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Note

Studies on the oxidation of 4-methyl phenol

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The liquid phase catalytic oxidation of 4-methyl phenol (*p*-cresol) and the effect of different parameters, viz., time, temperature and pressure on the final yield has been studied.

p-Hydroxy benzaldehyde (PHB) is an important chemical intermediate in the manufacture of agrochemicals, uv stabilizers, dyes, textile auxiliaries, food and pharmaceutical products[1-3]. It is generally manufactured from phenol and chloroform under alkaline conditions using Riemer Tiemann reaction[4]. Several indirect methods such as starting from phenol and formaldehyde (via 4-hydroxy benzyl alcohol followed by oxidation)[5] or from *p*-nitro toluene[6] (via reduction, diazotisation followed by the hydrolysis of the resultant diazonium salt), have been reported which consists of many steps with cumbersome procedures.

Direct oxidation of *p*-cresol has been widely reported using several types of simple and complex metal catalysts like cobalt chloride, cobalt acetate, cobalt phthalocyanins, cobalt (salen) and CuCl-py[7-10]. However, these reactions give complex by-products due to accompanied coupling, polymerization, and ring opening reactions[11,12] where the final yields are generally low.

In this communication, studies on the direct oxidation of *p*-cresol has been reported which were carried out in an autoclave with 1 – 5 bar pressure of oxygen by varying the parameters like reaction time and quantities of cobalt based catalyst. Alkali and charcoal which act as the oxygen absorbing media were used which provide more surface area for oxidation.

Experimental procedure—All the reagents used were of LR grade. High performance thin layer chromatography (HPTLC) of Camag (Switzerland) make has been used for qualitative and quantitative analysis of the reaction products. Precoated TLC aluminium sheets with silica gel 60 having fluorescent indicator of 0.2 mm thickness (E Merck) have been used for HPTLC analysis. Bands were applied with the Lino-met IV automatic applicator. The solvent system used for elution is EtOAc : Hexane (1:2). Indigeneously manufactured laboratory autoclave is used for carrying out the oxidation reactions.

p-Cresol in methanol and NaOH were placed in an autoclave. Cobalt catalyst mixed with charcoal is added to it which was pressurised with oxygen to 1 – 5 bar. The contents were stirred at 65 – 75°C for few hours, cooled, filtered and filtrate was concentrated to remove methanol. The residue was acidified and extracted with ethyl acetate, which was subjected to qualitative and quantative analysis by HPTLC using the standard samples.

Results and discussion—The results obtained by HPTLC analysis (Table 1) reveal that in most of the cases either the conversion or the selectivity of the reaction was poor depending upon the reaction time and oxygen pressure. As the time of reaction was increased the high polar impurities have been increased (Expt 13) whereas at less time the conversion was low (Expt 11). In general, the results show that cobalt phthalocyanine was relatively less active than cobalt acetate tetra hydrate. It is expected to be due to the insolubility of metal phthalocyanins in aqueous medium. Water soluble derivatives like sulfonates or carboxylates of metal phthalocyanins are reported to give higher yields in oxidation[13]. Better results were seen when the oxidation was carried out at 65 – 75°C, with cobalt catalyst mixed with excess charcoal in presence of alkali and methanol under 3 bar oxygen pressure for 6 h where negligible amount of high polar impurities were formed with 86% of PHB. The enhanced activity and selectivity may be attributed to high solubility of cobalt acetate in aqueous media as compared to cobalt phthalocyanin and the high surface area provided by charcoal.

