Russian Journal of Applied Chemistry, Vol. 78, No. 10, 2005, pp. 1715–1717. Translated from Zhurnal Prikladnoi Khimii, Vol. 78, No. 10, 2005, pp. 1745–1747. Original Russian Text Copyright © 2005 by Shteinberg.

BRIEF COMMUNICATIONS

Catalysis of the Reaction between 4-Nitrobenzoic Acid and Ammonia by Boric Acid + Polyehylene Glycol-400

L. Ya. Shteinberg

Institute of Chemical Technology and Industrial Ecology, Rubezhanskii Krasitel' Limited Liability Company, Rubezhnoe, Lugansk oblast, Ukraine

Received April 13, 2005

Abstract—Solvent effect on the synthesis of 4-nitrobenzamide by the reaction of 4-nitrobenzoic acid with ammonia in the presence of the catalytic system constituted by boric acid and polyethylene glycol-400 was studied.

4-Nitrobenzamide is the synthetic precursor of 4-aminobenzamide used for preparing a numbers of dyes [1].

In [2], we showed that the system constituted by boric acid and polyethylene glycol (PEG-400) effectively catalyzes the synthesis of 4-nitrobenzamide (NBA) by the reaction of 4-nitrobenzoic acid (NBAc) with ammonia in a mixture of 1,2,4-trichlorobenzene with o-xylene. It was noted that PEG-400 favors dissolution of boric acid and homogenization of the reaction mixture. In this study, we examined this catalytic reaction in various media:

$$\begin{array}{rcrcr} & 4-\text{NO}_2\text{C}_6\text{H}_4\text{COOH} + \text{NH}_3\\ & \text{NBAc} \\ & \xrightarrow{\text{H}_3\text{BO}_3 + \text{PEG-400}} & 4-\text{NO}_2\text{C}_6\text{H}_4\text{CONH}_2 + \text{H}_2\text{O}_3 \\ & & \text{NBA} \end{array}$$

Catalysis by boron compounds of amidation reactions performed in aromatic and aliphatic hydrocarbons, including hexane, benzene, toluene, cumene, isomeric xylenes, and trichlorobenzene, was considered in [3–5]. To carry out the reaction of NBA with ammonia, we took protic and aprotic solvents differing in the polarity and boiling point. The results obtained and dielectric constants of the solvents ε are listed in the table.

As seen, the reaction readily proceeds in various aromatic and aliphatic aprotic solvents and their mixtures. With an increase in the reaction time and catalyst amount, the NBA yield grows becoming almost quantitative (run nos. 4, 7, 8).

In the series of solvents with low (and similar) polarity, the yield of the target product varies in parallel with the reaction temperature (run nos. 1–3, 5, 12):

p-cymene (177°C) > decane (174°C) > white spirit (155–162°C) > *o*-chlorotoluene (155°C) > *o*-xylene (145°C). At close temperatures, the NBA yield varies in parallel with the solvent polarity in the order (run nos. 6, 7, 9) *o*-dichlorobenzene > 1,2,4-trichlorobenzene > decane. The same influence of the solvent polarity on the NBA yield is observed in amidation under similar conditions in binary mixtures *p*-cymenenitrobenzene (run nos. 13–17). As can be seen, the NBA yield steadily grows with increasing nitrobenzene zene content, and accordingly, solvent polarity.

The highest NBA yields were attained in *o*-dichlorobenzene and 1,2,4-thichlorobenzene even without refluxing of the reaction mixture and distillation of the water released, which is evidently removed from the reaction zone with excess ammonia (previously, in catalysis by titanium and boron compounds, intense azeotropic distillation of the released water was necessary for obtaining benzanilide [9]).

As known [10], boric acid readily reacts with various alcohols, including glycols, and polyethylene glycols (HOROH), to give complexes \mathbf{A} exhibiting elevated acidity. Such compounds can serve as acid catalysts in amidation. An increase in solvent polarity can favor stabilization of transition state \mathbf{B} and acid catalysis:



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Run no.	Solvent	** 8	T, °C	τ, h	H ₃ BO ₃ , mol % relative to NBAc	Yield of NBA, %
1	o-Xylene	2.57	145	6.0	5	2
2	o-Chlorotoluene	4.45	155	6.0	5	3
3	White spirit	-	155-162	6.0	5	4
4	n	—	155-162	6.5	34	70
				10.0	34	95
5	Decane	1.99	174	6.0	5	10
6	"	1.99	174	6.0	34	63
7	o-Dichlorobenzene	9.93	162-164	6.0	34	92
8	1,2,4-Trichlorobenzene	3.98	170-175	6.0	2	66
				10.0	2	93
9	"	3.98	170-175	6.0	34	79
				9.0	34	96
10	Decane ^{***}	1.99	174	6.0	0	Traces
11	1,2,4-Trichlorobenzene****	3.98	170-175	7.0	0	49
12	<i>p</i> -Cymene	2.24	177	6.0	5	13
13		2.24	177	8.0	2	13
	<i>p</i> -Cymene : nitrobenzene :					
14	10:1	5.21	177	8.0	2	40
15	8:1	5.89	177	8.0	2	59
16	5:1	7.68	177	8.0	2	67
17	3.5 : 1	9.51	177	8.0	2	72
18	Ethylene glycol	38.66	175-180	6.0	33	0
19	Diethylene glycol	31.69	175-180	6.0	33	0
20	Triethylene glycol	23.19	175–180	6.0	33	0

Synthesis of NBAc in various solvents*

* In all the experiments, the PEG-400 amount was taken as a half (in moles) of that of boric acid.

