

# KINETIC STUDIES OF THE CATALYTIC OXIDATION OF TOLUENE TO BENZOIC ACID IN THE LIQUID PHASE

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**ABSTRACT:** *The catalytic oxidation of toluene to benzoic acid in the liquid phase has been studied in an un-stirred tank reactor. Low concentration of acetic acid was added in order to increase the solubility of the catalyst in toluene. The dependence of the rate of reaction on the concentration of toluene catalyst and oxygen pressure was studied. It has been suggested that liquid phase oxidation of toluene to benzoic acid primarily is a diffusion controlled reaction and the order of reaction with respect to oxygen shifts to lower values by stirring.*

**KEY WORDS:** *Catalytic oxidation, Toluene, Benzoic acid, Rate of reaction, Diffusion controlled reaction.*

Oxidation of toluene to benzoic acid has been studied by many investigators [1-4]. However, kinetic and mechanistic studies of this reaction are very limited. *Bhattacharya* et al. [5] have studied the kinetics of reaction at high concentration of acetic acid in presence of cobalt acetate as catalyst and potassium bromate as catalyst promoter in a flow reactor with air flow of 2.8-3.3 lit/min. Under these conditions the reaction is first order with respect to catalyst and half order with respect to oxygen pressure.

*Panneerselvam* et al. [6] have studied the catalytic oxidation of toluene in concentrated solution of acetic acid in presence of cobalt acetate and potassium bromate in a packed bed reactor with air flow of 4.25 lit/min at atmospheric pressure. Under these condition the order of reaction with respect to catalyst is

0.25 and with respect to oxygen is 0.3 in the oxidation of toluene to benzaldehyde and 0.25 and 0.3 respectively in it's subsequent oxidation to benzoic acid.

Thermal oxidation of toluene to benzoic acid has been studied by *Blanco* and *Royo* [7] in a well stirred tank reactor with 300 r.p.m. mechanical mixing and air flow rate of 2.8 lit/min at oxygen partial pressure of 4.2 atmosphere. Reaction is independent of oxygen pressures under these conditions.

*Ivanov* [8] has studied the role of acetic acid in the catalytic oxidation of toluene and has shown that reaction is much slower in acetic acid solution than in the absence of it despite of considerably higher stability of catalyst in the presence of acetic acid. He has proposed that catalyst activators raises the kinetic equilibrium concentration of carbonyl com-

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pounds and peroxides.

In agreement with Ivanov results we have also found that the induction time, that is the time gap for absorption of oxygen, increases with acetic acid concentration. At very high concentration of acetic acid [more than 40% (V/V)] for oxygen pressure of 10.7 atmospheres at 145 °C and catalyst concentration of  $8.03 \times 10^{-3}$  mol/lit reaction stops completely.

Analysis of these results shows that the rate of reaction depends on acetic acid concentration and the rate of stirring (mechanical, flow or both). Therefore, in kinetic studies of the liquid phase oxidation of toluene to benzoic acid either the dependence of rate of reaction on the concentration of acetic acid and rate of stirring should be taken into account or the effect of these important factors should be minimized.

In order to minimize the effect of these parameters we have studied the catalytic oxidation of toluene to benzoic acid in the liquid phase in an un-stirred tank reactor and have reduced the amount of acetic acid to 5%(V/V).

Our experimental results suggest that the rate equation for catalytic oxidation of toluene to benzoic acid in an un-stirred tank reactor is:

$$\frac{-dr}{dt} = K[\text{Toluene}][\text{Catalyst}]^{0.21}[\text{PO}_2]^n$$

where  $n = 1$  in the range of 4 to 7 atmosphere pressure range. A lower pressures  $1 < n < 1.8$  and at higher pressures  $0 < n < 1$ .

These results in comparison with other results under different operational conditions suggest that the order of reaction with respect to toluene concentration does depend on the operational conditions, i.e., on the concentration of acetic acid, catalyst and stirring. Order of 0.21 with respect to other values obtained under different operational conditions suggest that although acetic acid increases the solubility of cobalt acetate in toluene, but at the same time decreases its activity because of the cage effect.

The order of reaction with respect to oxygen depends on the presence of oxygen in the reaction sites and this depends on the stirring rate of the reaction mixture and the diffusion of oxygen through the liquid.

## EXPERIMENTAL

The reactor consisted of a 140 mL stainless steel cylindrical vessel with two valves and one internal thermocouple for measuring the reaction temperature. Cobalt acetate was dissolved in 5 mL of glacial acetic acid and was added to 95 mL of toluene.

The reactor was flushed with oxygen and filled with oxygen to the desired pressure at room temperature. The oxygen valve was then closed and reactor was immersed in an oil thermostat bath set at the desired temperature within  $\pm 1$  °C. After thermal equilibrium oxygen valve was opened and oxidation was carried out at constant pressure. The reaction was quenched at desired time by removing the reactor from the oil bath and immersing it in an ice bath. The amount of benzoic acid present was measured by back titration and corrected for acetic acid in the reaction mixture.

The amount of benzaldehyde measured by oxime reaction was negligible and was not taken into account.

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