# *O*-Acetylation of 4-Hydroxybenzoic Acid with Acetic Anhydride

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The kinetics of the acetylation of 4-hydroxybenzoic acid with acetic anhydride without any solvent at 125 °C was investigated. The catalytic effectiveness of 23 substances was evaluated.

Aromatic polyesters represent a significant group of latest thermotropic polymeric materials. These substances are distinguished by the excellent mechanical properties and high thermal and chemical stability which are the consequence of their liquid-crystalline structure [1]. For the main part, they are the matter of the copolyesters of 4-hydroxybenzoic acid (PHBA) with 6-hydroxy-2-naphthoic acid, however, they include commonly also structural units of aromatic diols and aromatic dicarboxylic acids [2—6]. Their preparation is based mostly on the acidolytic melt copolycondensation of acetoxy derivatives of the above-mentioned components.

Methods of copolycondensation of beforehand prepared acetoxy derivatives, namely of 4-acetoxybenzoic acid (PABA), are the subject of a series of papers and numerous patents. However, the information about *in situ* prepared PABA exploiting procedures is inaccessible in the literature. It is possible to presume that such procedures would be from the viewpoint of achievement more convenient and in practice economically advantageous. For many reasons, only acetic anhydride is the suitable reagent for the acetylation of PHBA *in situ*. However, we have found the acetylation of PHBA is from the practical viewpoint too slow and, consequently, its catalysis is necessary, in contrary to acetylation of 6-hydroxy-2-naphthoic acid which reacts with acetic anhydride satisfactorily quickly even without any catalyst.

Preparation of PABA by means of acetylation of PHBA *in situ* for the subsequent copolycondensation should meet following requirements:

1. full conversion of PHBA;
2. minimum excess of acetic anhydride;
3. the reaction time as short as possible;
4. application only of such catalysts which support no side reaction by the acetylation and have no undesirable effect on the subsequent copolycondensation and on the properties of resulting copolyester.

*O*-Acylation of substances bearing the phenol group is generally catalyzed both with acids, and with bases. However, from the viewpoint of subsequent acidolysis of reaction mixture which is performed at the temperature about 280 °C, it is necessary to exclude many of commonly used effective catalysts (*e.g.* mineral acids). Therefore we aimed in particular at the testing of the effectiveness of the potential acetylation catalysts which are used for the acidolytic copolycondensation of PABA. We have tested 23 substances which may be sorted into three groups.

1. Substances referred in the literature to the catalysts of acidolytic (co)polycondensations, reesterification (co)polycondensations or (co)polyesterifications: sodium, potassium, magnesium, calcium, zinc, copper(II), and cobalt(II) acetates.

2. Chemically related substances to those of the previous group for which we assume they conform to the fourth of the above-mentioned requirements: lithium, barium, chromium(III), nickel(II), manganese(II), and diuranyl zinc acetates, dibutyltin maleinate (dibutyltin oxide is used for the catalysis of (co)polycondensations of acetoxyarenecarboxylic acids), zirconium(IV), vanadium(IV), and antimony(III) oxides, and nickel(II) hydroxide.

3. Other: pyridine (commonly known as the catalyst of *O*-acylations of hydroxy compounds), triphenylphosphane, triphenylphosphane oxide, disodium hydrogenphosphate, and disodium phenylphosphate.

## THEORETICAL

Reactions of alcohols and phenols with carboxylic acids anhydrides are irreversible. We assume the acetylation of PHBA with acetic anhydride without any catalyst is a second-order reaction (first-order for both components), its course at constant temperature is isochoric and molar volumes of the components are independent on the reaction mixture composition.

A B

Time dependence of molar concentration of the component A and component B is expressed with the rate law

$$-\frac{da}{dt} = kab \tag{1}$$

where $a$ and $b$ are molar concentrations of the components A and B, respectively, $t$ is the reaction time, and $k$ is the reaction-rate constant. If the mole ratio of components B and A ($n_B$ $n_A$) at the start of reaction is $Z$, the molar volume of the component A is $V_A$ and the ratio of molar volume of the component B to molar volume of the component A is $\beta$, it follows for the time corresponding to the conversion $z$ of the component A when $z = 0$ at $t = 0$ from eqn (1) for $Z \neq 1$

$$t = \frac{V_A}{k} \frac{Z\beta + 1}{Z - 1} \ln \frac{Z - z}{Z (1 - z)} \tag{2}$$

and for $Z = 1$

$$t = \frac{V_A}{k} (1 + \beta) \frac{z}{1 - z} \tag{3}$$

respectively.

