoxidation is easier than  $\alpha$ -pinene.

It should be noted that the peroxyacids attack on the double bond monoterpene hydrocarbons takes place from  $\alpha$ -field, therefore the reaction is stereospecific. Attack peroxyacids of the  $\beta$ -region is less likely, because here there are steric constraints.

Based on these results, we have calculated the transition state parameters  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$ , numerical values are given in Table. 4 and Table. 5. Parameters  $\Delta S^\ddagger$  is negative in all cases, indicating that the ordering transition state compared to the original. The numerical values of  $\Delta G^\ddagger$  for the process of  $\alpha$ -pinene epoxidation remote control for all the studied solvents are almost identical.

TABLE 3

THE TOTAL RATE CONSTANT OF PSEUDO FIRST-STAGE EPOXIDATION  $\alpha$ -PINENE AND  $\Delta^3$ -KARENE BY PEROXYDECANOIC ACID (PDA)

Solvent	$\alpha$ -pinene		$\Delta^3$ -karene	
	303 K			
	$k \cdot 10^3 \text{ c}^{-1}$	$E_{akt}$ , kJ/mol	$k \cdot 10^3 \text{ c}^{-1}$	$E_{akt}$ , kJ/mol
Dichloro-ethane	43,2	24,0	113	20,4
Benzene	68,6	29,7	99,5	40,4
Hlorbenzen	59,4	39,9	88,2	39,5
Tetra-hlormetan	74,6	31,0	103	23,2
Nitrobenzen	84,8	38,6	85,6	35,5
Acetic acid	58,9	57,9	85,1	31,6
Toluene	52,8	32,6	54,1	49,6
m-xylene	48,3	34,9	55,7	32,0
Acetone	6,82	39,2	20,3	39,5
Propanol-2	14,7	64,2	19,6	39,5
Ethyl acetate	14,8	36,4	12,5	57,1
Dioxane	24,3	27,3	11,9	40,9

Between the values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for two studied processes there is a linear relationship, that is, in our experiments was observed compensation effect. This suggests an elaborate effect of solvent on the study process.

On the basis of these studies we can be conclude that the solvent in which is reaction, changes the reactivity of terpenoids and epoxidation agent.

TABLE 4

PARAMETERS OF TRANSITION STATE FOR EPOXIDATION REACTION OF  $\alpha$ -PINENE BY PEROXYDECANOIC ACID (PDA)

Solvent	$\alpha$ -pinene		
	303 K		
	$\Delta H^\ddagger$ , kJ/mol	$-\Delta S^\ddagger$ , J/mol K	$\Delta G^\ddagger$ , kJ/mol
Dichloroethane	21.4	228	93.9
Benzene	27.1	205	92.3
Hlorbenzen	37.3	173	92.3
Tetrahlormetan	28.4	200	92.1
Nitrobenzen	36.0	174	91.3
Acetic acid	55.4	135	96.2
Toluene	30.0	197	92.7
m-xylene	32.3	191	93.0
Acetone	36.6	193	98.0
Propanol-2	61.6	103	94.2
Ethyl acetate	33.8	196	95.9
Dioxane	24.7	222	95.0

To find the dependence of oxidation rate constants ( $k$ ) of the basic physico-chemical parameters of solvents was used equation (1)

$$\lg k = a_0 + a_1 (n^2 - 1)/(n^2 + 2) + a_2 (\epsilon - 1)/(2\epsilon + 1) + a_3 B + a_4 E_T + a_5 \delta^2 + a_6 V_M \quad (1)$$

where,  $n$  and  $\epsilon$  – refractive index and dielectric constant of solvents that determine their polarizability and polarity are responsible for nonspecific solvation [6, 7] accordingly, determining the ability of solvents to acid-

base interactions, is specific solvation. The values of  $\delta$  and  $V_M$  – parameter of Hildebrandt solubility whose square is proportional to the cohesive energy environment and molar volume of solvent, expressing the influence of structural factors.

TABLE 5

PARAMETERS OF TRANSITION STATE FOR EPOXIDATION REACTION OF  $\Delta^3$ -KAREN BY PEROXYDECANOIC ACID (PDA).

