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# Reaction Pathway and Kinetics for Uncatalyzed Partial Oxidation of *p*-Xylene in Sub- and Supercritical Water

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In sub- and supercritical water, partial oxidation of *p*-xylene was performed by the batch reactor without a catalyst at the conditions of 240–400 °C and 220–300 bar. The loaded amount of hydrogen peroxide was set to 21–100% of the stoichiometric requirements for oxygen. Conversion of *p*-xylene was reached over about 89.02% (in subcritical conditions) and over 99% (in supercritical conditions) within 20 min. In sub- and supercritical water, we proposed a simplified reaction pathway in parallel and the possible reaction mechanism from major products that consist of *p*-tolualdehyde, *p*-toluic acid, terephthalic acid, 4-carboxybenzaldehyde, toluene, and benzaldehyde. The yield of major products in subcritical condition was higher than that of major products in supercritical condition. The values of rate constants and activation energy were determined. The overall rates of *p*-xylene were divided into two equations. Also, the kinetic constants obtained from a simplified reaction pathway showed good agreement with experimental results.

## 1. Introduction

The sub- and supercritical water is now used increasingly as a solvent for chemical reaction. It has been through the wide range of variations of the physical properties through pressure and temperature changes that reactions in a homogeneous phase were not limited through mass transport.<sup>1</sup> Also, water is cheap, nontoxic, neither combustible nor explosive, and, as a solvent and reaction partner, environmentally friendly. Furthermore, subcritical water can act as an acid or base catalyst. Also, in sub- and supercritical water, many chemical reactions that were previously only possible with the addition of support materials under normal conditions can take place. This specific property suggests that sub- or supercritical water may be used as a possible replacement for environmentally unacceptable solvents for a number of organic reactions.

The most common process used worldwide for the production of terephthalic acid (TPA), a *p*-xylene-oxidized derivative, has been produced and used to make useful products such as polyester fiber and poly(ethylene terephthalate) (PET). TPA has recently become an important, fast-growing chemical as a raw material for PET. In 1999, ca. 26 million tons of PET were manufactured worldwide, and its growth is estimated at a minimum of 5% annually to the year 2002. Nowadays, about 70% of the TPA used worldwide is produced by the catalytic oxidation of *p*-xylene discovered by Scientific Design and Amoco.<sup>3</sup> However, this process has some disadvantages, i.e., the use of bromine as a promoter which corrodes the reactor and the requirement of a solvent like acetic acid. The oxidation is catalyzed by a mixture of heavy metals, most com-

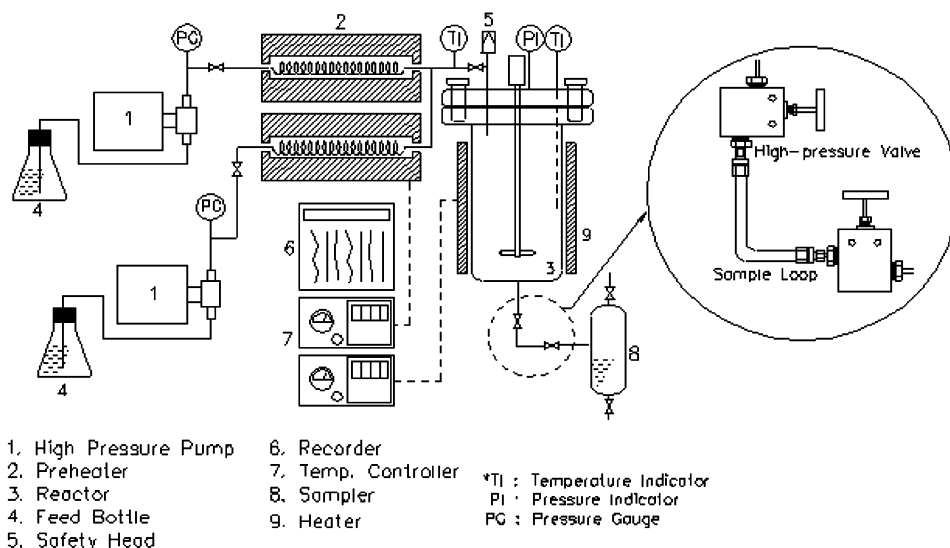
monly cobalt and manganese salts, and bromine, typically in the form of HBr, NaBr, or tetrabromoethane.<sup>4–7</sup> However, the catalysis of the Br group in these catalysts often causes critical corrosion. Also, from economical and environmental points of view, the development of a new oxidation system that overcomes these disadvantages for the production of TPA is desired. In this work, for the first time, sub- and supercritical water processes without catalysts were considered to work out the corrosive problem. A major drawback of the process in the sub- and supercritical water is the corrosion of reactor materials, which is extremely high when chlorine-, sulfur-, or phosphorus-containing compounds are oxidized and the corresponding acids are formed.<sup>8–10</sup> On the other hand, the corrosion problem when water is only used for the process was not found in the previous research.

