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Kinetics of Catalyzed Liquid-Phase Oxidation of *p*-Nitrotoluene by Air in Basic Medium

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Abstract:

An alternative method for the oxidation of nitrotoluenes is described, using air with a cobalt catalyst in basic medium. Different process parameters were studied to realize the true kinetics of the process. At 28 °C and 16 atm air pressure, 96% selectivity at a conversion level of 40% for *p*-nitrotoluene was achieved in 18 h using cobalt phthalocyanine. For a given initial concentration of *p*-nitrotoluene, the reaction was found to be of first-order kinetics.

Introduction

Toluene and its derivatives undergo base-catalyzed autoxidation, and the carbanion[1−3] formed by the reaction of the base and the reactant undergoes oxidation by a free radical mechanism.[4] *p*-Nitrotoluene undergoes base-catalyzed oxidation with oxygen. These reactions usually require strong bases, such as potassium *tert*-butoxide in dipolar aprotic solvents.[5−8] Catalyst[9] plays an important role in this type of reaction. Though the oxidation by air in basic medium is well known, information regarding the process parameters and the kinetics is less highlighted in the published literature. Thus, efforts have been made to find the most suitable process conditions and the true reaction kinetics of such oxidations from the viewpoint of process research and development.

Experimental Section

The reactions were carried out in a 750-mL-capacity bubble column reactor. The reactor consisted of stainless steel tube of 5-cm inside diameter and 44-cm length. It was provided with an air purger, a thermometer pocket, a pressure gauge, and a vertical condenser. The reactor was heated when necessary by use of a Nichrome heating element wound on the reactor, and the heat input was controlled by a Variac; with proper manipulation of the heat input, it was possible to maintain the desired temperature in the reactor within ±5 °C. The compressor was used for supplying air. The pressure inside the reactor and the air flow rate were controlled by means of needle valves provided at the inlet and the outlet of the reactor. A calibrated rotameter was provided at the exit to measure the air flow rate.

Predetermined amounts of the catalyst and the substrate were mixed with the solvent, and the solution was shaken thoroughly to make it homogeneous. The reactor was then kept at the desired temperature, and the flow of air was started. After the reaction was allowed to proceed for the predetermined period, the reactor was allowed to cool to room temperature if required, and the pressure was released.

The major products of the reaction were the carboxylic acid and the aldehyde. The reaction mixture was filtered and distilled under vacuum to remove solvent. It was then diluted with water and acidified with dilute hydrochloric acid. The organic compound was extracted in toluene or benzene. The organic layer, after thorough washing with water, was then taken for analysis.

Analytical Section

Analysis of the Acid Formed in the Reaction by Acid−Base Titration. The carboxylic acid present in the reaction mixture was analyzed by taking a measured volume of the extracted organic layer. The extract was titrated with standard methanolic sodium hydroxide to estimate the carboxylic acid.

Analysis of Unreacted Nitrotoluenes by Gas Chromatography. Samples of 1−2 mL withdrawn at regular intervals of time were analyzed by gas chromatography (Chemito 8510). The details are as follows: column used, Stainless Steel, 3.2 mm i.d. × 2 m; packing, 10% SE-30 on Chromosorb-W; carrier gas, nitrogen; flow rate, 30 mL/min; detector, FID; oven temperature, 220 °C; injector temperature, 300 °C; detector temperature, 300 °C.

Analysis of Aldehyde Formed in the Reaction by Oximation. In a typical procedure, an accurately measured organic layer was diluted with methanol, and the pH of the solution was adjusted to 3.0. For measuring the pH, an electronic pH meter (Chemito) was used. A solution of hydroxylamine hydrochloride in 90% methanol was made, and the pH was adjusted to 3.0 separately. Both solutions were mixed and kept at 45 °C for 1 h.

The liberated HCl was titrated potentiometrically to pH 3.0 using 0.1 N sodium hydroxide solution. The amount of the aldehyde present in the sample was calculated as follows:

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(1) Sosnovsky, G. In *Organic peroxides*; Swern, D., Ed.; Wiley: New York, 1971; Vol. 3, p 354.

(2) Russell, G. A.; Moye, A. J.; Janzen, E. G.; Mak, S.; Talaty, E. R. *J. Org. Chem.* **1967**, *32,* 137.

