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Effect of the Benzoic Acid Additives on the Catalytic Activity of Tetrabuthoxytitanium in the Synthesis of Benzanilide

L. Shteinberg[a], V. V. Marshalova[b], V. M. Dibrova[a], and S. M. Shein[a]

[a] *Institute of Chemical Technology and Industrial Ecology,*
pl. Khimikov 3, Rubezhnoe, Luganskaya oblast, 93000 Ukraine
e-mail: alex12-01@yandex.ru

[b] *Institute of Chemical Technology, East Ukrainian National University, Rubezhnoe, Luganskaya oblast, Ukraine*

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Abstract—Catalytic activity of tetrabutoxytitanium in the synthesis of benzanilide is changed at its pre-coordination with benzoic acid in boiling *ortho*-xylene. Upon increase in the amount of added benzoic acid the catalyst activity increases and then decreases. In the presence of aniline, benzoic acid does not activate tetrabutoxytitanium that may result from its binding to the H-complex with aniline. The formation of such complexes was confirmed indirectly by ^{1}H NMR spectroscopy. Under comparable conditions, the effective catalysts for the benzanilide synthesis are polytitanates obtained from tetrabutoxytitanium at its interaction with water and benzoic acid, and the still bottoms after their vacuum distillation.

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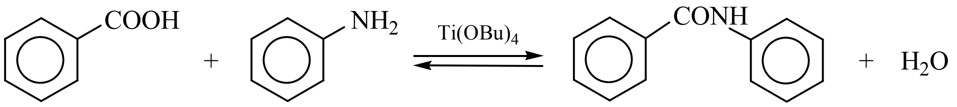
It was found previously that tetrabutoxytitanium, being an effective catalyst for the synthesis of benzanilide by aniline acylation with benzoic acid, alters its activity under the action of water: irreversibly at the preliminary hydrolysis [1, 2] and reversibly at the contact with water released in the reaction process [3]. Both initial compounds and benzanilide can form with tetrabutoxytitanium complexes of different hydrolytic stability [4]. The tetrabutoxytitanium complexes with benzoic acid and benzanilide are less prone to hydrolysis. It is presumable that they would differ by effeiciency in the catalysis.

The aim of this work is to study the effect of benzoic acid additives on the catalytic activity of tetrabutoxytitanium in the synthesis of benzanilide.



(1)

The reaction of tetrabutoxytitanium (two samples activated by pre-hydrolysis at the storage [1]) with benzoic acid was carried out in boiling *ortho*-xylene. We found that pretreatment of the catalyst with benzoic acid leads to a change in its activity (as judged from the yield of benzanilide within 1 h under comparable conditions). The increase in the amount of benzoic acid additive initially increases and then decreases the benzanilide yield (Fig. 1).

The maximum relative increase in the catalytic activity in two series of experiments was 67/20 = 3.35 times (Fig. 1, curve *1*) and 96/58 = 1.65 times (Fig. 1, curve *2*). With the less active sample of tetrabutoxytitanium (Fig. 1, curve *1*) the relative increase in the catalysis efficiency is higher. At the same time the initially more active sample of tetrabutoxytitanium showed higher absolute activity at the treatrment with benzoic acid.

In general, in both series of experiments, the maximum catalytic activity was higher than that of unhydrolyzed tetrabutoxytitanium: 96/12 = 8 times and in 67/12 = 5.5 times, respectively (the figure in the

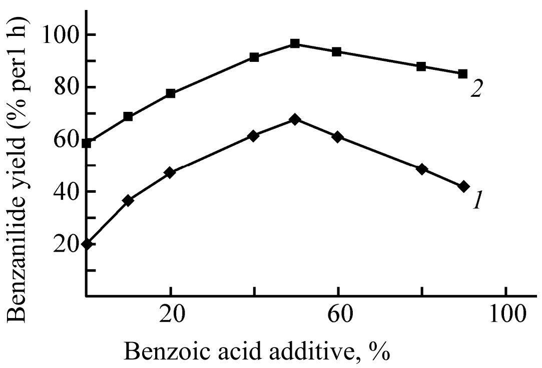


Fig. 1. Dependence of the benzanilide yield on the amount of benzoic acid additive (mol % relative to the total charge of benzoic acid).

denominator, 12%/h of benzanilide, is the activity of unhydrolyzed tetrabutoxytitanium [2]).

