# **Thermal Dehydration of 2-(4-Aminophenyl)ethanol**

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**Abstract**—The influence of inorganic nucleophilic agents on the liquid-phase process of thermal dehydration of 2-(4-aminophenyl)ethanol at 200–260°C was investigated. It was found that  $K_2CO_3$ , BaCO<sub>3</sub>, BaO, CaH<sub>2</sub>, and NaOH did not catalyze the dehydration, but the process takes place easily with the formation of 4-aminostyrene in high yield, using KOH in the range of 100–180 mol % with respect to 2-(4-aminophenyl)ethanol.

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One of the approaches to the synthesis of 4-amiostyrene is the liquid-phase catalytic dehydration of the isomeric 4-aminophenylethyl alcohols at elevated temperature. In this case the dehydration of 1-(4-aminophenyl)ethanol is a non-selective process and has no preparative value [1]. In contrast, the dehydration of 2-(4-aminophenyl)ethanol is important for organic synthesis and provides 4-aminostyrene as one product.

In general, the literature provides incomplete and unreliable information on this issue. We specify the publications [2–8], often referred while considering the process for dehydration of 2-(4-aminophenyl)ethanol. It should be noted that these publications do not include any description of experiments and the reaction conditions, which, however, did not prevent or interfere researchers to cite these works, and the authors of individual articles refered to each other [3, 4]. As for reliability, it enough to cite as an example the key paper [5], which reports on the dehydration of 2-(4-aminophenyl)ethanol in the presence of anhydrous potassium carbonate as catalyst, which instead of the reaction conditions and product yields describes some properties of the product. In fact, we established that  $K_2CO_3$  does not catalyze the dehydration of 2-(4-aminophenyl)ethanol.

Preparative method for the liquid-phase dehydration of 2-(4-aminophenyl)ethanol in the presence of KOH at 200–260°C and a pressure of 5–15 mm Hg, yielding 50.2% of the product was described in [9].

Thus, virtually only one publication describes this synthesis, and liquid-phase dehydration of 2-(4-aminophenyl)ethanol remains largely unexplored.

The aim of this work is the study of the influence of nucleophilic reagents on the formation and yield of 4-aminostyrene by thermal liquid-phase dehydration of 2-(4-aminophenyl)ethanol.



Pure 2-(4-nitrophenyl)ethyl nitrate was synthesized in 35.6% yield, its further catalytic hydrogenation in methanol over  $Ni_{Re}$  in the presence of  $N_2H_4$ ·H<sub>2</sub>O by a simplified method [10] gave the amino alcohol **III** in 83% yield which does not require further purification. Dehydration of 2-(4-aminophenyl)ethanol was performed at 200–260°C and a pressure of 10–14 mm Hg. As catalyst were tested such compounds as  $K_2CO_3$ , BaCO<sub>3</sub>, BaO, CaH<sub>2</sub>, NaOH and KOH. We found that anhydrous carbonates do not exhibit a catalytic effect,

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despite the publications about the use of potassium carbonate as a catalyst [5-8], as already reported above. Thus, when a mixture of K<sub>2</sub>CO<sub>3</sub> with BaCO<sub>3</sub> of 86/14 mol % composition was used, only the original 2-(4-aminophenyl)ethanol was distilled off from the reaction mixture. Use of the alkaline earth metal hydrides as the dehydrating agents should be effective, considering the formation of reactive intermediate oxide. However, vacuum distillation of 2-(4-aminophenyl)ethanol with a significant excess of CaH<sub>2</sub> at 250-255°C did not lead to the formation of 4-aminostyrene: the crystalline distillate obtained consisted of the parent compound, collected in an amount of 77.1% of the taken for reaction. Use as a dehydrating agent BaO together with K<sub>2</sub>CO<sub>3</sub> also did not cause dehydration. Thus, it reasonably to assume that other alkali metal carbonates and oxides and hydrides of other alkaline earth metals also do not catalyze this reaction.

The use of such strong nucleophilic reagents as NaOH and KOH in this reaction leads to mixed results. For example, in the presence of NaOH the formation of 4-aminostyrene does not occur, as in the case of the addition to NaOH of a small amount (3.8 mol %, based on the alkali) of  $CaH_2$  as a possible promoter. Therewith, the isolation of the source amino alcohol also failed.

Catalytically active compounds was only KOH, so that the fact that the dehydration of 2-(4-aminophenyl) ethanol proceeds as described in [9] is confirmed experimentally. However, the method of [9] has several drawbacks: consumption of KOH is excessive, more than 3.4-fold excess (342.3 mol %), which can cause oxidative processes, and inappropriate use of 4*tert*-butylpyrocatechol, which readily undergoes degradation in the presence of alkali resulting in a side reactions of 2-(4-aminophenyl)ethanol and 4-aminostyrene with the products of its oxidation and decomposition, leading to a decrease in the yield of 4-aminostyrene.

