

# Terephthalic Acid Synthesis in High-Temperature Liquid Water

Jennifer B. Dunn and Philip E. Savage\*

University of Michigan, Department of Chemical Engineering, Ann Arbor, Michigan 48109-2136

We have completed an exploratory study of the synthesis of terephthalic acid via the partial oxidation of *p*-xylene in liquid water at temperatures ranging from 250 to 350 °C. The reactions occurred in 1.54 mL stainless steel batch reactors, and the batch holding time was 60 min. We determined the influence of temperature, catalyst identity, *p*-xylene initial concentration, and oxidant initial concentration on the yield of terephthalic acid and intermediate products. The catalysts included in this study were manganese bromide, cobalt bromide, manganese acetate, nickel bromide, hafnium bromide, and zirconium bromide. Hydrogen peroxide was the oxidant. The maximum yield of terephthalic acid,  $49 \pm 8\%$ , occurred at 300 °C with manganese bromide as the catalyst. Other catalysts or catalyst combinations produced lower yields. Yields of terephthalic acid decreased as the oxidant-to-*p*-xylene ratio decreased, either by increasing the initial concentration of *p*-xylene or by decreasing the initial concentration of oxidant.

## Introduction

High-temperature water (HTW) is receiving increased attention as an environmentally benign medium for organic chemical reactions.<sup>1,2</sup> In contrast to many organic solvents, water does not pose an environmental hazard, and it is also inexpensive. The properties of HTW differ from those of liquid water at ambient conditions so that HTW is a suitable medium for organic chemical reactions. These properties include a decreased dielectric constant, permitting HTW to dissolve organic substances that would be insoluble in water at ambient conditions. Moreover, temperature can be used as a solubility switch in a HTW medium. As the reaction mixture is cooled, organic products become insoluble, separate from the aqueous phase, and are accessible for recovery. This article deals with the use of liquid-phase HTW as the reaction medium for terephthalic acid synthesis.

Terephthalic acid is a monomer used to produce poly(ethylene terephthalate), which is commonly used in injection-molded consumer product containers such as soft drink bottles. The main commercial route to terephthalic acid is partial oxidation of *p*-xylene in acetic acid at approximately 200 °C and 15–30 atm with a combination of manganese, bromine, and cobalt as catalyst. Nearly all new terephthalic acid plants employ this catalyst combination and similar reaction conditions. This process achieves 98% conversion of *p*-xylene and 95 mol % yield of terephthalic acid.<sup>3</sup>

The replacement of acetic acid with HTW as the reaction medium could lead to a more profitable and more environmentally benign process provided high terephthalic acid yields can be obtained. Opportunities for process improvement exist for several reasons. First, the use of acetic acid necessitates an expensive distillation step to separate the water formed during the oxidation reaction from the acetic acid so that it can be recycled back to the reactor. Additionally, acetic acid reacts with the bromine present in the system to form methyl bromide, a hazardous compound that must be removed before gas from the process can be released to

the environment. Finally, some acetic acid is oxidized during the reaction, and these losses must be offset by replenishing the solvent. Therefore, the use of HTW as the reaction medium for terephthalic acid synthesis would eliminate the economic and environmental burdens that currently accompany the use of acetic acid.

Most accounts of previous studies of the partial oxidation of *p*-xylene in HTW reside in the patent literature. One patent<sup>4</sup> specifies ruthenium oxide as the catalyst and reaction temperatures from 150 to 280 °C. This process, however, results in very low yields of terephthalic acid. Another patent<sup>5</sup> suggests inclusion of an iodine promoter to decrease the amount of impurities such as 4-carboxybenzaldehyde that form in the reaction. It specified a temperature range of 200–300 °C. A final patent<sup>6</sup> discloses a two-stage process that uses water as a solvent in levels up to a 1:1 ratio by weight with *p*-xylene and employs a bromine–manganese–cobalt mixture as catalyst. The first stage operates between 150 and 210 °C and converts 40–95% of the *p*-xylene to acid derivatives. More bromine and water are added to the effluent from the first stage before it passes to the second stage, which operates between 200 and 250 °C. The overall yield of terephthalic acid is 70–85%.