The shape of the curves (Fig. 1) resembles that of the change in the catalytic activity of tetrabutoxytitanium due to prior interactions with water [1, 2]: the growth of benzanilide yield upon increase in the amount of water added to the catalyst, reaching a maximum and then the decrease in the catalytic activity.

It was shown previously [2] that the effect of water on the efficiency of catalysis of the benzanilide synthesis catalyzed by tetrabutoxytitanium is associated with the formation of polytitanates of various structures. It was suggested that polyfunctional catalysis occurred because of the close and simultaneous interaction of benzoic acid and aniline with several few atoms of titanium and the ligands that serve as the nucleophilic centers of catalysis located in the polytitanate chain.

It is known [5, 6] that carboxylic acids, including benzoic acid, like water, contribute to the formation of polytitanates in the process of reaction with titanium alkoxides, which occurs with the substitution of a part of alcohol groups by the carboxylate ligands. In some cases these polytitanates are more active catalysts of esterification (polyesterification) reaction than the titanium alkoxides [6, 7].

In the benzanilide synthesis the mechanism of activation by tetrabutoxytitanium at the treatment with benzoic acid is possible through the formation of polytitanate and implementation of multifunctional catalysis (by analogy with [2]).

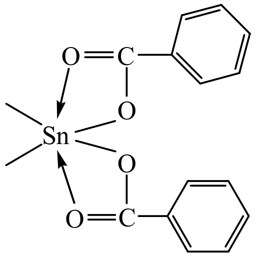
The reduction of the catalyst activity at the increase in amount of benzoic acid added for the treatment of tetrabutoxytitanium can originate from the variations in the composition and structure of the formed polytitanate. It is known [5] that at the interaction of titanium tetraalkoxides with carboxylic acids various polytitanates are formed depending on the ratio of the initial components [Eqs. (2)–(4)]:

$$n\,(RO)_4Ti + 2n\,R'COOH \rightarrow [-O-Ti(-OCOR')(OR)-]_n + n\,R'CO_2R + 2n\,ROH, \qquad (2)$$

$$2n\,(RO)_4Ti + 5n\,R'COOH \rightarrow [-(OR)(R'OCO-)Ti-O-Ti(-OCOR')_2-]_n + 2n\,R'CO_2R + 5n\,ROH, \qquad (3)$$

$$n\,(RO)_4Ti + 3n\,R'COOH \rightarrow [-(R'OCO-)_2Ti-O-]_n + n\,R'CO_2R + 3n\,ROH. \qquad (4)$$

As the amount of benzoic acid per 1 mol of the tetrabutoxytitanium grows, along with the formation of polytitanates, more and more labile alcohol groups in their composition will be replaced by benzoate residues. In addition, benzoate ligands can form stable chelate complexes due to additional coordination of the carbonyl groups with the central ion of the catalyst. For example, there is information on the stability of benzoate tin complexes **I**, catalysts for the synthesis of carboxylic acid amides [8]:

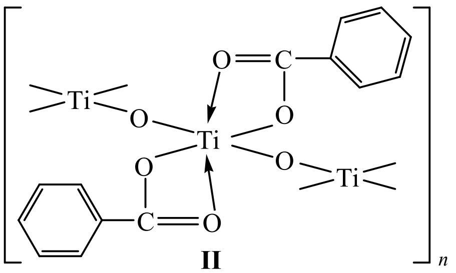


I

Benzoate ligands prevent access of the initial materials (amine and carboxylic acid esters) to the central tin ion, therewith, the ligands thmselves do not react with amines to form benzoic acid amides.