In the absence of initiators, 4-aminostyrene polymerizes by free-radical mechanism with great difficulty even at high (hundreds of Celsius degrees) temperatures, so during the dehydration of 2-(4-aminophenyl)ethanol there is no need for inhibitors of radical processes, or their precursors, and the alkaline reagent which is present in the reaction mixture elimi-nates the polymerization by the cationic mechanism.

Formation of 4-aminostyrene with the yield of 75.3% occurs easily at use KOH in the range 100-

180 mol % relative to the parent compound. In this case the dehydration of 2-(4-aminophenyl)ethanol usually begins at temperatures significantly above 200°C and proceeds more rapidly at 250–260°C, the optimal dynamic evacuation of product from the reaction zone is provided in the same range and at a pressure of 10–15 mm Hg but not below, since otherwise increases the quantity of distilled off initial amino alcohol, which reduces the 4-aminostyrene yield.

## EXPERIMENTAL

For nitration we used HNO<sub>3</sub>  $d_4^{20} = 1.488$  g cm<sup>-3</sup>, containing nitrogen oxides. Diethyl ether was purified to remove peroxides and distilled. Absolute ethanol was obtained by boiling rectified ethanol with CaH<sub>2</sub> excess with subsequent distillation, and then redistilled with a small amount of Na. As the dehydrateing agent were used caustic reagents of chemically pure grade and powdered calcium hydride of 93% purity. For the reduction was used 99% N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O and catalyst prepared from Ni–Al alloy of 50:50 composition.

The NMR spectra were taken from solutions in DMF- $d_7$  on a Bruker Avance II 400 spectrometer, <sup>1</sup>H at 400.1 MHz, <sup>13</sup>C at 100.6 MHz. Elemental composition was determined using a Vario Elemental C, H, N, S analyzer.

Synthesis of 2-(4-nitrophenyl)ethyl nitrate. To 250 ml of HNO<sub>3</sub> at -10 to -5°C under vigorous stirring was added dropwise 61.08 g (0.450 mol) of  $\beta$ phenethyl alcohol; last few ml of β-phenethyl alcohol was added at 10°C. After the end of the nitration, the reaction mixture was poured with stirring into 3 l of ice-water. After standing the mixture, the dilute acid was decanted from a heavy yellow liquid which was then repeatedly washed with water. Yield of crude nitration products was 102.77 g (96.9%). Nitro compounds were kept at -21°C to complete crystallization, the crystalline mass was then pressed on a vacuum filter to separate liquid o-isomer. The crystalline substance was then washed twice with ethanol and thoroughly separated by pressing from the residual 2-(2-nitrophenyl)ethyl nitrate which is insoluble in alcohol. After drying in air was obtained 46.26 g of crude 2-(4-nitrophenyl)ethyl nitrate, mp 44-45°C, which was then recrystallized from ethanol. Ethanol was removed under vacuum from the filtrate remaining after the separation of o-isomer, the residue was kept at -21°C for several days, and then from the crystallized

precipitate was isolated 8.9 g of 2-(4-nitrophenyl)ethyl nitrate. The total yield of crude product was 55.34 g (52.2%). The yield of pure 2-(4-nitrophenyl)ethyl nitrate 37.73 g (35.6%), mp 54–55°C, a needle with a slight greenish-yellow tinge.

Synthesis of 2-(4-aminophenyl)ethanol. To a solution of 1.28 g (0.2048 mol) of 2-(4-nitrophenvl)ethyl nitrate in 260 ml of methanol was added Ni<sub>Re</sub> prepared from 1.0 g of Ni-Al alloy, then 25 ml of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O was added and the mixture was stirred till exothermic reaction began. When the reaction intensity decreased, to the reaction mixture was added another 25 ml portion of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, the mixture was heated in a water bath to initiation of a violent reaction. After decomposition of most of the hydrazine, to the mixture was added 17 ml of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, and the reaction mixture was heated at 80°C until the reaction completion, and then kept at 40-45°C to complete cessation of gas evolution. Then catalyst was removed from warm solution by filtration, volatiles were distilled off by heating under vacuum in a rotary evaporator. To the liquid residue was added 50 ml of absolute ethanol, the solvent was distilled off and the residual suspension was left for crystallization. The crystals were filtered off from the mother liquor, washed with absolute ethanol and after drying in vacuum over P<sub>4</sub>O<sub>10</sub> was obtained 9.83 g of 2-(4aminophenyl)ethanol as white crystals, mp 107-108°C. The filtrate was evaporated in a vacuum, the residue was poured onto a petri dish and after the evaporation of volatile components, the substance was rubbed on the filter with a small amount of absolute ethanol. After filtration, the precipitate was washed with absolute ethanol and dried in air. As a result, 5.26 g of a white finely crystalline substance was obtained, mp 105°C. Total yield 15.09 g (83%). <sup>1</sup>H NMR spectrum, δ, ppm: 2.613, 2.632, 2.650 m (2H, CH<sub>2</sub>), 3.598, 3.617, 3,635 m (2H , CH<sub>2</sub>O), 6.593, 6.599, 6.604, 6.615, 6.620, 6.627 (2H, 2,6-Ar), 6.899, 6.906, 6.910, 6.922, 6.926, 6.933 (2H, 3,5-Ar).

