Terephthlic Acid Synthesis in Supercritical Water

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Abstract: We have demonstrated the feasibility of terephthalic acid synthesis from *p*-xylene in supercritical water at 380 °C and explored the effects of key process variables. Reactions were carried out batchwise and isothermally in 1.54 mL stainless steel vessels. Hydrogen peroxide served as the oxidant and manganese bromide as the catalyst. We determined the effects of batch holding time, water density, and catalyst, oxidant, and *p*-xylene initial concentrations on the yield of terephthalic acid and the product distribution. The highest yield of terephthalic acid obtained was 57 ± 15% at a water density of 400 kg m^{-3}, a batch holding time of 7.5 min, and initial concentrations of *p*-xylene, catalyst, and oxidant of 0.07 M, 7.7×10^{-3} M, and 0.58 M, respectively. At reaction times longer than 10 minutes, terephthalic acid yields decreased due to decarboxylation of terephthalic acid. Water density had little effect on the yield of terephthalic acid. When catalyst and oxidant were present in low levels, increasing their molar equivalents augmented the terephthalic acid yield. There was little additional increase in the terephthalic acid yield, however, after the levels of catalyst and oxidant reached 0.1 and 8 equivalents, respectively. The experimental results provided some insight into the reaction mechanism.

Keywords: green chemistry; partial oxidation; supercritical water; terephthalic acid; *p*-xylene

Introduction

One of the principles of green chemistry is to use innocuous solvents.[1] Therefore, synthesizing chemicals in high-temperature water (HTW) and supercritical water (SCW) instead of in less benign organic solvents is one approach to practicing green chemistry. Many chemical syntheses have been demonstrated in HTW or SCW.[2] Recent examples include Heck coupling,[3] alkylation,[4] and condensation.[5]

Whereas ambient liquid water is a poor solvent for many organic compounds, the properties of SCW ($T_c = 647$ K, $P_c = 221$ bar) enable it to function well in this role and therefore serve as a practical reaction medium. Figure 1 illustrates the changes in several properties of water with temperature at a fixed pressure of 280 bar.[6] Figure 1a shows that the density decreases as temperature increases, and there is a pronounced drop in density around 660 K. Figure 1b shows that the dielectric constant decreases steadily as the temperature approaches 660 K, where it decreases more sharply. This reduced dielectric constant greatly increases the ability of SCW to dissolve organic substances. Figure 1c shows a nearly 1000-fold increase in the ion product of water, K_w, in the range of approximately 300 K to 550 K. The increased dissociation of water into hydronium and hydroxide ions facilitates acid/base-catalyzed reactions, in some cases obviating the need for any added catalyst. Figure 1d illustrates the pronounced decrease in viscosity that water experiences with increasing temperature. These illustrations in Figure 1 show that the properties of HTW differ considerably from those of ambient liquid water, and that the properties vary continuously over a large range. This large variation in properties can be correlated with the water density and temperature, which hints at the possibility of using these variables to tune the reaction medium for a given reaction.

Figure 2 displays experimental data for the solubility of terephthalic acid, a representative organic compound, in liquid water as a function of temperature.[7] Clearly, the solubility of this compound is greatly enhanced at increased temperatures. As one exceeds the critical temperature, organic compounds and water exist in a single fluid phase.

The focus of this paper is the synthesis of terephthalic acid in SCW. Terephthalic acid is a monomer used in the production of polyethylene terephthalate, which is used for injection-molded consumer products such as soft drink bottles. Most industrial processes to synthesize terephthalic acid proceed via the partial oxidation of *p*-xylene in acetic acid at approximately 200 °C and 15–30 atm. The most common catalyst is a combination of manganese, bromine, and cobalt. The *p*-xylene conversion in this process is 98% and the terephthalic acid mol% yield is 95%.[7]