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(9) Svensson, A. (Nobel Chemicals A.B.). U.S. Patent 4,866,204, 1989; *Chem. Abstr.* **1990**, *112,* 118456.

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$$\text{grams of aldehyde} = \frac{VNM}{1000}$$

where V is the volume of sodium hydroxide solution required, in milliliters, N is the normality of sodium hydroxide solution, and M is the molecular weight of the aldehyde.

Results and Discussion

This type of reaction completely depends on the effectivity of the base to form the carbanion and of the catalyst to absorb oxygen in the liquid phase. Different types of catalysts, such as cobaltous chloride, cobaltous bromide, and cobalt phthalocyanine were used. Different process parameters which are important for this process were studied to determine the optimum reaction conditions and the true kinetics of this process, using *p*-nitrotoluene as the model compound.

Material Balance. In a typical run, 96.36% material balance on isolation basis was achieved (Table 1). The loss may be due to distillation or handling.

Effect of Air Flow Rate. The reactor employed in this investigation was a typical bubble column reactor, where no mechanical agitator was provided for agitation. To maintain a high superficial linear velocity for adequate mixing, a sufficiently high flow rate of 3.0 L/min was maintained.

At a lower air flow rate of 1.2 L/min (Table 2), the conversion was relatively poor, presumably because of effects of mass transfer. When the air flow rate was increased from 1.2 to 3.0 L/min, the conversion of *p*-nitrotoluene increased markedly. To ascertain whether mass transfer effects have been eliminated, the air flow rate was increased from 2.4 to 3.0 L/min, and it was observed that almost the same conversion was achieved. Therefore, in all the subsequent runs, the air flow rate was maintained at 3.0 L/min, so that the effects of mass transfer could be eliminated, and the results obtained represented the true kinetics of the process.

Effect of Air Pressure. In this work, pressure was varied from 4 to 20 atm (Table 3). When the pressure was increased from 4 to 16 atm, there was an increase in the conversion of *p*-nitrotoluene. But with further increase of pressure from 16 to 20 atm, the conversion leveled off. Hence, in subsequent reactions, a pressure of 16 atm was maintained.

Effect of Different Reactants. Under the given reaction conditions, the conversions for different reactants such as *p*-nitrotoluene, *o*-nitrotoluene, *p*-xylene, *o*-xylene, α-picoline, β-picoline, γ-picoline, and *2*-methylpyrazine were studied. It was observed that the rate of oxidation of *p*-nitrotoluene was much faster than those of other compounds (Table 4). Picolines can also be oxidized, but the conversion level was only 7−10%. *2*-Methylpyrazine was also oxidized to give only 6% conversion.

Effect of Period of Reaction and Concentration of *p*-Nitrotoluene. With an increase in period of reaction, the conversion increased, and with an increase in substrate concentration, there was a small increase in the rate of reaction (Figure 1).

Effect of Temperature. The reaction temperature was varied from 28 to 70 °C (Figure 2). It was observed that, at lower temperatures the specific rate of the reaction was very poor, but the selectivity was as high as 87%. With an increase in temperature from 28 to 70 °C, the rate of reaction increased markedly, but the selectivity decreased a lot. At 70 °C, the selectivity (Table 5) was as low as 14.3% due to side reactions at basic conditions. Even at 40 °C, the rate of formation of dimerized product was high, and the selectivity was only 57%. In view of this, a temperature of 28 °C appears to be suitable for the process.

Effect of Molar Concentration of Potassium Hydroxide. In this reaction, base plays the most vital role. In view of this, different molar concentrations of potassium hydroxide were used to study the effect on the rate of reaction (Figure 3). For 10% w/v reactant concentration, it was observed that, with an increase in the molar concentration of potassium

Table 1. **Material balance for the basic oxidation of *p*-nitrotoluene**[a]

material	amount (Gmol)	*p*-nitrotoluene accounted for (%)
p-nitrotoluene taken	0.2189	100
p-nitrotoluene recovered from reaction mixture after reaction	0.1549	70.8
p-nitrobenzoic acid	0.05144	23.5
p-nitrobenzaldehyde	0.00254	1.16
other byproducts	0.00197	0.90
unaccounted	0.0079	3.64
total	0.2187	100

[a] Reaction conditions: Initial concentration of *p*-nitrotoluene, 10% w/v; temperature, 28 °C, catalyst, $CoCl_2$; catalyst loading, 5 g/L; air pressure, 16 atm; air flow rate, 3.0 L/min; reaction time, 18 h; solvent, methanol; reaction volume, 300 mL.

