The selective, continuous, aerobic oxidations of \textit{para}-xylene (pX) and \textit{ortho}-xylene (oX) were performed in an identical fashion in supercritical water. The xylenes were oxidized without a catalyst and with hydrobromic acid, cobalt(II) and manganese(II) bromide catalysts. The conversions and yields to phthalic acid (OA) from oX were always significantly higher than those for terephthalic acid (TA) from pX. The formation of CO$_2$ was significantly higher for pX than oX despite the higher conversions to oX. These results are unexpected because the literature teaches that thermal and catalytic decarboxylation is much higher for OA than TA. The superior yields from oX are consistent with a lower steady-state concentration of hydroxyl radicals, OH$^\cdot$ due to the internal, concerted attack of the peroxides with the oX methyl group. This mechanism forms the phthalide directly from \textit{o}-tolualdehyde (oTOL) which is consistent with the observation that \textit{ortho}-tolualdehyde (oTA) is much lower in oX than \textit{para}-tolualdehyde, PTA, in pX oxidation. This mechanism also lowers the steady-state concentration of aromatic acids consistent with the observed lower benzoic acid and CO$_2$ yields. Overall, the results suggest that the metal catalysts can play more than one role, thereby opening up the opportunity for discovering new catalytic synergies which are explored in our next paper, Part 2 of this series.

**Introduction**

This is the first of two papers in which we report studies on the feasibility of producing terephthalic acid, TA, by aerobic oxidation of \textit{p}-xylene, pX, in high temperature water, HTW, or supercritical water, SCW. Our overall aim has been to develop a better understanding of the reaction and to discover new catalysts and better reaction conditions to give higher yields of TA and less burning of pX to CO$_2$. Previously, we have reported that (a) high yields of TA can be obtained by oxidation of pX in SCW using a continuous reactor,\textsuperscript{11} (b) more generally, aromatic acids can be obtained from oxidation of alkylaromatic compounds,\textsuperscript{1} (c) the simultaneous oxidation of mixtures of xylenes is feasible\textsuperscript{4} and (d) increased Bronsted acidity, increased bromide concentration, and the addition of aromatic acids can all substantially reduce the precipitation of manganese oxides that can occur when MnBr$_2$ is used as a catalyst.\textsuperscript{5}

In this paper, we compare the results of oxidizing \textit{ortho-} and \textit{para}-xylene, oX and pX. The differences in the product distribution between the two xylenes suggest differences in the mechanisms of the two oxidations and provide new insights into the role of the catalyst and the mechanisms of burn of the aromatics. The second paper,\textsuperscript{6} describes our successful attempts to find better catalysts and their optimization.

Research activity has been growing in the field of SCW (\(T_c = 374\ ^\circ\text{C}, p_c = 221\) bar) or more generally in high-temperature water because of the unusual properties of H$_2$O under these conditions.\textsuperscript{7} A wide range of chemical reactions have been studied where SCW plays the role of a solvent and/or reactant and/or catalyst.\textsuperscript{7–12} Research on the homogeneously catalysed oxidation of methylaromatics in HTW and SCW was first reported by Holliday et al.\textsuperscript{13} and subsequently by others.\textsuperscript{14–19} The aerobic oxidation of pX to TA is carried out industrially using acetic acid as the solvent. Despite its extraordinary efficiency (99\% selectivity, \textasciitilde 95\% yield), the process still has some drawbacks.\textsuperscript{22} The crude TA contains \textasciitilde 0.3\% of 4-carboxybenzaldehyde (4CBA) that must be removed via a costly and energy-consuming process. Another negative factor is loss of ca. 0.05 kg of acetic acid per kg of TA manufactured due to combustion.\textsuperscript{22} Moreover, solvent degradation generates the greenhouse gas CO$_2$ and the ozone-depleting agent CH$_3$Br. Finally, re-use of the solvent necessitates an energy-consuming
distillation step to remove the \( \text{H}_2\text{O} \) formed as a by-product (2 moles per TA mole produced). Replacing the acetic acid by water could overcome these drawbacks as well as giving more efficient heat recovery due to the higher oxidation temperatures utilised in HTW and SCW. Water is therefore a serious candidate for replacing acetic acid due to the combination of economic and environmental benefits that it offers.