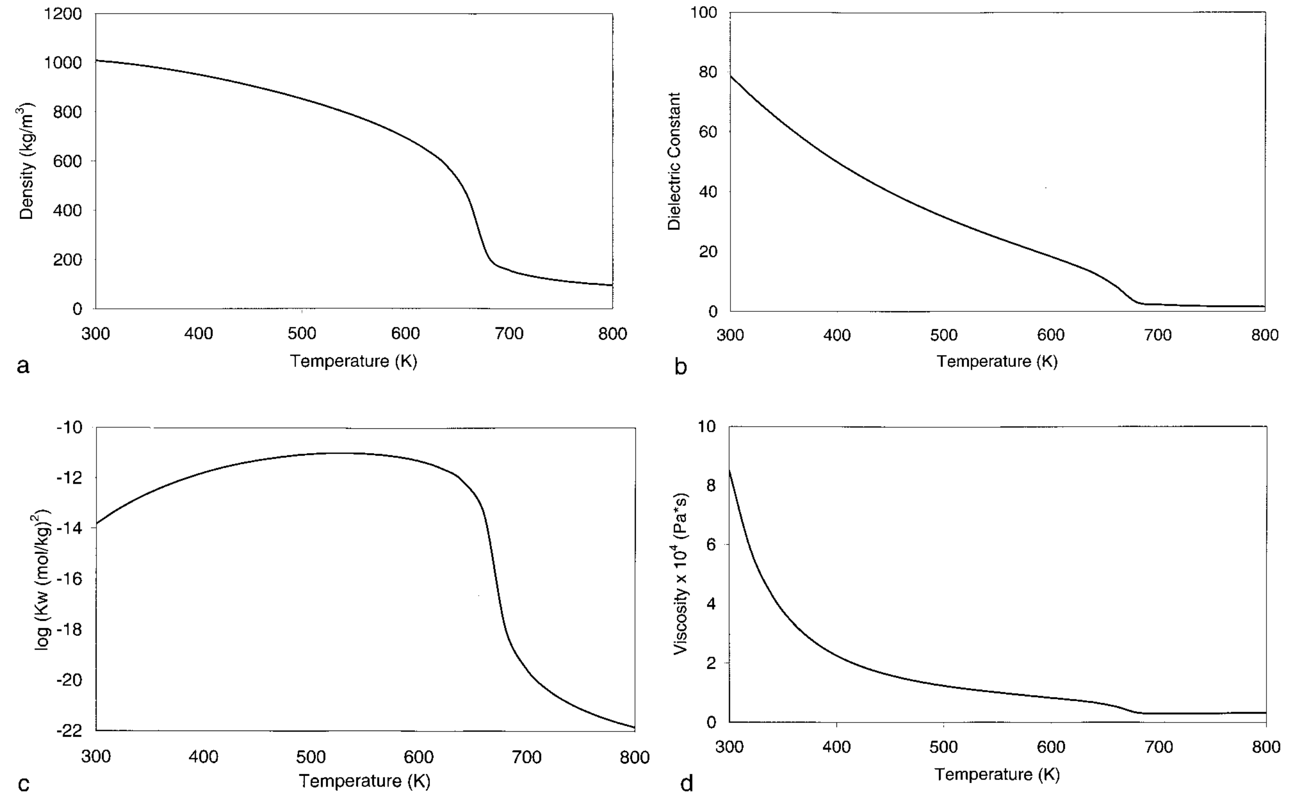

Figure 1. Variation in properties of water with temperature at 280 bar; (a) density, (b) dielectric constant, (c) ion product, (d) viscosity.

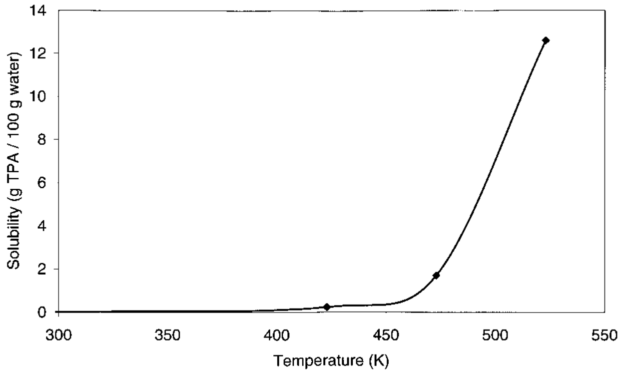

Figure 2. Variation in solubility of terephthalic acid (TPA) in liquid water with temperature.

Several economic and environmental benefits could ensue from the replacement of acetic acid by SCW in this process if yields of terephthalic acid in SCW are comparable to those in acetic acid. First, this replacement would eliminate the energy-intensive separation of acetic acid from water (that forms as a by-product during the reaction) before the acetic acid is recycled back to the reactor. Additionally, methyl bromide, an environmentally harmful compound, forms in the reaction system, possibly from acetic acid reacting with bromine. Finally, a portion of the acetic acid is oxidized during the reaction and must be replenished.

This article provides the results from an exploratory investigation of SCW as a reaction medium for synthesis of terephthalic acid via the homogeneously catalyzed partial oxidation of *p*-xylene. We provide information regarding the effects of the reaction time, water density, and concentrations of catalyst, oxidant, and *p*-xylene on the yields of different oxidation products from isothermal reactions at 380 °C. This article and one forthcoming from Poliakoff[8] are the first on terephthalic acid synthesis in supercritical water. Previous reports[9–14] of the partial oxidation of *p*-xylene in water have been limited to temperatures below the critical point.

Results and Discussion

We performed isothermal experiments at 380 °C to discover the influence of reaction time, water density, and the initial concentrations of *p*-xylene, oxidant, and catalyst on the product yields from *p*-xylene partial oxidation in SCW. Figure 3 displays the partial oxidation products we identified and quantified. These products are terephthalic acid, *p*-toluic acid, *p*-tolualdehyde, 4-carboxybenzaldehyde, terephthaldicarboxaldehyde, 4-hydroxymethylbenzoic acid, 4-methylbenzyl alcohol, and benzoic acid.

