

Aerial oxidation of substituted aromatic hydrocarbons catalyzed by Co/Mn/Br⁻ in water-dioxane medium

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Abstract

Aerial oxidation of substituted aryl aromatic hydrocarbons were carried out using Co/Mn/Br⁻ catalyst system in water-dioxane medium in the range 14–56 bar air and temperature 383–423 K. The combination of optimum catalyst concentration of salts Co(OAc)₂, Mn(OAc)₂ and NaBr (1:3:10 molar ratio) in water-dioxane (1:2 mole ratio) is found catalyze aerial oxidation of substituted aryl aromatic to give corresponding oxygenated products. Under the optimized conditions, *p*-cymene gave *p*-isopropyl benzaldehyde (33.1%), *p*-isopropylbenzyl alcohol (54.7%) and *p*-isopropyl benzoic acid (3.3%), respectively, at *p*-cymene conversion 40.2%. Similarly, oxidation of *p*-methoxy toluene gave *p*-methoxy benzaldehyde (87.4%), benzyl alcohol (5.5%), and *p*-methoxy benzoic acid (6%), while oxidation of *p*-*tert*-butyl toluene yielded *p*-*tert*-butyl benzaldehyde (87%), *p*-*tert*-butyl benzyl alcohol (5.7%) and *p*-*tert*-butyl benzoic acid (6.1%), at conversions 16.4% and 36.1%, respectively. It is found that Co/Mn/Br⁻ catalyst system in water-dioxane medium is effective in the aerial oxidation of substituted aromatic hydrocarbons to get corresponding alcohol and aldehydes in greater yields.

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1. Introduction

Oxidation reactions occupy a prominent place in both the sciences of catalysis and catalysis-based modern chemical industry [1,2]. They have vastly contributed to the development of the modern society, for their products are incorporated into an amazingly large proportion of the materials and commodities in daily use. In chemical industry more than 60% of products are obtained by catalytic oxidation routes. Terephthalic acid (TA) is commercially manufactured by the dioxygen oxidation of *p*-xylene using Co/Mn/Br⁻ catalyst system in acetic acid medium [3–5]. The issues to be addressed in liquid phase catalytic oxidation of aromatic hydrocarbons are to find efficient catalyst systems, free from bromide promoter and replacement of acetic acid solvent, both these factors cause corrosion problems in

operating system. In addition to these, there is a significant loss in acetic acid (5–10 wt% of TA) getting oxidized to CO and CO₂, which requires the lowering the reaction temperature without reducing reaction rates.

Oxidation of *p*-cymene is important, because, of its oxidation products *p*-isopropyl benzylalcohol and *p*-isopropyl benzaldehyde is used in perfumes and has export potential. The latter is also used as a flavoring agent for food materials and *p*-isopropyl benzoic acid is used as a pharmaceutical intermediate. Oxidation of *p*-cymene by molecular oxygen to *p*-isopropylbenzoic acid or its intermediate alcohol and aldehyde catalyzed by Co and Mn complexes in acetic acid medium with acetaldehyde or methyl ethyl ketone as radical initiators [6,7], cerium (IV) ammonium nitrate in acetic acid to give nitro and acetate substituted derivatives [8] and oxides of Cr, Mn and Se have been reported [9]. Similarly, liquid and vapor phase oxidation of *p*-methoxytoluene and *p*-*tert*-butyltoluene, wherein conventional catalysts consisting Co, Mn and NaBr salts in acetic acid

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medium and vanadium pentoxide based catalysts, for the vapor phase oxidation of *p*-methoxy toluene to *p*-methoxy benzaldehyde have also been reported [10–17]. Mechanisms of oxidations using Co/Mn/Br⁻ catalyst systems in acetic acid medium, are well established in the literature, however, the oxidation of substituted aryl aromatic hydrocarbons to get corresponding alcohol and aldehydes in higher yields is still important from industrial view point.

Therefore, we are reporting here our results on the oxidation of substituted aryl aromatic hydrocarbons in water-dioxane medium using conventional Co/Mn/Br⁻ catalyst system and optimized reaction conditions for higher substrate conversions and product yields.

2. Experimental

Cobalt acetate, manganese acetate, sodium bromide and 1,4-dioxane (AR grade) were procured from M/s. Loba Chemie, Mumbai. Double distilled water and air from the cylinder was used as a source of molecular oxygen in the oxidation reaction. *p*-Cymene, *p*-methoxy toluene and *p*-*tert*-butyl toluene supplied by M/s. Malti Chemicals, Baroda were distilled and purity checked from GC prior to their use in the oxidation experiments. Oxidation experiments were conducted in a 300 ml pressure reactor (M/s Parr Instruments Co., USA).