Other reasons are to determine the possible reaction pathway and the kinetics insight into partial oxidation of *p*-xylene in sub- and supercritical water and to confirm the possibility for high yield of the major products using sub- and supercritical water in uncatalyzed conditions as environmental and economical benefits. In this paper, we focus on the different series and new parallel reaction pathway obtained through our results for the reaction pathway proposed on the basis of the preliminary work. Therefore, we undertake the study of synthetic organic oxidations such as the selective oxidation pathway of alkyl aromatic compounds in sub- and supercritical water using hydrogen peroxide as the oxidant. The previous studies of the partial oxidation of *p*-xylene were used in the catalysis and specified the mechanism from their reaction.<sup>11–15</sup> However, the uncatalyzed partial oxidation of *p*-xylene in sub- and supercritical water has not been reported yet. This work is the first attempt at developing a detailed pathway for the sub- and supercritical water of the complex, the decomposition of *p*-xylene. We consider

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**Figure 1.** Schematic diagram of experimental setup.

free-radical chemistry only and use information in the previous research<sup>16–18</sup> on the reactivity hydroxyl radicals from hydrogen peroxide decomposition with our knowledge of the reaction intermediates in sub- and supercritical water.

Finally, the partial oxidation kinetics for each product in sub- and supercritical water were presented and discussed. They can be provided as useful information about the uncatalyzed partial oxidation of *p*-xylene in sub- and supercritical water.

## 2. Experimental Section

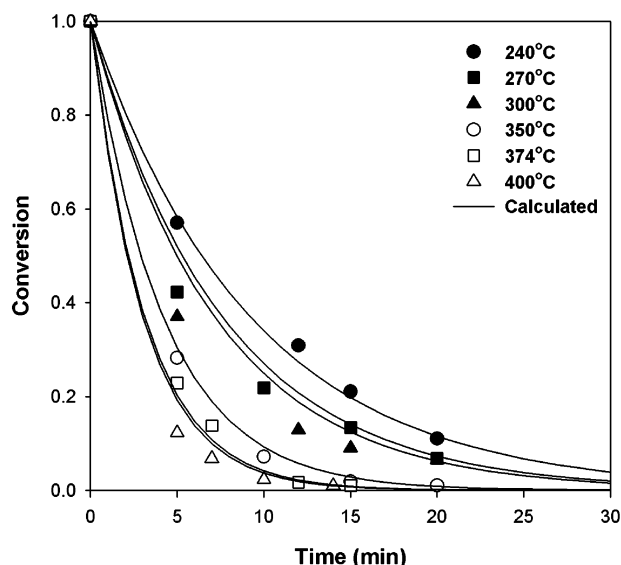
**2.1. Apparatus.** The experimental setup of this work is depicted in Figure 1 and is used in the batch type. The internal volume of the reactor is 1379 cm<sup>3</sup>; its material is used with a Hastelloy-C autoclave of cylindrical vessel type equipped with a magnet drive agitator having variable-speed arrangements. To be heated and kept at fixed temperature, the reactor was equipped with an electric heater. The reaction temperature was controlled by using a temperature controller of an accuracy of  $\pm 1$  °C. The pressure gauge was compensated for because a deadweight tester (Superb Instrument Ltd.), release valve, and safety rupture were placed on top of the reactor vessel. A thermocouple was well immersed in the reaction mixture. Water and hydrogen peroxide as an oxidant was fed by high-pressure minipumps (Milton Roy Co. model NSI-33R). The feeds were preheated to about 20 °C above the reaction temperature and mixed at the T-joint near the reactor.

The effluent mixture was depressurized to atmospheric pressure as it passed through a sample loop that consisted of high-pressure valves (HiP Equipment Co.) and a tube ( $1/4$  in. SUS 316).

**2.2. Procedure.** The autoclave was charged with a known concentration of *p*-xylene and water. The injected water was used to remove dissolved air from the distilled water. The reaction mixture was heated to the desired temperature with constant stirring (150 rpm). In this work, temperature was varied from 240 to 400 °C with regard to the initial concentration of *p*-xylene from 0.0444 to 0.393 mol/L. The amount of water supplied to the reactor with increasing temperature was varied from about 1100 to 120 mL, which resulted in

the pressure variance from 220 to 300bar. Once the temperature was attained, hydrogen peroxide was fed to the reactor at a desired experimental amount. Quantitative interpretation of the variance of hydrogen peroxide as the oxidant was investigated to obtain a target product. To quantify the effect of oxygen in the present work, the amount of hydrogen peroxide ranged from 21% to 100% of the stoichiometric requirements. However, most of the attempts were performed below 100% of the possibility for controlling the selectivity in the formation of TPA by partial oxidation. In addition, the added amount of water was then fed in the reactor to set the predetermined pressure at sub- and supercritical reaction temperatures. This time was considered as zero time for the reaction, and the samples (2–3 mL) were periodically withdrawn during the course of the reaction to generate the kinetic data. The samples were cooled instantly at conditions near the ambient pressure in the sample loop. They were finally collected in the sampling vessel for analysis. After sampling, the water pressure was maintained by adding a little water to keep the reaction condition at constant pressure.

