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> BRIEF COMMUNICATIONS

Use of Ozone for Preparing 4-Nitrobenzoic Acid in a Closed Process Cycle

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Abstract—The possibility of preparing 4-nitrobenzoic acid in a closed process cycle by oxidation of 4-nitrotoluene with an ozone–air mixture was examined. The optimal conditions of oxidation with multiple use of mother liquors were found, and the conditions for crystallization of 4-nitrobenzoic acid from the reaction mixture were determined. The effects of water, acetic anhydride, and catalyst on the oxidation performed in mother liquors after filtration of the target product were examined.

4-Nitrobenzoic acid is widely used in production of organic intermediates, dyes, and drugs [1]. In industry, it is produced by oxidation of 4-nitrotoluene with potassium dichromate in sulfuric acid [2], with dilute nitric acid [3], and with atmospheric oxygen in the presence of catalysts (metals of variable oxidation state and bromine compounds) [4]. Oxidation by mineral oxidants occurs under mild conditions but yields large amounts of toxic and difficult-to-utilize wastes. Oxidation by atmospheric oxygen occurs under rigorous conditions and, therefore, requires sophisticated equipment. In this context, low-temperature reaction of ozone with 4-nitrotoluene in acetic acid shows promise. In the presence of cobalt bromide catalyst, oxidation of 4-nitrotoluene by ozone-air mixture occurs under mild conditions (atmospheric pressure, 95°C), and the yield of 4-nitrobenzoic acid reaches 96% [5].

In this study, we developed a closed process cycle for production of 4-nitrobenzoic acid by oxidation of 4-nitrotoluene.

EXPERIMENTAL

Oxidation of 4-nitrotoluene was performed in a vertical cylindrical reactor equipped with a blade stirrer (7.5–13.3 rps) and a bubbler. The reactor was charged with 40 ml of glacial acetic acid, 4-nitrotoluene (0.5 M), cobalt(II) acetate (0.195 M), and potassium bromide (0.084 M). The stirring was switched on, and the mixture was heated to 95°C. After dissolution of the catalyst, an ozone–air mixture con-

taining 4.7×10^{-4} M ozone was fed at a rate of 8.3×10^{-3} l s⁻¹. Oxidation was performed until complete exhaustion of 4-nitrotoluene and was monitored by GLC [6].

After oxidation, the reaction mixture was cooled to 13–14°C, and the precipitated carboxylic acid was filtered off, washed on the filter with hydrochloric acid, and recrystallized from water; yield 96%. The filtrate was returned to the oxidation stage. The wash



Fig. 1. Oxidation of 4-nitrotoluene by ozone–oxygen mixture in mother liquor. [ArH] = 0.5, $[O_3] = 4.7 \times 10^{-4}$, $[CoAc_2] = 0.0195$, [KBr] = 0.084 M; $T = 95^{\circ}$ C; the same for Fig. 2. (*C*) Water concentration and (τ) time. Concentration of (*1*–4) 4-nitrotoluene and (*1*–4') 4-nitrobenzoic acid. Runs in the cycle: (*1*, *1'*) first; (2, 2') second with full catalyst loading; (*3*, *3'*) third with full catalyst loading; and (*4*, *4'*) second with addition of 0.495 M (CH₃CO)₂O, 0.01 M CoAc₂, and 0.063 M KBr.



Fig. 2. Effect of water on (1) accumulation rate and (2) yield of 4-nitrobenzoic acid. (ν) Accumulation rate, (η) yield, and (*C*) water concentration.

waters containing cobalt(II) chloride were evaporated, and the cobalt(II) salt was used as the reaction catalyst.

To optimize the crystallization conditions, we prepared standard mixtures consisting of 4-nitrobenzoic acid, cobalt(II) acetate, potassium bromide, and acetic acid taken in the same amounts as in the experiment on 4-nitrotoluene oxidation. The reaction solution obtained at 95°C was cooled with slow stirring. We found that the optimal conditions of quantitative isolation of 4-nitrobenzoic acid are cooling from 95 to 35°C at a rate of 1 deg min⁻¹ and from 30 to 14°C at a rate of 0.5 deg min⁻¹. With this schedule, 30– 60-µm crystals of the acid are formed.