It is not excluded that at the interaction of tetrabutoxytitanium with benzoic acid such stable complexes also can be formed. Upon increase in the amount of benzoic acid additive, the size of polytitanate and the number of titanium ions inaccessible for the catalysis increase. By the example of a fragment of such complex **II** it can be seen that all six coordination sites of the central titanium atom are occupied, and it becomes coordinatively saturated.

The benzoate ligands and the oxygen bridges prevent access of reacting substances (benzoic acid and aniline) to the titanium atom, which is equivalent



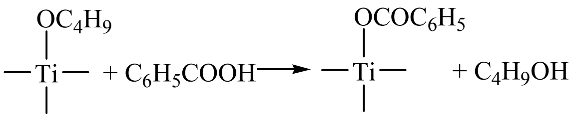
II

to reducing the concentration of active catalyst. This inhibition of catalysis can occur when the benzoate associated with titanium does not react with aniline with the formation of benzanilide.

Note that as a key stage in the catalysis of the synthesis of carboxylic acid esters and amides by tetrabutoxytitanium the polarization is considered of carbonyl bond at the coordination of carboxylic acid or ester with titanium ion [6, 7]. At the same time, the carboxylate ligands form mostly a ionic bond with titanium [6, 9], and it can be assumed that the activation of a carboxylic acid in the reactions of nucleophilic substitution in such a complex does not occur.

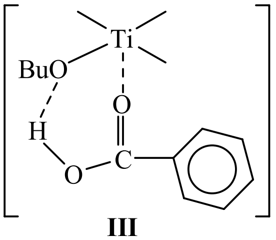
A separate question is, why just after pouring together all the components of the reaction mixture (benzoic acid, aniline, tetrabutoxytitanium, and *ortho*-xylene) and carrying out the reaction of acylation the above mentioned activation of the catalyst does not occur. Such an order of mixing may be formally regarded as the maximal addition of benzoic acid with respect to tetrabutoxytitanium,.

It is known [5, 6] that the first stage in the reaction of benzoic acid with tetrabutoxytitanium is the entrance of the benzoate ligand in the coordination sphere of titanium [Eq. (5)].



$$-\overset{\overset{OC_4H_9}{|}}{\underset{|}{Ti}}- + C_6H_5COOH \longrightarrow -\overset{\overset{OCOC_6H_5}{|}}{\underset{|}{Ti}}- + C_4H_9OH \quad (5)$$

This reaction occurs initially at the coordination of benzoic acid at the titanium and butoxy group, followed by simultaneous rupture and formation of bonds in the complex **III**:



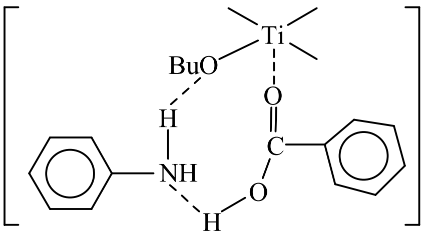
III

Such a mechanism is suggested in [10, 11] for the esterification of carboxylic acids.

However, in the studied catalytic benzanilide synthesis the benzoic acid in a non-polar *ortho*-xylene can bind aniline to form salt or H-complex **IV** [12]:

$$PhCOOH + H_2NPh \rightarrow \underset{\textbf{IV}}{[PhCOOH\cdots NH_2Ph]}. \quad (6)$$

Given that in the reaction mixture the aniline is in excess relative to benzoic acid, and especially to the tetrabutoxytitanium, we can assume the existence of significant competition for the benzoic acid hydrogen between aniline and butoxy ligand of the tetrabutoxytitanium. Such a competition can result in the formation of complex **V** in which the benzoate ligand does not enter the titanium coordination sphere:



V

To check the possible existence of complex **IV,** we studied the interaction of benzoic acid with aniline in *ortho*-xylene using ^{1}H NMR spectroscopy. This method allowed us to fix the presence of salts and H-complexes formed by amines and carboxylic acids [12, 13].

