Effect of Tertiary Amines on the Hydrolysis Kinetics of Benzoyl Chloride in Water-Dioxane Solutions

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The main object of this study was to study the effect of pyridine, 2-methyl pyridine, 3-methyl pyridine, 2,6-dimethyl pyridine, quinoline and tribenzylamine on the hydrolysis kinetics of benzoyl chloride in water-dioxane solutions. The investigation has been made by means of gas-liquid chromatography measurements. Almost equal rate constants have been determined for the hydrolysis reaction of benzoyl chloride in dioxane solutions. The catalytic effect of the studied range of tertiary amines on the hydrolysis reaction of benzoyl chloride was determined.

Key Words: Benzoyl chloride, Hydrolysis kinetics, Tertiary amines, Water-dioxane solutions.

INTRODUCTION

Benzoyl chloride, a typical acyl chloride, reacts with water to give benzoic and hydrochloric acids:

$$C_6H_5COCl + H_2O \rightarrow C_6H_5COOH + HCl$$
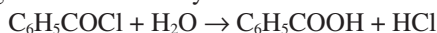
The interest in the kinetics and mechanism of hydrolysis of acyl chlorides has arisen for almost a century. The first study was published in 1927 by Berger and Olivier[1]. The hydrolysis kinetic studies of acyl chlorides are important due to the use of highly reactive acyl chloride, as one of the monomers, in methods of synthesizing high polymers by polycondensation on an interface. In addition, hydrolysis of acyl chlorides is the principal parasitic reaction tending to reduce the polymer yield because the interfacial polycondensation proceeds in the presence of aqueous alkali[2].

A number of kinetic studies have been reported on the hydrolysis of benzoyl chloride. They were carried out in aqueous acetone, alcohol and in pure water. Berger and Olivier[1] studied the hydrolysis of benzoyl chloride in aqueous acetone. The hydrolysis of benzoyl chloride in aqueous acetone, acetone-water mixtures and acetone-dioxan mixtures has been extensively studied by Hudson and co-workers[3-7]. They concluded that the hydrolysis of benzoyl chloride in solvents rich in acetone and water proceed by bimolecular S_N2 and S_N1 mechanisms, respectively.

Wang *et al.*[8] studied the kinetic reaction of benzoyl chloride and sodium carboxylate using pyridine 1-oxide as an inverse phase-transfer catalyst in a system of the two phases H_2O and CH_2Cl_2. They concluded that the reaction rate was strongly affected by the concentration of pyridine l-oxide in the organic phase and by the concentration of carboxylate ion in the aqueous phase.

The effect of tertiary amines on the hydrolysis kinetics of benzoyl chloride in water-dioxane solutions has so far remained unexplained. Therefore, this paper aimed to investigate this effect.

The kinetic reaction,

$$C_6C_5COCl + H_2O = C_6H_5COOH + HCl \qquad (1)$$

was carried out in dioxane at 25 ± 0.01 ºC. As a tertiary amine, pyridine, 2-methyl pyridine, 3-methyl pyridine, 2,6-dimethyl pyridine, quinoline and tribenzylamine were used.

It is well known that the hydrolysis of benzoyl chloride without a catalyst proceeds with a negligible rate. According to Cherkasova *et al.*[9], hydrolysis of benzoyl chloride in dioxane with different water content in the presence of a catalyst, a tertiary amine proceeds by the following scheme:
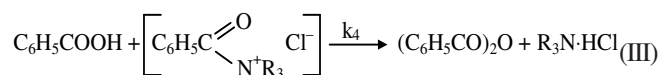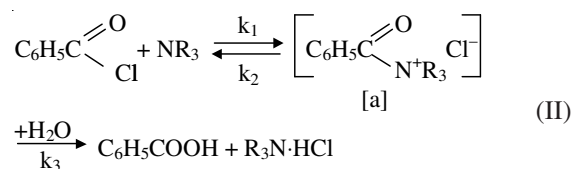
The intermediate group [a] obviously has the structure of acyl ammonium salt. Electrophilicity of the carbon atom in

such a structure increases sharply due to the neighborhood with ammonium nitrogen atom, which is apparently the main cause of acceleration of the acylation reaction in the presence of tertiary amines. Thus, amines play the role of intermediate carriers of acyl groups.