Table 2. **Effect of air flow rate on the rate of *p*-nitrotoluene oxidation**[a]

flow rate (L/min)	overall conversion of *p*-nitrotoluene (%)	conversion to acid (%)	conversion to aldehyde (%)	selectivity with respect to acid (%)
1.2	17	13	2.5	77
1.8	20	15.8	2.4	79
2.4	25	20.75	2	83
3.0	27	23.5	1.16	87

[a] Reaction conditions: initial concentration of *p*-nitrotoluene, 10% w/v; temperature, 28 °C; catalyst, $CoCl_2$; catalyst loading, 5 g/L; air pressure, 16 atm; reaction time, 18 h; solvent, methanol; reaction volume, 300 mL.

Table 3. **Effect of air pressure on the rate of *p*-nitrotoluene oxidation by air**[a]

air pressure (atm)	overall conversion of *p*-nitrotoluene (%)	conversion to acid (%)	conversion to aldehyde (%)	selectivity with respect to acid (%)
4	14	9.06	3.6	85.6
8	19	14.06	2.7	86.2
12	23	18.4	1.94	86.5
16	27	23.49	1.16	87.0
20	28	24.64	1.02	87.0

[a] Reaction conditions: initial concentration of *p*-nitrotoluene, 10% w/v; temperature, 28 °C; catalyst, $CoCl_2$; catalyst loading, 5 g/L; air flow rate, 3.0 L/min; reaction time, 18 h; solvent, methanol; reaction volume, 300 mL.

Table 4. **Effect of different reactants[a]**

reactant	overall conversion (%)	conversion to acid (%)	conversion to aldehyde (%)	selectivity to acid (%)
p-nitrotoluene	27	23.49	1.16	87.0
o-nitrotoluene	14	13.00	nil	92.8
p-xylene	4	3.87	nil	96.8
o-xylene	2	1.98	nil	99.0
α-picoline	8.5	8.07	nil	95.0
β-picoline	7	6.37	nil	91.0
γ-picoline	10	9.60	nil	96.0
2-methylpyrazine	6	5.34	0.45	89.0

[a] Reaction conditions: initial concentration of reactant, 10% w/v; temperature, 28 °C; catalyst, $CoCl_2$; catalyst loading, 5 g/L; air pressure, 16 atm; air flow rate, 3.0 L/min; reaction time, 18 h; solvent, methanol; reaction volume, 300 mL.

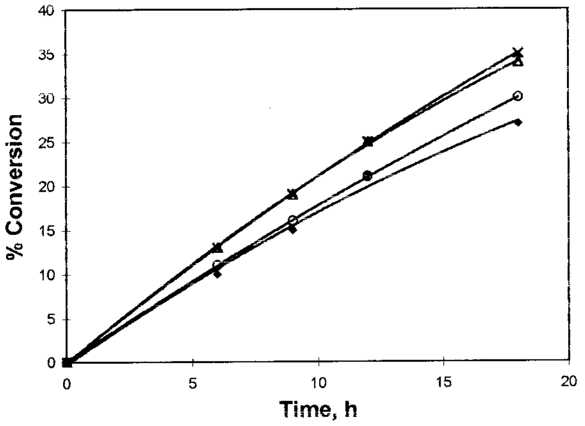

Figure 1. **Effect of initial concentration of reactant on overall conversion. Reaction conditions: temperature, 28 °C; catalyst loading, 5 g/L; air pressure, 16 atm; air flow rate, 3.0 L/min; reaction volume, 300 mL. Key to symbols (% w/v): ■, 10; ○, 15; △, 20; ×, 30.**