Refereed journals contain only two accounts of *p*-xylene partial oxidation in HTW without any added organic compounds. In one account,<sup>7</sup> transition-metal-substituted polyoxometalates were the catalyst for the partial oxidation of *p*-xylene in water at 180 °C. The main reaction product was *p*-toluic acid. The selectivity to terephthalic acid, which ranged from 0.99% to 5.05%, was the lowest of all reaction products. The other account<sup>8</sup> is a broad study of the partial oxidation of alkyl aromatics in HTW. These authors reported a 64% yield of terephthalic acid from *p*-xylene with manganese bromide as the catalyst at nominal reaction conditions of 375 °C and 40 min. They also reported a 15% yield of *p*-toluic acid and a 3% yield of *p*-tolualdehyde. With cobalt acetate as the catalyst at the same reaction conditions, the authors reported no terephthalic acid but 24% yields of both *p*-toluic acid and *p*-tolualdehyde. The information in this account is not useful for quantitative kinetics because the heatup time for the reactors was

\* Corresponding author. E-mail: psavage@umich.edu. Phone: (734) 764-3386. Fax: (734) 763-0459.

comparable to the total reaction time. Thus, the reactions were not isothermal. Additionally, the yield for terephthalic acid was determined gravimetrically, and it is unclear how the authors separated terephthalic acid from other products, such as 4-carboxybenzaldehyde, to quantify its yield. It may be that the yields reported for terephthalic acid include contributions from other compounds as well.

The potential importance of a HTW-based process for *p*-xylene oxidation and the scant information available about the effects of the key process variables on the product yields and selectivity motivated the work presented herein. This article reports, for the first time, the effects of different catalysts, reaction temperatures, and initial concentrations of *p*-xylene and oxidant on the products from the isothermal partial oxidation of *p*-xylene in high-temperature, liquid water. A separate article<sup>9</sup> reports our results for this reaction in supercritical water.

## Experimental Section

We desired to discover the influence of catalyst identity, temperature and the initial concentration of *p*-xylene and oxidant on the product yields from *p*-xylene partial oxidation in HTW. All experiments were done isothermally in constant volume batch reactors. The first set of experiments explored the following catalysts: manganese bromide ( $\text{MnBr}_2$ ), cobalt bromide ( $\text{CoBr}_2$ ), nickel bromide ( $\text{NiBr}_2$ ), zirconium bromide ( $\text{ZrBr}_4$ ), hafnium bromide ( $\text{HfBr}_4$ ), and manganese acetate ( $\text{Mn}(\text{OAc})_2$ ).

A literature search guided our choice of catalysts. We evaluated  $\text{MnBr}_2$  because it is the most commonly used catalyst for this reaction and produced the highest terephthalic acid yield in an earlier study.<sup>8</sup> To mimic the catalyst combination used in industry,  $\text{Mn}/\text{Co}/\text{Br}$ , we combined  $\text{MnBr}_2$  and  $\text{CoBr}_2$  in equimolar proportions. We also tested  $\text{CoBr}_2$  alone. To reduce the  $\text{Br}/\text{Mn}$  ratio and thereby reduce the corrosivity of the reaction environment, we combined  $\text{Mn}(\text{OAc})_2$  with  $\text{MnBr}_2$  to produce a molar proportion of  $\text{Br}:\text{Mn} = 1.1$ . We chose two other catalyst combinations based on information in patents (but not for aqueous-phase oxidation). One patent<sup>10</sup> disclosed a combination of  $\text{MnBr}_2$ ,  $\text{NiBr}_2$ , and  $\text{ZrBr}_4$  in molar proportions of  $\text{Mn}:\text{Ni}:\text{Zr} = 29:32:1$ , which we reproduced in our experiments. Another patent<sup>11</sup> disclosed a combination of  $\text{MnBr}_2$ ,  $\text{CoBr}_2$ , and  $\text{HfBr}_4$ , which we used in molar proportions of  $\text{Mn}:\text{Co}:\text{Hf} = 24:12:1$  based on information in the patent.  $\text{HfBr}_4$  reportedly reduces the deactivating effect of water on the catalyst. We also assessed the effectiveness of  $\text{MnBr}_2$  and  $\text{HfBr}_4$  without  $\text{CoBr}_2$  in a molar proportion of  $\text{Mn}:\text{Hf} = 31:1$ . For these catalyst evaluation experiments, the reaction temperature was 300 °C, the catalyst-to-*p*-xylene-to- $\text{H}_2\text{O}_2$  molar ratio was 1:10:138, and the batch holding time was 60 min.

