HYDROLYSIS OF 2-PHENYLBENZOXAZOLE AND o-BENZAMIDOPHENOL IN AQUEOUS SOLUTIONS OF SULFURIC ACID

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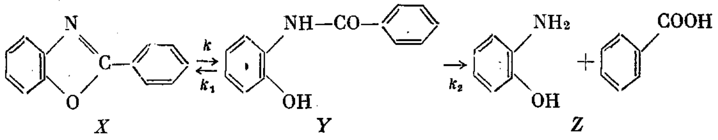
In the thermal destruction of polymers, water and acid and basic substances are formed, which can initiate reactions of ionic destruction of the polymer. In view of this, in the present work we studied the kinetics and mechanism of the hydrolysis of 2-phenylbenzoxazole (PBO) and o-benzamidophenol (BAP), which are models of cyclized and noncyclized fragments of polybenzoxazoles [1].

EXPERIMENTAL METHOD

We used PBO (mp 101-102°), BAP (mp 169-169.5°), o-amidophenol and benzoic acid (cp grade), the characteristics of which corresponded to the data of [2, 3]. The acid hydrolysis of BAP was investigated at 100-150° and a H_2SO_4 concentration of 8-66% by mass. Aqueous solutions of H_2SO_4 were prepared from grade especially pure conc. H_2SO_4. At a reagent concentration of $(0.5\text{-}1.5) \cdot 10^{-4}$ M, the influence of the reagents on the thermodynamic parameters of the medium is practically excluded. The experiments were conducted in an atmosphere of argon. The kinetics of the hydrolysis of BAP was studied spectrophotometrically according to the change in the absorption at 249 and 304 nm, where the greatest differences are observed in the absorption spectra of the starting materials and reaction products (Fig. 1).

When PBO is heated [4] in aqueous solutions of mineral acids, BAP is formed and is converted under the same conditions to PBO



We investigated the kinetics of the conversion of BAP. The change in X, Y, and Z with time is described by the equations [5]

$$X = -B_0 k_1 \frac{e^{r_1 t} - e^{r_2 t}}{r_2 - r_1}$$

$$Y = -B_0 \frac{(k + r_1) e^{r_1 t} - (k + r_2) e^{r_2 t}}{r_2 - r_1}$$

$$Z = B_0 - (X + Y)$$

$$r_1 = \frac{-a + \sqrt{a^2 - 4b}}{2}$$

$$r_2 = \frac{-a - \sqrt{a^2 - 4b}}{2}$$

$$a = k + k_1 + k_2$$
$$b = k \cdot k_2$$

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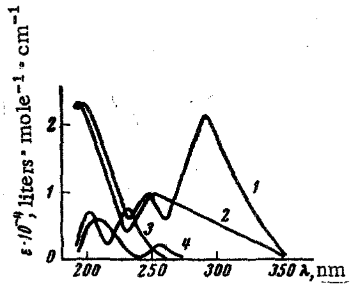


Fig. 1

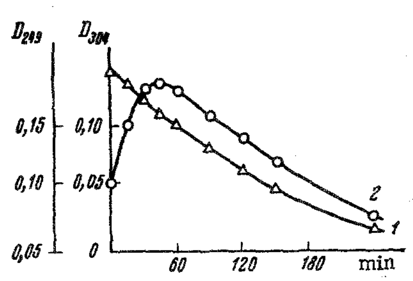


Fig. 2

Fig. 1. UV spectra: 1) 2-phenylbenzoxazole; 2) o-benzamidophenol; 3) benzoic acid; 4) o-aminophenol.

Fig. 2. Change in the optical density at wavelengths 249 (1) and 304 (2) nm during the conversion of o-benzamidophenol in H_2SO_4.

The optical density at 249 and 304 nm (see Fig. 1) can be expressed as follows:

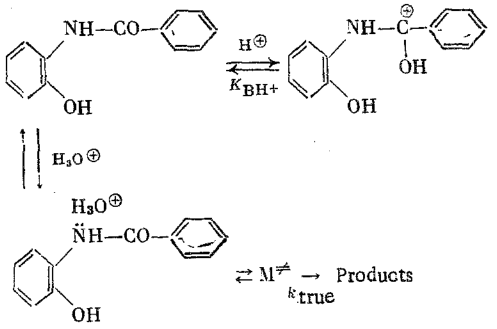
$$D_{249} = X\varepsilon'_{249} + Y\varepsilon''_{249} + Z\varepsilon'''_{249}$$

$$D_{304} = X\varepsilon'_{304} + Y\varepsilon''_{304}$$

where ε', ε", and ε‴ are the coefficients of extinction of PBO, BAP, and the reaction products. As was established by preliminary experiments, for the individual substances and their mixtures, the Beer–Lambert law is observed. The values of the effective rate constants of all the reactions were found by treatment of the experimental data (Fig. 2) on a BÉSM-6 electronic computer. As a rule, the error in the calculation did not exceed 10% (in experiments with 8% H_2SO_4 it reached 20%). The constants found (Table 1) are satisfactorily described by an Arrhenius equation. The calculated values of the effective activation energy of the hydrolysis of PBO and BAP and the cyclization of o-benzamidophenol were practically independent of the concentration of H_2SO_4 and were 29 ± 1, 24 ± 1, and 32 ± 1 kcal/mole, respectively.