Due to limitations in the reactor system, we were not able to close the carbon balance in the experiments. A

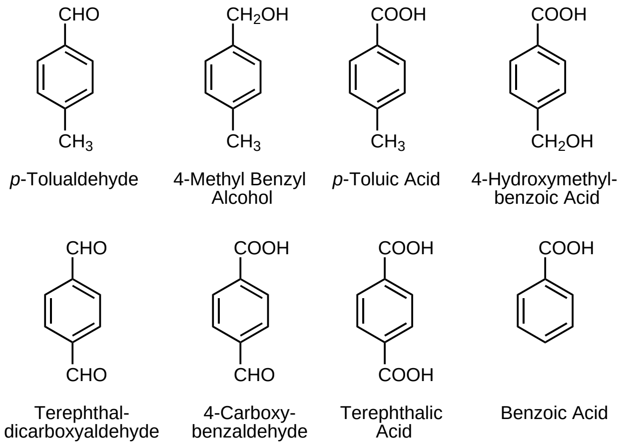

Figure 3. Reaction products identified from the partial oxidation of *p*-xylene in SCW.

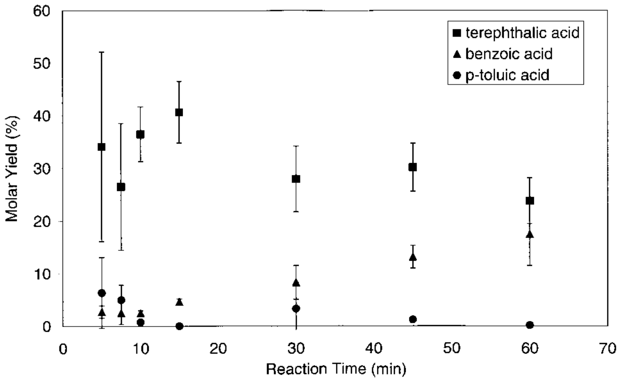

Figure 4. Temporal variation of product yields from *p*-xylene oxidation in SCW at 380 °C ([*p*-xylene]$_0$ = 0.07 M, [H_2O_2]$_0$ = 0.91 M, [$MnBr_2$] = 8.4×10^{-3} M, [H_2O] = 500 kg m^{-3}).

portion of the carbon was likely converted to CO and CO_2 during the reaction, but the reactors did not provide any reliable means of collecting or analyzing gaseous products. Additionally, background experiments revealed[14] that a fraction of the *p*-xylene (at least 20%) initially loaded into the reactors could escape during the course of the reaction. We believe this escape is related to the volatility of *p*-xylene. Because product yields were calculated based on the amount of *p*-xylene loaded into the reactors, this loss of *p*-xylene implies that the product yields reported herein are best taken as lower bounds.

All concentrations reported herein are those that existed at reaction conditions. We performed between three and eight experiments at each set of conditions so we could determine the uncertainties in the experimental results. All results reported herein represent mean values, and the uncertainties shown are standard deviations.

Effect of Reaction Time

Figure 4 displays the temporal variations of the molar yields of terephthalic, toluic, and benzoic acids from reactions at 380 °C and a water density of 500 kg m^{-3}. These data show that the terephthalic acid yield reaches a maximum of 41% (± 6%) after 15 minutes of reaction. Longer reaction times result in a lower yield. At these longer times where the terephthalic acid yield decreases, the benzoic acid yield increases. These trends are consistent with terephthalic acid undergoing a decarboxylation reaction to produce benzoic acid. Clearly, this degradation of the target product is undesired. The yields of *p*-toluic acid in Figure 4 are highest at short times, and they gradually decrease with increasing time. This behavior is consistent with this product being further oxidized to terephthalic acid at the longer times. Taken collectively, the temporal variations in Figure 4 show trends consistent with the operation of a sequential reaction network, as one would expect for this particular system. *p*-Xylene is oxidized to intermediate products, such as *p*-toluic acid. These intermediates are then further oxidized to terephthalic acid, which can then undergo decarboxylation to produce benzoic acid.

Effect of Water Density

One of the potential advantages of performing chemical reactions in a fluid above its critical point is that one can easily manipulate the fluid density. As discussed in the introduction, many properties of the fluid are density (or pressure) dependent, so there exists the opportunity to use density to engineer, or tune, the fluid properties for specific chemical transformations. We conducted a series of experiments to determine the effect of the SCW density on the product yields from *p*-xylene oxidation. These experiments were conducted at 380 °C for 15 min, with nominal *p*-xylene, hydrogen peroxide (H_2O_2), and manganese bromide ($MnBr_2$) concentrations of 0.07 M, 0.86 M, and 7.5×10^{-3} M, respectively.

