ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 4, pp. 613−617. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © L.Ya. Shteinberg, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 4, pp. 619−623.

ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Effect of Boric Acid Concentration on the Catalysis of the Reaction of 4-Nitrobenzoic Acid with Ammonia

L. Ya. Shteinberg

Institute for Chemical Technology and Industrial Ecology, Research Institution, Rubezhnoe, Lugansk oblast, Ukraine

Received August 13, 2007

Abstract—Effect of the catalyst concentration (boric acid + PEG-400) on the formation rate and yield of 4-nitrobenzamide in the reaction of 4-nitrobenzoic acid with ammonia was studied.

DOI: 10.1134/S1070427209040156

It has been found previously that the system boric acid + PEG effectively catalyzes formation of 4-nitrobenzamide (PNBAm) in the reaction of 4-nitrobenzoic acid (PNBA) with ammonia [1–3]. The effect of the nature of solvents, PEG and other cocatalysts, and the reaction temperature on the yield of the target product has been studied. It has been noted that the catalysis is efficient at various boric acid : PNBA and PEG : PNBA ratios when the reaction is performed in aprotic solvents. No PNBAm is formed in the absence of PEG or in amidation of PNBA in protic solvents (polyalcohols).

The aim of this study was to examine the influence exerted by the amount of boric acid and PEG on the yield and formation rate of 4-nitrobenzamide.

PNBA was reacted with ammonia in aprotic solvents with different polarities (trichlorobenzene, *o*-dichlorobenzene, *n*-decane), in which, as it has been shown previously [2], PNBA can be obtained in high yield. PEG-400 was used as a cocatalyst; in all the experiments, the boric acid : PEG-400 molar ratio was 2 : 1:

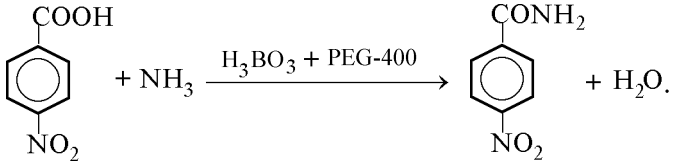


Figure 1 shows kinetic curves of PNBAm accumulation in the course of time in relation to the amount of boric acid used. It was found that the kinetic curves have two different shapes in various solvents, depending on the solvent nature. When the reaction is performed in *o*-dichlorobenzene and trichlorobenzene (Figs. 1a and 1b), the kinetic curves are linear up to large degrees of conversion (70–75%). PNBAm is formed in nearly quantitative yield in 8–9 h. When the amidation is performed in decane (Fig. 1c), the kinetic curves are linear up to conversions of 8–60%, depending on the amount