**2.3. Analysis.** For quantitative analysis of a gas phase such as CO and CO<sub>2</sub>, a gas chromatograph equipped with a thermal conductivity detector and a packed column of length 3 m ( $1/8$  o.d. Porapak-Q) was used, and helium was employed as the carrier gas. Liquid products were analyzed by using a high-performance liquid chromatograph that consisted of an isocratic pump (Younlin model M930) with a (Waters) column of symmetry 5  $\mu$ m C-18 at ambient condition and with a flow rate of 1 mL/min by applying the following solvents of the mobile phase: 91% HPLC-grade water (J. T. Baker), 2% HPLC-grade acetic acid (J. T. Baker), 7% HPLC-grade 2-propyl alcohol (Fisher Scientific), and 600  $\mu$ L of 85 wt % phosphoric acid (Aldrich). Standard solutions for calibration and identification of each product were prepared using the following: *p*-xylene, *p*-tolualdehyde, *p*-toluic acid, 4-carboxybenzaldehyde, and TPA obtained from Acros Organics. Toluene, *p*-toluic alcohol, 4-carboxybenzyl alcohol, benzoic acid, terephthaldehyde, and benzaldehyde obtained from Aldrich Chemical. All of the reagents were pure for analytical use. Hydrogen peroxide as an oxidant is used as an aqueous solution of 35 wt % (Yakuri Pure



**Figure 2.** *p*-Xylene conversion versus reaction time in 220 bar, 50% of  $\text{H}_2\text{O}_2$  stoichiometric requirement.

Chemical). The respective response factors for each liquid product in this work were estimated from the correlation of the response factors of known similar compounds. Also, previous work on the analysis of *p*-xylene oxidation products provided us sources for determining unknowns.<sup>2</sup> Further confirmation of the products was made by GC-MS (HP 5890 series II using a HP-1 column of length 30 m coupled to a HP 5970 mass-selective detector) to reconfirm the identification of the HPLC peaks for the liquid products. In this work, the total carbon balance was between 93% and 100% based on the compounds detected by HPLC and GC-TCD.

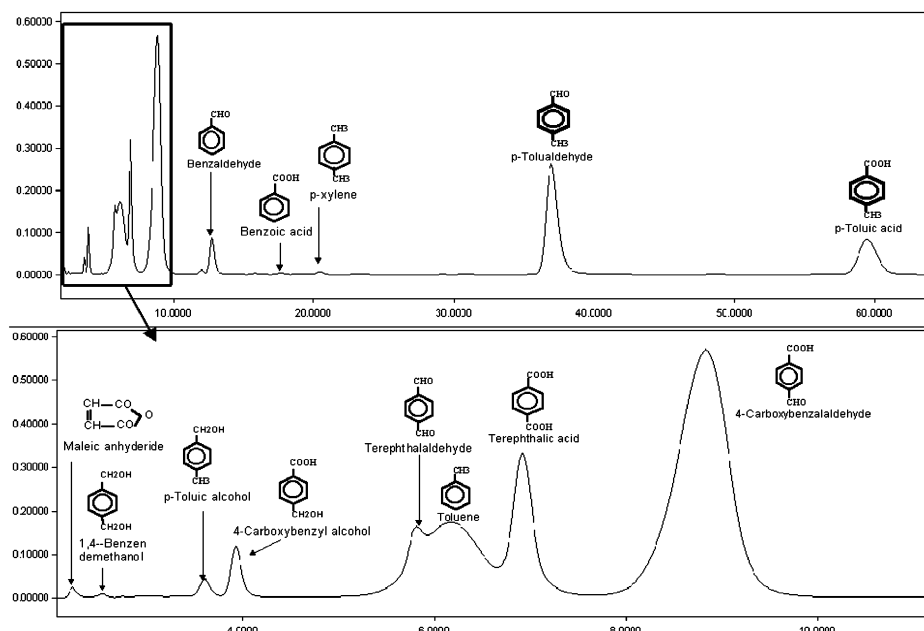
### 3. Results and Discussion

#### 3.1. Consideration of the Heat-Up Effect and Conversion of *p*-Xylene for Partial Oxidation.

Because heating of the reactor to the desired reaction

temperature took from 30 to 50 min, the conversion of *p*-xylene during the heat-up period in the absence of oxygen was investigated first. The initial solution concentration of *p*-xylene in the hot water was from 0.0046 to 0.042 wt %, and most of samples were collected at the end of this heat-up period. When *p*-xylene was further heated from 240 to 400 °C, there was higher decomposition. The *p*-xylene conversion from 240 to 400 °C by simple thermal decomposition was achieved below 6.82%. Particularly, at 400 °C, the composition for generated products was 7.25% for *p*-tolualdehyde, 30.76% for *p*-toluic alcohol, and 5.26% for toluene. When the homolytic reaction in high temperature was followed, the hydroxyl radical ( $\text{OH}^\bullet$ ) was first produced from the initial reaction of water as  $\text{H}_2\text{O} \rightarrow \text{H}^\bullet + \text{OH}^\bullet$ . The generation of the hydroxyl radical could be dehydrated for the methyl group of *p*-xylene and broke the C-C bond. This phenomenon had been reported on the decomposition of organic compounds in WAO and SCWO from earlier research.<sup>19,20</sup> In this work, because the heat-up period needed a longer time to increase the temperature, through negligible conversion for the overall *p*-xylene conversion obtained, the heat-up period represents the time required to form the free radicals. However, it is a well-known fact that the reproducibility of the heat-up period under otherwise similar conditions is rather poor because of adventitious impurities. Hence, most of the reactions in high temperature were performed with a sufficient amount of initiator along with water. Figure 2 shows the overall conversion of *p*-xylene partial oxidation that involves the heat-up period. Most of *p*-xylene was decomposed into other products within 20 min. The *p*-xylene conversion in 240, 270, 300, and 350 °C obtained 89.02%, 93.19%, 93.51%, and 98.98%, respectively, and over 99% for 374 and 400 °C.

