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Combined acid additives and the MC catalyst for the autoxidation of *p*-xylene to terephthalic acid

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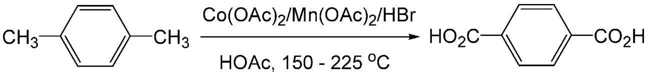
Abstract

The autoxidation of *p*-xylene (pX) was carried out with the $Co(OAc)_2/Mn(OAc)_2/Br^-$ catalyst in the presence of a strong acid, such as trifluoroacetic acid (TFA), heptafluorobutyric acid (HFBA) and *p*-toluenesulfonic acid. The initial reaction rates, measured by the rate of oxygen uptake, and the yields of terephthalic acid were used to compare the effectiveness of acid additives. All the acid additives improved significantly the effectiveness of the catalyst at their low concentrations. The autoxidation reaction increased with the $Mn(OAc)_2$ concentration. The reaction involves the formation of manganese(III) salts of strong acids, which are more powerful oxidizing agents than manganese(III) acetate. Thus, the cycles of free-radical chain reactions that involve formation of dibromide radical take place rapidly. Dibromide radical abstracts a hydrogen atom from the methyl group of *p*-xylene to form $ArCH_2^\bullet$, and then the sequence progresses through alcohol, aldehyde and carboxylic acid. Manganese(III) salts of strong acids also directly react with *p*-xylene. This was confirmed by studying the reaction between $Mn(OAc)_3$ and *p*-xylene in the presence of trifluoroacetic acid.

Keywords: Autoxidation; *p*-Xylene; Terephthalic acid; Acid catalysts; Fluorinated acids

1. Introduction

The catalytic autoxidation of *p*-xylene provides the route for the commercial production of terephthalic acid [1–4]. It is used to manufacture poly(ethylene terephthalate), a polymer commonly made into fibers, resins, films, etc. [5]. $Co(OAc)_2$ is used as a catalyst for this reaction with a compatible promoter, HBr, and a cocatalyst $Mn(OAc)_2$ [6–9].



(1)

The promoter and cocatalyst enhance the activity of $Co(OAc)_2$ catalyst and eliminate a long induction period [9,10]. This combination of reagents, originally discovered by Mid-Century Corporation and later developed by Amoco Chemicals, is known as the MC catalyst [11]. A drawback is the fact that bromide corrodes expensive titanium reactors, however, and it also forms $CH_3Br(g)$, [12] which can deplete the ozone layer [13]. Eastman Kodak Co. and Mobil Chemical Co. have used a lower carbonyl compound as promoter, but relatively large amount of cobalt salt is required [11]. Recently, *N*-hydroxyphthalimide (NHPI) and its substituted derivatives have been reported to be highly efficient promoters for the aerobic oxidation of *p*-xylene, [14,15] but NHPI is not without its problems. NHPI decomposes, particularly when the chain reaction is fast, and therefore, continuous addition of NHPI is recommended [15].

Besides promoters, the oxidizing power of catalyst metals plays an important role in this process. The oxidation of methylarenes with manganic and cobaltic acetates have been reported to improve significantly in the presence of strong acids [16–18]. The result is attributed to the formation of manganic and cobaltic salts of strong acids which are stronger oxidizing agents than their corresponding acetates. In this study, we describe the effectiveness of the MC cata-

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lyst in the presence of trifluoroacetic acid (aqueous pK_a 0.26), heptafluorobutyric acid (0.34) and *p*-toluenesulfonic acid. Studies have been carried out at the variable concentrations of acid additives and $Mn(OAc)_2$ to define the mechanistic roles.

2. Experimental

2.1. Materials

The following reagents were used as obtained commercially without further purification: cobalt(II) acetate tetrahydrate, manganese(II) acetate, manganese(III) acetate, glacial acetic acid, trifluoroacetic acid, heptafluorobutyric acid, *p*-toluenesulfonic acid, sodium bromide, pX, *p*-tolualdehyde, *p*-toluic acid and terephthaldicarboxaldehyde (TPA). 4-Carboxybenzaldehyde was supplied by the BP Chemicals Company.