In a typical run, known amounts of substrate, metal salts Co(OAc)₂ · 4H₂O, Mn(OAc)₂ · 4H₂O, NaBr, water, 1,4-dioxane was mixed in the reactor. The reactor was pressurized with air from the cylinder and the bomb was heated to attain the required temperature. At this stage, the agitation was started to initialize the reaction and sample was withdrawn through sample valve. The reaction was continued for a period of 2–3 h and stopped. At the end of a run, reactor was cooled to room temperature and the reaction mixture was transferred to a beaker. The reaction mixture withdrawn in the beginning and at the end of the reaction were analyzed by gas chromatography (Shimadzu, GC-14B) with a 6 ft 10% SE-30 S.S.packed column, 1/8 in O.D and FID (detector). From GC analysis, the conversion of substrate and selectivities for products were obtained. The identities of the oxidation products were made by GC-MS (Shimadzu GCMS QP 5400).

3. Results and discussion

Oxidation of *p*-cymene catalyzed by Co/Mn/Br⁻ catalyst system with air gave *p*-isopropylbenzyl alcohol, *p*-isopropyl benzaldehyde and *p*-isopropyl benzoic acid and the results along with reaction conditions are presented in Table 1. Similarly, aerial oxidation of *p*-*tert*-butyl toluene and *p*-methoxy toluene gave corre-

sponding aldehydes, alcohols and carboxylic acids and the results along with the reaction conditions are presented in Table 2. The oxidation reactions and their products obtained are shown in Schemes 1–3, respectively.

The oxidation of *p*-cymene was carried with different mole ratios of catalyst salts to know their effect of on the conversion of *p*-cymene and product selectivities. From the results (entry nos. 1–3, Table 1), it is found that Co:Mn:Br⁻ (1:3:10, mole ratio) gave marginally higher conversion (39.1%) of *p*-cymene at 42 bar air and 423 K after 3 h. However, the selectivities for *p*-isopropyl benzyl alcohol were higher than *p*-isopropyl benzaldehyde and *p*-isopropyl benzoic acid. Hence, Co:Mn:Br⁻ (1:3:10, mole ratio) was used for studying the effect of temperature, air pressure and time on stream on the conversion and product distribution in the oxidation of *p*-cymene reaction.

3.1. Effect of temperature

The influence of temperature on the oxidation of *p*-cymene was studied by varying the temperature from 383 to 443 K, with Co:Mn:Br⁻ (1:3:10, mole ratio), 42 bar air and 2 h. From the results (entry nos. 4A–4C, Table 1) it is seen that maximum conversion of *p*-cymene (49.5%) was observed at 443 K. Corresponding alcohol and aldehyde selectivities were found to be 54.1% and 39.1%, respectively. However, at lower temperature conversions was comparatively less, while selectivities for *p*-isopropylbenzyl alcohol were higher. The selectivities for *p*-isopropyl benzaldehyde increased with increase in temperature, because, of consecutive reactions steps involved in the oxidation of *p*-cymene. The side products were higher particularly at lower temperatures and for a reasonable conversion minimum temperature should be around 403 K for the oxidation of *p*-cymene.

3.2. Effect of pressure (Air)

The oxidation of *p*-cymene was carried out to know the effect of air (O₂) pressure ranging between 14 and 56 bar at 423 K. From the results (entry nos. 5A–5D, Table 1), it is seen that the conversion of *p*-cymene increased from 20.6% to 60.2% with increase in pressure. The selectivity for *p*-isopropylbenzyl alcohol steadily increased and *p*-isopropyl benzaldehyde decreased with increase in pressure. Higher pressure seems to stabilize a primary oxidation product *p*-isopropyl benzyl alcohol leading to its higher selectivity.

3.3. Effect of Br⁻ concentration

To find the effect of Br⁻ concentration in the aerial oxidation of *p*-cymene, the mole ratio of Co:Mn:Br is varied in such a way that the total moles (moles added) varied was in the range 3.5–14 mmol. The variation in