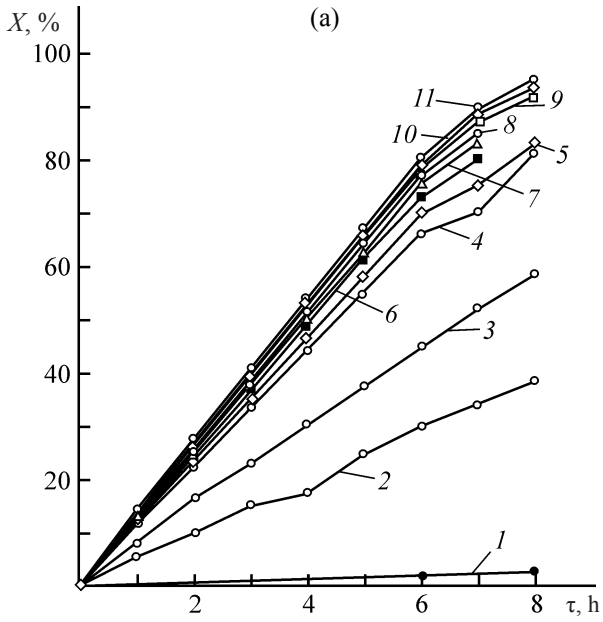


Fig. 1. PNBAm yield X vs. time τ at various amounts of boric acid used. Solvent: (a) 1,2,4-trichlorobenzene, 173°C; (b) *o*-dichlorobenzene, 163°C; and (c) *n*-decane, 174°C. H_3BO_3 (mol % relative to PNBA): (a, b) (*1*) 0, (*2*) 0.5, (*3*) 1, (*4*) 2, (*5*) 5, (*6*) 10, (*7*) 15, (*8*) 20, (*9*) 28, (*10*) 34, and (*11*) 43; (c) (*1*) 0, (*2*) 2, (*3*) 5, (*4*) 10, (*5*) 15, (*6*) 20, (*7*) 28, (*8*) 34, and (*9*) 43.

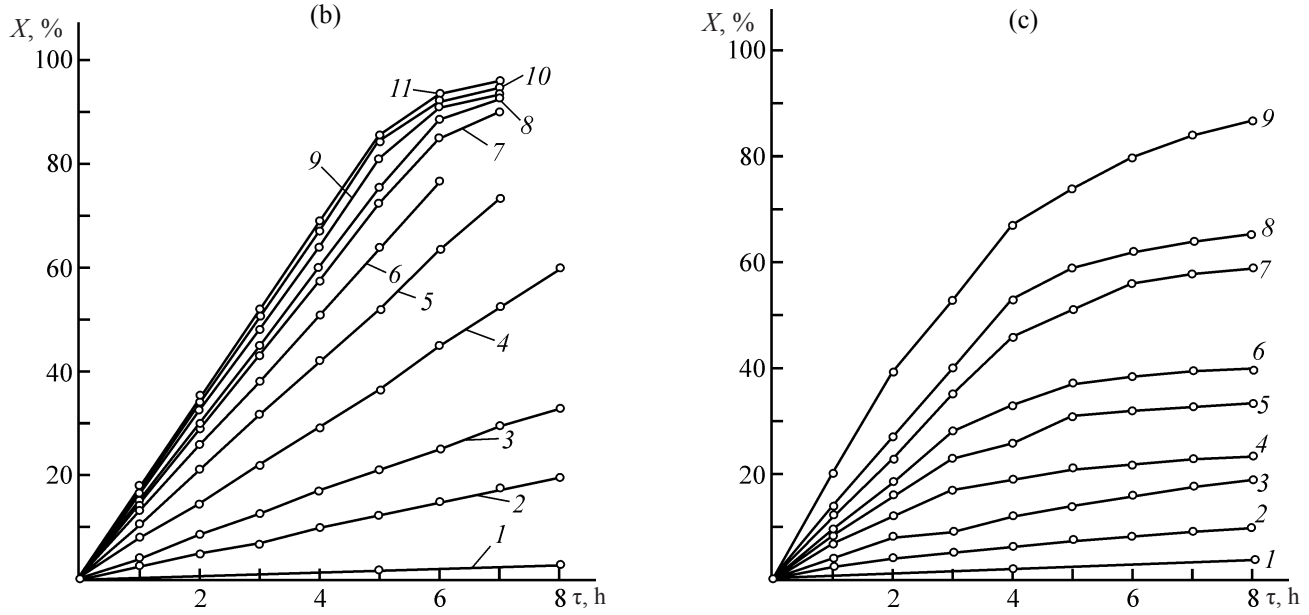


Fig. 1. Contd.

of boric acid used, and then the reaction is strongly decelerated, with the kinetic curves almost leveling-off.

In addition, two dependences of the initial rates of PNBAm accumulation on the amount of boric acid are observed (Fig. 2). With the comparatively poor accuracy and complicatedness of kinetic measurements taken into account, the accumulation rates were calculated as average rates W_{av} (M h^{-1}) from the linear portions of the kinetic curves by the formula [4]:

$$W_{av} = c_0 a/(100\tau),$$

where c_0 is the initial PNBA concentration (M), a, PNBAm yield (%); and τ, reaction duration (h).

