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Studies of Acylation Kinetics of Aspen Wood with Aromatic Carboxylic Acids

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Abstract—With the help of Erofeev–Kolmogorov and Eiring equations kinetic characteristics of acylation of the aspen wood with the aromatic carboxylic acids in presence of thionyl chloride in the trifluoroacetic acid medium were calculated and thermodynamic parameters of this process were established.

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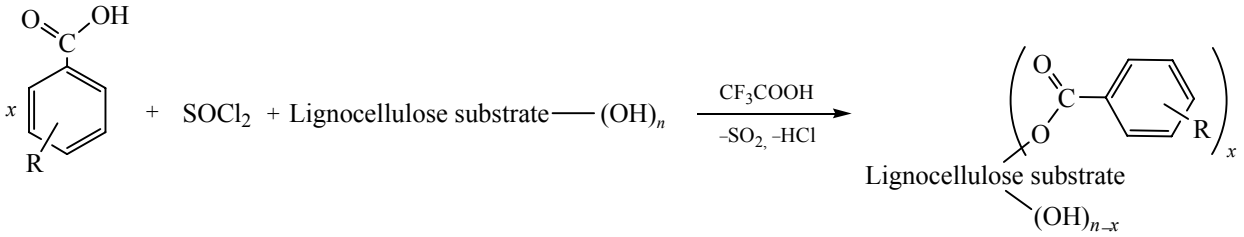
Nowadays cellulose esters have not lost their value. They are widely used in industry [1]. Such cellulose esters as benzoates and phthalates are most thoroughly studied. They exhibit many useful properties which makes them valuable artificial polymers having practical use. But the procedures of their synthesis are significantly limited. They are based on treating cellulose with the unstable reagents like benzoyl chloride and phthalic anhydride in the presence of basic catalysts. At the same time, syntheses of cellulose esters with the other substituted aromatic carboxylic acid are scarce and are poorly described [2].

In the previous works we have shown the possibility of preparing cellulose esters with the other aromatic carboxylic acids directly from the wood [3–5]. A mixture of carboxylic acid, thionyl chloride, and trifluoroacetic acid was used as the acylating agent. As the above-mentioned esters present practical interest for industry, kinetic studies of the process of their formation permit the establishment of the optimal technological parameters of their manufacturing.

In this work the results on the evaluation of the kinetic and thermodynamic parameters of the aspen wood (lignocellulose substrate) with different aromatic carboxylic acids in the system including the acid, thionyl chloride, and trifluoroacetic acid are presented.

With the purpose of removing the extractive substances and gemicellulose the aspen wood was exposed to extraction and prehydrolysis according to the procedures described in [6]. The substrate obtained was further acylated in the system including carboxylic acid, thionyl chloride, and trifluoroacetic acid. The process can be described by the following reaction scheme.



R = H, 2(4)-NH_2, 2(4)-OH, 2-NO_2, 2-COOH, 2-OH, 5-SO_3H, 5-NH_2.

The kinetic data obtained were treated using the Erofeev–Kolmogorov equation [7].

$$\ln [-\ln(1 - \alpha)] = \ln k + n \ln \tau. \quad (1)$$

Here α is the degree of conversion of the hydroxy groups to ester ones, k is the empiric coefficient comparable with the reaction rate constant, n is the empiric coefficient characterizing the number of elementary

Table 1. Reaction rate constants of acylation of lignocellulose substrate

Aromatic carboxylic acid included in the composition of lignocellulose subtstrate	Rate constant (K), s^{-1}			
	25°C	35°C	45°C	55°C
Benzoic	2.651×10^{-6}	3.532×10^{-6}	5.075×10^{-6}	7.098×10^{-6}
p-Aminobenzoic	1.946×10^{-5}	1.633×10^{-5}	1.548×10^{-5}	1.051×10^{-5}
p-Oxybenzoic	3.831×10^{-6}	0.876×10^{-6}	0.599×10^{-6}	0.071×10^{-6}
p-Nitrobenzoic	6.480×10^{-7}	8.327×10^{-9}	5.080×10^{-11}	1.298×10^{-11}
o-Aminobenzoic	1.781×10^{-6}	3.911×10^{-6}	6.828×10^{-6}	14.030×10^{-6}
o-Oxybenzoic	4.924×10^{-7}	2.275×10^{-5}	4.259×10^{-5}	2.614×10^{-4}
o-Phthalic	7.022×10^{-8}	1.440×10^{-8}	2.803×10^{-11}	1.492×10^{-11}
5-Sulfosalicylic	0.860×10^{-7}	2.508×10^{-7}	7.310×10^{-7}	35.570×10^{-7}
5-Aminosalicylic	1.890×10^{-7}	1.372×10^{-7}	1.031×10^{-7}	0.425×10^{-7}