Currently, a potential major economic inconvenience of the water-based method is the undesired total oxidation (burn) of pX and decarboxylation of the aromatic acids. Minimizing burn and decarboxylation in HTW is therefore an important goal in making this new methodology commercially viable for TA manufacture. This paper reports differences in yields, selectivity and burn of xylene between oX and pX oxidation in SCW, which provide evidence for the mechanisms that cause total oxidation.

The metal/bromide catalyzed autoxidation of pX and oX as well as \( \text{p}-\) and \( \text{o}-\)toluic acid have been reviewed and summarized but there is only a small amount of literature which directly compares results from oX and pX even in acetic acid. Oxidation of oX in SCW has been reported previously, but without any data for formation of CO\(_2\). Recently, we studied catalyst stability in the oxidation of oX in SCW and, although we have noticed differences between the isomers of xylene, this paper is the first time that we have studied these differences systematically.

**Method**

A simplified schematic of our tubular continuous flow reactor is shown in Fig. 1. The reactions were carried out at a temperature of 380 °C and a pressure of 230 bar. More details of the experimental equipment and procedure can be found in the Experimental section and in the second paper of this series.

![Simplified schematic of the continuous reactor used in this work](image)

**Fig. 1** Simplified scheme of the tubular continuous flow reactor used in this work. O\(_2\) is generated from aqueous \( \text{H}_2\text{O}_2 \) by high temperature decomposition in a pre-heater, PH. The mixture \( \text{O}_2/\text{H}_2\text{O}_2 \) pure xylene, and an aqueous solution of the catalyst are continuously fed into the reactor by means of HPLC pumps. After the reactor, the mixture is quenched with a cold solution of NaOH that neutralizes any CO\(_2\) to form carbonate. An average residence time of 5.8 s is calculated from the reactor volume, the total flow rate and the density of pure water, obtained from the NIST database.

The concentrations of dicarboxylic acids and the intermediates in the product stream were analysed by HPLC. The yield of dicarboxylic acid, \( Y_A \), was then calculated by eqn (1).

\[
Y_A = 100 \frac{[A]}{[X]} \quad (1)
\]

where \([A]\) is the molar concentration of the acid, \([X]\) is the molar concentration of pX or oX if the conversion had been 0, i.e. allowing for dilution. \([X] = \left( F_X \rho_X / (F_{\text{total}} M_X) \right) \), where \( F_X \), \( F_{\text{total}} \) are the flow rates of the xylene and the total flow after quench; \( \rho_X \) and \( M_X \) are the density and molar mass of the xylene, respectively. CO\(_2\) yield was calculated from the carbonate concentration obtained from titration by eqn (2), with \([BA]\) being subtracted to avoid counting the CO\(_2\) molecules arising from decarboxylation.

\[
Y_{\text{CO}_2} = \frac{100[\text{CO}_2^2] - [BA]}{8[X]} \quad (2)
\]

Finally we define “burn” as \( Y_{\text{CO}_2}/Y_A \); that is the number of moles of xylene totally oxidized per mole of dicarboxylic acid produced. Hence burn is a measure of the amount of xylene that is lost through combustion.

**Results**

Our strategy has been to run the oxidation of pX and oX in the same reactor and in an identical fashion so that genuine similarities and differences can be identified and directly compared. The following catalysts were used: four concentrations of HBr, CoBr\(_2\), and MnBr\(_2\) by itself or with either HBr or benzoic acid added to increase the solubility of the catalyst. Control experiments were run without any added catalyst.

Fig. 2 summarizes the yields of the dicarboxylic acids and CO\(_2\). It can be seen that, for both oX and pX, all of the catalysts have the effect of increasing the yield of diacid compared to the control experiments. Also, under these conditions, CoBr\(_2\) is a much poorer catalyst than MnBr\(_2\) for the selective oxidation of both xylenes.

However, it is the differences in the oxidation of these two apparently similar substrates that are particularly striking. The yields of \( \text{o}-\)phthalic acid, OA, are always higher than those of TA, with and without the presence of catalyst. That is surprising in view of the fact that OA is known to deactivate the Co/Mn/Br catalyst in acetic acid, due to catalytic decarboxylation and lower yields are observed for oX than pX. