

# Effect of Water on the Kinetics of the Catalytic Reaction between Benzoic Acid and Aniline

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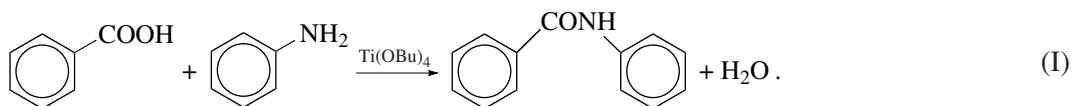
**Abstract**—Water forming in benzanilide synthesis from benzoic acid and aniline catalyzed by titanium tetrabutoxide does not influence the activity of the catalyst. The role of mass transfer processes associated with water removal from the system is revealed. The reversible deactivation of titanium tetrabutoxide by water occurs in the absence of vigorous water boiling and distillation. The stability of titanium tetrabutoxide to water is explained by the formation of titanium benzoate complexes at the initial stage of the reaction. These complexes enhance the resistance of the catalyst structure to hydrolysis.

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## INTRODUCTION

It was shown previously [1, 2] that the pretreatment of titanium tetrabutoxide (TTB) with water

vapor leads to essential changes in the catalytic activity of TTB in the reaction of benzoic acid with aniline:



After the absorption of up to 2 mol of water per mole of TTB, catalytic activity first increases by a factor of 3–5 and then falls to zero. The amount of water needed for the preactivation and subsequent complete deactivation of the catalyst is 40–45 times smaller than the amount of water resulting from reaction (I) (considering the extent of conversion).

Here, we report the effect of water on the kinetics of reaction (I).

## EXPERIMENTAL

### General

Benzoic acid, aniline, *ortho*-xylene, and TTB were purified and used according to published procedures [1–3]. The concentration of unreacted benzoic acid was determined by nonaqueous potentiometric titration [3]. Benzanilide was synthesized according to a standard procedure [3]. The catalyst was TTB, either activated by storage or freshly distilled. The resulting water was removed into a Dyne–Stark trap filled with *ortho*-xylene. A flask or a test tube with the reaction mixture was placed in a thermostat maintaining the temperature with an accuracy of 0.1 K. The reaction volume was 40

and 10 cm<sup>3</sup>, respectively. If necessary, air, nitrogen, or argon was bubbled through the boiling reaction mixture at a rate of 20–30 cm<sup>3</sup>/min. For minimization of the solvent carry-over, an effective water condenser was placed at the outlet of the Dyne–Stark trap.

### Interaction between Benzoic Acid and TTB

One gram (8.2 mmol) of benzoic acid, 1 g (2.9 mmol) of TTB, and 30 ml of *ortho*-xylene were placed into a flask fitted with a reflux condenser. The mixture was warmed to boiling and kept there for 5 min. The reaction mixture was analyzed by GLC on a Khrom-5 chromatograph (flame ionization detector, 2-m-long capillary column 3 mm in diameter packed with 1% silicon elastomer E-301 and 10% Apieson N on Chromaton N-AW-DMCS (0.2–0.25 mm), argon as the carrier gas, gas flow rate of 1.8 l/h, oven temperature of 160–230°C, evaporator temperature of 275°C). The marker was butyl benzoate obtained from benzoyl chloride and butanol according to a standard procedure [4] and purified by vacuum distillation.

## RESULTS AND DISCUSSION

It was noted previously [1–3], that, in an open system, a high conversion in reaction (I) is reached only under conditions of efficient water stripping. For this reason, the role of the mass transfer processes controlling the rate of water removal under conditions of boiling and stirring was studied qualitatively. The following regularities were observed with activated TTB as the catalyst:

(1) In a closed system (sealed tube), exposure of the mixture to 145°C for 1 h does not initiate reaction (I).

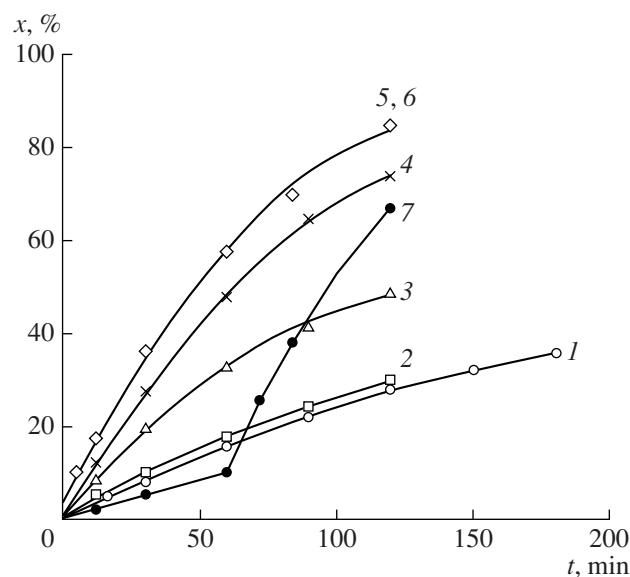
(2) In an open system under vigorous stirring, but in the absence of boiling, which was prevented by reducing the temperature by 1 K (to 144°C), benzanilide forms in low yield (5–15% in 1 h).