As can be seen in Fig. 2 (curves *1, 2*) a pronounced increase in the rate of PNBAm formation in trichlorobenzene and *o*-dichlorobenzene is observed as the amount of boric acid is raised to 2 mol % relative to PNBA. With a larger amount of boric acid, the rate curves are close to leveling-off. At low boric acid concentrations, the reaction rate in trichlorobenzene is higher, whereas at higher boric acid concentrations, it is lower than that in *o*-dichlorobenzene.

For the reaction performed in decane (Fig. 2, curve *3*), the dependence of the initial rate on the boric acid concentration in the range 5–43% is described by a straight line, with the initial rates being lower than that for the reaction in *o*-dichlorobenzene and trichlorobenzene at low catalyst concentrations, and comparable or even higher, at high boric acid concentrations.

To understand the dependences obtained, the known concepts of catalysis by boron compounds in amide formation reactions can be used. It has been shown that one of roles played by PEG in catalytic synthesis of PNBAm consists in solubilization of boric acid in a low-polarity solvent, which may occur via formation of PEG-borate ester:

$$\text{>B–OH} + \text{H(OCH}_2\text{CH}_2)_n\text{OH} \longrightarrow \text{>B–O(CH}_2\text{CH}_2)_n\text{OH} + \text{H}_2\text{O},$$

and just this compound may be the true catalyst of the process.

Numerous studies devoted to synthesis of carboxylic acid amides in the presence of boron compounds have postulated [5, 6] that boron carboxylates are synthesized via an activated form of carboxylic acid, which is easily attacked by an amine:

$$\text{R–C(=O)–OH} + \text{HOB<} \longrightarrow \text{R–C(=O)–O–B<} + \text{H}_2\text{O}.$$

It can be assumed that, for an ester of this kind to be formed, at least one free oxy group should be present at the boron atom. This group can also be involved in various transformations that lead to a decrease in the total concentration of free oxy groups and decelerate the catalytic amidation process.

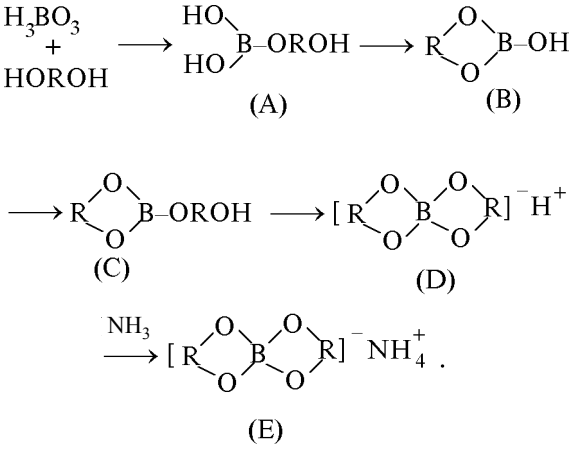
For example, dependences of the reaction rate on the amount of a catalyst, similar to those obtained for synthesis

of PNBAm in *o*-dichlorobenzene and trichlorobenzene, are known for the reactions of nucleophilic substitution of carbonyl compounds with amines and may occur for several reasons considered below.

(1) Binding of an amine by the acid catalyst, with the loss of nucleophilic properties by the amine and deceleration of the amidation reaction [7]. Such a counterproductive interaction of weak boron-containing acids with ammonia will hardly occur in PNBAm synthesis.

As shown previously [2], even 4-nitrobenzoic acid, which is stronger than boric acid, does not bind ammonia and a separately synthesized ammonia salt of 4-nitrobenzoic acid rapidly and completely decomposes into the starting components (ammonia and 4-nitrobenzoic acid) under the reaction conditions.

Formation of ammonium salts is known [8, 9] for strongly acidic alcoholic complexes of boron, synthesized from polyols and boric acid. Therefore, boric acid can react with PEG (HOROH) to give a number of linear and cyclic esters (A)–(C), which are transformed to an acid complex (D). This complex reacts with ammonia to give an ammonia salt (E):



However, complexes (E) are formed in a sufficient amount only in interaction of boric acid with an excess amount of PEG. With the fact that PEG-400 is present in the reaction mass in deficiency with respect to boric acid, and ammonia, in a large excess, taken into account, it can be concluded that its binding by the acid catalyst, with loss of nucleophilic properties, would be hardly occurring.