Table 1
Catalytic data of oxidation of *p*-cymene^a

Run	Catalyst composition ^b (mmol)	Conversion (wt%)	TOF ^c	Product distribution (wt%) ^d			
				A	B	C	Others
1	Co (1) + Mn (3) + NaBr (10) (3 h)	39.1	0.31	54.7	33.1	3.3	8.9
2	Co (3) + Mn (1) + NaBr (10) (3 h)	35.2	0.28	57.7	32.1	2.7	7.5
3	Co (1) + Mn (1) + NaBr (10) (3 h)	32.6	0.30	59.2	31.2	2.3	7.3
Effect of temperature ^e							
4A	Co (1) + Mn (3) + NaBr (10) (2 h)	6.8	0.04	71.7	15.5	1.6	11.2
4B	Co (1) + Mn (3) + NaBr (10) (2 h)	42.0	0.25	67.3	25.4	1.7	5.6
4C	Co (1) + Mn (3) + NaBr (10) (2 h)	49.5	0.30	54.0	39.1	1.8	5.1
Effect of pressure ^f							
5A	Co (1) + Mn (3) + NaBr (10) (2 h)	20.6	0.13	50.7	36.9	6.7	5.7
5B	Co (1) + Mn (3) + NaBr (10) (2 h)	36.3	0.22	53.2	35.0	5.8	6.0
5C	Co (1) + Mn (3) + NaBr (10) (2 h)	49.5	0.30	55.0	33.1	4.9	7.0
5D	Co (1) + Mn (3) + NaBr (10) (2 h)	60.2	0.36	59.7	31.3	2.4	6.6
Effect of Br ⁻ concentration ^g							
6	Co (1) + Mn (3) + NaBr (10) (2 h)	49.5	0.30	54.0	34.1	1.8	10.1
7	Co (0.5) + Mn (1.5) + NaBr (5) (2 h)	44.0	0.27	51.8	38.1	1.7	8.4
8	Co (0.25) + Mn (0.75) + NaBr (2.5) (2 h)	37.2	0.25	49.8	39.5	1.5	9.2
Time on stream ^h							
9A	Co (1) + Mn (3) + NaBr (10) (2 h)	40.2	0.47	54.7	33.1	3.3	8.9
9B	Co (1) + Mn (3) + NaBr (10) (4 h)	74.8	0.45	63.5	19.4	3.8	13.3
9C	Co (1) + Mn (3) + NaBr (10) (6 h)	93.8	0.38	54.2	14.4	14.8	16.6

^a Reaction conditions: medium *p*-cymene (33.58 mmol) + NaBr (10 mmol) + H₂O (311 mmol) + 1,4-dioxane (568 mmol), time = 3 h, air pressure = 42 bar, temperature = 423 K.

^b The sources of Co and Mn are Co(OAc)₂ · 4H₂O and Mn(OAc)₂ · 4H₂O, respectively. Values in the parenthesis refer to the number of mmol of catalyst. In runs 1–5D, 10 mmol of NaBr was used.

^c Turnover frequency (TOF) = mole of *p*-cymene converted per mole of metal salt per hour.

^d A = *p*-isopropylbenzyl alcohol, B = *p*-isopropyl benzaldehyde, C = *p*-isopropyl benzoic acid.

^e In runs 4A–4C, *p*-cymene = 17.16 mmol, time = 2 h, temperature = 383, 403, 423 K, respectively.

^f In runs 5A–5D, *p*-cymene = 17.16 mmol, time = 2 h, air pressure = 14, 28, 42, 56 bar, respectively.

^g In runs 6, 7, 8, *p*-cymene = 17.16 mmol, time = 2 h, air pressure = 42 bar, temperature = 423 K.

^h In runs 9A–9C, *p*-cymene = 33.58 mmol, air pressure = 56 bar, temperature = 423 K, time = 2 h, 4 h, 6 h, respectively, (each time reactor was cooled, gas discharged and fresh air charged to continue the run).

Table 2
Catalytic data of oxidation of different substrates

Run	Substrates	Conversion (wt%)	TOF ^j	Product distribution (wt%)			
				A	B	C	Others
1	<i>p</i> -cymene	40.2	0.47	33.1 ^a	54.7 ^b	3.3 ^c	8.9
2	<i>p</i> -methoxy toluene	36.1	0.43	87.4 ^e	5.5 ^h	6.0 ⁱ	1.1
3	<i>p</i> - <i>tert</i> -butyl toluene	16.4	0.20	87.0 ^d	5.7 ^c	6.1 ^f	1.2

Conditions: medium substrate (33.58 mmol), Co (1 mmol) + Mn (3 mmol) + NaBr (10 mmol) + H₂O (311 mmol) + 1,4-Dioxane (568 mmol), time = 2 h, air pressure = 56 bar, temperature = 423 K. The sources of Co and Mn are Co (OAc)₂ · 4H₂O and Mn (OAc)₂ · 4H₂O, respectively.

^a *p*-isopropyl benzaldehyde.

^b *p*-isopropylbenzyl alcohol.

^c *p*-isopropyl benzoic acid.

^d *p*-*tert*-butyl benzaldehyde.

^e *p*-*tert*-butyl benzyl alcohol.

^f *p*-*tert*-butyl benzoic acid.

^g *p*-methoxy benzaldehyde.

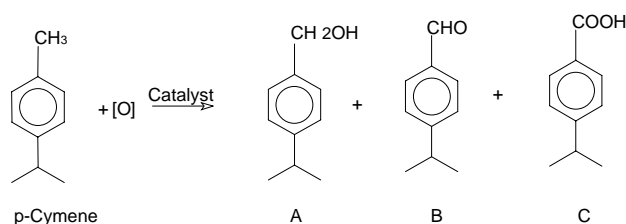
^h *p*-methoxy benzyl alcohol.

