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

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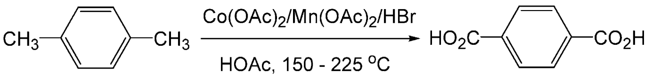
Abstract

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.

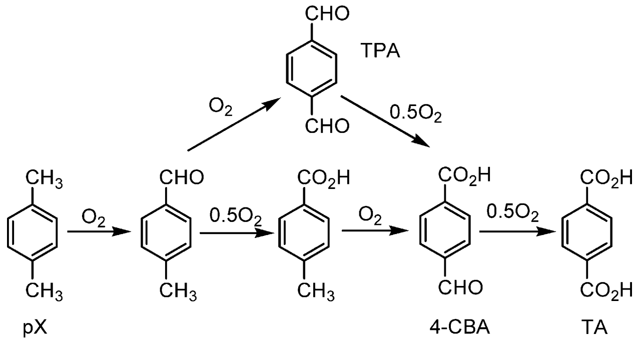
3. Results

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, $v_i = 13 \times 10^{-6}$ mol L^{-1} s^{-1} (Fig. S2 in Supporting information). The same reaction with 5 wt% TFA took place at a higher rate, $v_i = 40 \times 10^{-6}$ mol L^{-1} 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

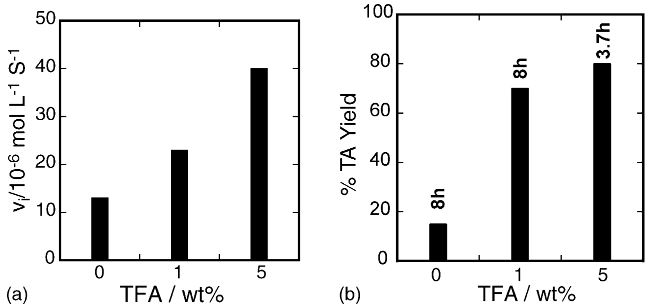


Fig. 1. Dependence of (a) initial rates, and (b) terephthalic acid yields, on the concentration of trifluoroacetic acid on the autoxidation of pX in HOAc at 70 °C. Reaction conditions: 100 mM pX, 10 mM $Co(OAc)_2$, 5 mM $Mn(OAc)_2$ and 15 mM NaBr.

this occurred, the observed beneficial effect was apparently for HBr, not for the presence of TFA. To check this argument, controlled experiments were performed using HBr as a bromide source and the result was compared with combined TFA and NaBr containing system (Table 1). Entry #1 in Table 1 shows the initial reaction rate and yield of terephthalic acid during the autoxidation of 100 mM pX with 5 wt% TFA, 15 mM NaBr, 5 mM $Co(OAc)_2$ and 10 mM $Mn(OAc)_2$; in effect, this is HBr + NaTFA, considering the relative acidities of the two. The same reaction with 15 mM HBr in place of NaBr and no TFA took place at lower rate; $\upsilon_i = 29$ mol L^{-1} s^{-1} and produced less terephthalic acid (entry #2). The third reaction containing 15 mM HBr and 5 wt% TFA took place at a comparable rate with a reaction maintaining 15 mM NaBr and 5% TFA (entry #3). Thus, the results in Table 1 confirmed that the enhanced activity of the MC catalyst is due to the presence of TFA.

The oxidation in the presence of TFA showed a noticeable difference in the reaction progress; O_2 uptake rate is fast at the beginning, followed by a slow uptake, and then rapid again (Fig. 2). Note that without TFA, the volume of O_2 uptake follows first-order kinetics.