stages in the course of the transformation of seed into the actively growing nucleus and the number of directions of the nuclei growth, τ is the time of synthesis.

The conversion was evaluated according to formula (2).

$$\alpha = S/S_{max}. \quad (2)$$

Here S is the current degree of substitution of the obtained cellulose esters at the time τ; S_{max} is the maximum degree of substitution of the OH groups in cellulose equal to 3 per its elementary unit.

Under the studied reaction conditions a linear dependence between ln [–ln (1 – α)] and ln τ was observed (correlation coefficient value varied in the range 0.97–0.99). Therefrom the reaction rate constant (K) was evaluated using the Sakovich method.

$$K = nk^{1/n}. \quad (3)$$

Here n and k are the empiric coefficients of the Erofeev–Kolmogorov equation, K is the reaction rate constant, s^{-1}.

Thermodynamic parameters of acylation of the aspen wood were evaluated on the basis of the Eiring equation (4). With this purpose the graph in the ln ($K\hbar/Tk_b$) was plotted and the activation enthalpy and entropy were calculated.

$$\ln K\hbar/Tk_b = \Delta S^{\neq}/R - (\Delta H^{\neq}/R)(1/T), \quad (4)$$

where K is the rate constant, s^{-1}; T is temperature, K; $\hbar$ is the Plank constant, $\hbar = 6.62\times10^{-34}$ J s; k_b is the Boltzmann constant, $k_b = 1.38\times10^{-23}$ J K^{-1}; R is the universal gas constant, $R = 8.31$ J mol^{-1} K^{-1}; $\Delta S^{\neq}$ is the activation entropy, J mol^{-1} K^{-1}; $\Delta H^{\neq}$ is the activation enthalpy, kJ mol^{-1}.

Results presented in Table 2 show that the activation free energy of acylation is not sensitive to the presence of substituents in the benzene ring of the aromatic carboxylic acid, and the mean $\Delta G^{\neq}$ value is 114 kJ mol^{-1}, but this substituent affects significantly the activation entropy and enthalpy.

The obtained values of the activation enthalpy (Table 2) for the acylation of lignocellulose substrate with *p*-aminobenzoic, 5-aminosalicylic, and *p*-oxybenzoic acids indicate the fast achievement of the transition state of the activated complex. In this case the formation of intermolecular H-bonds between the aromatic carboxylic acids and lignocellulose complex probably takes place. It is accompanied by the rupture of the lignin-carbohydrate bonds and amorphyzation of cellulose. The activation entropy values shows the energetic stability of the transition complex. But whereas in the *p*-aminobenzoic acid the amino group is protonated with trifluoroacetic acid complicating the formation of hydrogen bonds, in *p*-oxybenzoic acid this obstacle is absent, and it is reflected in the obtained values of thermodynamic parameters.

In the reaction of lignocellulose substrate with 5-aminosalicylic acid the process of formation of the transition complex is complicated evidently by the formation of intermolecular hydrogen bonds as well as by intramolecular interactions (Table 2).

The absence of the formation of H-bonds between the nitro group and the hydroxy groups of lingo-

Table 2. Thermodynamic parameters of acylation of lignocellulose substrate with the substituted aromatic carboxylic acids

Aromatic carboxylic acid included in the composition of lignocellulose subtstrate	Activation energy ($\Delta H^{\neq}$), kJ mol^{-1}	Activation entropy ($\Delta S^{\neq}$), J mol^{-1} K^{-1}	Free energy of activation ($\Delta G^{\neq}$), kJ mol^{-1}
Benzoic	32.04	–243.51	108.25
p-Aminobenzoic	–17.92	–396.60	106.22
o-Aminobenzoic	74.76	–113.29	110.22
p-Oxybenzoic	–101.60	–690.84	114.63
o-Oxybenzoic	152.81	151.56	105.37
5-Sulfosalicylic	97.14	–57.08	115.00
5-Aminosalicylic	–50.34	–539.66	118.57
p-Nitrobenzoic	269.09	448.72	128.64
o-Phthalic	–259.56	–1250.97	131.99