Oxidation of 4-nitrotoluene by an ozone–oxygen mixture in a closed process cycle $(95^{\circ}C)^{*}$

Run no.	Degree of ozone utilization, %	4-Nitrobenzoic acid		
		yield, %	mp, °C	content, %
1	90.2	78.0	242.0	99.2
2	89.6	92.9	241.5	99.4
3	89.3	93.0	241.0	99.1
4	91.0	93.1	241.5	99.3
5	90.1	92.9	242.5	99.2
6	89.9	93.1	242.0	99.3
7	89.0	92.9	241.5	99.3
8	89.3	93.0	242.5	99.1
9	90.4	93.2	242.0	99.4
10	90.1	93.1	241.5	99.3

Charged, M: 4-nitrotoluene 1.01, KBr 0.095 (in run no. 1, 0.126), Co(II) acetate or chloride 0.014 (in run no. 1, 0.023), acetic anhydride 3.7 (in run no. 1, 0); in run no. 1, CH₃COOH (40 ml); in run nos. 2–10, filtrate after filtering off 4-nitrobenzoic acid (36.3 ml) containing cobalt(II) and bromine compounds.

Then we studied the effect of the crystallization time at 14° C. Below are given the crystallization time (min) and acid yields (%): 0, 52; 3, 60; 6, 70; 10, 78; 15, 78; and 20, 78. Thus, it is appropriate to perform crystallization for 10 min.

After keeping for 10 min, 4-nitrobenzoic acid was washed with concentrated HCl to remove the absorbed cobalt(II) acetate. After fivefold use in the washing stage, hydrochloric acid was distilled off, and cobalt chloride was used in the oxidation stage without additional treatment.

When we used the filtrate from crystallization of the target product as the solvent, we noticed a progressing decrease in the accumulation rate and yield of the aromatic acid with increasing number of recycles (Fig. 1). This might be due to partial loss of the catalyst. However, even addition of a full portion of the catalyst in experiments with the filtrate had no noticeable effect on the oxidation results (Fig. 1, second and third runs of the cycle).

The oxidation deceleration may also be due to formation of oxidation inhibitors: phenols, nitrobenzene, and water. The effect of inhibitors on the oxidation was studied after compensating for the partial loss of the catalyst in the previous run. We found that the rate of 4-nitrotoluene oxidation in the presence of phenol and nitrobenzene does not change noticeably, whereas addition of water appreciably decreases the oxidation rate and the process selectivity (Fig. 2). Therefore, under conditions of multiple use of the filtrate, when the content of water formed by the reaction increases from run to run, the oxidation selectivity will decrease.

To bind the water formed by the reaction, we performed experiments with addition of acetic anhydride. We found that at a concentration of acetic anhydride in the primary filtrate of 0.495 M (provided that the catalyst loss is compensated for, see table), the oxidation rate becomes equal to the rate of 4-nitrotoluene oxidation in glacial acetic acid, and the yield of the aromatic acid reaches 93%. Further increase in the concentration of acetic anhydride decreases the oxidation rate and selectivity, because, when the water formed by the reaction is completely bound, excess acetic anhydride starts to react with intermediate 4-nitrobenzaldehyde to form 4-nitrobenzylidene diacetate, which is more resistant to ozone [7].

The amount of the catalyst lost in the cycle was determined in the presence of acetic anhydride (0.495 M). We found that, on adding potassium bromide (0.063 M, 75%) and cobalt diacetate (0.012 M, 61.5%) to the recycling filtrate, the selectivity of 4-ni-

trotoluene oxidation fluctuates about 93%, i.e., the amount of the added components corresponds to the catalyst loss.

To check the possibility of multiple use of mother liquors, we performed seven cycles, with ten runs in each, with addition of the catalyst, to compensate for its loss in the previous run, and acetic anhydride. The yield of 4-nitrobenzoic acid in oxidation of 4-nitrotoluene in the mother liquor was obtained at a level of 93% (see table).

CONCLUSION

It is feasible to prepare 4-nitrobenzoic acid by oxidation of 4-nitrotoluene in a closed process cycle with multiple use of mother liquors.

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