After identifying the best catalyst, we used it and then varied the reaction parameters (temperature, initial *p*-xylene concentration, and initial hydrogen peroxide concentration) over a sufficiently wide range to determine their effects on the product yields. We conducted one set of experiments at 250, 300, and 350 °C and nominal *p*-xylene, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and  $\text{MnBr}_2$  concentrations of 0.08, 1.1, and  $8.9 \times 10^{-3}$  M, respectively. All concentrations reported here are at reaction conditions. In other sets of experiments, all at 300 °C with  $8.9 \times 10^{-3}$  M  $\text{MnBr}_2$ , we varied the molar ratio of

$\text{H}_2\text{O}_2$  to *p*-xylene by manipulating the initial concentration of either *p*-xylene (between 0.08 and 0.24 M) or  $\text{H}_2\text{O}_2$  (between 0.3 and 1.1 M). We performed multiple experiments at each set of conditions so we could determine the uncertainties in the experimental results. All results reported herein represent mean values.

**Materials.** All reactions were carried out in 1.54 mL tubing-bomb batch reactors made from stainless steel Swagelok fittings. Each reactor comprised two  $3/8$ -in. caps and one  $3/8$ -in. port connector. Before their use in oxidation reactions, the reactors were loaded with water and held at 300 °C for 1 h. All chemicals were purchased from Aldrich Chemical at high purity and used as received. An aqueous solution of 30 wt %  $\text{H}_2\text{O}_2$  was the oxidant. We used  $\text{H}_2\text{O}_2$  for experimental convenience. We recognize that  $\text{H}_2\text{O}_2$  is too costly for a commercial-scale terephthalic acid process.  $\text{H}_2\text{O}_2$  rapidly decomposes into  $\text{O}_2$  and  $\text{H}_2\text{O}$  via hydroxide radical intermediates at the experimental conditions.<sup>12</sup> Therefore, either these radicals or  $\text{O}_2$  may serve as the oxygen source in these experiments.

**Procedure.** All reactants were weighed to within  $\pm 0.1$  mg on an analytical balance after they were added to the reactors. All experiments used *p*-xylene loadings such that essentially all of the *p*-xylene would reside in the aqueous phase at reaction conditions. The highest nominal *p*-xylene concentration used was 0.24 M, which is below the saturation concentration of 0.41 M reported at 299 °C<sup>13</sup> and below the 1.3 M saturation concentration we calculated from UNIFAC at 300 °C. After the *p*-xylene, catalyst, and  $\text{H}_2\text{O}_2$  solution were added to a reactor, water was added in an amount that ensured nearly all of the reactor volume would be occupied by the liquid phase at reaction conditions. The average water loadings were  $1.15 \pm 0.09$ ,  $1.02 \pm 0.04$ , and  $0.76 \pm 0.01$  mL for experiments at 250, 300, and 350 °C, respectively.

After the reactors were loaded and sealed they were weighed and then placed in a preheated, isothermal fluidized sand bath. We determined experimentally that the reactor contents reach the temperature of the sand bath within three minutes and then remain at that temperature. After the desired reaction time elapsed, the reactors were removed from the sand bath and placed in front of a fan to cool. Upon removal from the sand bath, the temperature of the reactor contents decreases 100 °C within a minute, effectively quenching the reaction. Therefore, the reactions conducted in the sand bath are essentially isothermal because the batch holding time (60 min) greatly exceeds the heating and cooling times ( $< 5$  min).

The reactors were weighed before and after each reaction to determine whether they had leaked. If the mass of a reactor's contents decreased by more than 15% during the course of the reaction, the data from it were discarded. The cooled reactors were then opened and their nongaseous contents were collected by successive additions of methyl sulfoxide (DMSO). We made no attempt to collect or analyze gaseous products. The reactor contents were removed by pipet and collected in a 25 mL volumetric flask. After the reactor contents were recovered, more DMSO was added to the flask to bring the total solution volume to 25 mL. A 500  $\mu\text{L}$  aliquot was removed from the flasks, diluted to 1 mL with DMSO, and transferred to HPLC sample vials for analysis. Filtration of the contents of the 25 mL flasks

using borosilicate glass filters isolated solid residue that formed during the reaction and was insoluble in DMSO.