^{**} The values of ε were taken from [6, 7]; for the mixture of *n*-cumene with nitrobenzene, the ε values were calculated using an additive scheme from the volume fractions of the components [8] (listed in table).

*** Filtrate from run no. 6 was taken as a solvent.

**** Filtrate from run no. 8 was taken as a solvent.

However, an attempt to obtain NBA in more polar solvents, glycols, failed (run nos. 18–20). A TLC analysis of the reaction mixture showed that NBAc rapidly (during 1 h) disappeared, but there was no NBA among the reaction products. Probably, in glycols, NBAc in the presence of boric acid forms glycol esters, which then do not react with ammonia.

A high polarity of the solvent may also favor homogenization of the reaction mixture. We found that, in amidation in low-polar decane (run nos. 5, 6), crystalline NBA precipitates already within 2 h. In more polar *o*-dichlorobenzene and 1,2,4-trichlorobenzene, the reaction mixture is homogeneous, amidation proceeds faster, and crystalline NBA precipitates only after cooling the reaction mixture to room temperature after the reaction is complete (run nos. 7–9).

Thus, with decane as a solvent, the reaction proceeds in the heterogeneous system gas-liquid-solid, formed within 2 h after the beginning of the reaction. Probably, the crystalline NBA precipitate is bound with a part of the catalyst, which may hinder its interaction with the reactants and the catalytic reaction as a whole.

To study the catalyst distribution in the reaction mixture, we performed experiment nos. 10 and 11, using as solvents the filtrates from separation of the solid target product in experiment nos. 6 and 8, respectively, without adding the catalytic system. It was found that the filtrate showed no catalytic power in decane (run no. 10), i.e., the whole amount of the catalyst was probably removed from the filtrate with NBA. In 1,2,4-trichlorobenzene, the filtrate showed fairly high catalytic power (run no. 11), thus confirming the uniform distribution of the catalyst. The degree of NBAc binding with ammonia can vary with the solvent polarity. As known, carboxylic acids form salts with amines. The reactivity of carboxylate anions and protonated amines in nucleophilic substitution at the carbonyl carbon atom may be substantially lowered [11, 12].

Since NBA is not formed from NBAc ammonium salt in the presence of the catalytic system [2], it was of interest to test the stability of this salt under the reaction conditions.

We found that the NBAC ammonium salt undergoes no changes on heating to 120° C for 20 h without solvents or on washing with *o*-xylene or *o*-chlorobenzene at room temperature, followed by filtration and drying: its melting point remains unchanged. However, on heating of the suspension of NBAc ammonium salt in these solvents to $60-80^{\circ}$ C, it decomposes with liberation of ammonia. Heating of such a suspension in *o*-xylene at 145°C for 10 min causes complete decomposition of the ammonium salt: after cooling, only NBAc is recovered from the reaction mixture. Probably, NBAc reacts in the free state but not as ammonium salt under the reaction conditions, even in the presence of a large excess of ammonia.

EXPERIMENTAL

Boric acid, NBAC, PEG-400, *o*-xylene, decane, 1,2,4-trichlorobenzene, *o*-dichlorobenzene, and nitrobenzene were of the same quality as in [2, 9, 13]. *o*-Chlorotoluene and white spirit were vacuum-distilled. Ethylene glycol, diethylene glycol, and triethylene glycol were dried over sodium sulfate and vacuum-distilled. *n*-Cymene was washed with sulfuric acid, water, solutions of potassium permanganate, sodium hydroxide, and again water, dried over sodium sulfate, and vacuum-distilled. NBA and ammonium salt of NBAc were prepared, the mixtures were analyzed, and the purity of the products was determined as in [2] with separation of an additional amount of the target product and vacuum distillation of the solvent from the reaction mixture.

CONCLUSIONS

(1) The catalytic system constituted by boric acid and polyethylene glycol-400 is the most efficient in synthesis of 4-nitrobenzamide from 4-nitrobenzoic acid and ammonia in aprotic solvents at 145–177°C. Under the reaction conditions, ammonium salt of 4-ni-trobenzoic acid rapidly decomposes, with ammonia liberated and no 4-nitrobenzamide formed.

(2) In polar proton-donor glycols, 4-nitrobenzoic acid rapidly transforms into unidentified products without formation of 4-nitrobenzamide.

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