The HPLC determination of oxidation products as a function of time confirmed the formation of 4.4–3.0 mM TPA (retention time = 5.1 min; Fig. S1 in Supporting information) during the time scale of 120–180 min, and then completely disappeared during the second rapid step due to the formation of next oxidation product. The oxidation of 100 mM TPA was studied separately with the combined MC catalyst and 5 wt% TFA. Under comparable conditions, the initial reaction rates, υ_i, with and without TFA were 320×10^{-6} and 26×10^{-6} mol L^{-1} s^{-1}, respectively. However, it is not clear why such a high reactive TPA would first accumulate and then rapidly oxidize. It is useful to note that the MC catalyzed oxidation of pX without TFA produced no TPA as an intermediate [15,19].

Table 1
Dependence of the initial rates and yields of terephthalic acid on different bromide sources and trifluoroacetic acid for the autoxidation of 100 mM pX with 5 mM $Co(OAc)_2$, 15 mM Br^-, 10 mM $Mn(OAc)_2$ at 70 °C in HOAc

Entry #	Br^- source	TFA (wt%)	υ_i ($\times 10^{-6}$ mol L^{-1} s^{-1})	Time (h)	Terephthalic acid (mM)
1	NaBr	5	40	8	86
2	HBr	0	29	8	48
3	HBr	5	39	7.5	70

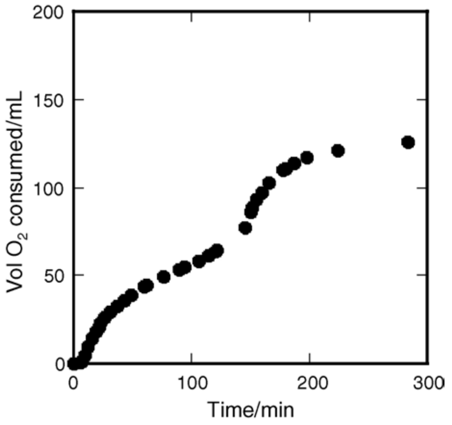


Fig. 2. Volume of O_2 consumed as a function of time for the autoxidation pX in the presence of 5 wt% TFA using the following reaction conditions: 5 mM $Co(OAc)_2$, 10 mM $Mn(OAc)_2$, 15 mM NaBr, and 100 mM pX at 70 °C. The mid-point break is a natural characteristic of the time course.

3.3. *Oxidation of intermediate products*

The intermediate products of the oxidation of pX with combined MC catalyst and TFA are *p*-tolualdehyde, *p*-toluic acid, terephthaldicarboxaldehyde and 4-carboxybenzaldehyde. These intermediates are commercially available. To explore the beneficial effect of TFA on these intermediates, the oxidation reaction of each intermediate was studied with 100 mM intermediate, 5 mM $Co(OAc)_2$, 10 mM $Mn(OAc)_2$, 15 mM NaBr and 5 wt% TFA. One set of each reaction was also carried out without TFA. The initial reaction rates are summarized in Table 2, and reveals that the reaction with TFA is 8–30 times faster than that without TFA.

3.4. *TFA versus HFBA*

As demonstrated above, the effectiveness of the MC catalyst improved significantly in the presence of TFA. But, the boiling point of TFA is 70 °C. Therefore, a substantial

Table 2
The directly evaluated initial rates for the autoxidation of partially oxidized forms of pX intermediates with the MC catalyst in the presence and absence of TFA

Intermediate	υ_i ($\times 10^{-6}$ mol L^{-1} s^{-1})	
	5 wt% TFA	0 wt% TFA
p-Tolualdehyde	240	35
p-Toluic acid	6	0.7
Terephthaldicarboxaldehyde	320	26
4-Carboxybenzaldehyde	158	5.4

Reaction conditions: 100 mM intermediate, 5 mM $Co(OAc)_2$, 10 mM $Mn(OAc)_2$, and 15 mM NaBr at 70 °C in HOAc.