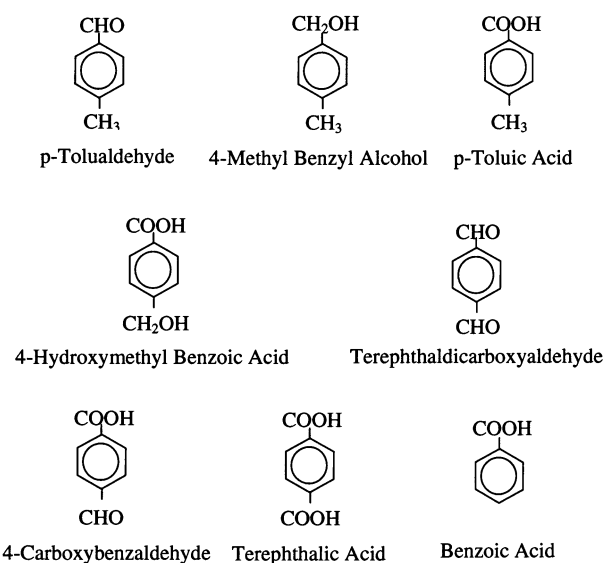
**Analysis.** All product analyses were conducted on a Waters High-Performance Liquid Chromatography (HPLC) system with ultraviolet detection at 254 nm. An Alltech LC-18 column with an internal diameter of 4.6 mm, a length of 250 cm and a particle size of 5  $\mu$ m was used. We used the analytical method developed by Viola and Cao.<sup>14</sup> The method involves gradient elution, with the mobile phase increasing in polarity over 22 min. The mobile phase components are water, DMSO, phosphoric acid, acetonitrile, and methanol. Initially, the mobile phase consists of 5% acetonitrile and 95% of an aqueous mixture containing 0.1% phosphoric acid and 0.5% DMSO by weight. At 5 min, methanol is introduced to the mobile phase with its concentration increasing linearly until the mobile phase consists of 10% methanol. At the same time, the amount of acetonitrile also increases and the amount of the aqueous mixture in the mobile phase decreases. The injection volume is 20  $\mu$ L. A constant flowrate of 1.5 mL/min is maintained. Between injections, the system is allowed to reequilibrate at the initial mobile phase concentration for 15 min. To facilitate the quantification of product yields, standards containing the compounds relevant to this study at three different concentrations were analyzed on the HPLC. Plotting peak area versus concentration for each species generated calibration curves. Molar yields were calculated by dividing the number of moles of each product present after the reaction by the initial number of moles of *p*-xylene loaded into the reactor.

We used CHN analysis and a scanning electron microscope (SEM) to analyze the solid residue collected on filter paper. For the CHN analysis, both unused filter paper and filter paper with solids were analyzed, so we could account for any contributions of the filter paper toward the organic content of the solids. In the CHN analysis, the gases resulting from the combustion of the samples were converted to water, nitrogen, and carbon dioxide, and then quantified using a thermal conductivity detector. We also used a Philips XL30FEG SEM to characterize the solid residue, coating samples with carbon to make them conductive. BP conducted further analysis of the solid residue through X-ray Diffraction (XRD) and elemental analysis by Inductively Coupled Plasma (ICP) Spectroscopy.

## Results and Discussion

The oxidation of *p*-xylene in HTW produced terephthalic acid, numerous intermediate products, and benzoic acid, a degradation product. These compounds are displayed in Figure 1. In this section, we present the results of experiments that elucidated the effect of different catalysts, temperatures, and *p*-xylene and H<sub>2</sub>O<sub>2</sub> initial concentrations on the yields of these products. The results are presented as mole % yields, and these represent mean values. The uncertainties that accompany these means are standard deviations. We first discuss closure of the mole balance, and then present the experimental results.

**Product Recovery.** We are confident that our experimental and analytical procedures enabled us to recover and quantify all DMSO-soluble oxidation products present in the cooled reactors. This confidence comes from background experiments wherein we were able to recover known amounts of *p*-xylene and indi-



**Figure 1.** Reaction products from the partial oxidation of *p*-xylene in HTW.

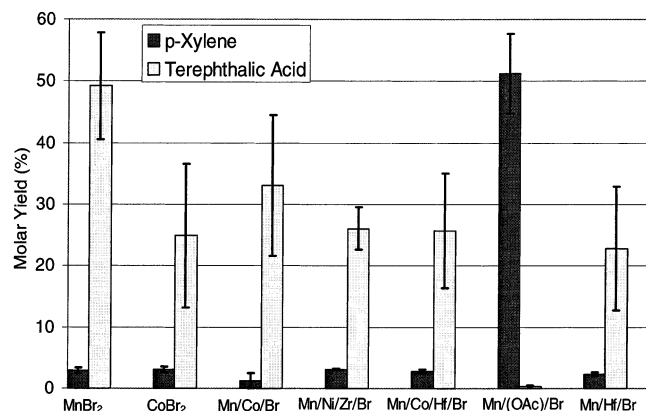
vidual reaction products that had been loaded into a reactor (and kept at room temperature). As an example,  $97 \pm 6\%$  of *p*-xylene added to the reactors was recovered in these experiments. Moreover, we were able to assign product identities to all of the peaks in the chromatograms arising from analysis of the reactor contents after reaction. Our quantitative results, however, showed that the sum of the yields of the DMSO-soluble products never accounted for more than 75% of the *p*-xylene initially loaded into the reactor. Recall, too, that the mass balance closure on the reactor contents always exceeded 85%. Therefore, it appeared that we were recovering most ( $>85\%$ ) of the mass of the material loaded into the reactors but somehow losing a portion ( $>25\%$ ) of the carbon-containing material.