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Table 1—Experimental data on the oxidations of *p*-cresol

Expt No.	Chemicals used/g, g	Catalyst used	O_2 pressure, bars	Temp, °C	Time, h	Product analysis by HPTLC
1	*p*-Cresol = 10.8 NaOH = 4.4 Charcoal = 2.2 Methanol = 100.0	Cobalt phthalocyanine (120 mg)	2	65 – 75	2	*p*-Cresol = 93.0 % PHB = 5.8 %
2	*p*-Cresol = 10.8 NaOH = 14.0 Charcoal = 7.5 Methanol = 30.0	Cobalt phthalocyanine (60 mg)	1	65 – 75	4	*p*-Cresol = 92.0 % PHB = 7.6 %
3	*p*-Cresol = 10.8 NaOH = 14.0 Charcoal = 7.5 Methanol = 30.0	Cobalt phthalocyanine (60 mg)	2	65 – 75	10	*p*-Cresol = 85.0 % PHB = 11.6 % Others = 3-4 %
4	*p*-Cresol = 10.8 NaOH = 14.0 Charcoal = 7.5 Methanol = 30.0	Cobalt phthalocyanine (60 mg)	5	100	8	*p*-Cresol = 82.0 % PHB = 10.5 % Others = 5.6 %
5	*p*-Cresol = 10.8 NaOH = 12.0 Charcoal = 0.5 Methanol = 60.0	Cobalt chloride (500 mg)	2	65 – 75	2.5 5.5	*p*-Cresol = 22.0% PHB = 60.0 % Others = 16.0 % *p*-Cresol = 12.0% PHB = 50.0 % Others = 34.0 %
6	*p*Cresol = 10.8 NaOH = 8.0 Charcoal = 0.5 Methanol = 60.0	Cobalt chloride (250 mg)	atmospheric	65 – 75	10	*p*-Cresol = 92.9% PHB = 5.6 %
7	*p*-Cresol = 10.8 NaOH = 14.0 Charcoal = 00.5 Methanol = 100.0	Cobalt acetate (250 mg)	4	65 – 75	3	*p*-Cresol = 29.6 % PHB = 50.0 % Others = 18.0 %
8	*p*-Cresol = 10.8 NaOH = 10.0 Charcoal = 00.5 Methanol = 100.0	Cobalt acetate (500 mg)	2	65 – 75	5	*p*-Cresol = 20.0 % PHB = 50.0 % Others = 27.0 %
9	*p*-Cresol = 10.8 NaOH = 04.3 Charcoal = 00.5 Methanol = 20.0	Cobalt acetate (400 mg)	3	65 – 75	4	*p*-Cresol = 18.0 % PHB = 52.0 % Others = 25.7 %
10	*p*-Cresol = 10.8 NaOH = 14.0 Charcoal = 00.4 Methanol = 100.0	Cobalt acetate (250 mg)	1.5	60 – 65	3 6	*p*-Cresol = 50.0 % PHB = 45.4 % Others = 4.1 % *p*-Cresol = 15.0 % PHB = 50.2 % Others = 34.5 %
11	*p*-Cresol = 10.8 NaOH = 14.0 Charcoal = 7.5 Methanol = 60.0	Cobalt acetate (400 mg)	3	65 – 75	2	*p*-Cresol = 50.1 % PHB = 46.5 % Others = 2.2 %
12	*p*-Cresol = 10.8 NaOH = 14.0 Charcoal = 7.5 Methanol = 60.0	Cobalt acetate (400 mg)	3	65 – 75	6	*p*-Cresol = 11.6 % PHB = 85.1 % Others = 0.8 %
13	*p*-Cresol = 10.0 NaOH = 14.0 Charcoal = 7.5 Methanol = 60.0	Cobalt acetate (400 mg)	3	65 – 75	8	*p*-Cresol = 8.9 % PHB = 76.7 % Others = 14.4 %
14	*p*-Cresol = 10.8 NaOH = 14.0 Charcoal = 7.5 Methanol = 60.0	Cobalt acetate (400 mg)	3	65 – 75	6	*p*-Cresol = 11.2 % PHB = 86.7 % Others = 0.8 %
15	*p*-Cresol = 43.2 NaOH = 56.0 Charcoal = 30.0 Methanol = 240.0	Cobalt acetate (1600 mg)	3	65 – 75	6	*p*-Cresol = 12.1 % PHB = 86.2 % Others = 0.7 %

Others = Unidentified high polar impurities seen on HPTLC.

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