If the values of the quantities $V_A$ and $\beta$ are unknown, it is impossible to determine the constant $k$ from the time dependence of the conversion $z$. Defining the quantity

$$\alpha = \frac{k}{V_A} \frac{Z + 1}{Z\beta + 1} \tag{4}$$

eqn (2) can be written in the form

$$t = \frac{1}{\alpha} \frac{Z + 1}{Z - 1} \ln \frac{Z - z}{Z (1 - z)} \tag{5}$$

and eqn (3) in the form

$$t = \frac{2}{\alpha} \frac{z}{1 - z} \tag{6}$$

If the molar volumes of the components A and B are equal ($\beta = 1$), the expression (4) is simplified to

$$\alpha = \frac{k}{V_A} \tag{7}$$

and consequently the quantity $\alpha$ is independent on the ratio $Z$. Provided the molar volumes of components are unequal ($\beta \neq 1$) the quantity $\alpha$ is the function of components mole ratio at the start of the reaction $Z$, which is monotonous in the domain $Z \in \langle 0; \infty)$, for $\beta < 1$ it is increasing, and for $\beta > 1$ it is decreasing. It is possible to presume for the ratio of densities of the components A and B $\frac{\rho_A}{\rho_B}$ that it is valid

$$0.5 \leq \frac{\rho_A}{\rho_B} \leq 2 \tag{8}$$

and from this follows the assumption for the value of $\beta$

$$0.67 \leq \beta \leq 2.70 \tag{9}$$

The time dependence of conversion $z$ of the component A was investigated for the domain

$$1 < Z < 1.2 \tag{10}$$

If the condition (9) is valid, the value of dependent variable $\alpha$ cannot vary more than by 4.1 % when the value of independent variable $Z$ varies from 1.0 to 1.2. This is the systematic error in the extreme considering the value of quantity $\alpha$ calculated from eqn (5) is constant, $\alpha = \alpha(Z\beta = 1)$.

Defining the function for $Z \neq 1$

$$F = \frac{Z + 1}{Z - 1} \ln \frac{Z - z}{Z (1 - z)} \tag{11}$$

and for $Z \to 1$

$$F = 2 \frac{z}{1 - z} \tag{12}$$

respectively, from eqns (5) and (6) follows the linear time dependence of this function

$$F = \alpha t \tag{13}$$

The development of catalyzed reaction in time is expressed with the rate law

$$-\frac{da}{dt} = kab + k_K cab \tag{14}$$

where $k_K$ is catalytic constant and $c$ is molar concentration of the catalyst. Neglecting the volume of catalyst, integration of eqn (14) for isochoric isothermal process and for $Z \neq 1$, analogously as derivation of eqn (2), yields

$$t = \frac{1}{\frac{k}{V_A} + \frac{k_K \rho}{V_A M_K} w_K} \frac{Z\beta + 1}{Z - 1} \ln \frac{Z - z}{Z (1 - z)} \tag{15}$$

where $\rho$ is reaction mixture density, $M_K$ is molar mass of catalyst, and $w_K$ is mass fraction of catalyst in the reaction mixture. Incorporating the quantity $\alpha$ defined in eqn (4) into eqn (15) one obtains the relation

$$t = \frac{1}{\alpha \left(1 + \frac{k_K \rho}{k M_K} w_K\right)} \cdot \frac{Z + 1}{Z - 1} \cdot \ln \frac{Z - z}{Z (1 - z)} \tag{16}$$

If the rate constant of reaction without catalyst $k$ and reaction mixture density $\rho$ are unknown, it is impossible to evaluate the catalytic constant $k_K$ from eqn (16). However, the effectiveness of catalyst can be characterized by the constant

$$\kappa = \frac{k_K \rho}{k M_K} \tag{17}$$

Substituting the expressions (*11*) and (*17*) into (*16*) one obtains

$$\kappa = \frac{1}{w_K}\left(-1 + \frac{1}{t\alpha}\ F\right) \qquad (18)$$

If the function is defined

$$D = \frac{F - t\alpha}{\alpha w_K} \qquad (19)$$

eqn (*18*) can be transformed into a straight line equation

$$D = \kappa t \qquad (20)$$

Acceleration of the reaction at a defined mass fraction $w_K$ of catalyst in reaction mixture can be characterized by the ratio $u$ of reaction time corresponding to defined conversion without catalyst (eqn (*5*)) to that corresponding to the same conversion with catalyst (eqn (*16*)); substituting the expression (*17*) into this ratio one obtains the relation