**3.2. Reaction Intermediate Compounds and a Possible Reaction Pathway.** In this work, various organic compounds were produced during the reaction as intermediate products. Typical results from HPLC analysis in sub- and supercritical condition are shown in Figure 3. The main products were found to be



**Figure 3.** Typical HPLC chromatographs: *p*-xylene oxidation products in sub- and supercritical water.



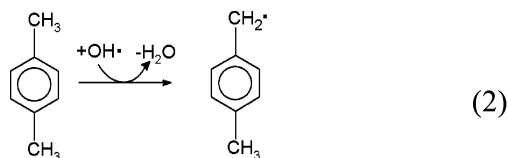
*p*-tolualdehyde, *p*-toluic acid, 4-carboxybenzaldehyde, TPA, toluene, and benzaldehyde. Also, the products of subpathways were formed to the products such as *p*-toluic alcohol, 1,4-benzendimethanol, 4-carboxybenzyl alcohol, and benzoic acid or the acids of low molecular weight products such as maleic anhydride. In the subcritical region but not the supercritical region, gaseous products such as CO and CO<sub>2</sub> were negligibly small. Parts a–d of Figure 4 show the yields of the organic compounds found in the reaction mixture at each temperature. As a result, the best product yields in the liquid phase from *p*-tolualdehyde (1.97%), *p*-toluic acid (5.15%), 4-carboxybenzaldehyde (5.95%), TPA (28.9%), and toluene (21.9%) were obtained in subcritical condition ( $T = 300\text{ }^{\circ}\text{C}$ ), while the yields in supercritical condition were less than those in subcritical condition because of rapid oxidation. On the basis of the intermediate products identified, we proposed a simplified reaction pathway, as shown in Figure 5. This reaction pathway includes parallel reactions that form *p*-tolualdehyde, *p*-toluic acid, 4-carboxybenzaldehyde, TPA, and several other products that have been detected from subsequent of *p*-xylene oxidation in sub- and supercritical water.

**3.3. Reaction Mechanism.** Recently, hydrothermal experiments of the organic compounds have been developed by a few researchers to describe free-radical mechanisms using hydrogen peroxide.<sup>7,23</sup> Also, in earlier research,<sup>21,22,27</sup> they demonstrated that when hydrogen peroxide was added, hydroxyl radicals were used as promoters, which had a significant effect on the rate, becoming the rate-controlling step when hydrogen peroxide had been consumed.

At this possible reaction pathway, the overall reaction can be described by a series of elementary steps such as the following. The presence of reactive free radicals (OH<sup>•</sup>) from the hydrogen peroxide reaction enhances the overall reaction rates. Here, hydrogen peroxide is a powerful source of highly reactive hydroxyl radicals for *p*-xylene decomposition.



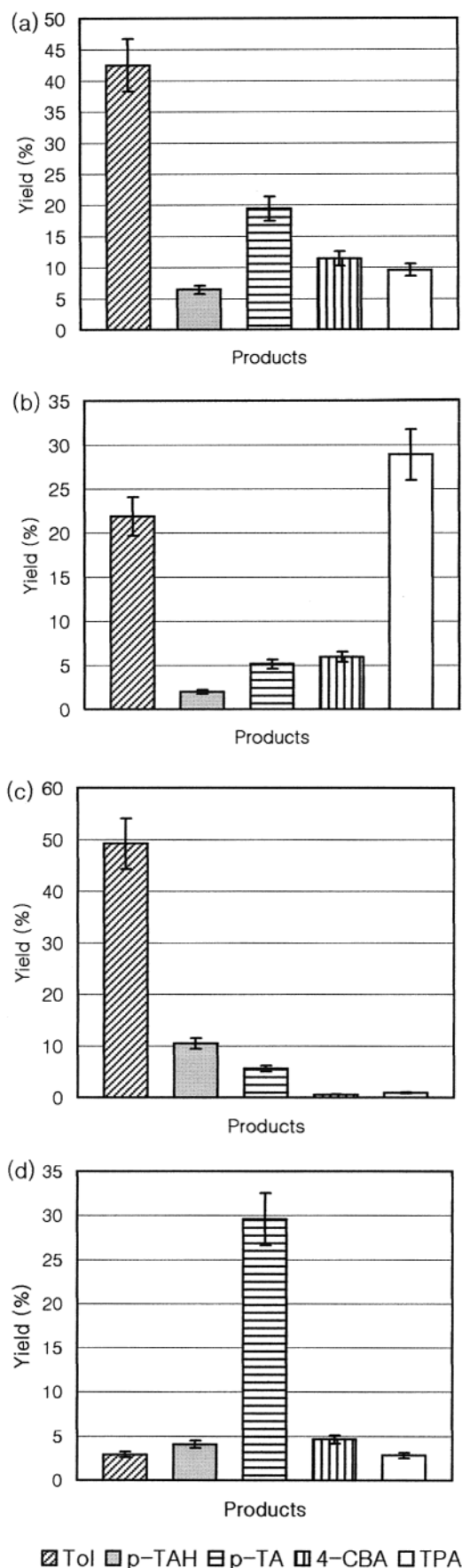
Once generated, hydroxyl radicals rapidly and unselectively react with all organics present in the reaction medium as in reaction (1). Therefore, hydroxyl radicals for *p*-xylene can be reacted such as in the following.