loss of expensive TFA would occur during the industrial process of pX oxidation at high temperature (220 °C). Thus, a higher boiling point acid additive is needed to minimize its loss at high temperature. Heptafluorobutyric acid (HFBA) has relatively higher boiling point, 120 °C, and therefore, more promising as an acid additive. The effectiveness of the combined MC catalyst and 5 wt% HFBA was studied for the oxidation of pX. Under comparable conditions of 100 mM pX, 5 mM $Co(OAc)_2$, 10 mM $Mn(OAc)_2$, 15 mM NaBr, 5 wt% HFBA and at 70 °C, the beneficial effect of HFBA was immediately realized from the initial reaction rate measurement, $v_i = 51 \times 10^{-6}\ \mathrm{mol\ L^{-1}\ s^{-1}}$, which is 22% higher than that of TFA activated reaction and 75% higher than without any acid additives. The yield of terephthalic acid was 95% in 4 h, as compared to 80% with TFA in the same time. The results are shown in Fig. 3. The plot of the volume of O_2 consumption against time was similar to that observed for TFA activated oxidation.

3.5. Effects of other acids

The effectiveness of the MC catalyst in the presence of inorganic acids, such as H_2SO_4 and H_3PO_4 was studied for the oxidation of 100 mM pX. An experiment with 5 mM $Co(OAc)_2$, 10 mM $Mn(OAc)_2$, 15 mM NaBr and 5% H_3PO_4 resulted in the formation of a purple precipitate immediately. Another experiment with 5% H_2SO_4 also produced a brown precipitate. In both cases, no O_2 consumption took place. Therefore, it is believed that H_2SO_4 and H_3PO_4 formed insoluble metal complexes with the catalyst metals. Both experiments with 0.5% H_2SO_4 or H_3PO_4 (one-tenth of previous concentration) also resulted in similar precipitation. As shown in Fig. 4, the O_2 uptake rate decreased immediately when 0.5% H_3PO_4 was injected into the reactor of an ongoing oxidation.

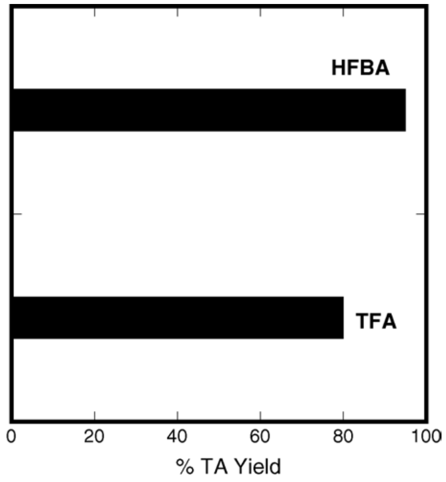


Fig. 3. Yields of terephthalic acid formed from the autoxidation of 100 mM pX with combined MC catalyst and 5 wt% acid additive at 70 °C in HOAc. Catalyst composition: 5 mM $Co(OAc)_2$, 10 mM $Mn(OAc)_2$, and 15 mM NaBr.

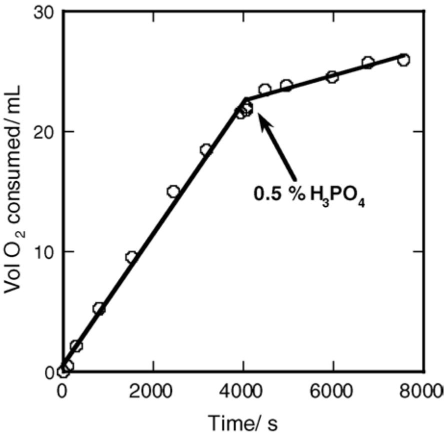


Fig. 4. Effect of H_3PO_4 on the autoxidation of 100 mM pX catalyzed by 5 mM $Co(OAc)_2$, 10 mM $Mn(OAc)_2$, 15 mM NaBr, at 70 °C in HOAc.