(2) Polycondensation of a catalyst, with a decrease in its total concentration and formation of species with lower catalytic activity and a smaller number of oxy groups at the boron atom. It is known [10] that boric acid transformed at elevated temperatures to boric anhydride, with release of water:

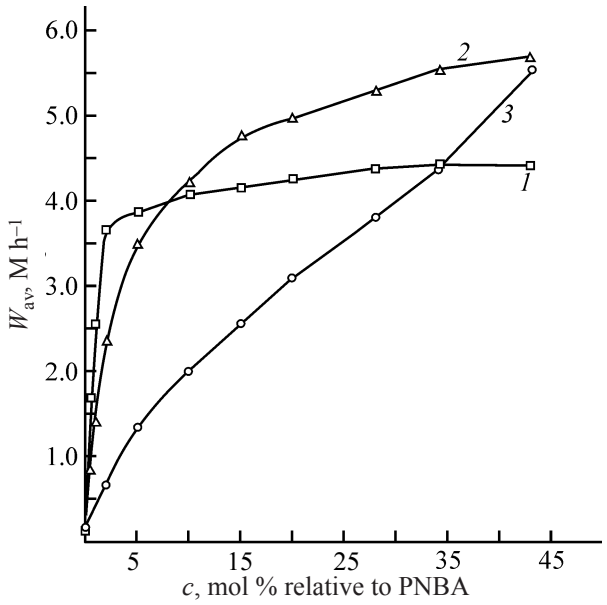
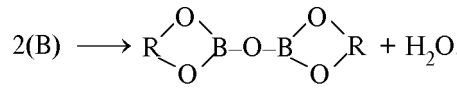


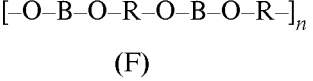
Fig. 1. PNBAm yield X vs. time τ at various amounts of boric acid used. Solvent: (a) 1,2,4-trichlorobenzene, 173°C; (b) *o*-dichlorobenzene, 163°C; and (c) *n*-decane, 174°C. H_3BO_3

$$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O$$

The polycondensation may also occur for products formed in interaction of PEG with boric acid [8, 9]. For example, for compound (B), such a cross-linking can be described by the equation



Also known is polycondensation of boric acid with polyols to give not only dimers, but also polymeric products (F) with a degree of polymerization, *n*, exceeding two:



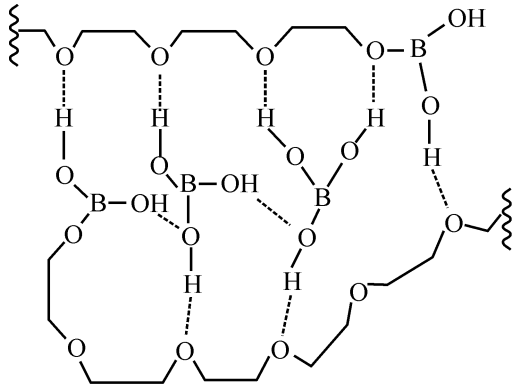
(F)

$n > 2$

It is demonstrated in separate experiments that, under the reaction conditions, boiling of boric acid in decane for 3 h results in water release in an amount of 70% relative to the theoretical value; under the comparable conditions, boric anhydride does not catalyze PNBAm formation in a reaction performed in *o*-dichlorobenzene.

It is not improbable that polycondensation of a boron-containing catalyst does occur in amidation of 4-nitrobenzoic acid, and the presence of oxy groups at the boron atom, whose number decreases, plays an important part in catalysis.