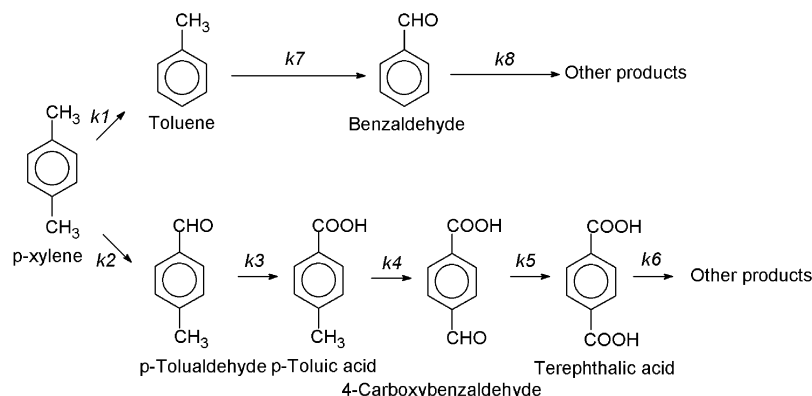
Reaction (3) provides a means to promote the oxidation of organics by generating radicals R<sup>•</sup>. Hydrogen peroxide can also react with oxygen such as in reaction (4) because of the high reactivity of hydroxyl radicals.<sup>17,24,25</sup> Moreover, the *p*-methylbenzyl radical can



form *p*-tolualdehyde through a reaction with HO<sub>2</sub><sup>•</sup>, and

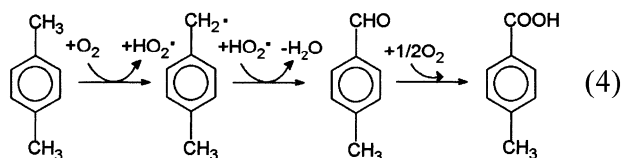


**Figure 4.** Yield (%) of the main organic compounds in the liquid phase in 220 bar, 50% of H<sub>2</sub>O<sub>2</sub> stoichiometric requirement: (a) 240 °C; (b) 300 °C; (c) 374 °C; (d) 400 °C.

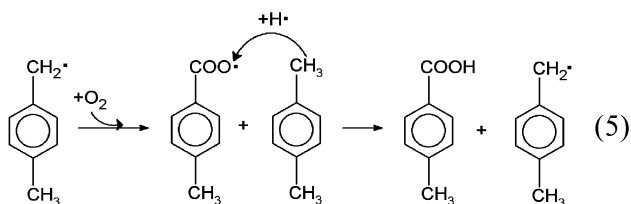


**Figure 5.** Proposed reaction pathway of *p*-xylene in this work.

*p*-tolualdehyde is expected to form *p*-toluic acid through a reaction with oxygen.



Also, the commonly accepted mechanism of the auto-oxidation of organics with oxygen in the absence of promoters starts with reaction (5).



The *p*-methylbenzyl radical at high temperatures is a variable source of radicals. However, it is very slow at low temperatures because ground-state oxygen does not react readily with most organic molecules because of its spin restrictions.<sup>22</sup> The *p*-methylbenzyl radical is formed by the above reactions; it can react readily with oxygen to form a peroxy compound that is able of reacting with the parent compounds constituting the chain propagation of the cycle.

Also, it is important to point out that OH and HOO radicals accelerate initial reaction rates but, once hydrogen peroxide is consumed, oxygen is the actual oxidant that really carries out most of the oxidation process.<sup>7</sup> Thus, it will react readily to form the carboxyl group of compounds such as *p*-toluic acid.

In particular, toluene of the products in intermediate compounds occurs rapidly at high temperatures, which is not occurring in other convenient reactions. Toluene occurs through breaking of the C–C bond into a benzyl group (–C<sub>6</sub>H<sub>5</sub>) and a methane group (–CH<sub>3</sub>) in *p*-xylene, and the methane group is predicted to form methyl alcohol with the excess water in the reactor as in reaction (6). Toluene is formed to hydrogenate for the benzyl group with formed H• in this reaction (6).