We analyzed the solid residue that formed during the reaction to determine whether it contained organic material. The total mass of these DMSO-insoluble solids was always less than 10 mg per reactor. The carbon content of this residue, as determined by CHN analysis, was very low ( $5.4 \pm 3.8\%$ ). At most, these solids can account for only 5 wt % of the carbon initially loaded into the reactor. The scanning electron microscope, the XRD analysis, and the ICP analysis all revealed that these solids were mostly composed of iron oxide. The bromine present in most of the reactions can be expected to corrode the stainless steel reactors, and these analyses confirm that this solid residue consists primarily of corrosion products.

Not finding much carbon in the solid residue, we next considered the possibility of carbon being present in the gas phase because these partial oxidation reactions typically produce CO and CO<sub>2</sub>. We calculated that if gaseous products accounted for the missing carbon, the pressure in the reactors at ambient conditions after the reaction would be approximately 8 atm. When we opened the cooled reactors, however, we did not observe any phenomena that would be consistent with such a rapidly escaping high-pressure gas phase. Therefore, we concluded that the presence of CO and CO<sub>2</sub> in the gas phase cannot account for all of the missing carbon.

One final hypothesis we considered is that the reactors lost *p*-xylene sometime after being placed in the sand bath. To test this hypothesis, we loaded reactors with about 12 mg of *p*-xylene and 1.1 g of water (without





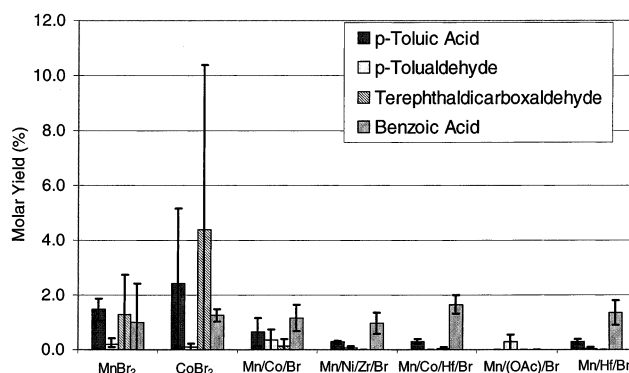
**Figure 2.** *p*-Xylene and terephthalic acid yields from different catalysts ( $T = 300\text{ }^{\circ}\text{C}$ ,  $[p\text{-xylene}]_0 = 0.08\text{ M}$ ,  $[\text{H}_2\text{O}_2]_0 = 1.1\text{ M}$ ,  $[\text{catalyst}] = 8.9 \times 10^{-3}\text{ M}$ ,  $t = 60\text{ min}$ ).

$\text{H}_2\text{O}_2$  and catalyst) and placed them in the sand bath for a batch holding time of 60 min at  $300\text{ }^{\circ}\text{C}$ . *p*-Xylene is thermally stable at these conditions, so a 100% recovery was expected. Recovery and analysis of the reactor contents, however, accounted for only  $78 \pm 2\%$  of the carbon initially loaded into the reactor. Additionally, the mass balance indicated that  $100 \pm 0.7\text{ wt } \%$  of the initial reactor contents had been recovered. We next performed an identical experiment in which we replaced *p*-xylene with biphenyl, which is much less volatile. The biphenyl recoveries were  $110 \pm 6\%$ . These experiments suggest that *p*-xylene, presumably because of its volatility, can be lost from the reactors after they are placed in the sand bath. Biphenyl, due to its lower volatility, is not lost. The loss of *p*-xylene is not reflected in the mass balance because *p*-xylene accounts for only 1% of the total mass of the reactor contents. Losing a fraction of the *p*-xylene, therefore, would not result in a significant change in mass over the course of the reaction.

The foregoing discussion indicates that the reactors might have lost *p*-xylene after being immersed in the sand bath. Because we calculated product yields on the basis of the amount of *p*-xylene initially charged to the reactor, the product yields reported herein represent lower bounds. Even higher yields of terephthalic acid, for example, might have actually been achieved.