Solvent	$\Delta^3$ - karene		
	303 K		
	$\Delta H^\ddagger$ , kJ/mol	$-\Delta S^\ddagger$ , J/mol K	$\Delta G^\ddagger$ , kJ/mol
Dichloroethane	17.9	236	89.4
Benzene	37.9	169	89.3
Hlorbenzen	36.9	173	89.4
Tetrahlormetan	20.8	225	89.1
Nitrobenzen	32,9	183	91,3
Acetic acid	29,1	199	89.2
Toluene	47.0	146	91.1
m-xylene	29.4	199	92.6
Acetone	36.9	186	93.2
Propanol-2	36.9	184	92.7
Ethyl acetate	54.6	130	93.9
Dioxane	38.9	185	97.4

Generalization of the equation (1) data results of aniline oxidation at 313K in 13 solvents leads to six parameters equation with very low numerical value of the output of multiple correlation coefficient  $R = 0, 7240$ . With the exclusion of the data array acetic acid solvent, coefficient of correlation increases to 0.8868. It is known [8] aniline and acetic acid form a solid compound that affects the effective rate constant of oxidation and can change the mechanism of the process.

To achieve good R preclude another solvent – acetone. As a result, we obtain the six parameters equation with good source of multiple correlation coefficient – 0.9709 and the standard deviation

$$S = 0,0359.$$

$$\lg k = 0,4697 + (4,3915 \pm 1,0712) \cdot f_1(n^2) + (-0,6956 \pm 0,2186) f_2(\epsilon) + (-0,2 \pm 0,5) 10^{-3} \cdot B + (-3,8 \pm 0,4) \cdot 10^{-3} \cdot E_T + (0,0336 \pm 0,0061) \cdot \delta^2 + (-5,0 \pm 1,5) \cdot 10^{-3} \cdot V_M. \quad (2)$$

The influence of individual members of (1) on the value of  $\lg k$  determined by their alternate exception. In addition, each time observed decrease in R for the obtained equations with fewer members. As a result of the oxidation rate of An by PDA satisfactorily described by three parameters equation (3) with a correlation coefficient  $R = 0,9593$  and standard deviation  $s = 0,04$ .

$$\lg k = -3,9817 + (-0,0011 \pm 0,0002) B + (0,0458 \pm 0,0053) \cdot E_T + (-0,0004 \pm 0,0002) \cdot \delta^2 \quad (3)$$

Thus, the factor that determines and increases the intensity of the process is elektrophylity environment (Et). To achieve the value of multiple correlation coefficient

$R > 0,9503$  necessary to take into account energy cohesive environment  $\delta^2$ , which increases the speed of the process, basicity B and elektrophylity  $E_T$ . The refractive index n (polarizability) and the molar volume of the solvent  $V_M$  in this case is negligible.

Generalization data results of the equation (1) oxidation of  $\Delta^3$ -karen at 308K in 12 solvents leads to six parameters equation with coefficients of pair correlation  $r_i$  0,6577, -0,1117, -0,2286, -0,8808, -0,1054, 0,1483, very large numerical value output multiple coefficient of correlation  $R = 0, 9929$  and standard deviation  $S = 0,0430$ .

$$\lg k = 0,4697 + (4,3915 \pm 1,0712) \cdot f_1(n^2) + (-0,6956 \pm 0,2186) f_2(\epsilon) + (-0,2 \pm 0,5) 10^{-3} \cdot B + (-3,8 \pm 0,4) \cdot 10^{-3} \cdot E_T + (0,0336 \pm 0,0061) \cdot \delta^2 + (-5,0 \pm 1,5) \cdot 10^{-3} \cdot V_M. \quad (4)$$

Similarly, the impact of individual members of (1) on the value of  $\lg k$  determined by their exclusion and the observed decrease in R for the obtained equations with fewer members. As a result,  $R = 0, 9928$  with basicity (B),  $R = 0, 9859$  without solvent molar volume ( $V_M$ ) and  $R = 0,9709$  with refractive index (n).