Benzaldehyde, like the preceding, is expected to form through the methylbenzyl radical with oxygen. Further, benzaldehyde goes to benzoic acid. Also, methyl ben-

**Table 1.** Experimental Measurements of Kinetic Constants for *p*-Xylene Decomposition

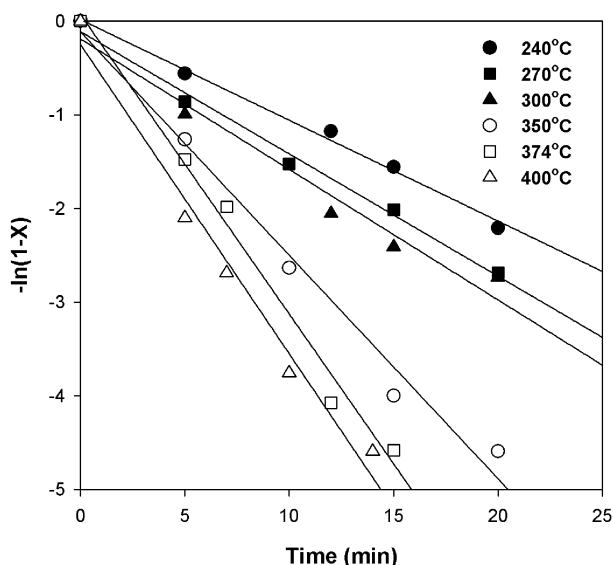
reaction			reaction		
<i>T</i> (°C)	time (min)	<i>k</i> (min <sup>−1</sup> )	<i>T</i> (°C)	time (min)	<i>k</i> (min <sup>−1</sup> )
240	20	0.108 ± 0.015	350	20	0.238 ± 0.051
270	20	0.131 ± 0.021	374	15	0.319 ± 0.059
300	20	0.139 ± 0.043	400	14	0.330 ± 0.080

zoate (C<sub>6</sub>H<sub>5</sub>–COOCH<sub>3</sub>) of the other decomposition products was identified from HPLC analysis. This product is formed through the reaction of benzoic acid with methyl alcohol. It is assumed that this methyl alcohol was formed in reaction (6).

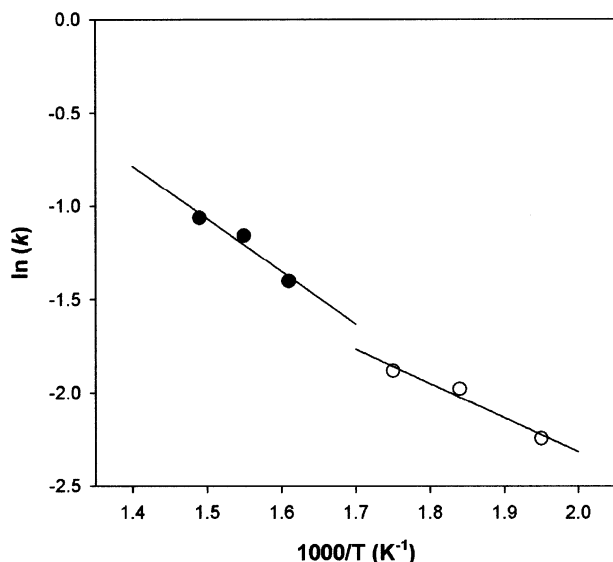
The *p*-methylbenzyl radical can also react with another *p*-methylbenzyl radical, but because the concentration of this *p*-methylbenzyl radical is low, the rate of this reaction is much lower than the rate of reaction (5). Because organics from reaction (5) become complex enough to form a condensation product, complex organics such as the coupling of benzylics were not identified in our experiments. Narayan and Antal<sup>28</sup> reported that the coupling mechanism in the heterolytic reaction with increasing water, where aromatic radicals react with each other to form a condensation product, could be prohibited. Also, with the substitution of a hydroxyl group,  $\pi$  electrons become delocalized and the benzene ring can be destabilized. Further substitution and oxygen attacks result in the complete destabilization of the benzene ring and lead to a ring-opening reaction. Therefore, they are more likely to crack and/or eliminate. Last, a pathway eventually is the formation of stable low molecular weight products and CO<sub>2</sub>.

At a proposed reaction pathway from our experiments, the main path of the products was considered to be especially significant because these products are applied to sources of industrial processes.<sup>11–15</sup> This reaction pathway would incorporate the effect of process variables into the maximum formation of the desired products.

**3.4. Kinetic Study.** The overall decomposition rates at each temperature were evaluated as shown in Table 1. The results of  $\ln(1 - X)$  versus time are straight lines, suggesting first-order kinetics (Figure 6). The overall rate kinetics can be made by the Arrhenius equation using multiple linear regression of Fortran software from nonisothermal kinetic data; these values were determined as  $r_A = 1.332 \pm 0.698 \exp[(-15.16 \pm 3.134 \text{ kJ/mol})/RT]$  for subcritical conditions (240 °C < *T* < 350 °C) and  $r_A' = 3.16 \pm 1.119 \exp[(-23.42 \pm 5.994 \text{ kJ/mol})/RT]$  for supercritical conditions (350 °C < *T* < 400 °C). The standard errors of the regression were 0.0535 in



**Figure 6.** Experimental data of the disappearance of *p*-xylene plotted as  $\ln(1 - X)$  versus time at 240–400 °C.



**Figure 7.** Arrhenius plot with an assumed first-order rate constant ( $\text{min}^{-1}$ ) for *p*-xylene oxidation in sub- and supercritical water.

subcritical conditions and 0.0612 in supercritical conditions. Also, the concentration of TPA as a target product was decreased with increasing temperature. The intermediate as the byproduct as well as the products of the main reaction pathway is affected to a higher extent in supercritical condition. This means the temperature is the major factor which influences the reaction pathway of *p*-xylene oxidation. Also, the partial oxidation method that retards the pathway to the final product was preferred for the purpose of improving the selectivity of the target intermediate and tracing the pathway.