DISCUSSION OF RESULTS

Hydrolysis of o-Benzamidophenol. The limiting step in the hydrolysis of amides is attack of the hydroxonium ion on the unprotonated amide bond [6]. Protonation of the carbonyl oxygen atom leads to the formation of a nonreactive form, since it prevents approach of the hydroxonium ion to the amide bond



The change in k_{eff} of the hydrolysis of amides in acid media is described by the equation

$$k_{eff} = \frac{k_{true} C_{H_3O^+}}{1 + h_A/K_{BH^+}} \tag{1}$$

where k_{true} is the true rate constant of the hydrolysis reaction; $C_{H_3O^+}$ is the concentration of hydroxonium ions [7]; h_A is the amide acidity ($-\log h_A - H_A$) [8]; K_{BH^+} is the thermodynamic constant of the basicity of the carbonyl oxygen of the amide bond.

This equation explains the passage of k_{eff} of the reaction of hydrolysis of amides through a maximum relative to the acid concentration (Fig. 3). In dilute solutions of acid, when the concentration of the nonprotonated form of the amide is much greater than the concentration of the protonated form

$$k_{eff} = k_{true} C_{H_3O^+} \tag{2}$$

TABLE 1. Effective Rate Constants of the Hydrolysis of 2-Phenylbenzoxazole (k), the Hydrolysis (k_2) and Cyclization (k_1) of o-Benzamidophenol

$C_{H_2SO_4}$, %	Constant $\cdot 10^2$, min^{-1}	100°	110°	120°	130°	140°	150°
8	k	3,0	8,7	22	57		
	k_1	0,18	0,55	1,7	5,2		
	k_2	0,26	0,81	1,7	4,3		
17	k	1,9	5,0	14	36		
	k_1	0,50	1,6	4,8	11		
	k_2	0,63	1,2	2,4	5,5		
31	k		4,4	11	25	63	
	k_1		2,8	8,7	18	48	
	k_2		1,3	3,0	8,3	13	
57	k			0,91	2,7	6,0	16
	k_1			2,7	7,9	17	49
	k_2			1,1	3,0	4,4	12
66	k			0,60	1,7	4,2	11
	k_1			1,7	4,5	12	32
	k_2			0,68	1,2	3,5	7,8

TABLE 2. Effective Rate Constants of the Hydrolysis of 2-Phenylbenzoxazole (k), Hydrolysis (k_2) and Cyclization (k_1) of o-Benzamidophenol at 25° and Various Concentrations of Sulfuric Acid

$C_{H_2SO_4}$, %	k, min^{-1}	k_1, min^{-1}	k_2, min^{-1}
8	$1{,}55 \cdot 10^{-6}$	$3{,}54 \cdot 10^{-8}$	$8{,}0 \cdot 10^{-7}$
17	$9{,}15 \cdot 10^{-7}$	$8{,}51 \cdot 10^{-8}$	$1{,}37 \cdot 10^{-6}$
31	$7{,}1 \cdot 10^{-7}$	$1{,}44 \cdot 10^{-7}$	$2{,}0 \cdot 10^{-6}$
57	$6{,}17 \cdot 10^{-8}$	$4{,}9 \cdot 10^{-8}$	$6{,}03 \cdot 10^{-7}$
66	$5{,}13 \cdot 10^{-8}$	$3{,}16 \cdot 10^{-8}$	$3{,}9 \cdot 10^{-7}$
k_{true}	$6 \cdot 10^{-6}$*	$0{,}6 \cdot 10^{-6}$	$4{,}0 \cdot 10^{-6}$
K_{BH+}	—	190	210

*$k_{true} \cdot K_{BH+}$.

In concentrated solutions of acid, where the carbonyl oxygen of the amide bond is substantially protonated

$$k_{eff} = \frac{k_{true} K_{BH+} C_{H_3O+}}{h_A} \tag{3}$$

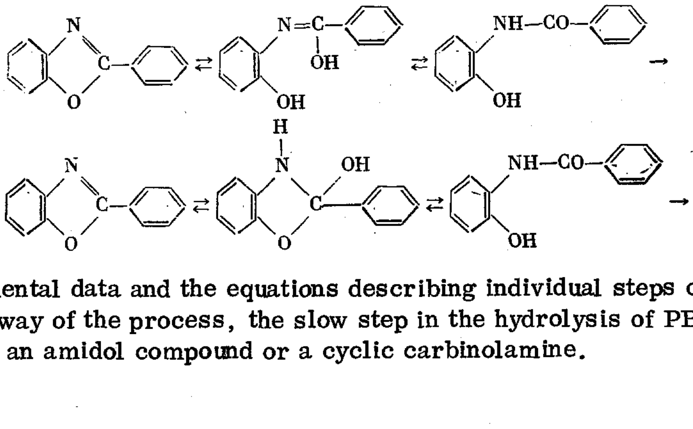
The thermodynamic parameters of H_2SO_4 were most reliably determined at 25°; therefore k_{eff} of the rate were extrapolated to 25° (Table 2). To determine the values of k_{true} and K_{BH+}, let us represent Eq. (1) in the following form

$$\frac{C_{H_3O+}}{k_{eff}} = \frac{1}{k_{true}} + \frac{1}{K_{BH+} k_{true}} h_A \tag{4}$$