Synthesis of 4-aminostyrene. *a*. A mixture of 5.25 g (0.0383 mol) of 2-(4-aminophenyl)ethanol, 2.12 g (0.0153 mol) of  $K_2CO_3$  and 0.5 0 g (0.0025 mol) of BaCO<sub>3</sub> was heated in an oil bath in the setup for distillation up to 200°C, the system pressure was reduced to 30 mm Hg. The formed light-brown liquid gently boiled. Heating continued for a short time, then the pressure was reduced to 10 mm Hg and the temperature was increased stepwise to 245°C. Initially distilled off the source 2-(4-aminophenyl)ethanol, part

of which crystallized on the condenser walls. Heating was stopped, the reaction mixture was allowed to cool, then the pressure in the system was equalized with atmospheric one, 2.15 g (0.0383 mol) of KOH was added, the mixture heating was continued and pressure was reduced to 10 mm Hg. The liquid became black, and 4-aminostyrene distilled off in the temperature range 250-260°C. The collected distillate was decanted from a small amount of the vellow crystals of 2-(4aminophenyl)ethanol, receiver was washed with a small amount of cooled diethyl ether, the extract was combined with the distillate. The condenser and allonge working surfaces were washed with diethyl ether to recover residual 4-aminostyrene, while the crystalline 2-(4-aminophenyl)ethanol remained on the glass surface. The etheral solutions were combined together, washed with a little water and dried over two portions of KOH. Then the solvent was removed under vacuum on a rotary evaporator, finally at 2 mm Hg, at 30-40°C. 3.18 g (69.7%) of 4-aminostyrene was isolated, yellow liquid crystallized upon cooling.

For purification, the 4-aminostyrene was distilled in the presence of small amount of KOH at 6–7 mm Hg on a bath with temperature 130–150°C. Yield 2.46 g (54%), mp 23–24°C (plates).

Use of BaO instead of BaCO<sub>3</sub> has no effect on the course of the process.

b. A mixture of 5.49 g (0.0400 mol) of 2-(4aminophenyl)ethanol and 4.0 g (0.0713 mol) of powdered KOH was heated to 200°C, left for 1 min, then pressure was reduced stepwise for 1 min to 12 mm Hg, and after 30 s to 10 mm Hg, while the bath temperature was raised to 210°C. On the walls of the condenser and nozzle crystallized original 2-(4aminophenyl)ethanol, which then was washed back to the distillation flask by the distilling liquid. The reaction mixture was heated further at 250-260°C at 11-14 mm Hg, while distillate soaked in a crystalline mass on the condenser walls. After about 1 h the heating was stopped, aminostyrene and original 4amino alcohol were washed off with diethyl ether from the walls, the ether was removed under vacuum, from the residue was extracted with water a part of 2-(4aminophenyl)ethanol. The mixture without separation was frozen and then water phase was allowed to melting, the solution was decanted, the crystalline solid phase was mixed with 50 ml of H<sub>2</sub>O, then 4aminostyrene was extracted with diethyl ether, dried over KOH and the solvent was removed from the

extract under vacuum, initially at 10 mm Hg and then finally at 1 mm Hg. Yield: 3.59 g (75.3%), liquid rapidly stained in the air, crystallized upon cooling.

After distillation the 4-aminostyrene in argon at 2 mm Hg and bath temperature  $120-140^{\circ}$ C was isolated 5.3 g (64%) of colorless substance. From the residue after pyrolysis was isolated 0.86 g of brown resin, partially soluble in DMF. Found, %: C 76.07, H 7.82. C<sub>8</sub>H<sub>9</sub>N. Calculated, %: C 76.01, H 7.89.

Treatment of 2-(4-aminophenyl)ethanol with other reagents. *a*. A mixture of 4.28 g (0.0359 mol) of 2-(4-aminophenyl)ethanol and 4.0 g (0.0951 mol) of CaH<sub>2</sub> was distilled in a vacuum at 250–255°C. The distillate obtained contained 3.3 g (77.1%) of the starting amino alcohol.

b. A mixture of 3.29 g (0.0240 mol) of 2-(4aminophenyl)ethanol, 2.5 g (0.0625 mol) of NaOH and 0.1 g (0.0024 mol) of CaH<sub>2</sub> was treated under similar conditions. No distillate was distilled off and 4aminostyrene did not form.

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