In the spectrum of aniline (0.35 M) in *ortho*-xylene there is a broadened peak at 2.4–3.0 ppm corresponding to the protons of the amino group, and a group of signals of aromatic protons in the region of 6.06–6.18 ppm [13] (Fig. 2, curve *1*).

In the spectrum of benzoic acid (0.35 M) in *ortho*-xylene a group of signals of aromatic protons is observed in the region of 7.80–7.96 ppm, the signal of hydroxy group is located in a weak field [13] (Fig. 2, curve *2*).

In the spectrum of a mixture of benzoic acid with aniline a peak appears at 5.1 ppm, which corresponds to a new common signal of hydroxy and amino groups (Fig. 2, curve *3*) indicating the interaction between these groups. The previously observed peak of the individual amino group disappears. Signals of aromatic protons of aniline undergo an upfield shift by 0.11 ppm, and signals of the aromatic protons of benzoic acid are

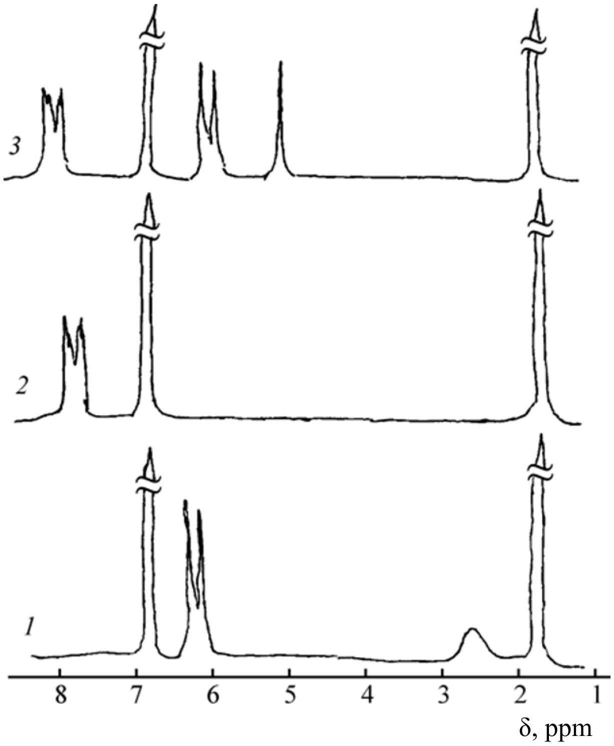


Fig. 2. ^{1}H NMR spectra (in *ortho*-xylene): (*1*) aniline (0.35 M), (*2*) benzoic acid (0.35 M), (*3*) aniline (0.35 M) + benzoic acid (0.35 M).

shifted downfield by 0.06 ppm. These shifts of the signals also indicate a change in the charges on the hydroxy and amino groups and the effect of such changes on the shift of the signals of aromatic protons.

Signals of aromatic protons at 6.83 ppm and aliphatic protons at 1.91 ppm correspond to *ortho*-xylene, as shown previously [2].

Thus, at mixing in *ortho*-xylene benzoic acid with aniline they interact with each other forming a heteroassociate, which could prevent the entry of the benzoate ligand in the titanium coordination sphere and creating a structure of the active catalyst.

In general, we can note that the two substances, benzoic acid and water, act in a similar manner on the tetrabutoxytitanium, contributing to the formation of the polymer structure of a more efficient catalyst. It can be assumed that other methods of obtaining polytitanate from tetrabutoxytitanium can lead to the same result (increase of the catalytic activity).

The table contains the results of testing several versions of such activation. For comparison, the table contains also the results the activation of tetrabutoxytitanium obtained previously.

As seen from the table, the least active is freshly distilled tetrabutoxytitanium (run no. 1). Its efficiency varies in some series of experiments, due, apparently, to the uncontrolled hydrolysis of the catalyst during vacuum distillation, storage and conducting experiments on the synthesis of benzanilide. Note that in the works of other researchers on the esterification and transesterification also a difference was observed in the catalytic activity and other properties even at the use of freshly distilled tetrabutoxytitanium. Therefore, as a base of comparison in such cases the least hydrolyzed catalyst is taken, assuming that it corresponds to the maximally pure tetrabutoxytitanium [14].