Based on preliminary kinetic studies, benzoic acid and tertiary amine hydrochloride (NR·HCl) released during the hydrolysis of benzoyl chloride did not influence the rate of the studied reaction. Hence, stage (III) practically does not occur. Accordingly, the hydrolysis reaction of benzoyl chloride in the presence of tertiary amines can be presented by the following scheme:

$$C_6H_5COCl + NR_3 + H_2O \rightarrow C_6H_5COOH + R_3N \cdot HCl (IV)$$
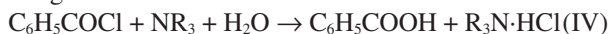
As follows from the Scheme (IV), hydrogen chloride released during the process binds the tertiary amine. In this regard, the concentration of tertiary amine in the reaction mixture will be changed over time.

Kuritsin[10] studied the kinetics of the hydrolysis reaction of benzoyl chloride in dioxane containing 1 to 3 mol/L of water. He found that the reaction obeys the laws of first-order reaction. The kinetic equation for the reaction (IV) is:

$$-\frac{d(c_{0,bc} - x)}{d\tau} = k_{ob}(c_{0,bc} - x) \cdot (c_{0,ta} - x) \quad (1)$$

where, $c_{0,bc}$ and $c_{0,ta}$ are the initial concentrations of benzoyl chloride and tertiary amine, respectively; x is the change in concentration of benzoyl chloride to time τ; k_{ob} is the observed rate constant, which can be calculated as follows:

$$k_{ob} = k_0 c_{0,H_2O} \quad (2)$$

Since in all the kinetic experiments the initial concentration of water $c_{0,H_2O} \gg c_{0,ta}$ and $c_{0,bc}$ [eqn. (2)], the rate constant (k) of reaction (IV) is referred to a single concentration of water. Therefore, from eqn. (1), it follows that:

$$k_{ob} = \frac{1}{\tau(c_{0,ta} - c_{0,bc})} \ln \frac{c_{0,bc}(c_{0,ta} - x)}{c_{0,ta}(c_{0,bc} - x)} \quad (3)$$

or

$$k_{ob} = \frac{x}{\tau \cdot c_{0,bc}(c_{0,bc} - x)} \quad (4)$$

if the kinetic experiment $c_{0,bc} = c_{0,ta}$.

EXPERIMENTAL

Purifications of benzoyl chloride, tertiary amines and dioxane were carried out by the method described by Vorobuv *et al.*[11]. Kinetic experiment and analysis of mixture reaction was adopted from Shebanova and Ivanova[12].

Benzoyl chloride (chemically pure grade) was distilled under vacuum [boiling temperature (T_b) of 65 ºC at pressure (P) of 6 mm Hg]. Water was twice distilled at atmospheric pressure. The first distillation was carried out by adding KMnO_4 (T_b = 99.8 ºC at P = 756 mm Hg). Tertiary amines: pyridine (pure grade), 2-methyl pyridine (pure grade), 2,6-dimetilpiridin (pure grade), quinoline (pure grade) were dried by solid potassium hydroxide and then distilled. Pyridine was distilled at atmospheric pressure, while 2-methyl pyridine, 2,6-dimethyl pyridine were distilled under reflux at atmospheric pressure. Quinoline was distilled under a vacuum. Boiling temperature of tertiary amines are listed in Table-1.

TABLE-1
BOILING TEMPERATURE OF TERTIARY AMINES

Tertiary amine	b.p. (ºC)	Pressure, mm Hg
Pyridine	114.5	760
2-methyl pyridine	127.0	745
2,6-Dimethyl pyridine	143.0	760
Quinoline	124.1	18

For the treatment of acidic compounds, a solvent of dioxane (pure grade) shaken with 50 % aqueous NaOH was used. After separation from alkali, dioxane was boiled for 6 h with sodium metal and then distilled on a column at atmospheric pressure (T_b = 100.5 ºC at P = 757 mm Hg). The water content, which was determined by gas-liquid chromatography, was 0.107 %. In all experiments, only freshly prepared dioxane and water were used.