(3) Catalysis by a monomer, self-association of the bifunctional catalyst, which affects the oxy group at the boron atom [7, 11]. The dependence of the reaction rate on the catalyst concentration (Fig. 2, curves *1* and *2*) has a form typical of this case. Use of boron-containing bifunctional catalysts in acyl transfer processes is known [12]. Since the catalytic amidation occurs at rather high temperatures (which, as a matter of fact, leads to disintegration of associates), it is not improbable that not only boric acid is involved in the association process, but the forming PEG-borate esters as well. It is known that PEG can bind several cations or molecules [13]. Below is presented the hypothetical structure of a fragment of such an associate of borate esters and boric acid (G), which can be formed at comparatively high catalyst concentrations:



(G)

As can be seen in an analysis of this structure, there are 10 oxy groups per 4 boron atoms, of which there is only one free oxy group that can be involved in catalysis.

It is not improbable that both effects, association and polycondensation of a boron-containing catalyst, do occur, which may result in a slower rise in the PNBAm formation rate upon an increase in the boric acid concentration.

The different dependence of the PNBAm formation rate on the amount of boric acid for the reaction occurring in decane can be attributed to the low solubility of the components of the reaction mixture in this solvent. As shown previously [2], the forming PNBAm precipitates in decane, with, in all probability, a larger part of the catalyst bound, and the reaction occurs in the gas–liquid–solid heterophase system. Presumably, only a minor part of PEG-borate esters, which are soluble in decane and are permanently removed from the reaction zone, is involved in the catalysis in this case and the catalyst association is not important.

Anomalous dependences of this kind, associated with the formation of the solid phase of the target product (which, by the way, occurs in this same decane), are also known for other amidation reactions, e.g., for acylation of aniline with benzene sulfochloride and benzoyl chloride [14, 15].

The results obtained necessitate a new approach to the effect of the solvent nature (solvent polarity) on the PNBAm yield. Previously, the faster formation of this compound in aprotic media with a comparatively high dielectric constant has been attributed to the possibility of formation and stabilization of acid borate complexes of (D) type, involved in the catalysis. Presumably, the solvent polarity affects the association of a boron-containing catalyst to a greater extent. Therefore, the amidation best occurs at comparatively high boric acid concentrations in *o*-dichlorobenzene having a higher polarity than trichlorobenzene and decane (despite the lower reaction temperature), which favors disintegration of catalyst associates.

Other reactions of nucleophilic substitution at the carbonyl carbon atom, catalyzed by boron compounds (boron trifluoride: esterification [16] and acylation of amines [17]; boric acid: hydrolysis of esters [18] and salicylic acid imines [19]) also show complex dependences of the reaction rate and of the yield of target products on the catalyst concentration (bell-shaped or leveling-off curves). In some cases, they are also related to the possible formation of boric acid esters [17]. Presumably, the presence of an oxy group at the boron atom and the possibility of its free interaction with the starting substances are important conditions for occurrence of catalysis in the amidation process.

EXPERIMENTAL

4-Nitrobenzoic and boric acids, *o*-dichlorobenzene, trichlorobenzene, *n*-decane, ammonia, and PEG-400 were purified and used as it was done in [1–3]. Boric anhydride of pure grade was additionally dehydrated [10] and used in an amount of 2 mol % relative to 4-nitrobenzoic acid.

In a study of the polycondensation process, 10 of boric acid in 50 cm^3 of *n*-decane was boiled in a flask

equipped with a Dean–Stark receiver and a water reflux condenser.

4-Nitrobenzoic acid was obtained, the mixtures were analyzed, and the purity of the synthesized substances was determined as it was done in [1, 2]. In kinetic measurements, 5 g (29.9 mol) of PNBA was used in a run, the yield of PNBAm was determined by gravimetry.

Prior to being introduced into a flask, ammonia (1000 cm^3 h^{-1}) was additionally heated to 120°C. Immediately after terminating the keeping, the flow of ammonia into the flask was switched-off.

The content of the main substance was additionally determined in the isolated PNBAm. For this purpose, 0.5–0.7 g of the target product was dissolved in 30 cm^3 of acetone, the solution was transferred to a 50-cm^3 volumetric flask, brought to the mark by addition of acetone, and a 1-cm^3 sample was taken, dissolved in 20 cm^3 of acetone, and 4-nitrobenzamide was titrated with a 0.1 N solution of perchloric acid in acetic acid on an EV-74 pH-meter. An ESL-43-07 glass electrode served as the working electrode, and an EVL-1M3 silver chloride electrode, as reference. The yield of PNBAm was calculated from the mass of the recovered product and the content of the main substance. The accuracy of the kinetic measurements was ±2 abs %.