As shown in Figure 7, the rate constants in the supercritical condition were comparatively higher than those in the subcritical condition. The reason for the higher reaction rates in the supercritical condition is probably because of changes in the properties of water with pressure and temperature. In the subcritical condition, the decomposition rate constants of *p*-xylene were found not to vary greatly with changes in temperature. As shown in Table 2, the rate constants of each product as well as the overall decomposition rates in the subcritical condition change less than those in the

**Table 2.** Reaction Rate Constants for the Proposed *p*-Xylene Oxidation Pathway in 220 bar and 50% of  $\text{H}_2\text{O}_2$  Stoichiometric Requirement

reaction rate constant ( $k_i/\text{min}$ )	subcritical conditions			supercritical conditions		
	240 °C	270 °C	300 °C	350 °C	374 °C	400 °C
$k_1$	0.098	0.115	0.121	0.204	0.249	0.225
$k_2$	0.011	0.015	0.018	0.034	0.071	0.105
$k_3$	0.118	0.219	0.215	0.097	0.073	0.124
$k_4$	0.080	0.144	0.275	0.178	0.186	0.015
$k_5$	0.094	0.276	0.241	0.226	0.194	0.123
$k_6$	0.088	0.080	0.087	0.144	0.213	0.180
$k_7$	0.066	0.174	0.192	0.043	0.081	0.076
$k_8$	0.243	0.263	0.348	0.081	0.097	0.138

supercritical condition. This can be explained as a result of very small changes of properties of water in the subcritical condition. In these experiments, the water density is varied widely from 0.81  $\text{g}/\text{cm}^3$  (at 240 °C) up to 0.123  $\text{g}/\text{cm}^3$  (at 400 °C). Also, it was reported that the reaction rate at the transient region like the supercritical condition shows dramatic increases in the work of Russell et al.<sup>29</sup>

The reaction kinetics was evaluated from the reaction pathway elucidated as shown in Figure 5, which corresponds to the possible reaction pathway discussed in section 3.3. Also, the values of the reaction rate constants provide insight into the relative significance of the different steps in the reaction pathway. The rate expression of the oxidation reaction used by the earlier workers is adopted here.<sup>30,31</sup> Experimental results of *p*-xylene oxidation were fit by using the differential equations given as the reaction conducted with a negligible change in specific volume in an isothermal, isobaric, batch reactor. The mole balance can be written as  $dC_i/dt = r_i$ , where  $C_i$  is the concentration of species  $i$  in the reaction,  $t$  is the reaction time, and  $r_i$  is the rate of formation of species  $i$ . The differential equations that describe the concentration of each product as functions of time, based on the reaction pathway shown in Figure 5, are the following:

$$dC_{p\text{-xylene}}/dt = -k_A C_{p\text{-xylene}} \quad \text{where } k_A = k_1 + k_2 \quad (1)$$

$$dC_{\text{Tol}}/dt = k_1 C_{p\text{-xylene}} - k_7 C_{\text{Tol}} \quad (2)$$

$$dC_{p\text{-TAH}}/dt = k_2 C_{p\text{-xylene}} - k_3 C_{p\text{-TAH}} \quad (3)$$

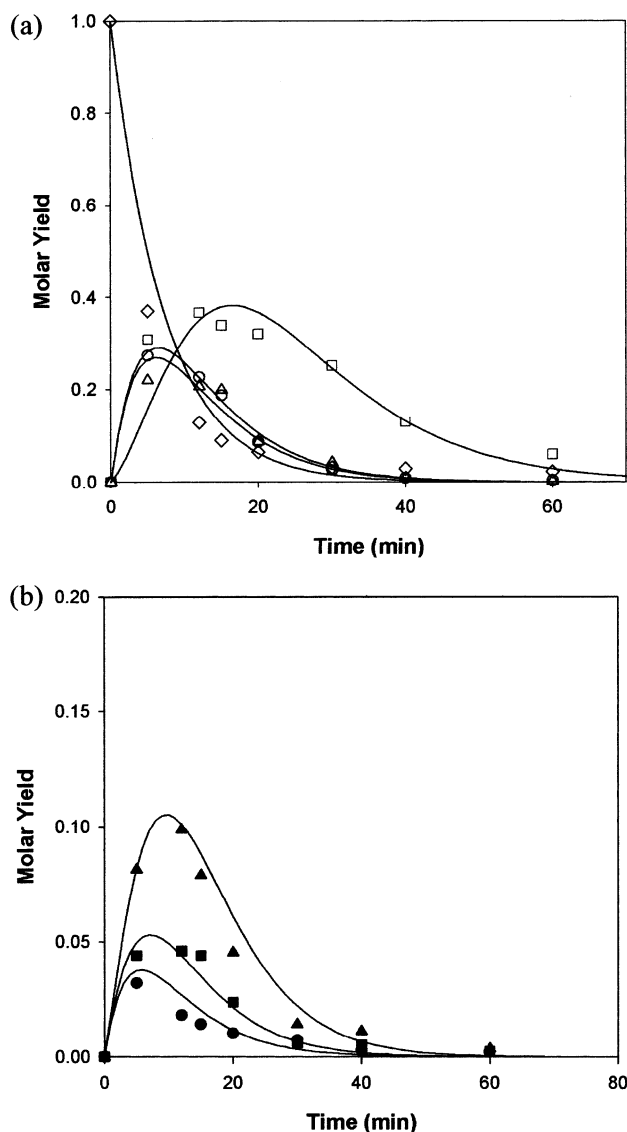
$$dC_{p\text{-TA}}/dt = k_2 C_{p\text{-xylene}} + k_3 C_{p\text{-TAH}} - k_4 C_{p\text{-TA}} \quad (4)$$