**Effect of Catalyst.** We assessed the performance of the different oxidation catalysts at  $300\text{ }^{\circ}\text{C}$  and a 60 min batch holding time. The nominal *p*-xylene,  $\text{H}_2\text{O}_2$ , and catalyst concentrations were 0.08, 1.1, and  $8.9 \times 10^{-3}\text{ M}$ , respectively. Figure 2 shows that six of the seven catalyst combinations provided nearly complete conversion of *p*-xylene. Moreover, terephthalic acid was the product formed in the highest yield for each of these six catalysts. The combination of  $\text{MnBr}_2$  and  $\text{Mn}(\text{OAc})_2$  ( $\text{Mn}(\text{OAc})/\text{Br}$  in Figure 2) was the only unusual catalyst. It produced a *p*-xylene conversion of only  $49 \pm 6\%$  and a terephthalic acid yield of  $0.4 \pm 0.1\%$ . The highest terephthalic acid yield was  $49 \pm 8\%$ , and it was obtained from reactions using  $\text{MnBr}_2$  alone.

Figure 3 shows the molar yields of terephthalaldehyde, *p*-tolualdehyde, *p*-toluic acid, and benzoic acid from the different catalysts. With the exception of benzoic acid, these products are intermediates in the pathway to terephthalic acid. Therefore, high yields of these products represent an opportunity for additional terephthalic acid production. Only the  $\text{MnBr}_2$  and  $\text{CoBr}_2$  catalysts, when used alone, produced yields of two products exceeding 1%. The yields of benzoic acid are



**Figure 3.** *p*-Toluic acid, *p*-tolualdehyde, terephthalaldehyde, and benzoic acid yields from different catalysts ( $T = 300\text{ }^{\circ}\text{C}$ ,  $[p\text{-xylene}]_0 = 0.08\text{ M}$ ,  $[\text{H}_2\text{O}_2]_0 = 1.1\text{ M}$ ,  $[\text{catalyst}] = 8.9 \times 10^{-3}\text{ M}$ ,  $t = 60\text{ min}$ ).

about 1% for all of the catalyst combinations that produced terephthalic acid in high yields. Benzoic acid likely forms from terephthalic acid decarboxylation.

Taken collectively, Figures 2 and 3 clearly show that  $\text{MnBr}_2$  is the most effective catalyst for the production of terephthalic acid. It provided the highest yields of terephthalic acid and nearly complete *p*-xylene conversion. 4-Carboxybenzaldehyde, which is an undesirable, colored byproduct in the commercial process was produced in only  $0.03 \pm 0.04\%$  yield in the experiments using  $\text{MnBr}_2$ .

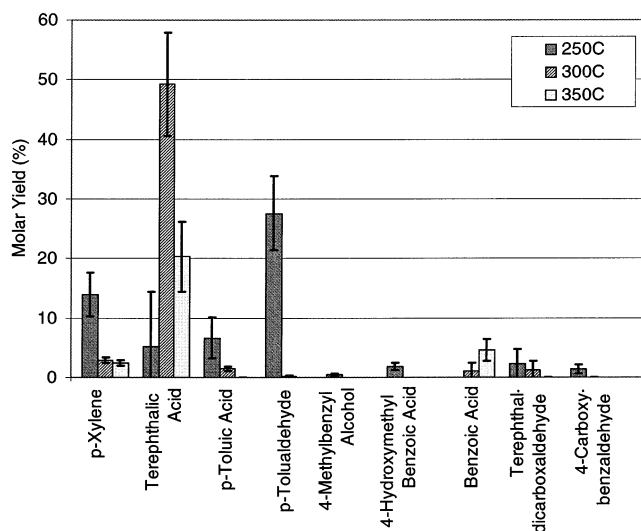
The least effective catalyst proved to be the combination of manganese acetate with manganese bromide. The total yield of oxidation products was only  $0.7 \pm 0.3\%$ .

Hafnium, when added to the catalyst combination of manganese, cobalt, and bromide (and thereby replacing some of the Mn and/or Co), appeared to decrease the terephthalic acid yield. Experiments including hafnium produced terephthalic acid in  $26 \pm 9\%$  yield. The yield of terephthalic acid with the catalyst combination of manganese, cobalt, and bromine was  $33 \pm 11\%$ . These reduced yields in the presence of hafnium stand in contrast with the claims in a patent.<sup>11</sup>

In summary,  $\text{MnBr}_2$  was the most effective catalyst tested. Replacing Br with acetate, though rendering the solution less corrosive, has an enormous negative effect on the performance of the catalyst. Replacing Mn with other metals also has a negative effect, but a much smaller one. Thus it appears that the Br concentration in solution is the most important aspect of the catalyst system. The identity of the metal atom is less important.