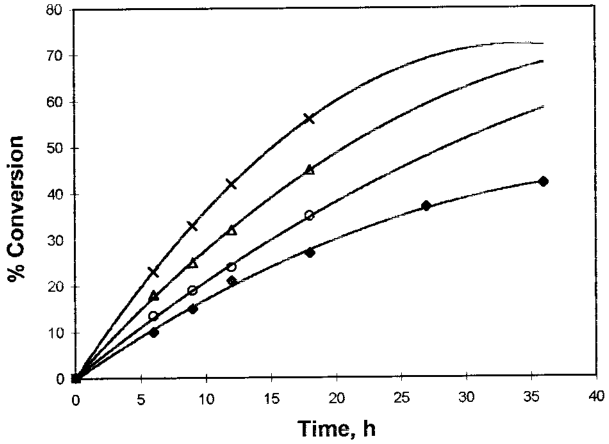

Figure 2. **Effect of temperature on overall conversion. Reaction conditions: initial concentration of reactant, 10% w/v; catalyst loading, 5 g/L; air pressure, 16 atm; air flow rate, 3.0 L/min; reaction volume, 300 mL. Key to symbols (°C): ◆, 28; ○, 40; △, 55; ×, 70.**

Table 5. **Effect of temperature on the rate of *p*-nitrotoluene oxidation by air[a]**

reaction temperature (°C)	overall conversion of *p*-nitrotoluene (%)	conversion to acid (%)	conversion to aldehyde (%)	selectivity with respect to acid (%)
28	27	23.5	1.16	87.0
40	42	23.94	Nil	57.0
55	65	21.645	Nil	33.3
70	86	12.30	Nil	14.3

[a] Reaction conditions: initial concentration of *p*-nitrotoluene, 10% w/v; catalyst, $CoCl_2$; catalyst loading, 5 g/L; air flow rate, 3.0 L/min; air pressure, 16 atm; reaction time, 18 h; solvent, methanol; reaction volume, 300 mL.

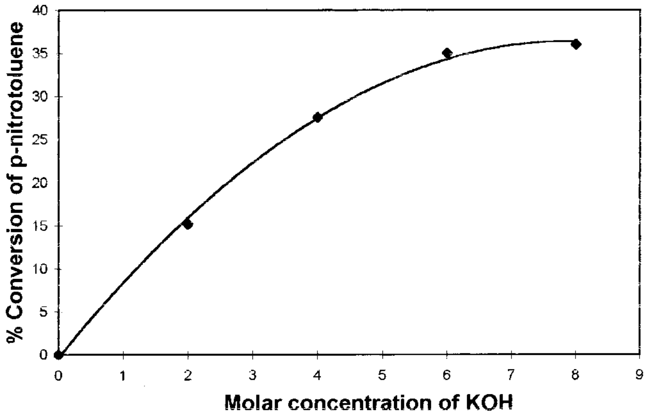

Figure 3. **Effect of molar concentration of potassium hydroxide. Reaction conditions: reaction temperature, 28 °C; reaction time, 18 h; air flow rate, 3 L/min; air pressure, 16 atm; catalyst loading, 5 g/L; reaction volume, 300 mL.**

Table 6. **Effect of different bases on the rate of *p*-nitrotoluene oxidation by air[a]**

base	overall conversion (%)	conversion to acid (%)	selectivity with respect to acid (%)
potassium hydroxide	23	19.7	85.7
sodium hydroxide	15	12.3	82.0
tert-butoxide	46	44.0	95.65

[a] Reaction conditions: initial concentration of *p*-nitrotoluene, 10% w/v; temperature, 28 °C; catalyst, $CoCl_2$; catalyst loading, 5 g/L; air flow rate, 3.0 L/min; air pressure, 16 atm; reaction time, 18 h; solvent, dimethylformamide; reaction volume, 300 mL.

hydroxide from 0 to 4 M, the conversion increased. With a further increase of base concentration from 4 to 6 M, the conversion increased, but the selectivity decreased from 87 to 83%. A further increase of base concentration from 6 to 8 M did not increase the rate of reaction. Thus, 4 M base concentration was found to be the best to obtain maximum selectivity, and further reactions were carried out at this base concentration.

Effect of Different Types of Base. Different types of bases, such as potassium hydroxide, sodium hydroxide, and potassium *tert*-butoxide, were used. In sodium hydroxide, it was found that the rate of reaction was slow, and in potassium *tert*-butoxide, the rate was very fast. Dimethylformamide was used as the solvent (Table 6).