The oxidation of 100 mM pX in the presence of 0.2 wt% *p*-toluenesulfonic acid was studied under comparable conditions. The initial rate increased from 13 to $22 \times 10^{-6}\ \mathrm{mol\ L^{-1}\ s^{-1}}$. However, as shown in Fig. 5, the reaction stopped after ca. 75% oxidation of pX to terephthalic acid. As the reaction stopped the solution took on a brown color with a UV–vis spectrum that matched that of $Mn(OAc)_3$. Higher concentration of *p*-toluenesulfonic acid (>0.2 wt%) caused precipitation of catalyst metals.

3.6. Dependence on metal cocatalysts

Metal cocatalysts, $Mn(OAc)_2$ and $Ce(OAc)_3$ are known to accelerate reactions in which bromide [19–22] and *N*-hydroxyphthalimide [15] are used to promote the oxidation. In each case, the oxidation rate attains a maximum value at a particular concentration of cocatalyst: 0.3 mM $Mn(OAc)_2$; 0.15 mM $Ce(OAc)_3$. The subsequent rate then declines slowly at higher manganese or cerium concentrations. In the present study, the effectiveness of combined

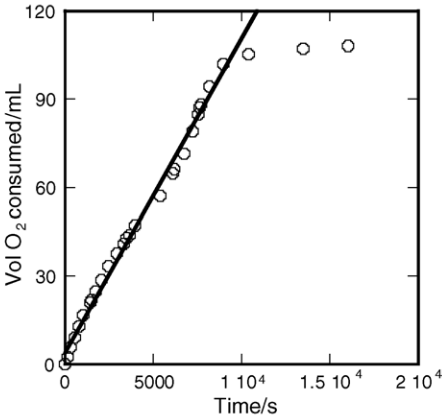


Fig. 5. Volume of O_2 consumed as a function of time for the autoxidation of pX with combined MC catalyst and 0.2 wt% *p*-toluenesulfonic acid. Reaction conditions: 5 mM $Co(OAc)_2$, 10 mM $Mn(OAc)_2$, 15 mM NaBr, and 100 mM pX at 70 °C.

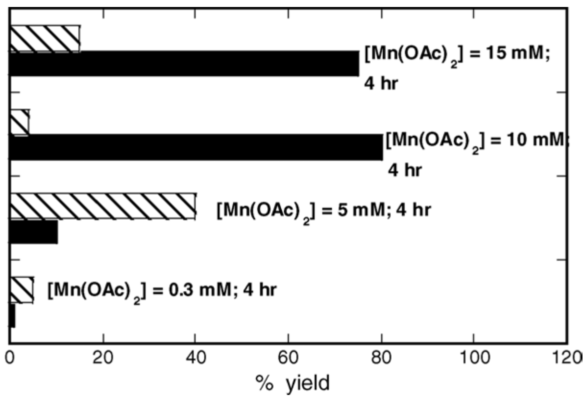


Fig. 6. Dependence of yields of terephthalic acid (solid bar) and *p*-toluic acid (striped bar) on the $Mn(OAc)_2$ concentration for the autoxidation of 100 mM pX with the fixed concentrations, 5 mM $Co(OAc)_2$, 15 mM NaBr, and 5 wt% TFA in HOAc at 70 °C. The yields at 10 and 15 mM $Mn(OAc)_2$ with TFA are the same within experimental error.

MC catalyst and TFA is also pronounced on $Mn(OAc)_2$ and $Ce(OAc)_3$. Experiments were preformed at varying concentrations of $Mn(OAc)_2$ in the range of 0.3–15 mM, with the fixed concentrations of $Co(OAc)_2$ (5 mM), pX (100 mM) and NaBr (15 mM). The results as shown in Fig. 6 and Table S2 indicating that the yields of terephthalic acid improved with increased in [$Mn(OAc)_2$] and then remained almost constant at concentrations greater than 10 mM.