In general, the activity of the tetrabutoxytitanium is so low that such pure catalyst hardly ever can be of practical interest.

Prolonged storage of tetrabutoxytitanium in a xylene solution or forced hydrolysis in a moist chamber increases the catalytic activity more than 10 times relative to the least active fresh catalyst (the table, run nos. 2, 3). Almost the same effect can be achieved at

Activation techniques in the synthesis of tetrabutoxytitanium benzanilide

Run no.	Method of activation	Yield of benzanilide, % per h
1	Freshly distilled tetrabutoxytitanium	7–12
2	Long-term storage and the use of tetrabutoxytitanium in *ortho*-xylene for 1 year	58–78
3	Hydrolysis of tetrabutoxytitanium in *ortho*-xylene with the water vapor in a moist chamber for 1–6 h	44
4	Pre-boiling of tetrabutoxytitanium in *ortho*-xylene with benzoic acid	55–76
5	Still bottoms after vacuum distillation of tetrabutoxytitanium at 170–250°C	23–29
6	Polytitanate **VI**	60

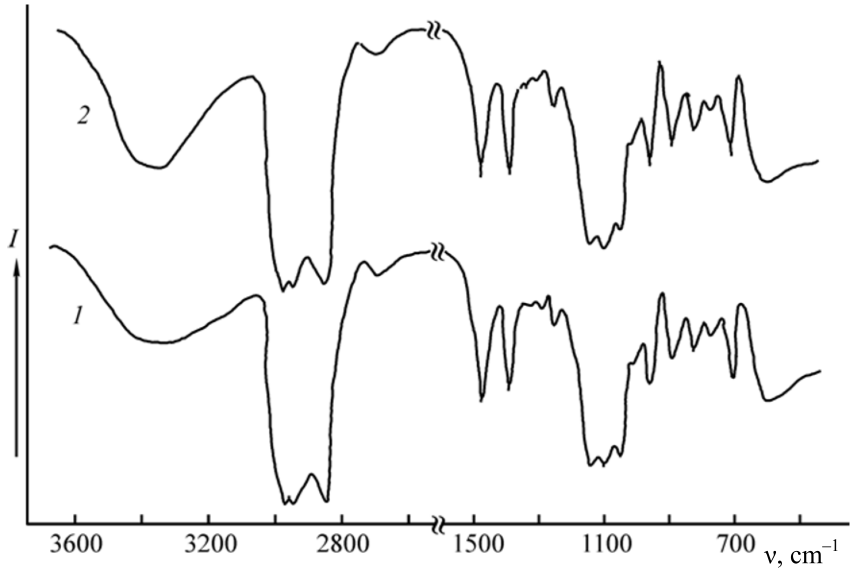


Fig. 3. IR absorption spectra (thin layer): (*1*) still bottoms after vacuum distillation of tetrabutoxytitanium and (*2*) tetrabutoxytitanium.

treatment with benzoic acid of the tetrabutoxytitanium partially activated during the storage in *ortho*-xylene (the table, run no. 4).

After vacuum distillation of tetrabutoxytitanium remain still bottoms that possess a high catalytic activity (see the table, run no. 5), apparently also polytitanates. It was shown in [6] that the thermolysis of titanium alkoxides, including tetrabutoxytitanium, at high temperature, under the conditions close to distilling the tetrabutoxytitanium and the formation of still bottoms, results in decomposition of the ethers leading to the formation of polytitanates containing hydroxy and alkoxy groups.