The study of hydrolysis kinetics reaction of benzoyl chloride was carried out in an oven at a temperature of 298.15 ± 0.01 ºC. Kinetic experiment began with the preparation of working solutions of reagents in dioxane. Working solution of benzoyl chloride was prepared in one pycnometer and water with catalyst was in another.

After the preparation of working solutions, 5 mL of benzoyl chloride was poured into reaction flasks. Then, water was added to flasks and the solution was stirred. The moment of water addition was considered to be the beginning of the reaction. In the all experiments, the initial concentration of benzoyl chloride and water in dioxane were 0.005 and 1 mol/L, respectively, while the concentration of catalyst was in the range of 0.005-0.02 mol/L.

The reaction propagation was observed by monitoring the change of unreacted benzoylchloride in the reaction sample. The reaction was determined using diethylamine toluene solution. The reaction was stopped using diethylamine toluene solution. Since diethylamine is a strong base and many times more reactive than water, it almost instantly connects unreacted benzochloride. Excess diethylamine was titrated with a solution of hydrogen chloride in isopropyl alcohol. As an indicator, bromophenol blue dissolved in isopropyl alcohol was used.

RESULTS AND DISCUSSION

As an example, the rate constants, which were calculated by using eqn. (3) in one of the kinetic experiments are listed in Table-2. From the data listed in Table-2, the rate constants are approximately constant in the range of degrees of conversion of 11 to 55 %.

Once again, the constancy of k_{obs} values with time confirms that the benzoic acid and tertiary amine hydrochloride formed during the hydrolysis do not influence the rate of the studied reaction.

The arithmetic means of the reaction (I) rate constants at various concentrations of benzoyl chloride and tertiary amine in the reaction mixture are listed in Table-3.

As in Shebanova and Kulibaba[13], we have carried out many kinetic experiments in which tribenzylamine was injected as an acceptor of hydrogen chloride. In this case, the catalyst concentration remained constant in the reaction mixture. In the presence of tribenzylamine, the kinetic rate equation takes the form:

$$-\frac{d(c_{0,bc} - x)}{d\tau} = k'_{obs}(c_{0,bc} - x) \qquad (3)$$

In equation (3),

$$k'_{obs} = k_{obs} \cdot c_{0,ta} \qquad (4)$$

where, $c_{0,ta}$ initial concentration of tertiary amine. Integrating equation (3), gives:

$$k'_{ob} = \frac{1}{\tau} \ln \frac{c_{0,bc}}{c_{0,bc} - c} \qquad (5)$$

An example of the rate constants k_{ob} and k'_{ob} for the studied reaction in the presence of pyridine is presented in Table-4.

TABLE-2
RESULTS OF KINETIC MEASUREMENTS FOR THE HYDROLYSIS REACTION OF BENZOYL CHLORIDE IN DIOXANE CONTAINING 1 mol/L OF WATER
($c_{0,bc}$ = 0.005 mol/L; $c_{0,pyridine}$ = 0.01 mol/L)

τ (min)	$\frac{x}{c_{0,bc}} \cdot 100\%$	k_{obs} (L/mol min)
10.0	11.0	1.20
12.0	12.5	1.15
15.0	16.3	1.24
25.0	24.8	1.22
37.1	34.8	1.28
40.0	36.2	1.25
45.0	40.9	1.32
45.1	41.8	1.30
50.2	43.2	1.29
60.0	46.7	1.21
70.0	54.9	1.30
$k_{average}$ = 1.25 ± 0.099		

TABLE-3
ARITHMETIC AVERAGE VALUES OF REACTION (I) RATE CONSTANTS AT VARIOUS CONCENTRATIONS OF BENZOYL CHLORIDE AND TERTIARY AMINE IN THE REACTION OF MIXTURE