Given the superior performance of the  $\text{MnBr}_2$  catalyst, we chose it as the catalyst in the remaining experiments to investigate the effects of other reaction variables.

**Effect of Temperature.** We assessed the effect of temperature on *p*-xylene partial oxidation in HTW with the  $\text{MnBr}_2$  catalyst and a 60 min batch holding time. The nominal *p*-xylene,  $\text{H}_2\text{O}_2$ , and  $\text{MnBr}_2$  concentrations were 0.08, 1.1, and  $8.9 \times 10^{-3}\text{ M}$ , respectively. Figure 4 displays the results from these experiments. The conversion of *p*-xylene increased as the reaction temperature increased from 250 to  $300\text{ }^{\circ}\text{C}$ . Another  $50\text{ }^{\circ}\text{C}$  increase in temperature to  $350\text{ }^{\circ}\text{C}$  did not produce much additional increase in the *p*-xylene conversion. The terephthalic acid yield increased tremendously from 250 to  $300\text{ }^{\circ}\text{C}$  but then decreased to about 20% when the temperature increased further to  $350\text{ }^{\circ}\text{C}$ . The decrease in the terephthalic acid yield is accompanied by a



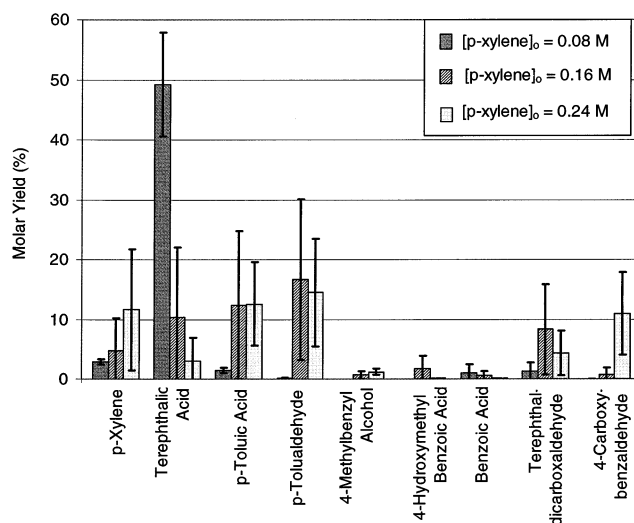
**Figure 4.** Product molar yields from *p*-xylene oxidation at different temperatures ( $[p\text{-xylene}]_0 = 0.08\text{ M}$ ,  $[\text{H}_2\text{O}_2]_0 = 1.1\text{ M}$ ,  $[\text{MnBr}_2] = 8.9 \times 10^{-3}\text{ M}$ ,  $t = 60\text{ min}$ ).

modest increase in the benzoic acid yield, so we attribute the reduced terephthalic acid yield at the highest temperature, at least in part, to more rapid decarboxylation. The yields of the oxidation products that are intermediates in the pathway to terephthalic acid are highest at 250 °C and lowest at 350 °C. This trend is consistent with a sequential reaction network being operative.

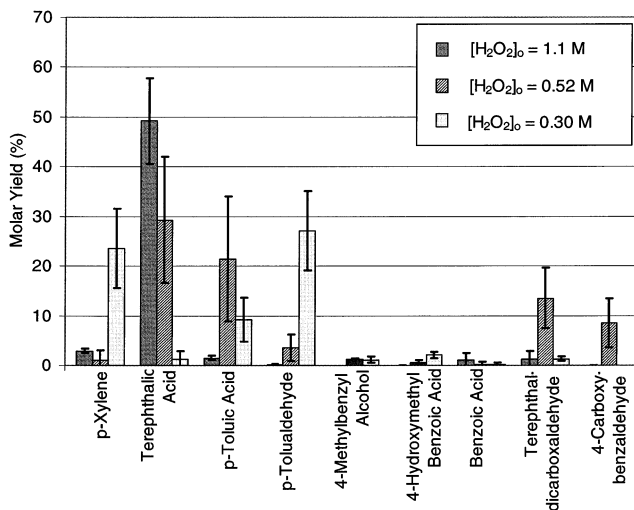
The results in Figure 4 suggest that after 60 min, the oxidation reaction is incomplete at 250 °C and that more decarboxylation of terephthalic acid occurs at 350 °C. A reactor temperature of 300 °C appears to provide the necessary balance between production and preservation of terephthalic acid.