$$dC_{\text{BDH}}/dt = k_1 C_{p\text{-xylene}} + k_7 C_{\text{Tol}} - k_8 C_{\text{BDH}} \quad (5)$$

$$dC_{4\text{-CBA}}/dt = k_2 C_{p\text{-xylene}} + k_3 C_{p\text{-TAH}} + k_4 C_{p\text{-TA}} - k_5 C_{4\text{-CBA}} \quad (6)$$

$$dC_{\text{TPA}}/dt = k_2 C_{p\text{-xylene}} + k_3 C_{p\text{-TAH}} + k_4 C_{p\text{-TA}} + k_5 C_{4\text{-CBA}} - k_6 C_{\text{TPA}} \quad (7)$$

Here, the  $k_i$  parameters for the above system were obtained by a nonlinear least-squares curve-fitting method.<sup>32</sup> Also, we used the Scientist package to solve simultaneously eqs 1–7 by using the Runge–Kutta 4th method. Figure 8a,b compares the experimental data and the above model predictions for reactions at 300 °C as a function of the reaction time by using Table 2. The solid curves represent the concentrations calculated, and the discrete points represent the experimental data. The



**Figure 8.** Comparison of experimental data and model prediction as a function of time for *p*-xylene partial oxidation at 300 °C, 220 bar and 50% of H<sub>2</sub>O<sub>2</sub> stoichiometric requirement. (Symbols: ◇ *p*-xylene, □ TPA, △ Tol, ○ BDH, ● *p*-TAH, ■ *p*-TA, ▲ 4-CBA and — predicted.)

model calculations and experimental data show good agreement. Therefore, the model in eqs 1–7 with the parameters in Table 2 should provide reliable predictions of the product concentration at all other temperatures as well as at 300 and 400 °C. Also, in supercritical condition, generation of the products except the main products was found to be a larger effect than in the subcritical condition. The oxidation rates of *p*-xylene were increased as the temperature increased under the same conditions (i.e., pressure and feed amount of hydrogen peroxide). This may be a result of the cage effect of water being around molecular of the reaction products, the same as the previous researches<sup>33–35</sup> because of the decreased partial volume of water in supercritical condition with increasing temperature.

#### 4. Conclusion

On the basis of the characteristics of SCW, partial oxidation of *p*-xylene was performed with water and hydrogen peroxide without catalyst. Also, *p*-xylene was decomposed into other products, of which the reaction

rates were divided into two equations. This values were determined as  $r_A = 1.332 \pm 0.698 \exp[(-15.16 \pm 3.134 \text{ kJ/mol})/RT]$  for subcritical conditions (240 °C <  $T$  < 350 °C) and  $r_A' = 3.16 \pm 1.119 \exp[(-23.42 \pm 5.994 \text{ kJ/mol})/RT]$  for supercritical conditions (350 °C <  $T$  < 400 °C). In addition, a simplified reaction pathway and reaction mechanism was proposed, and the reaction pathway shows that the reaction started in parallel, *p*-tolu-aldehyde and toluene. In particular, the path toward toluene in our experimental results is not occurring in other convenient reactions. Also, we obtained the best product yield for TPA in subcritical condition ( $T = 300$  °C). The kinetic constants obtained from a simplified reaction pathway showed a good agreement with experimental results. Compared with the former catalytic reaction, though the yield of target products (such as 4-CBA and TPA) was less than that of the former catalytic reaction, our results have economical, environmentally friendly advantages in matters of noncatalytic reaction and nonhazardous solvent. Also, we offered the possibility of controlling the selectivity in the synthesis of useful products through partial oxidation followed by subcritical water.

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#### Notation

Tol = toluene  
*p*-TAH = *p*-tolualdehyde  
*p*-TA = *p*-toluic acid  
 BDH = benzaldehyde  
 4-CBA = 4-carboxybenzaldehyde  
 TPA = terephthalic acid  
 $k$  = reaction rate constant

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