(3) Under conditions of water stripping, other things being equal, the benzanilide yield depends on the contact area between the liquid and the gas phase. The larger this area, the faster the reaction. For example, in catalytic acylation in test tubes 1 cm in diameter and in flasks 3 and 5 cm in diameter, the benzanilide yield in 1 h is 10, 18, and 48%, respectively.

The boiling rate can be controlled by varying the difference between the temperature of the thermostat with a flask and the boiling point of the reaction mixture (145°C). As follows from Fig. 1 (curves 2–5), as this difference increases, the reaction rate increases and reaches its limit at a temperature drop of 11°C. Under these conditions, the formation of a stable foam layer over the boiling mixture was noticed. If the temperature drop exceeds 11°C, the reaction rate no longer depends on it (Fig. 1, curve 6).

Efficient water stripping favors achieving the maximum benzanilide yield (58% in 1 h). A similar influence of mass transfer factors was previously observed in esterification and polyesterification reactions catalyzed by TTB, which are also accompanied by water release [5, 6]. Water can be removed not only by vigorous boiling, but also by bubbling a gas (nitrogen, argon, and air) through the reaction mixture. Under these conditions, reaction (I) can occur already at 135°C with a yield of up to 58–60% in 1 h.

These results indicate the important role of mass transfer in reaction (I). At a moderate water removal rate, the rate of reaction (I) is limited by mass transfer, specifically water evaporation. At a high mass transfer rate, the rate of reaction (I) is determined by the amidation rate and the reaction proceeds under kinetic control. This is indicated by the presence of a limit after which the rate of reaction (I) no longer depends on the difference between the thermostat temperature and the boiling point of the reaction mixture (Fig. 1). The absence of interaction between benzoic acid and aniline in a closed system cannot be explained by the reversibility of process (I). The equilibrium constant of the amidation reaction cannot be very small (for instance, in the similar reaction of acetic acid with aniline, the equilibrium constant is 1–5 [7]). Under the assumption



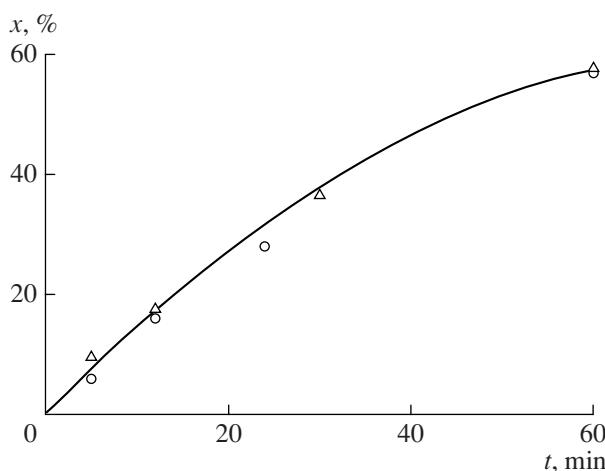
**Fig. 1.** Dependence of the conversion of benzoic acid into benzanilide on the reaction time at  $[PhCOOH]_0 = 0.2$  mol/l,  $[PhNH_2]_0 = 0.4$  mol/l, and  $[TTB]_0 = 0.004$  mol/l in boiling *ortho*-xylene at 145°C under conditions of water stripping: (1) freshly distilled TTB, thermostat temperature ( $T$ ) of 159.0°C; (2) activated TTB,  $T = 148.6^\circ\text{C}$ ; (3–6) activated TTB,  $T = (3) 151.9^\circ\text{C}$ , (4)  $154.2^\circ\text{C}$ , (5)  $156.6^\circ\text{C}$ , and (6)  $159.0^\circ\text{C}$ ; (7) activated TTB, exposure for 1 h at  $144^\circ\text{C}$  without boiling followed by rapid distillation at  $T = 159.0^\circ\text{C}$ .

that the equilibrium constant of reaction (I) is equal to ~0.5–1, the equilibrium conversion will be 40–60% for the reactant concentrations considered.