Effect of Solvent. With a view to use the homogeneous catalyst system under consideration, the use of methanol, dimethylformamide, dimethyl sulfoxide, and 1,4-dioxane were considered. In all cases, the results obtained were

Table 7. **Effect of solvent on the rate of *p*-nitrotoluene oxidation by air**[a]

solvent	overall conversion (%)	conversion to acid (%)	selectivity with respect to acid (%)
methanol	27	23.5	87
DMF	23	19.7	85.7
DMSO	19	16.4	84.6
1,4-dioxane	11	9.53	86.2

[a] Reaction conditions: initial concentration of *p*-nitrotoluene, 10% w/v; temperature, 28 °C; catalyst, $CoCl_2$; catalyst loading, 5 g/L; air flow rate, 3.0 L/min; air pressure, 16 atm; reaction time, 18 h; reaction volume, 300 mL.

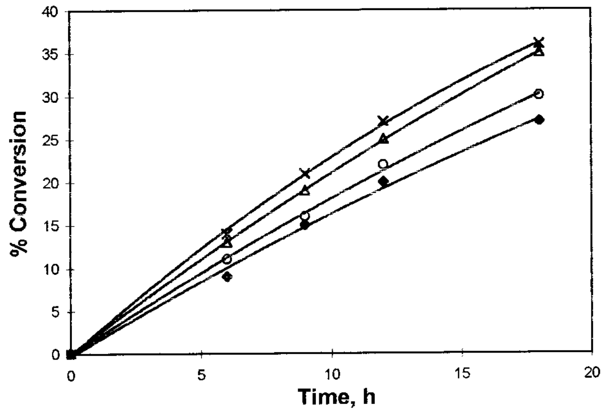

Figure 4. **Effect of catalyst loading on overall conversion. Reaction conditions: temperature, 28 °C; initial concentration of reactant, 10% w/v; catalyst, $CoCl_2$; air pressure, 16 atm; air flow rate, 3.0 L/min; reaction volume, 300 mL. Key to symbols (g/L): ◆, 5; ○, 8; △, 10; ×, 15.**

satisfactory (Table 7). In dioxane, the conversion was as low as 11%, and in methanol it was as high as 27% in 18 h.

Effect of Catalyst Loading. A range of 0−15 g/L of catalyst loading was studied. It was observed that, with an increase in catalyst loading from 0 to 10 g/L, the conversion of *p*-nitrotoluene increased significantly (Figure 4). When the catalyst loading was increased from 10 to 15 g/L, it was observed that there was no significant change in the conversion level. The selectivity remained almost the same.

Different Types of Catalysts. Cobaltous chloride, cobaltous bromide, and cobalt phthalocyanine were used as catalysts. It was observed that the conversion of *p*-nitrotoluene was almost the same when cobaltous chloride or cobaltous bromide (Table 8) was used. Under similar conditions, in the case of cobalt phthalocyanine, the conversion was very high.

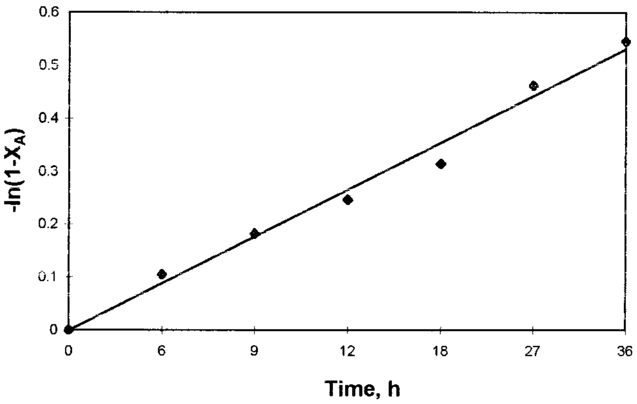

Figure 5. **Time vs $-\ln(1 - X_A)$. Reaction conditions: temperature, 28 °C; initial concentration of reactant, 10% w/v; catalyst loading, 5 g/L; air pressure, 16 atm; air flow rate, 3.0 L/min; reaction volume, 300 mL.**