CONCLUSIONS

(1) The catalytic system boric acid + PEG-400 is effective in the reaction of 4-nitrobenzoic acid with ammonia only in a narrow range of boric acid concentrations (up to 2 mol % relative to 4-nitrobenzoic acid).

(2) It is preferable to use more polar solvents (trichlorobenzene, *o*-dichlorobenzene) for performing the reaction.

REFERENCES

1. Shteinberg, L.Ya., *Zh. Org. Khim*., 2003, vol. 39, no. 7, pp. 1033–1035.
2. Shteinberg, L.Ya., *Zh. Prikl. Khim*., 2005, vol. 78, no. 10, pp. 1745–1747.
3. Shteinberg, L.Ya., *Zh. Prikl. Khim*., 2006, vol. 79, no. 8, pp. 1296–1299.
4. Panchenkov, G.M. and Lebedev, V.P., *Khimicheskaya kinetika i kataliz. Uchebnoe posobie dlya vuzov* (Chemical Kinetics and Catalysis: Textbook for Higher School), Moscow: Khimiya, 1985.
5. Nelson, P. and Pelter, A., *J. Chem. Soc*., 1965, no. T-9, pp. 5142–5144.
6. Pelter, A. and Levitt, T.E., *Tetrahedron*, 1970, vol. 26, no. 6, pp. 1539–1544.
7. Savelova, V.A. and Oleinik, N.M., *Mekhanizmy deistviya organicheskikh katalizatorov. Bifunktsional'nyi i vnutrimolekulyarnyi kataliz* (Operation Mechanisms of Organic Catalysts: Bifunctional and Intramolecular Analysis), Kiev: Naukova dumka, 1990.
8. Shvarts, E.M., *Vzaimodeistvie bornoi kisloty so spirtami i oksikislotami* (Interaction of Boric Acid with Alcohols and Oxyacids), Riga: Zinatne, 1990.
9. Gren', A.I. and Kuznetsov, V.V., *Khimiya tsiklicheskikh efirov bornykh kislot* (Chemistry of Cyclic Boric Acid Esters), Kiev: Naukova dumka, 1988.
10. Handbuch der Praparativen Anorganischen Chemie, Brauer, G., Ed., vol. 2, Ferdinand Enke Verlag, Stuttgart, 1978.
11. Litvinenko, L.M. and Oleinik, N.M., *Organicheskie katalizatory i gomogennyi kataliz* (Organic Catalysts and Homogeneous Catalysis), Kiev: Naukova dumka, 1981.
12. Litvinenko, L.M. and Oleinik, N.M., *Usp. Khim.,* 1978, vol. 47, no. 5, pp. 777–780.
13. *Phase-Transfer Catalysis. New Chemistry, Catalysts, and Applications*, Starks, C.M., Ed., Washington: Am. Chem. Soc., 1987.
14. Kuritsyn, L.V. and Vorob'ev, N.K., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1964, vol. 7, no. 3, pp. 400–405.
15. Vorob'ev, N.K. and Kuritsyn, L.V., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1964, vol. 7, no. 1, pp. 34–40.
16. Sowa, F.J. and Nieuwland, J.A., J. *Am. Chem. Soc*., 1936, vol. 58, no. 2, pp. 271–272.
17. Bel'skii, V.E., Ivankova, N.L., and Vinnik, M.I., *Zh. Fiz. Khim.,* 1965, vol. 39, no. 6, pp. 1426–1431.
18. Bezsudnova, E.Yu., Sakodynskaya, I.K., and Yatsimirskii, A.K., *Kinet. Kataliz,* 1995, vol. 17, no. 4, pp. 569–575.
19. Rao, G. and Philipp, M., *J. Org. Chem*., 1991, vol. 56, no. 4, pp. 1505–1510.