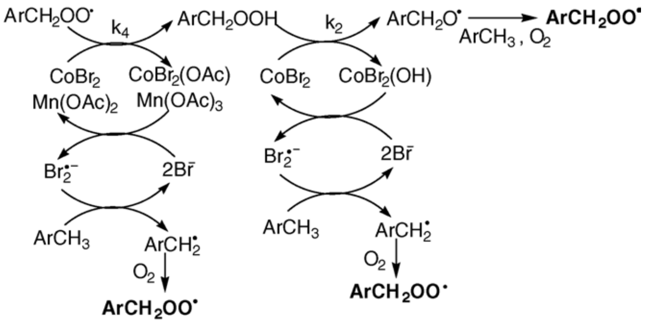
An experiment was performed with 10 mM $Ce(OAc)_3$. With 100 mM pX, 5 mM $Co(OAc)_2$, and 15 mM NaBr at 70 °C, the initial rates with and without 5% TFA were 22 and 13×10^{-6} mol L^{-1} s^{-1}. The result is shown in Fig. S3 in Supporting information.

4. Discussion

To discuss the beneficial effect of the MC catalyst with acid additives, it is useful to review briefly on the mechanism of the MC catalyzed autoxidation of methylarenes. It has been demonstrated [15,19,21,23] that the reaction follows a free radical chain mechanism. The chain can be initiated by a trace quantity of aralkyl hydroperoxide; one can also rely on the trace of hydroperoxide that is inevitably present in the *p*-xylene that has been stored for a while. In the initiation step, aralkyl hydroperoxide reacts with $CoBr_2$ to generate reactive species, cobalt(III) and aralkoxyl radicals.

$$ArCH_2COOH + Co(II)Br_2 \rightarrow ArCH_2O^\bullet + Co(III)Br_2OH \quad (3)$$

The catalyst metal $Co(OAc)_2$ exists as $CoBr_2$ in the reaction medium. We have independently demonstrated that $CoBr_2$ reacts at this step[24]. Here and elsewhere, the Co species are written as monomers, even though dimers and trimers are known to exist in HOAc, especially in aged solutions [25,26]. Once the reaction begins, monomeric Co(IIIa) is formed and it cycles quite rapidly to carry repeated cycles of reaction.



Scheme 1. Chain branching of peroxyl radicals in the autoxidation of pX with the $Co(OAc)_2/Mn(OAc)_2/Br^-$ catalyst.

The highly reactive $ArCH_2O^\bullet$ then reacts with pX (denoted as $ArCH_3$) to form an aralkyl radical.

$$ArCH_2O^\bullet + ArCH_3 \rightarrow ArCH_2^\bullet + ArCH_2OH \quad (4)$$

The subsequent oxygenation of $ArCH_2^\bullet$ produces the important alkylperoxyl radical:

$$ArCH_2^\bullet + O_2 \rightarrow ArCH_2OO^\bullet \quad (5)$$

The peroxyl radical reacts with $ArCH_3$, Co(II) and Mn(II) to propagate and branch the radical chain reactions (Eqs. (6–8)).

$$ArCH_2OO^\bullet + ArCH_3 \rightarrow ArCH_2OOH + ArCH_2^\bullet \quad (6)$$

$$ArCH_2OO^\bullet + CoBr_2 + HOAc \rightarrow CoBr_2(OAc) + ArCH_2OOH \quad (7)$$

$$ArCH_2OO^\bullet + Mn(OAc)_2 + HOAc \rightarrow Mn(OAc)_3 + ArCH_2OOH \quad (8)$$

The second-order rate constants of reactions (7) and (8) are 720 and $\sim 10^5$ L mol^{-1} s^{-1}, respectively [22]. In the subsequent step, $CoBr_2(OAc)$ and $Mn(OAc)_3$ oxidize the bromide ion to dibromide radical. The formation of dibromide radical was studied directly by laser flash photolysis, and thus confirmed independently [27]. Hence, a single peroxyl radical becomes three by a sequence of pathways, as shown in Scheme 1, in which the numbering of rate constants corresponds to the prior usage [19,23].