Initial concentration (mol/L)		k_{obs} (L/mol min)
Benzoyl chloride	Tertiary amine	
Pyridine		
0.005	0.000	1.25 ± 0.099
0.005	0.010	1.28 ± 0.060
0.005	0.005	1.32 ± 0.097
0.005	0.015	1.19 ± 0.032
0.005	0.075	1.23 ± 0.098
0.005	0.020	1.24 ± 0.057
0.025	0.010	1.20 ± 0.072
2-Methyl pyridine		
0.005	0,015	0.155 ± 0.012
0.005	0.020	0.156 ± 0.006
2,6-Dimethyl pyridine		
0.005	0.010	0.8260 ± 0.0250
0.005	0.015	0.7860 ± 0.0200
0.005	0.020	0.7940 ± 0.0330
0.001	0.020	0.8090 ± 0.0230
Quinoline		
0.01	0.020	0.0587 ± 0.0016

From the data listed in Table-4, it follows that the magnitude of the rate constant k_{obs}, which was calculated by using eqns. (3,4,5) is matched within the limits of experimental error.

TABLE-4
VALUE OF THE RATE CONSTANTS k_{obs} AND k'_{ob} FOR THE HYDROLYSIS REACTION OF BENZOYL CHLORIDE AT 25 ºC (CATALYST-PYRIDINE)

Initial concentration Cº (mol/L)	k_{obs} (L/mol min)	k'_{obs} (min^{-1})
0.005	1.21	0.00604
0.010	1.26	0.01260

Based on the data listed in Table-3, the calculated average values of the rate constants of the hydrolysis reaction of benzoyl chloride in dioxane containing one mole per liter of water in the presence of various catalysts are listed in Table-5.

Analyzing the data given in Table-5, from the studied range of tertiary amines, pyridine and 3-methylpyridine have the strongest catalytic effect on the reaction of (IV), whereas quinoline has the weakest effect.

In the transition from quinoline to 3-methyl pyridine, the values of the catalytic rate constant increased 38 times and the catalytic activity (k_{ob}/k'_{obs}) of 3-methyl pyridine and quinoline increased 2100 and 57 times, respectively.

TABLE-5
CATALYTIC RATE CONSTANT k_{obs} FOR REACTION (IV) AT 25 ºC AND THE BASICITY OF TERTIARY AMINES

Catalyst	k_{obs} (L/mol·min)	pKa (H$_2$O, 25 ºC)
Pyridine	1.2400 ± 0.0740	5.17
2-Methyl pyridine	0.1560 ± 0.0089	5.97
3-Methyl pyridine	2.3100 ± 0.0950	5.68
2,6-Dimethyl pyridine	0.8040 ± 0.2500	6.75
Quinoline	0.0612 ± 0.0027	5.01
Without a catalyst, k'_{ob} = 1.08 × 10^{-3} ± 0.06		

From the data listed in Table-5, the catalytic activity of tertiary amine is not determined by its basicity only, but also by sterical factors. Introduction of methyl groups in any position of pyridine nucleus leads to an increase in the basicity of the tertiary amine. However, these same groups have very different effects on catalytic activity: in the positions 2 and 6, they reduce the catalytic activity (2 - 8 times) and cause the growth of catalytic activity in position 3 ($\approx$ 2 times). Quinoline has a weak catalytic effect on the speed of the process than pyridine and its derivatives. This can be explained, probably, by the low basicity of quinoline and the filmed effect of nitrogen substituent in the α-position.

Conclusion

The effect of tertiary amines on the hydrolysis kinetics of benzoyl chloride in water-dioxane solutions was investigated successfully. From the results of kinetic measurements for the hydrolysis reaction of benzoyl chloride in dioxane containing 1 mol/L of water, the rate constants were approximately constant in the range of degrees of conversion of 11 to 55 %. From the studied range of tertiary amines, it was found that pyridine and 3-methyl pyridine have the strongest catalytic effect on the hydrolysis reaction of benzoyl chloride, whereas quinoline has the weakest effect. It also found that the catalytic activity of tertiary amine was not determined by its basicity only, but also by sterical factors.

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