$$u = 1 + \kappa w_K \qquad (21)$$

We investigated the kinetics of the reaction of PHBA with acetic anhydride at 125 °C. The reaction proceeds at this temperature with measurable rate even without catalyst. We do not know any suitable and procurable instrumental method of monitoring of changes in the investigated, an anhydride and three acids containing, system. Therefore, we directed our attention to classical analytical methods. As the most viable approach to solve this problem, we regarded to determine acetic anhydride which is present in reaction mixtures.

We chose the modified method [7] which is based on the quantitative conversion of unreacted acetic anhydride to acetanilide by means of known excess of standard aniline solution in chloroform. Unreacted aniline can be titrated, just as salts of carboxylic acids [8], with titrimetric solution of perchloric acid in ethylene glycol—isopropyl alcohol—water medium [9] using methyl red as indicator. We verified that the presence of PHBA does not affect the determination of acetic anhydride by this method. However, we found, admixture of PABA causes decreasing of consumption of standard solution of perchloric acid when aniline solution is added at room temperature. Spontaneous increasing of temperature follows due to the heat of reaction and the difference between the true and theoretical consumption increases with the time between the addition of aniline solution and the dilution with mentioned mixture of alcohols. This is the evidence of aminolysis of PABA with aniline. Therefore, we modified this procedure. We found that the aminolysis of acetic anhydride proceeds quantitatively during 5 min without noticeable aminolysis of PABA when the aniline solution is added at 0—5 °C. After making-up the exact volume of solution by the above-mentioned mixture of alcohols, the aminolysis of PABA is very slow even at room temperature and the stock solution can be titrated with invariable results in course of several hours.

## EXPERIMENTAL

The exact concentration of *ca.* 0.1 M-NaOH was determined by titration of exactly known mass of oxalic acid dihydrate in aqueous solution using phenolphthalein as indicator. Aniline was distilled *in vacuo* in the presence of zinc powder, its purity was confirmed through the conformity of its refractive index value with the tabulated one. Standard 0.1 M aniline solution was prepared solving aniline (9.3129 g; 0.1000 mol) in chloroform and adjusting the volume exactly to 1 $dm^3$

At the preparation of the standard solution, commercial (Laborchemie Apolda) 68 % (11.5 mol $dm^{-3}$) perchloric acid (17.4 $cm^3$, 0.2 mol) was added dropwise to the mixture ethylene glycol—isopropyl alcohol ($\varphi_r$ = 1 1, 500 $cm^3$) under shaking (heat development) and, after tempering to room temperature, the solution was diluted to 1 $dm^3$ with the same mixture solvent. It was standardized against standard aniline solution using methyl red as indicator.

At the determination of purity of 4-hydroxybenzoic acid the commercial (Merck) product PHBA (*ca.* 1.4 g; 0.01 mol) was dissolved in the mixture pyridine—water ($\varphi_r$ = 1 1, 40 $cm^3$) and the solution was diluted with ethanol exactly to 100 $cm^3$ Pipetted volume (10 $cm^3$) of this stock solution was titrated with 0.1 M-NaOH, phenol red being used as indicator. The value 0.9900 ± 0.0043 of mass fraction of PHBA was found (three stock solutions, ever titrated three times).

At the determination of purity of acetic anhydride an exact mass of commercial (Lachema) acetic anhydride, anal. grade (*ca.* 1.0 g; 0.01 mol) was dissolved in chloroform (20 $cm^3$) in an 100 $cm^3$ volumetric flask and 0.1 M standard chloroform solution of aniline (20 $cm^3$) was pipetted to this solution. After short shaking, the flask was left in quiet for 5 min at room temperature and then the content was completed with ethylene glycol—isopropyl alcohol ($\varphi_r$ = 1 1) mixture. From this stock solution, 10 $cm^3$ samples were pipetted and titrated with 0.2 M perchloric acid using methyl red as indicator. The value 0.9774 ± 0.0022 of mass fraction of acetic anhydride was found (3 stock solutions, ever titrated three times).