Terephthalic acid was the major product in these experiments. Benzoic acid and *p*-toluic acid were the only other products detected, and the benzoic acid yields were always the higher of the two. Figure 5 displays the results. The yield of terephthalic acid was always between 30 – 41%, with the higher yields being achieved at the intermediate densities (400 and 500 kg m^{-3}). With the exception of the experiment at 400 kg m^{-3}, which has the largest uncertainty, the benzoic acid yields were always about 5%. These results indicate that the water density does not have a strong influence on the product yields from *p*-xylene oxidation in SCW.

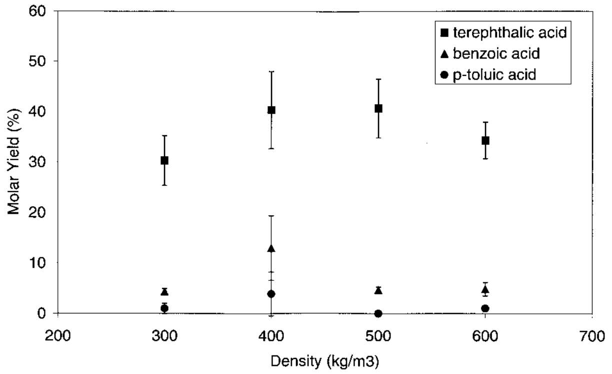

Figure 5. Product molar yields from p-xylene oxidation in SCW at 380 °C at different water densities ($[p\text{-xylene}]_0 = 0.07$ M, $[H_2O_2]_0 = 0.86$ M, $[MnBr_2] = 7.5 \times 10^{-3}$ M, t = 15 min).

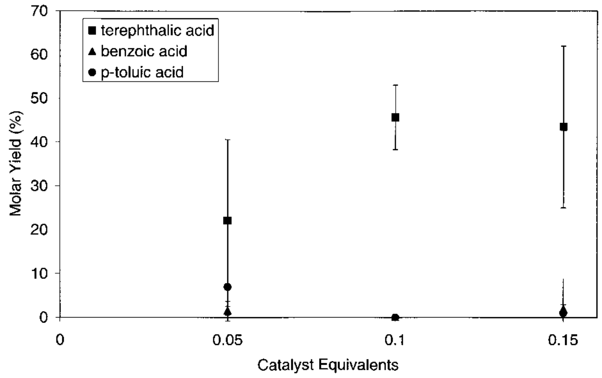

Figure 6. Product molar yields from p-xylene oxidation in SCW at 380 °C at different catalyst loadings ($[p\text{-xylene}]_0 = 0.07$ M, $[H_2O_2]_0 = 0.91$ M, $[H_2O] = 400$ kg m^{-3}, t = 7.5 min).

Effect of Catalyst Loading

Manganese bromide was the catalyst used in all experiments. We conducted a set of experiments at 380 °C and a water density of 400 kg m^{-3} wherein the amount of catalyst added to the reactor was varied. All of these experiments used the same nominal initial concentrations of p-xylene and H_2O_2 of 0.07 M and 0.91 M, respectively. Figure 6 provides the experimental results. Increasing the catalyst loading from 0.05 to 0.10 equivalents increased the terephthalic acid yield from 22 to 45%. An additional increase in loading to 0.15 equivalents had no additional effect on the terephthalic acid yield. Terephthalic acid was the product in highest yield in all of the experiments. Benzoic acid and p-toluic acid were also formed.

Effect of Oxidant Loading

The amount of oxidant available for the partial oxidation reaction can be expected to influence the product distribution and product yields. To isolate the influence of this variable we conducted experiments at 380° C and a water density of 400 kg m^{-3} for 7.5 min with nominal p-xylene and catalyst concentrations of 0.08 M and 7.7 × 10^{-3} M, respectively. We explored cases wherein the oxidant was present in excess and wherein it was the limiting reactant. The stoichiometric requirement for terephthalic acid synthesis is six equivalents of H_2O_2. Figure 7 presents the experimental results. Figure 7a shows that four equivalents of hydrogen peroxide led to p-toluic acid and p-tolualdehyde as the most abundant products, each with yields of about 20%. Moreover, Figure 7b shows that about 20% of the p-xylene initially loaded into the reactor was recovered after the reaction. Terephthalic acid was produced, but only in about a 2% yield. Clearly, the production of terephthalic acid was inhibited by this substoichiometric amount of H_2O_2.