For qualitative estimation of the structure of the still bottoms we recorded its IR spectrum to compare with the spectrum of partially hydrolyzed tetrabutoxytitanium (Fig. 3). The IR spectrum of the still bottoms contains the same absorption bands as that of tetrabutoxytitanium (Fig. 3, curve *2*): 600–900 cm^{-1} (Ti–O), 1375–1450 and 2850–2050 cm^{-1} (butyl groups), 3100–3500 cm^{-1} (diffuse hydroxyl peaks) [15]. These data indicate that the still bottoms have the same functional groups as tetrabutoxytitanium.

Polytitanate **VI**, the cured product of the reaction of tetrabutoxytitanium with dimethylvinylethynylcarbinol [Eq. (7)] applied on silica gel [9], was also tested as catalyst. It also showed a high activity (the table, run no. 6).

$$\begin{aligned}&(\mathrm{BuO})_4\mathrm{Ti} + \mathrm{HOC(CH_3)_2 - C{\equiv}C{-}CH{=}CH_2}\\ &\quad\rightarrow (\mathrm{BuO})_3\mathrm{TiOC(CH_3)_2 - C{\equiv}C{-}CH{=}CH_2}.\end{aligned} \tag{7}$$

Thus, different methods of treatment of tetrabutoxytitanium, the catalyst for the synthesis of benzanilide, resulting in the formation of polytitanate oligomers showed a similar effect of the tetrabutoxytitanium activation. These methods include the addition of benzoic acid and water, the reagent and the final product involved in the formation of active catalyst, that allows controlling the catalytic reaction without the use of special additives and ligands.

The role of benzoic acid is rather contradictory: On the one hand, it promotes the formation of active polytitanate chain, but on the other hand, it forms a stable complex with tetrabutoxytitanium [4] and thereby prevents its hydrolysis and activation by water. In the presence of aniline, benzoic acid does not activate tetrabutoxytitanium, that is, both the initial materials involved in the formation of effective catalyst serve as regulators of the catalytic activity, which can vary, depending on the order of their charging.

EXPERIMENTAL

Benzoic acid, aniline, *ortho*–xylene, and tetrabutoxytitanium were purified and used as in [1–3, 16]. The samples of hydrolyzed tetrabutoxytitanium with different degree of catalytic activity were prepared as in [1, 2]. Tetrabutoxytitanium was distilled in a vacuum at 150–200°C and residual pressure 10–12 mm Hg, collecting the main fraction at 173–175°C.

^{1}H NMR spectra were recorded on a Tesla BS-487C spectrometer (80 MHz) at 20°C with internal reference hexamethyldisiloxane. IR spectra were recorded on a Specord UR-75 instrument from thin films.

The concentration of unreacted benzoic acid was determined by potentiometric titration on an EV-74 ionomer [16]. As the working electrode a glass electrode ESL-43-07 was used, as the reference, a silver chloride electrode.

The synthesis of benzanilide was performed as described in [1] using a catalyst activated during storage, freshly distilled tetrabutoxytitanium, the still bottoms after vacuum distillation of tetrabutoxytitanium, and polytitanate **VI**.

In all experiments on testing the catalytic activity the amount of catalyst was 2 mol % calculated on titanium. The tetrabutoxytitanium still bottoms obtained after vacuum distillation was used as the catalyst, taking its average molecular weight equal to that of tetrabutoxytitanium.

The catalyst **VI** contained 0.5% of polytitanate on silica gel and was applied proceeding from the percentage of the titanium content.

Studies on the effect of benzoic acid additives on the catalytic activity of tetrabutoxytitanium. A flask equipped with a Dean–Stark trap and reflux condenser was charged with a varied amount of benzoic acid and 40 cm^3 of *ortho*-xylene, heated to 140°C. Tetrabutoxytitanium, 0.05 g (0.16 mmol), was charged, and the mixture was quickly heated to boiling, kept for 30 min, then cooled by 1–2°C to stop the boiling, and to the flask was added 1.53 g (16.4 mmol) of aniline and then benzoic acid to the desired molar ratio (tetrabutoxytitanium : benzoic acid : aniline = 1 : 50 : 100), the mixture was heated to boiling and thus maintained for 1 h.

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