The noncatalytic reaction occurs slowly (the benzanilide yield is 0.5–1% in 1 h); therefore, it can be neglected. It was previously established [1] that *ortho*-xylene even after drying over sodium and distillation contains 0.026–0.028 wt % water. This amount is >3 times larger than the equivalent amount of the catalyst introduced into the reaction. Therefore, the absence of the catalytic reaction in the closed system can be explained by catalyst deactivation by the water initially present in *ortho*-xylene.

In order to evaluate the effect of water, we analyzed kinetic curves obtained for catalysts differing in activity, namely, freshly distilled TTB (low-activity catalyst) and the catalyst activated by storage [1, 2]. The kinetic curve for freshly distilled TTB under intensive water stripping is not S-shaped (Fig. 1, curve 1). According to earlier data [8, 9], this might indicate autocatalysis and TTB activation by resulting water. The kinetic curves for activated TTB do not show typical evidence of reaction slowdown caused by TTB autoinhibition. For example, there is no sharp decrease in the reaction rate at a moderate conversion (Fig. 1).

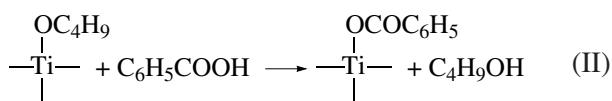
If water is not distilled off at the early stages of the reaction, the process kinetics will be significantly different. The following experiment was performed. A solution of the initial reagents and the catalyst in *ortho*-



**Fig. 2.** Superimposition of kinetic curves 6 ( $\Delta$ ) and 7 ( $\circ$ ) from Fig. 1 after the shift of the former to the origin of coordinates.

xylene was held at 144°C for 60 min (without boiling). The reaction mixture was sampled at 10-min intervals. Next, the mixture was rapidly (within 1–2 min) brought to vigorous boiling at 145°C and sampling was continued. As is clear from Fig. 1, kinetic curve 7 has a distinct kink at  $t = 60$  min, which corresponds to the onset of water stripping. If the onset point of intense boiling ( $t = 60$  min) is taken to be the initial point of curve 7 and the conversion reached by that time is ignored, curve 7, after being shifted, will coincide well with curve 6; that is, curves 6 and 7 will become identical (Fig. 2). Considering that the kinetic curves are monotonic throughout the time interval examined, it can be inferred that the catalyst does not react with water irreversibly to change its catalytic activity.

Since pure TTB is unstable even in the presence of traces of water, undergoing rapid hydrolysis and condensation, resulting in polybutoxytitanates (titanoxane polymers) [1, 2], the nature of the catalyst should be clarified. It was noted earlier [10, 11] that the interaction of carboxylic acids with TTB under esterification conditions results in catalytically active titanium(IV) acylates having an increased hydrolytic stability. Likewise, treatment with a carboxylic acid makes titanoxane polymers more resistant to hydrolysis [12]. From this standpoint, the stability of the catalytic activity of TTB during amidation and the fact that it is not affected by the resulting water can be explained by the formation of titanium(IV) benzoate complexes at the early stages of the reaction. These complexes seem to be the true catalysts:

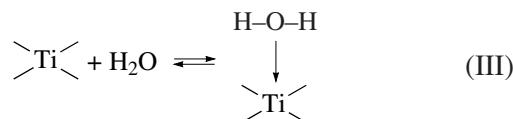


The substitution of acylate groups for two alkoxide groups in titanium tetraalkoxides occurs rapidly and

may be accompanied by the formation of butyl esters of carboxylic acids as a result of the interaction of the latter with nascent butanol [13, 14].

It was demonstrated by GLC that boiling benzoic acid with TTB in *ortho*-xylene for 5 min results in butyl benzoate. Apparently, due to the appearance of a benzoate group in the coordination sphere of titanium, the structure of the titanoxane backbone of the catalyst used in reaction (I) becomes stronger and does not undergo significant changes later.

In view of this, the strong effect of mass transfer processes (reaction slowdown in the absence of boiling and the restoration of the reaction rate under conditions of rapid water removal) can be explained by the reversible binding of water to the catalyst with the formation of catalytically inactive complexes:



The possibility of this reversible process taking place was discovered by studies of the effect of water on the transesterification kinetics of dicarboxylic acid esters in the presence of TTB [15, 16]. The shapes of the corresponding kinetic curves [15, 16] are the same as the shape of curve 7 in Fig. 1, which accounts for the reversible TTB deactivation by water in benzylidene synthesis.

Thus, the integrated system catalyst–reagents–product (water) forms under conditions of reaction (I). The catalytic process involves not only the action of the catalyst on the reactants, yielding products, but also the action of the reactants on the catalyst. This stabilizes the catalyst structure and prevents catalyst deactivation by water, one of the reaction products.

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