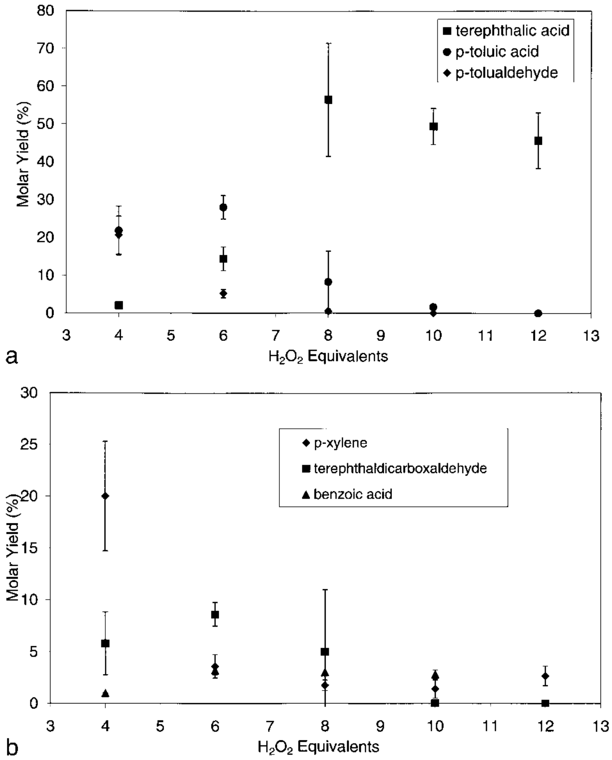

Figure 7. Product molar yields from p-xylene oxidation in SCW at 380 °C at different H_2O_2 initial concentrations ($[p\text{-xylene}]_0 = 0.08$ M, $[MnBr_2] = 7.7 \times 10^{-3}$ M, $[H_2O] = 400$ kg m^{-3}, t = 7.5 min); (a) major products, (b) minor products.

Partial oxidation products dominated the product spectrum.

At a stoichiometric H_2O_2 loading, the yields of products further along the oxidation network (e.g., p-toluic acid, terephthalic acid) increased, whereas the amount of p-xylene recovered and the yields of products that appear earlier in the network (e.g., p-tolualdehyde) decreased. As the H_2O_2 loading increased further, the yields of partial oxidation products decreased nearly to zero, whereas the yield of terephthalic acid increased to a nearly steady value of about 50%. These results indicate that a slight excess of oxidant could be advantageous for terephthalic acid synthesis in SCW.

Effect of *p*-Xylene Loading

The effect of the *p*-xylene loading was investigated in two ways. First, we varied the initial concentration of *p*-xylene at 380 °C, a water density of 400 kg m^{-3}, and a batch holding time of 7.5 min, while keeping the nominal H_2O_2 and $MnBr_2$ concentrations fixed at 0.80 M and 8.6×10^{-3} M, respectively. The results of these experiments are in Figure 8, which shows that the terephthalic acid yield was largely unaffected by the change in *p*-xylene concentration. The yield of *p*-toluic acid, however, which is a reaction intermediate, increased as the *p*-xylene loading increased. We note here that the molar equivalents of H_2O_2 and $MnBr_2$ decreased as the *p*-xylene concentration increased, so these changes might have also affected the results. Therefore, we also conducted additional experiments in which we changed the initial loading of *p*-xylene, but also altered the concentrations of H_2O_2 and $MnBr_2$ to keep their molar equivalents fixed at 8 and 0.1, respectively. The nominal *p*-xylene concentrations were 0.03 M, 0.07 M, and 0.13 M. Figure 9 displays the results of these experiments. The yield of terephthalic acid increased from 25% to 56% as the initial *p*-xylene concentration increased from 0.03 M to 0.07 M but then did not significantly change with the final increase in initial *p*-xylene concentration. Figure 9b shows that the conversion of *p*-xylene increased and the yields of terephthaldicarboxaldehyde and *p*-tolualdehyde decreased as the initial *p*-xylene concentration increased. Therefore, increased initial *p*-xylene concentrations appear favorable for higher *p*-xylene conversion. The yield of terephthalic acid, however, was unaffected by increasing the initial *p*-xylene concentration beyond 0.07 M.

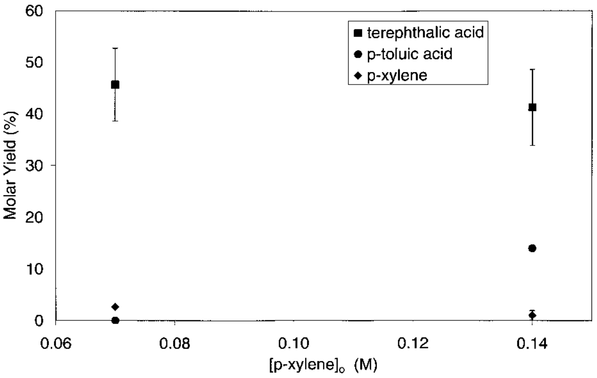

Figure 8. Product yields from p-xylene oxidation in SCW at 380 °C at different *p*-xylene initial concentrations ($[H_2O_2]_0 =$ 0.8 M, $[MnBr_2] = 8.6 \times 10^{-3}$ M, $[H_2O] = 400$ kg m^{-3}, t = 7.5 min).