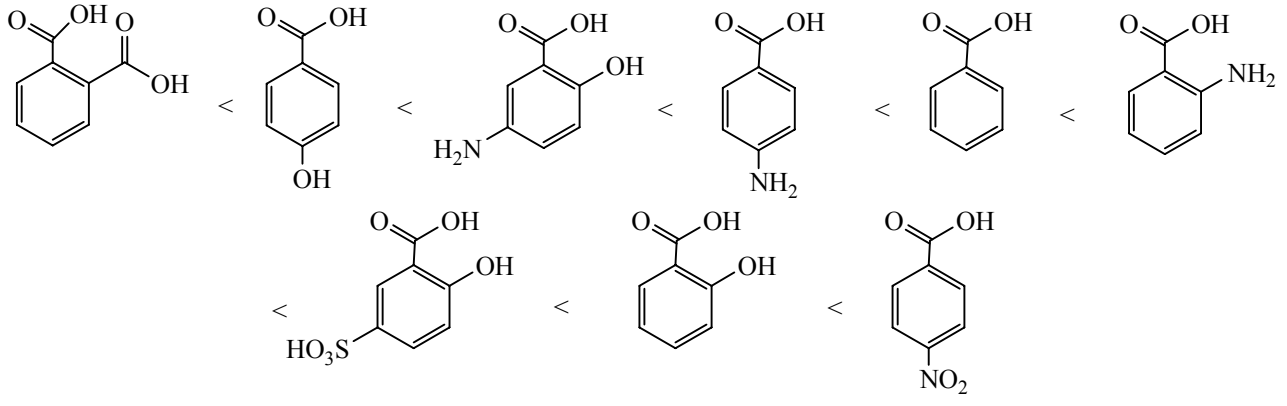
cellulose substrates complicates direct interaction between the acylating agent and the lignin-carbohydrate complex. Positive value of activation enthalpy shows the existence of high energy barrier which must be surmounted for the diffusion of acylating agent in the supramolecular structure of lignocellulose material to the hydroxy groups of cellulose. It creates complications for the formation of transition complex. The activation entropy value (Table 2) shows the absence of hydrogen bonds which leads to the energetic loosening of the activated complex and accelerates the formation of the final product. Analogous situation is observed in the acylation of lignocellulose material with benzoic acid which indicates the fast achievement of the state of activated complex.

ortho-Location of the amino and hydroxy groups complicates the formation of activated complex, and negative value of the activation enthalpy shows the energy consumption for the diffusion of the acylating agent to the polymer. On the basis of the data obtained on the activation entropy a suggestion can be made on the energy stability of the activated complex. The formation of intramolecular hydrogen bonds in the reaction with *o*-oxybenzoic acid obviously favors the loosening of the activated complex in contrast to the acylation with *o*-aminobenzoic acid where intramolecular bonds are weakened due to the formation of the complex with trifluoroacetic acid.

Note also that the obtained values of thermodynamic parameters in the reaction of acylation of lignocellulose substrate with *o*-phthalic acid show the high stability of the transition complex and energetic complications in the formation of the final product.

While acylation of lignocellulose substrate with 5-sulfosalicylic acid the reaction of thionyl chloride with the sulfonic group of this acid is possible [8] which complicates finally the formation of activated complex.

The consideration of the effect of the structure of carboxylic acid on the activation enthalpy and entropy of acylation of the aspen wood permits to construct the following series.



Hence, thermodynamic parameters and kinetics of acylation of lignocellulose substrate with the aromatic carboxylic acids are evaluated. It is shown that the activation free energy of the reaction is practically independent of the nature of substituent in benzene ring, and its mean value is 114 kJ mol^{-1}. It is established that aromatic carboxylic acids form a series reflecting the effect of substituent in benzene ring on the values of activation enthalpy and entropy of acylation reflecting its nature and location in the molecule.

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