### Determination of the Conversion of PHBA

PHBA (*ca.* 0.01 mol), contingent catalyst, and acetic anhydride were weighed into 10 $cm^3$ distillation flask. Magnetic stirring bar was placed into the mixture, the flask was equipped with reflux condenser with drying tube with calcium chloride and immersed

half neck into glycerol bath kept at 125 °C and the stirring was switched on. The clear solution arose during *ca.* 1.5 min from which, in some experiments, solid PABA precipitated during keeping at this temperature. The mixture did not boil at any experiment and only the negligible amount of condensate settled in the inlet of condenser. After the definite time since immersion, heating bath was replaced with ice bath in which the flask was shaken for one minute. Amount of solid in reaction mixture essentially enlarged due to cooling. The inside surface of condenser was rinsed with chloroform (5 $cm^3$) into the flask and its content was transferred into a 100 $cm^3$ volumetric flask quantitatively by means of the same solvent (15 $cm^3$). After 10 min cooling in an ice bath, 0.1 M standard chloroform solution of aniline (20 $cm^3$) was pipetted to the arisen clear solution. After short shaking, the flask was left in quiet for 5 min at room temperature and then the content was completed with ethylene glycol— isopropyl alcohol ($\varphi_r$ = 1 1) mixture. From this stock solution, 10 $cm^3$ samples were pipetted and titrated with 0.2 M perchloric acid by use of methyl red as indicator. The conversion of PHBA was calculated according to the formula

$$z = \frac{M_A}{m_A w_A}\left(\frac{m_B w_B}{M_B} - v\frac{m_K}{M_K} - V_{S1}c_{S1} + V_{S2}c_{S2}\right)$$

where $M_A$ is the molar mass of PHBA, $m_A$ is the mass of used PHBA, $w_A$ is the mass fraction (purity) of the used PHBA, $m_B$ is the mass of the used acetic anhydride, $w_B$ is the mass fraction (purity) of the used acetic anhydride, $v$ is the number of the molecules of water in the formula unit of the catalyst, $m_K$ is the mass of the catalyst, $V_{S1}$ is the volume of the aniline standard solution, $c_{S1}$ is the molar concentration of the aniline standard solution, $V_{S2}$ is the volume of the perchloric acid standard solution, and $c_{S2}$ is the molar concentration of the perchloric acid standard solution.

## RESULTS AND DISCUSSION

The conditions of individual experiments (reaction time $t_i$ and the mole ratio of reactants at the start $Z_i$), and corresponding values of conversion of PHBA $z_i$, the quantity $\alpha_i$, and the function $F_i$ are given in Table 1. The reaction rate characterized by constant $\alpha$ was evaluated as weighted average of value $\alpha_i$ when the mass is directly proportional to the time $t_i$; its value which was used in calculations to evaluate experiments with the catalysts is 0.165 $min^{-1}$ with standard deviation $s_\alpha$ = 0.028 $min^{-1}$ The sum of deviations of values $F_i$ from the according to eqn (*11*) expected values $F$ is equal to zero. The time dependence of the function $F$ and $F_i$ values are plotted in Fig. 1. Ten of 18 experiments were carried out at the initial reactants mole ratio $1.03 < Z < 1.06$, the remaining at $1.18 < Z < 1.20$. Both sets of points ($t_i$, $F_i$) are spread in diagram about both sides of the evaluated straight line. The evaluation of the first set of experiments by the same manner as given above for all experiments gave the $\alpha$ value 0.161 $min^{-1}$ with standard deviation $s_\alpha$ = 0.027 $min^{-1}$, the analogical evaluation of the second set gave the values $\alpha$ = 0.170 $min^{-1}$ and $s_\alpha$ = 0.032 $min^{-1}$ Consequently, the quantity $\alpha$ is really independent of the $Z$ in the error interval.

By the same method as described for the acetylation of PHBA, the kinetics of acetylation of 6-hydroxy-2-naphthoic acid was also investigated [10], evaluation of 10 experiments in the domain $1.01 < Z < 1.07$ gave