In the case of graphical solution of this equation, values of k_{true} and K_{BH+} were obtained (see Table 2).

Hydrolysis of 2-Phenylbenzoxazole and Cyclization of o-Benzamidophenol. As can be seen from Fig. 3, the effective rate constant of the hydrolysis of PBO decreases with increasing acid concentration, while the cyclization of BAP passes through a maximum. In the establishment of the mechanism of the two processes, it is advisable to consider them jointly, since according to the principle of detailed equilibrium, the intermediate compounds in these reactions should have the same structure. Since reactions both at the C=N bond and at the C–O bond can occur during hydrolysis of PBO, two reaction pathways are possible. In the investigation of the synthesis of polybenzoxazoles it was postulated that the formation of the benzoxazole ring in the vacuum heat-treatment of polyoxyamides should proceed through an amidol compound [9-11]. The possibility of amide–amidol tautomerism was assumed in [12-14]. In a number of studies on the hydrolysis of Schiff's bases, benzimidates [15, 16], and 2-methyloxazoline [17], it was assumed that the process occurs through the formation of a carbinolamine.

On the basis of the literature data, let us assume that the acid catalytic hydrolysis of PBO and the cyclization of BAP can proceed through the formation of an amidol compound or a cyclic carbinolamine



An analysis of the experimental data and the equations describing individual steps of the reaction show that regardless of the pathway of the process, the slow step in the hydrolysis of PBO and in the cyclization of BAP is the formation of an amidol compound or a cyclic carbinolamine.

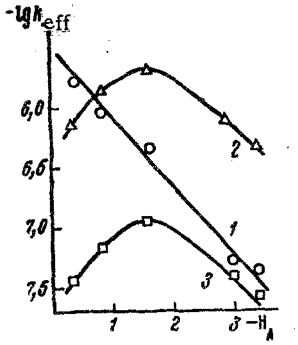


Fig. 3

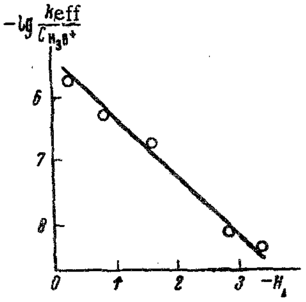


Fig. 4

Fig. 3. Dependence of the effective rate constant of the hydrolysis of 2-phenylbenzoxazole (1), the hydrolysis (2), and cyclization (3) of o-benzamidophenol on the acidity of the medium at 25°.

Fig. 4. Dependence of $C_{H_3O^+}/k_{eff}$ on H_A for the hydrolysis of 2-phenylbenzoxazole at 25°.

The dependence of k_{eff} of the cyclization of BAP on the acid concentration is satisfactorily described by Eq. (1). The values of the thermodynamic constant of the basicity of the carbonyl oxygen of the amide bond, calculated from the data on the hydrolysis and cyclization of BAP, proved close (see Table 2).

The dependence of k_{eff} of the hydrolysis of PBO on the acid concentration is described by Eq. (3) (Fig. 4); consequently, the nonprotonated form of PBO is reactive, while the protonation of PBO occurs chiefly at the oxygen and is accompanied by the formation of a nonreactive form. It can be assumed that the hydrolysis of PBO proceeds analogously to the hydrolysis of amides, but in relatively dilute solutions of acid, PBO is already substantially protonated. At the present time it does not seem possible to determine the pathway of the hydrolysis of PBO and cyclization of BAP: through the formation of an amidol compound or a cyclic carbinolamine, since the two pathways are kinetically indistinguishable.

CONCLUSIONS

1. The kinetics of the hydrolysis of 2-phenylbenzoxazole, the hydrolysis and cyclization of o-benzamidophenol were studied spectrophotometrically.

2. The effective rate constant of the hydrolysis of 2-phenylbenzoxazole decreases with increasing H_2SO_4 concentration, while the effective rate constants of the hydrolysis and cyclization of o-benzamidophenol have maxima.

3. The dependence of the effective rate constants of the hydrolysis of 2-phenylbenzoxazole and the cyclization of o-benzamidophenol on the acid concentration is described by the same equations as the hydrolysis of amides, but in contrast to amides, in relatively weak solutions of acids 2-phenylbenzoxazole is already appreciably protonated.

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