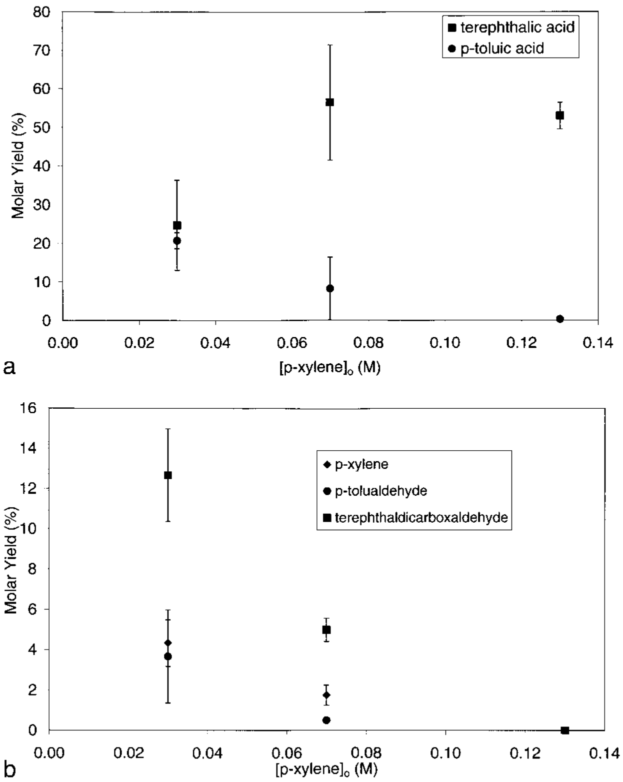

Figure 9. Product molar yields from *p*-xylene oxidation in SCW at 380 °C at different initial concentrations of *p*-xylene, H_2O_2, and $MnBr_2$ (H_2O_2 equivalents = 8, $MnBr_2$ equivalents = 0.1, $[H_2O] = 400$ kg m^{-3}, t = 7.5 min); (a) major products, (b) minor products.

Reaction Mechanism

We suspect that the partial oxidation of p-xylene proceeds in SCW via the same general pathway as it does in acetic acid/water mixtures because the same intermediate oxidation products form in water that form in acetic acid. The mechanism of this reaction in acetic acid/water mixtures has been the focus of much study.[15] It is instructive to consider how this mechanism may change when SCW replaces acetic acid. We first briefly outline the catalytic mechanism of the reaction in acetic acid and then discuss possible changes in the mechanism when SCW is the solvent.

As mentioned earlier, the most common method for synthesis of terephthalic acid in acetic acid uses three catalyst components: cobalt, manganese, and bromine. These catalyst components, which exhibit a high degree of synergy, usually are added to the system as cobalt acetate, $Co(OAc)_2$, manganese acetate, $Mn(OAc)_2$, and HBr. When $M(OAc)_2$, where M = Co or Mn, is added to acetic acid, little dissociation of the $M(OAc)_2$ occurs, and the metal is surrounded by both acetate and acetic acid ligands.[16] These structures vary in the number and placement of acetic acid and acetate ligands but all are thought to be members of the active catalyst system.

Acetic acid ligands play an important role in the reaction mechanism because they can be replaced by other species that require access to the transition metal to continue the reaction. These ligands are only weakly attached to the metal nucleus and therefore ligands such as peroxo radicals, peroxides, and peracids, which also weakly attach to the metal, can easily replace them. Reaction between these ligands and the transition metals are important steps along the reaction pathway. For example, Co^{2+} reacts with peracids to produce acids such as *p*-toluic acid and terephthalic acid. This reaction is very fast and has a high selectivity to the carboxylic acids. Additionally, both Mn and Co react with hydroperoxides to produce peroxo radicals and alkoxy radicals, which are also precursors to intermediate products such as aldehydes and peracids. Moreover, aqua ligands can also replace acetic acid ligands and form hydrogen bonds with bromide in the system, drawing the ion into the second coordination sphere of the metal. This placement makes reaction between the metal and the bromide, as in Equation (3) below, easier than if the bromide were completely dissociated from the metal.

In acetic acid, the Co, Mn, and Br are thought to undergo the series of reactions outlined in Equations (1)–(5).

$$Co^{2+} \longrightarrow Co^{3+} \quad (1)$$

$$Co^{3+} + Mn^{2+} \longrightarrow Mn^{3+} + Co^{2+} \quad (2)$$

$$Mn^{3+} + Br^{-} \longrightarrow Mn^{2+} + Br^{\bullet} \quad (3)$$

$$Br^{-} + Br^{\bullet} \longrightarrow Br_2^{\bullet -} \quad (4)$$

$$Br_2^{\bullet -} + ArCH_3 \longrightarrow HBr + ArCH_2^{\bullet} + Br^{-} \quad (5)$$