Rate of  $\Delta^3$ -karen oxidation satisfactorily described of two parameters equation.

$$\lg k = 1,2685 + (-4,8 \pm 0,4) \cdot 10^{-3} \cdot E_T + (0,0259 \pm 0,0058) \cdot \delta^2. \quad (5)$$

As a result, a factor that determines and increases the intensity of the process is elektrophylity environment ( $E_T$ ). To achieve the value of multiple correlation coefficient  $R > 0,9859$  necessary to take into account energy cohesive environment  $\delta^2$ , which increases the speed of the process, its polarizability n and elektrophylity  $E_T$ , which reduces the speed. Basicity B and solvent molar volume  $V_M$  in this case is negligible.

Similar results were obtained for the epoxidation process of  $\alpha$ -pinene at 308K.

Equations of six parameters was find with a sufficiently high multiple correlation coefficient  $R 0,9739$  where by none of the parameters of the solvent has a determining influence on the value of  $\lg k$ , since the value paired correlation coefficients ( $r_i$ ) is in the range – 0.7587 to 0.7497. Relationship between  $\lg k$  values in 12 solvents and their properties can obtain equation (6).

$$\lg k = -1,2971 + (6,2414 \pm 1,9475) \cdot f_1(n^2) + (-2,3744 \pm 0,3974) f_2(\epsilon) + (0,4 \pm 0,9) 10^3 \cdot B + (2,3 \pm 0,7) \cdot 10^{-3} \cdot E_T + (0,0536 \pm 0,0110) \cdot \delta^2 + (1,1 \pm 2,8) \cdot 10^{-3} \cdot V_M. \quad (6)$$

With the exclusion of six parameters equation one of the parameters, such as molar volume of the solvent, we obtain an equation with  $R = 0,9736$

$$\lg k = -1,2256 + (6,5979 \pm 1,7169) \cdot f_1(n^2) + (-2,3177 \pm 0,3706) f_2(\epsilon) + (0,3 \pm 0,9) 10^{-3} \cdot B + (2,2 \pm 0,7) \cdot 10^{-3} \cdot E_T + (0,0518 \pm 0,0100) \cdot \delta^2. \quad (7)$$

Characteristics that define the basicity and molar volume of the solvent does not affect the speed of the process. Excluding them from the equation leads to four parameters equation with slightly worse correlation.

$$\lg k = -1,3765 + (7,1084 \pm 1,1227) \cdot f_1(n^2) + (-2,2707 \pm 0,3530) f_2(\epsilon) + (-2,0 \pm 0,4) \cdot 10^{-3} \cdot E_T + (54,6 \pm 7,0) \cdot 10^{-3} \cdot \delta^2 \quad (8)$$

Excluded other parameters of correlation equation reduces the correlation coefficient.

Thus, the reaction rate of  $\alpha$ -pinene epoxidation unlike aniline and  $\Delta^3$ -karen described by equation four parameters correlations with higher coefficient  $R = 0,9732$ .

Unequal effects of solvents on the processes of oxidation  $\alpha$ -pinene and  $\Delta^3$ -karene explained by different solvation investigated terpenoids. It should be noted that the solvation epoxidation agent by peroxydecanoic acid is the same in both cases.

### Conclusion

The oxidation of aniline by PDA of various organic solvents was studied. An effective rate constant and energy of activation of the studied process was found. It is shown that the nature of the reaction medium has impact on both the rate constants and the energy of activation.

The activation parameters of aniline oxidation was calculated. Between the activated parameters of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  is a linear relationship, therefore in a series of our experiments there is a compensation effect.

The heats of formation of the reactants and reaction products was calculated of various semi-empirical quantum-chemical methods. The heat of the oxidation

reaction of aniline by PDA on the first two stages was calculated according to the Hess equation.

The effect of solvents on the epoxidation reaction of  $\alpha$ -pinene and  $\Delta^3$ -karene by PDA was investigated. A general kinetic equation process was proposed. The processes of oxidation studied compounds by PDA include rapid formation of an intermediate compound which gives decomposing reaction products.

The equation of correlation was resulting relating the rate of reaction with the basic physicochemical properties of solvents.

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