The oxidation of alkylarenes with the manganic acetate, $Mn(OAc)_3$, in HOAc has been reported to be drastically enhanced in the presence of strong acids, e.g., trifluoroacetic acid, trichloroacetic acid, perchloric acid, etc [16]. Mn(III) salts of these strong acids are more powerful oxidizing agents than that of $Mn(OAc)_3$. In this study, TFA and HFBA also enhanced the effectiveness of the MC catalyst, indicative of the formation of polyfluorinated Mn(III) acetates, $Mn(TFA)_3$, and $Mn(heptafluorobutyroacetate)_3$ in the catalytic cycle. Consequently, the oxidation of bromide ion to dibromide radical $HBr_2^\bullet$ takes place quite rapidly, and hence, the overall oxidation rate becomes faster. However, the concentration of polyfluorinated Mn(III) acetate salt must be very low considering the fact that trifluoroacetate and heptafluorobutyric acetate ions are weaker ligands than acetate ion. Also, low concentrations (5 wt%) of acid additives were used.

In our earlier publications, the effectiveness of the MC catalyst without any acid additives has been reported to be maximum at 0.3 mM $Mn(OAc)_2$, followed by a slow decline at higher concentration [15,19]. But, in the presence of acid additives, the effectiveness of the catalyst increases with increase in $Mn(OAc)_2$ concentrations, even at its concentration greater than 10 mM. As the concentration of $Mn(OAc)_2$ increases, more polyfluorinated Mn(III) acetate species are formed, and participated in the catalytic cycles. Thus, the free-radical chain reactions become faster. These higher oxidizing species may also directly react with pX, as shown in Eq. (9):

$$Mn(TFA)_3 + ArCH_3 \rightarrow Mn(TFA)_2 + ArCH_2^{\bullet} + TFA \quad (9)$$

$$ArCH_2^{\bullet} + O_2 \rightarrow ArCH_2OO^{\bullet} \quad (5)$$

This extra path further increases total concentration of peroxyl radical, and hence enhances the overall oxidation.

The reaction between pX and $Mn(OAc)_3$ was separately examined in the presence of TFA to justify the occurrence of reaction (9). An experiment with 2 mM $Mn(OAc)_3$, 100 mM pX and in the absence of TFA showed no absorbance change of $Mn(OAc)_3$ at 455 nm (trace a in Fig. 7). The same reaction, when repeated in the presence of TFA, took place quite rapidly, as indicated by fast absorbance change of $Mn(OAc)_3$ (traces b, c and d).

The useful observations in Fig. 7 are: (i) TFA initiates the reaction between $Mn(OAc)_3$ and pX, and the reaction with 50% TFA is faster than that with 5% TFA. (ii) The reaction in air saturated solution is significantly faster (trace d) than in deaerated solution. HPLC analysis of reaction solutions determined the formation of *p*-tolualdehyde in trace d, which certainly justifies the direct oxidation of pX with Mn(III) in the presence of acid additive, as shown by Eq. (9).

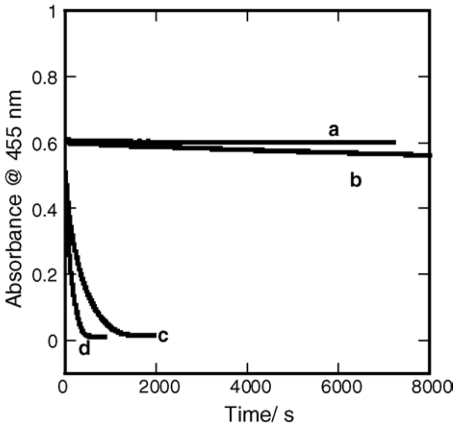


Fig. 7. Kinetic traces of the reaction of 2 mM $Mn(OAc)_3$ with 100 mM pX at 25 °C. Other reaction conditions are: (a) 0% TFA and deaerated solution, (b) 5% TFA and deaerated solution, (c) 50% TFA and deaerated solution, and (d) 50% TFA and air saturated solution.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2005.06.007.

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