In the first step Co^{2+} is oxidized to Co^{3+}. Possible oxidants are a peracid formed from acetic acid[17] or dioxygen.[18] Co^{3+} then oxidizes Mn^{2+} to Mn^{3+}. In the next step Mn^{3+} oxidizes a bromide ion and forms a bromine radical ($Br^{\bullet}$). This radical reacts with Br^{-}, forming an adduct ($Br_2^{\bullet -}$), which then abstracts hydrogen from a methyl group in *p*-xylene. It has been suggested, alternatively, that $Br_2^{\bullet -}$ forms directly from reaction between Mn^{3+} and Br^{-}, i.e., steps 3 and 4 above occur as a single step as in Equation (6), because $Br_2^{\bullet -}$, with a lower reduction potential than $Br^{\bullet}$, is the thermodynamically favored product.[19,20]

$$Mn^{3+}Br_2 \longrightarrow Mn^{2+} + Br_2^{\bullet -} \quad (6)$$

After the benzylic radical forms in step 5, it reacts with oxygen and forms an alkylperoxy radical, and the reaction continues toward the formation of terephthalic acid.

The reaction conditions used in this present study differ from industrial reaction conditions in two main ways, and these differences could have mechanistic implications. First, cobalt is not present in our reaction system. Therefore, there must be a path other than step 2 above to formation of Mn^{3+}. One possibility is that Mn^{2+} is oxidized by H_2O_2 to begin the reaction sequence. It is known that Mn(II) oxo-cluster complexes in acetic acid form Mn(III) oxo-cluster complexes instantaneously in the presence of H_2O_2.[18] A second possibility is that the reaction is initiated in a different way, such as by oxidative attack on the hydrocarbon itself,[21] as in Equation (7).

$$ArCH_3 + O_2 \longrightarrow ArCH_2^{\bullet} + HO_2^{\bullet} \quad (7)$$

We did experiments at 380 °C for 7.5 minutes to assess the importance of this uncatalyzed initiation. The experiments used initial concentrations of *p*-xylene and H_2O_2 of 0.08 M and 0.64 M, respectively, but no $MnBr_2$. The terephthalic yield was $1 \pm 0.3\%$, whereas the yield of other oxidation products was $17 \pm 0.9\%$. These low yields of oxidation products without $MnBr_2$ addition suggest that uncatalyzed oxidative attack on the hydrocarbon is not the main path for terephthalic acid formation in our experiments.

The second major difference from industrial reaction conditions is that neither acetic acid nor acetate were present in our experiments. Therefore, these ligands cannot be involved in the chemistry in SCW as they are in industrial practice. Perhaps the lower terephthalic acid yields we obtained in SCW (relative to the yields obtained commercially in acetic acid) may be the result of impeded access of peroxo radicals, peroxides, and peracids to the coordination sphere of the transition metal catalyst. When $MnBr_2$ is used in SCW, the pathway to this coordination sphere *via* replacement of an acetic acid ligand is nonexistent.

The effectiveness of $MnBr_2$ as a catalyst for the partial oxidation of *p*-xylene in SCW may depend on the extent to which it dissociates. Mn^{3+} can reduce bromide as in Equation (3) more quickly if the dissociation of $MnBr_2$ is minimal than if it is complete.[16] The dielectric constant of the solvent provides an indication of the extent of dissociation of $MnBr_2$ that may occur. The dielectric constant of SCW in our experiments ranges from 4.84 to 9.97.[6] The dielectric constant of acetic acid at ambient conditions, in which $MnBr_2$ remains coordinated,[22] is 6.18. The proximity of the dielectric constants for these two solvents suggests that $MnBr_2$ might remain coordinated in SCW as well.

To summarize, the reaction mechanism in SCW may be similar to the reaction mechanism in acetic acid. The absence of cobalt in the SCW-phase experiments is possibly circumvented by the oxidation of Mn^{2+} by H_2O_2. The key $Br_2^{\bullet -}$ adduct may be formed via reductive elimination of $Mn^{3+}Br_2$ as is possible in acetic acid/water mixtures. It is also conceivable that in a purely aqueous environment $Br_2^{\bullet -}$ is less important that $Br^{\bullet}$. In this case, the reaction in Equation (4) would not occur and $Br^{\bullet}$ would replace $Br_2^{\bullet -}$ in Equation (5).[16] Finally, the lower yields obtained in our work as compared to yields commonly obtained in industrial practice may be a result of changes in the interaction between intermediates such as peroxo radicals, peroxides, and peracids and the manganese, stemming from the absence of acetic acid ligands. Further study of the reaction mechanism in the absence of acetic acid would assist in the design of a catalyst system to optimize the yield of terephthalic acid in SCW.

Practical Significance of Terephthalic Acid Synthesis in SCW

This work (along with that of Poliakoff[8]) has demonstrated, for the first time, the technical feasibility of synthesizing terephthalic acid via the partial oxidation of *p*-xylene in SCW. The highest molar yield of terephthalic acid that was obtained was 57 ± 15%. Recall that the yields we report must be viewed as representing the lower boundary of what is chemically possible because of the loss of *p*-xylene from the reactors in the early stages of reaction. SCW, then, is a promising medium for this reaction.