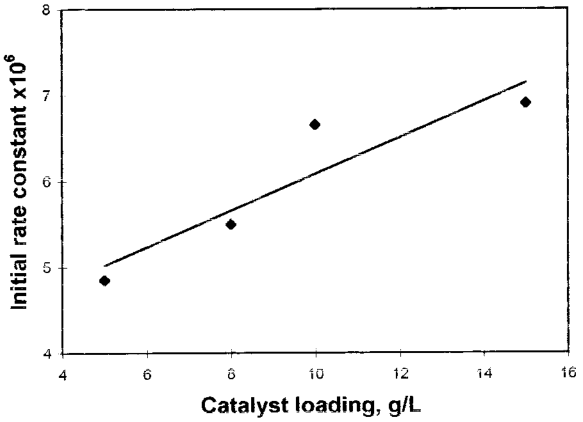

Figure 6. **Effect of catalyst loading on initial rate. Reaction conditions: temperature, 28 °C; initial concentration of reactant, 10% w/v; catalyst, $CoCl_2$; air pressure, 16 atm; air flow rate, 3.0 L/min; reaction volume, 300 mL.**

Kinetic Interpretation

To determine the true kinetics of the reaction, it was necessary to eliminate the mass transfer effects. To ensure that the mass transfer has been completely eliminated, the reactions were studied at higher flow rate and air pressure.

A plot of $-\ln(1 - X_A)$ vs t (Figure 5) gives a straight line passing through the origin. It proves that, under the given reaction conditions, the reaction is first order for a particular initial substrate concentration. From Figure 6, it is observed that the initial rate of reaction increased linearly with the increase in catalyst loading, which further supports the fact that it is a first-order reaction.

Table 8. **Effect of different types of catalysts on the rate of *p*-nitrotoluene oxidation by air**[a]

catalyst	overall conversion of *p*-nitrotoluene (%)	conversion to acid (%)	conversion to aldehyde (%)	selectivity with respect to acid (%)
cobaltous bromide	25	21.5	1.4	86
cobaltous chloride	27	23.5	1.16	87
cobalt phthalocyanine	40	38.4	1.02	96

[a] Reaction conditions: initial concentration of *p*-nitrotoluene, 10% w/v; temperature, 28 °C; catalyst loading, 5 g/L; air flow rate, 3.0 L/min; air pressure, 16 atm; reaction time, 18 h; solvent, methanol; reaction volume, 300 mL.

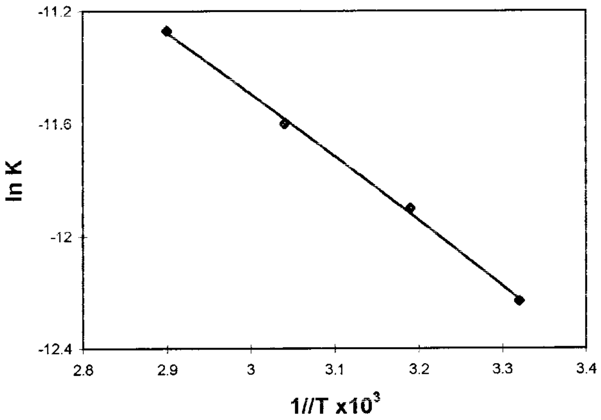

Figure 7. **Arrhenius plot. Reaction conditions: initial concentration of reactant, 10% w/v; catalyst loading, 5 g/L; air pressure, 16 atm; air flow rate, 3.0 L/min; reaction volume, 300 mL.**

From the Arrhenius plot, the energy of activation was found to be 4.5 kcal/mol (Figure 7). The low activation energy indicates that the reaction is intrinsically slow, as the mass transfer effect has already been removed.

Conclusions

The reaction follows a first-order kinetics with respect to *p*-nitrotoluene. The low activation energy indicates that the reaction is an intrinsically slow reaction.

Under the most suitable conditions, using cobalt phthalocyanine as the catalyst, dimethylformamide as the solvent, and *tert*-butoxide as the base, it was possible to achieve a conversion as high as 56% in 18 h.

Certain compounds, such as *o*-nitrotoluene, which are very difficult to oxidize to *o*-nitrobenzoic acid in acidic medium, can be oxidized in high selectivity by this method. As the reactions were conducted at 28 °C and the specific reaction rate was very low, there was absolutely no risk of formation of anthranilic acid by a base-catalyzed rearrangement.

Less expensive catalysts, such as cobaltous chloride or bromide, can be used to get a good conversion to benzoic acid instead of using much more costly catalysts, like metal porphines.

Unlike oxidations in acidic medium, the construction material is not at all a problem, as the reaction can be carried out at room temperature without any corrosive promoter like bromide salts.

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