**Table 1.** Kinetic Data of the Acetylation of PHBA at 125 °C

| | $t_i$ / min | | $Z_i$ | $F_i$ | $\alpha_i$ / $min^{-1}$ |
|---|---|---|---|---|---|
| 1 | 7 | 0.35631 | 1.1850 | 0.98 | 0.140 |
| 2 | 7.5 | 0.35700 | 1.0353 | 1.08 | 0.144 |
| 3 | 15 | 0.60846 | 1.1833 | 2.57 | 0.171 |
| 4 | 15 | 0.60007 | 1.0345 | 2.88 | 0.192 |
| 5 | 30 | 0.72662 | 1.1860 | 4.09 | 0.136 |
| 6 | 30 | 0.70354 | 1.0384 | 4.47 | 0.149 |
| 7 | 40 | 0.83871 | 1.0389 | 9.32 | 0.233 |
| 8 | 45 | 0.81702 | 1.1919 | 6.19 | 0.137 |
| 9 | 46 | 0.82216 | 1.0319 | 8.51 | 0.185 |
| 10 | 55 | 0.86575 | 1.1806 | 8.29 | 0.151 |
| 11 | 65 | 0.81925 | 1.0392 | 8.21 | 0.126 |
| 12 | 90 | 0.86076 | 1.0359 | 11.01 | 0.122 |
| 13 | 90 | 0.92278 | 1.1926 | 12.24 | 0.136 |
| 14 | 120 | 0.92649 | 1.0568 | 18.73 | 0.156 |
| 15 | 120 | 0.97609 | 1.1907 | 23.20 | 0.193 |
| 16 | 120 | 0.97961 | 1.1948 | 24.55 | 0.205 |
| 17 | 180 | 0.95790 | 1.0384 | 32.41 | 0.180 |
| 18 | 240 | 0.96712 | 1.0425 | 37.87 | 0.158 |

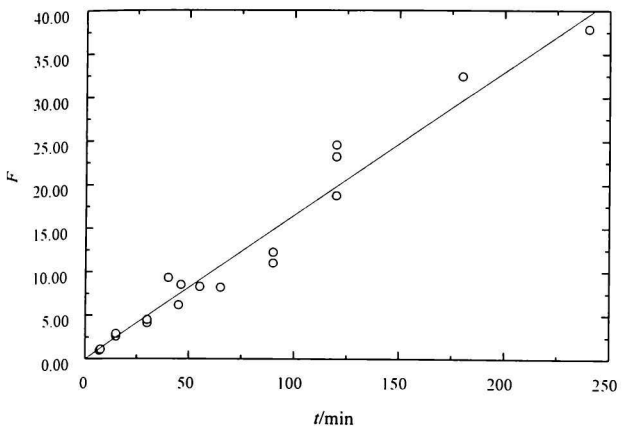


**Fig. 1.** Time dependence of the function $F$ at 125 °C.

$\alpha$ value 1.616 $min^{-1}$ Consequently, the acetylation of 6-hydroxy-2-naphthoic acid is 17 times more rapid than the acetylation of PHBA, which can be explained by lower acidity of phenol group in contrast to PHBA.

The experiments with catalysts were carried out, in most cases, at their mass fractions in the range from $1.26 \times 10^{-3}$ to $8 \times 10^{-3}$, reaction times between 4 min and 60 min and at initial reactants mole ratio $Z$ in the range from 1.04 to 1.08. These limits were exceeded in cases of sodium acetate ($0.95 < Z < 1.20$ and $0.72 < z < 0.99$), calcium acetate hydrate ($1.04 < Z < 1.17$ and $0.75 < z < 0.98$), disodium hydrogenphosphate dodecahydrate ($1.06 < Z < 1.11$), potassium acetate ($1.06 < Z < 1.16$), and pyridine ($1.00 < Z < 1.03$). In cases of substances with bound water, the mass of acetic anhydride for the calculations of ratios $Z$ and conversions $z$ was calculated as the difference between the weighed mass multiplied with mass fraction and the mass which was theoretically hydrolyzed with bound water.

The results of the experiments with catalysts are given in Table 2 where $n$ is a number of performed experiments. The $\kappa$ values were evaluated as weighted averages of $\kappa_i$ values which had been calculated for individual experiments from eqn (*18*), the masses being directly proportional to reaction times. Standard deviations values $s_\kappa$ indicate the values $\kappa$ afford no exact but semiquantitative information about catalytic effectiveness of tested substances. The results vacillation is caused not only by a small number of experiments but, in most cases, mainly by the fact that the time needed for the dissolution of solid catalyst is significant and, in addition, rather inreproducible. The same is valid for relative reaction acceleration $u_{0.001}$ values at catalyst mass fractions $w_K$ values 0.001 which were evaluated according to eqn (*21*) and their vacillations are illustrated by their standard deviations $s_{u(0.001)}$.