2.2. General oxidation procedures

The progress of the autoxidation reactions was monitored in HOAc by the oxygen uptake method using a manometric apparatus similar to the one described in the literature [1,15,19] The reactor, which contains an impeller to maintain oxygen saturation of the solution, was thermostated at 70 °C by means of a circulating water bath. Oxygen consumption was measured by monitoring the decrease in volume at constant 1 atm pressure of pure oxygen in a burette connected to the reactor. The initial reaction rates were calculated from the slope of the linear plots of the volume of oxygen consumption against time.

Oxidation products of some reactions were monitored by HPLC, having calibrated the method with known compounds, qualitatively and quantitatively. For HPLC analysis, a 20 μL aliquot was removed from the reactor at different times during the reaction and diluted to 1 mL with 1:4 DMSO/CH_3CN (v/v). The diluted solution was then run through the HPLC column. A Waters model 501 solvent delivery system, Waters 996 photodiode array detector and a Novapak C_{18} 3.9 mm × 150 mm column were used for this method. A binary solvent of 50% H_2O/0.5% CH_3COOH and 50% CH_3CN was used to analyze the sample in both isocratic and gradient modes. The oxidation products were identified by their retention times in comparison with authentic samples. Each peak of the HPLC chromatogram was properly integrated and the actual concentration of each component was obtained from the pre-calibrated plot of peak area against concentration, as presented in Fig. S1 in Supporting information.

The reaction between 2 mM $Mn(OAc)_3$ and 100 mM pX in the presence of TFA was followed using Shimadzu UV-2101PC or UV-3101PC spectrophotometers. The progress of the reaction was determined by monitoring the decrease of $Mn(OAc)_3$ absorbance at 455 or 370 nm. A quartz cell of 1.0 cm path length was used for absorbance measurement.

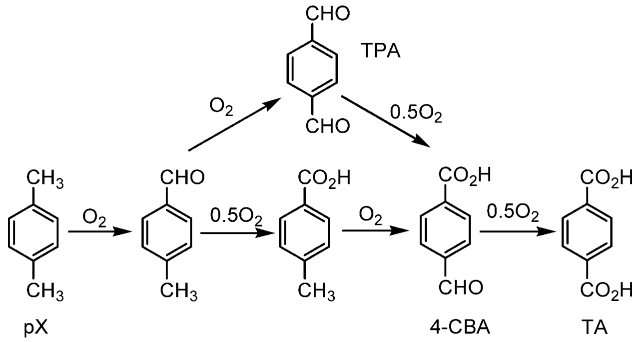
3. Results

3.1. Autoxidation reaction

The oxidation of pX to terephthalic acid occurs through a complicated multi-step process. The stoichiometric equation is given below:

$$C_6H_4(CH_3)_2 + 3O_2 \rightarrow C_6H_4(COOH)_2 + 2H_2O \qquad (2)$$

Several partially oxidized forms of pX are produced during the course of free-radical chain reaction, namely *p*-tolualdehyde, *p*-toluic acid, terephthaldicarboxaldehyde (TPA) and 4-carboxybenzaldehyde (4-CBA). Alcohol was not detected, presumably due either to rapid oxidation of alcohols to aldehydes or to esterification with acetic acid. The sequential oxidation process is shown below:



3.2. Effect of TFA

A preliminary reaction was carried out with 100 mM pX, 5 mM $Co(OAc)_2$, 10 mM $Mn(OAc)_2$ and 15 mM NaBr in HOAc at 70 °C. The initial change in the volume of O_2 consumption was linear as a function of time. The slope of the linear plot gave the initial reaction rate as, $v_i = 13 \times 10^{-6} \text{mol L}^{-1} \text{s}^{-1}$ (Fig. S2 in Supporting information). The same reaction with 5 wt% TFA took place at a higher rate, $v_i = 40 \times 10^{-6} \text{mol L}^{-1} \text{s}^{-1}$. The oxidation with 5 wt% TFA produced 86% terephthalic acid in 8 h as compared to only 15% terephthalic acid without TFA. Thus, the effectiveness of the catalyst is enhanced in the presence of TFA. Comparisons of the initial reaction rates of oxygen uptake and HPLC yields of terephthalic acid are shown in Fig. 1a and b. Table S1 in Supporting information shows the yields of various partially oxidized pX intermediates as a function of TFA concentration.

However, the above experiment was carried out using NaBr as a bromide source, while the industrial process uses HBr. The latter is believed to be more efficient promoter than the former. A question therefore arises as to whether HBr is produced in situ, due to coexistence of TFA and NaBr. If