The economic feasibility of using SCW in a commercial-scale process to manufacture terephthalic acid from the partial oxidation of *p*-xylene remains to be explored. On the positive side, water is less expensive than acetic acid, and unlike acetic acid, it cannot be oxidized, so there would be no reaction-induced solvent losses. Moreover, replacing acetic acid with water may reduce methyl bromide formation and the expense associated with its removal from process vents. Additionally, the use of water as the reaction medium would eliminate the need for the expensive distillation step in the current process that separates acetic acid solvent from water formed during the reaction. On the negative side, an SCW-based process will involve higher temperatures and pressures, which will certainly drive up costs. Also, it is desirable to obtain yields of terephthalic acid higher than those reported herein if one is contemplating commercial use.

Experimental Section

All reactions were carried out in 1.54 mL batch reactors fashioned from a 3/8-inch stainless steel Swagelok port connector and two 3/8-inch caps. All chemicals were obtained from Aldrich Chemical at high purity and used as received. An aqueous solution of 30 wt% H_2O_2 served as the oxidant source. We used H_2O_2 for experimental convenience, recognizing that it is too costly for a commercial-scale process. $MnBr_2$ was selected as the catalyst because both Mn and bromide are used commercially for this reaction and $MnBr_2$ produced the highest terephthalic acid yields in previous[13,14] aqueous-phase oxidations at subcritical temperatures.

Each reagent (*p*-xylene, H_2O_2, $MnBr_2$, and water) was weighed to within ± 0.1 mg on an analytical balance as it was added to the reactors. After the reactors were loaded and sealed they were weighed and then immersed in a preheated, isothermal fluidized sand bath. The reactor contents reach the temperature of the sand bath in about two minutes. Reaction likely occurred as the reactors were heating. Figure 10 provides a representative heat-up curve for one of the reactors. After the desired reaction time had elapsed, the reactors were removed from the sand bath and placed in front of a fan to cool, effectively quenching the reaction. Figure 11 provides a cool-down curve for one reactor, which cooled 78 °C during the first minute.

We weighed the cooled reactors, and then compared the masses of the reactor contents before and after reaction. We discarded all data from reactors wherein this comparison revealed more than a 10% loss in mass. The cooled reactors were then opened and their non-gaseous contents were collected by successive additions of dimethyl sulfoxide (DMSO). We had no means of collecting or analyzing gaseous

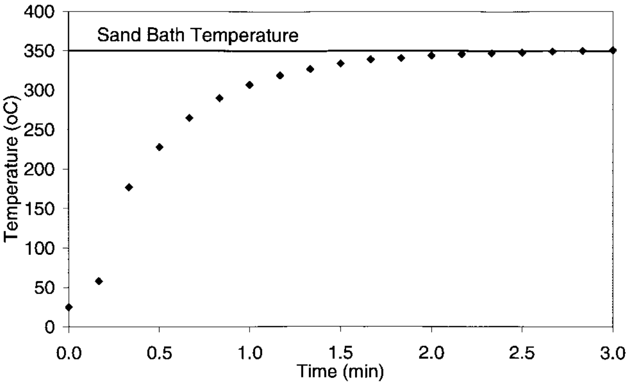

Figure 10. Temperature of a reactor loaded with water versus time in 350 °C sand bath.

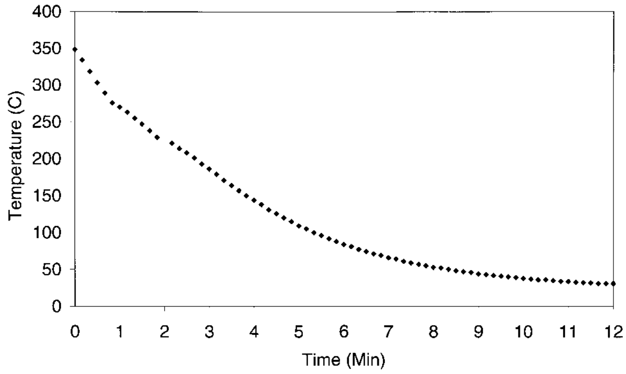

Figure 11. Temperature of a reactor loaded with water versus time as it is cooled by a fan.

products, but such products were clearly present in many of the experiments because the sound of escaping gas accompanied the opening of the reactors. We recovered and isolated a DMSO-insoluble solid residue that formed during the reaction. Previous analysis showed that these solids consisted largely of iron oxide, and are most likely corrosion products.[14]

All product analyses were conducted on a high-performance liquid chromatograph (HPLC) equipped with an Alltech LC-18 column. The injection volume was 20 μL, and a constant flow rate of 1.5 mL/min was maintained. We used ultraviolet detection at 254 nm and the gradient elution method developed by Viola and Cao.[23] Experimental calibration curves were developed for each compound to facilitate the quantification of product yields. These molar yields were calculated by dividing the number of moles of each product formed by the initial number of moles of *p*-xylene loaded into the reactor.

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