ⁱ *p*-methoxy benzoic acid.

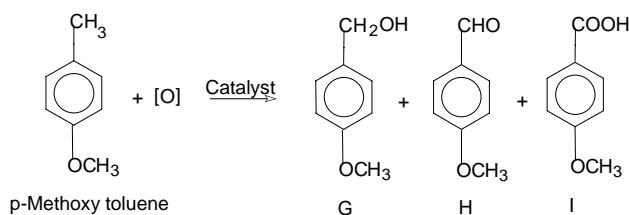
^j Turnover frequency (TOF) = mole of substrate converted per mole of metal salt per hour.

total moles of catalyst components, actually amounts to the variation in total catalyst concentration in the reaction mixture. It is seen from the results presented in

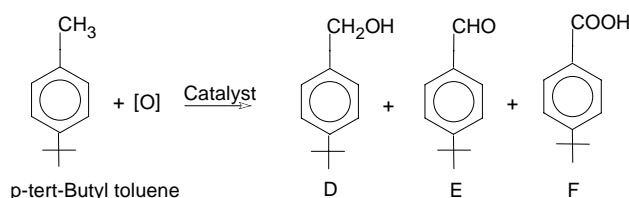
Table 1 (entry nos. 6–8), that the conversion of *p*-cymene decreased with decrease in catalyst concentration. At all catalyst concentrations, the selectivities for



Scheme 1. Oxidation of *p*-cymene. A, *p*-isopropylbenzyl alcohol; B, *p*-isopropyl benzaldehyde; C, *p*-isopropyl benzoic acid.



Scheme 2. Oxidation of *p*-*tert*-butyl toluene. G, *p*-methoxy benzyl alcohol; H, *p*-methoxy benzaldehyde; I, *p*-methoxy benzoic acid.



Scheme 3. Oxidation of *p*-methoxy. D, *p*-*tert*-butyl benzyl alcohol; E, *p*-*tert*-butyl benzaldehyde; F, *p*-*tert*-butyl benzoic acid.

p-isopropylbenzyl alcohol and *p*-isopropyl benzaldehyde were higher with smaller amounts of *p*-isopropyl benzoic acid. Side products were higher at higher conversion of *p*-cymene.

3.4. Time on stream

In order to obtain maximum conversion of *p*-cymene, the oxidation reaction was carried out for the total period of 6 h. After every 2 h, the reactor was cooled and charged with fresh air. From the results presented in Table 1 (entry nos. 9A–9C), that a maximum conversion of *p*-cymene (93.8%) was obtained at the end of 6 h with *p*-isopropylbenzyl alcohol and *p*-isopropyl benzaldehyde selectivities 54.2% and 14.4%, respectively. Entry no. 9B (Table 1) at *p*-cymene conversion (74.8%), the highest selectivity of 63.5 for *p*-isopropylbenzyl alcohol was obtained.

3.5. Oxidation of *p*-methoxytoluene and *p*-*tert*-butyl-toluene

Under the optimized conditions of *p*-cymene oxidation, the aerial oxidation of *p*-methoxy toluene and

p-*tert*-butyl toluene was conducted and the results obtained are presented in Table 2. It is seen that, *p*-cymene and *p*-methoxy toluene could be oxidized easily than *p*-*tert*-butyl toluene. In comparison with *p*-cymene, the oxidation of *p*-methoxy toluene and *p*-*tert*-butyl toluene is found to be more selective to corresponding aldehydes under the reaction conditions.

4. Conclusions

Thus, the specific activity (TOF) for *p*-cymene conversion is enhanced by the presence of Co, Mn and NaBr concentrations in water-dioxane medium. The conversion of *p*-cymene increased at higher temperature and air pressure. High yields of aldehydes and alcohols could be obtained if reactions were carried out at a low temperature under conditions of oxygen starvation (pressure requirement). On the other hand if the reaction temperatures and oxygen concentration (air pressure) are at higher levels, the intermediate product aldehyde quickly oxidizes to carboxylic acid.

A decrease in catalyst mole ratio from 14 to 3.5 decreased the conversion of *p*-cymene. From the observations made, it is concluded that the optimum conditions for maximum conversion of *p*-cymene (>93%) and high product selectivity for alcohol and aldehyde is to carry out the reaction at 423 K and 56 bar air for 6 h, with Co/Mn/Br⁻ catalyst mole ratio 1:3:10 in water-dioxane medium. Similarly, *p*-methoxy toluene and *p*-*tert*-butyl toluene are oxidized more selectively to corresponding aldehydes under the optimized reaction conditions. Therefore, we conclude that the aerial oxidation of substituted aryl hydrocarbons could be effectively carried out with the conventional catalyst system under liquid phase conditions in water-dioxane medium, which avoids the loss of acetic acid and minimize corrosion problems of the conventional system.

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