**Effect of *p*-Xylene Initial Concentration.** We assessed the effect of the *p*-xylene initial concentration on the product yields with the  $\text{MnBr}_2$  catalyst at 300 °C and a 60 min batch holding time. The nominal  $\text{H}_2\text{O}_2$  and  $\text{MnBr}_2$  concentrations were 1.1 M and  $8.9 \times 10^{-3}\text{ M}$ , respectively. The nominal *p*-xylene concentrations were 0.08, 0.16, and 0.24 M, which resulted in molar ratios of  $\text{H}_2\text{O}_2$  to *p*-xylene of 14, 6.8, and 4.3, respectively. The stoichiometric ratio is 6:1. Figure 5 displays the results of these experiments. As the *p*-xylene concentration increased, the conversion and the yield of terephthalic acid decreased, whereas the yields of intermediate byproducts generally increased. The benzoic acid yields decreased as the terephthalic acid yields decreased, again suggesting that terephthalic acid decarboxylation forms this product. The larger shift in product distribution corresponded with the greater decrease in the  $\text{H}_2\text{O}_2$ –*p*-xylene molar ratio—from 14 to 6.8. When the ratio decreased further to 4.3, which indicates a substoichiometric amount of  $\text{H}_2\text{O}_2$ , a less pronounced shift in product distribution occurred. These results show that the product distribution is highly sensitive to the ratio of  $\text{H}_2\text{O}_2$  to *p*-xylene and that the terephthalic acid yields increase as this ratio increases even above the stoichiometric amount.

**Effect of Initial Oxidant Concentration.** We assessed the effect of the  $\text{H}_2\text{O}_2$  initial concentration with the  $\text{MnBr}_2$  catalyst at 300 °C and a 60 min batch holding time. The nominal *p*-xylene and  $\text{MnBr}_2$  concentrations were 0.08 and  $8.9 \times 10^{-3}\text{ M}$ , respectively. The nominal hydrogen peroxide concentrations were 1.1, 0.52, and



**Figure 5.** Product molar yields from *p*-xylene oxidation at different *p*-xylene initial concentrations ( $T = 300\text{ °C}$ ,  $[\text{H}_2\text{O}_2]_0 = 1.1\text{ M}$ ,  $[\text{MnBr}_2] = 8.9 \times 10^{-3}\text{ M}$ ,  $t = 60\text{ min}$ ).



**Figure 6.** Product molar yields from *p*-xylene oxidation at different  $\text{H}_2\text{O}_2$  initial concentrations ( $T = 300\text{ °C}$ ,  $[p\text{-xylene}]_0 = 0.08\text{ M}$ ,  $[\text{MnBr}_2] = 8.9 \times 10^{-3}\text{ M}$ ,  $t = 60\text{ min}$ ).

0.30 M, which resulted in  $\text{H}_2\text{O}_2$ -to-*p*-xylene molar ratios of 14, 6.9, and 4.0, respectively. Figure 6 provides results from these experiments. The *p*-xylene conversion showed a pronounced decrease as the oxidant concentration decreased from 0.52 to 0.30 M. The yield of terephthalic acid also decreased sharply as the oxidant concentration decreased. Correspondingly, the yields of most oxidation intermediates increased. The trends in Figure 6 are similar to those in Figure 5, which suggests that the  $\text{H}_2\text{O}_2$ -to-*p*-xylene ratio may be the key variable rather than the absolute concentrations of these reactants.

## Summary and Conclusions

This work confirms the technical feasibility of synthesizing terephthalic acid via the partial oxidation of *p*-xylene in HTW. The highest yield obtained was  $49 \pm 8\%$ , achieved from reaction at 300 °C for 60 min with  $\text{MnBr}_2$  as the catalyst. Our results reveal the effects of catalyst identity, reaction temperature, and the initial concentrations of  $\text{H}_2\text{O}_2$  and *p*-xylene on the product distribution.

$\text{MnBr}_2$  proved to be the most effective catalyst for producing terephthalic acid. The Br content in the

catalyst was far more important than the identity of the metal atom. For reactions at 60 min, the terephthalic acid yield was higher at 300 °C than at 250 or 350 °C. The lower temperature led to higher yields of intermediate oxidation products; the higher temperature led to higher yields of benzoic acid, a decarboxylation product. It is possible, however, that shorter reaction times at 350 °C could produce higher terephthalic acid yields. Finally, the reaction showed a strong dependence on the H<sub>2</sub>O<sub>2</sub>-*p*-xylene molar ratio. When this ratio was decreased, either by increasing the initial concentration of *p*-xylene or decreasing the initial concentration of oxidant, the yield of terephthalic acid decreased and the yield of most intermediate oxidation products increased.

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