The negative values $\kappa$ were found for triphenylphosphane, antimony(III) oxide, dibutyltin maleinate, and zirconium(IV) oxide but their standard deviations $s_\kappa$ demonstrate that a retardation effect of them is not indicative. On the other hand, no positive catalytic effect is indicative for chromium(III) ac-

**Table 2.** Catalytic Effectiveness of Tested Catalysts at 125 °C

| Catalyst | $n$ | $\kappa$ | | $u_{0.001}$ | $s_{u(0.001)}$ |
|---|---|---|---|---|---|
| Triphenylphosphane oxide | 4 | −143 | 256 | 0.86 | 0.26 |
| Antimony(III) oxide | 4 | −138 | 206 | 0.86 | 0.21 |
| Dibutyltin maleinate | 4 | −75 | 83 | 0.93 | 0.08 |
| Zirconium(IV) oxide | 4 | −7 | 68 | 0.99 | 0.07 |
| Chromium(III) acetate | 4 | 40 | 80 | 1.04 | 0.08 |
| Diuranyl-zinc acetate | 4 | 100 | 518 | 1.10 | 0.52 |
| Triphenylphosphane | 4 | 293 | 69 | 1.29 | 0.07 |
| Copper(II) acetate monohydrate | 4 | 347 | 213 | 1.35 | 0.21 |
| Disodium hydrogenphosphate dodecahydrate | 6 | 771 | 475 | 1.77 | 0.47 |
| Disodium phenylphosphate dihydrate | 4 | 1 033 | 275 | 2.03 | 0.28 |
| Zinc acetate dihydrate | 4 | 1 201 | 255 | 2.20 | 0.26 |
| Potassium acetate | 4 | 1 357 | 196 | 2.36 | 0.20 |
| Vanadium(IV) oxide | 4 | 2 018 | 652 | 3.02 | 0.65 |
| Sodium acetate | 8 | 2 396 | 961 | 3.40 | 0.96 |
| Lithium acetate dihydrate | 4 | 3 876 | 329 | 4.88 | 0.33 |
| Nickel(II) acetate tetrahydrate | 4 | 4 675 | 430 | 5.67 | 0.43 |
| Barium acetate monohydrate | 4 | 4 841 | 2 867 | 5.84 | 2.87 |
| Magnesium acetate tetrahydrate | 5 | 5 040 | 706 | 6.04 | 0.71 |
| Manganese(II) acetate | 4 | 5 656 | 2 569 | 6.66 | 2.57 |
| Cobalt(II) acetate | 6 | 6 547 | 1 030 | 7.55 | 1.03 |
| Nickel(II) hydroxide | 4 | 8 050 | 1 678 | 9.05 | 1.68 |
| Calcium acetate monohydrate | 6 | 9 023 | 3 422 | 10.02 | 3.42 |
| Pyridine | 6 | 13 359 | 1 895 | 14.36 | 1.90 |

etate, diuranyl-zinc acetate, and triphenylphosphane for which positive $\kappa$ values were found from the viewpoint of their standard deviations.

It is evident from Table 2, inspite of the abovementioned variances of results that a series of tested substances significantly accelerates the acetylation of PHBA with acetic anhydride. Pyridine exhibits the highest catalytic effect that is not surprising. However, the removal of pyridine spots from the product of acetylation *in situ* before the next treatment would make a complication and it is not exactly known yet, how their presence will affect the subsequent acidolytic copolycondensation. From this viewpoint, favourable results were found in cases of acetates of nickel(II), barium, magnesium, manganese(II), and, especially, in cases of cobalt(II) acetate and nickel hydroxide. The substances of the last series can be altogether used as catalysts of acidolytic copolycondensation, as given in patent literature, and their presence in the reaction mixture is, consequently, rather favourable from the viewpoint of its subsequent treatment. However, it is worth mentioning that even 0.1 % content of the most effective catalyst accelerates the reaction approximately 14 times, that is less than the ratio of rate constants of uncatalyzed acetylations of 6-hydroxy-2-naphthoic acid and PHBA.

There is evident from the given results that the preparation of PABA *in situ* for the subsequent acidolytic copolycondensation to aromatic polyesters is possible. It is possible namely to extrapolate from our results that, using 0.1 % content of the catalysts given in the lower part of Table 2, the conversion should reach 99.99 % in 10 to 15 h and in 2 to 4 h at 1 % and 5 % excess of acetic anhydride, respectively. The final choice of suitable catalyst has to be optimized with respect to the subsequent acidolysis.

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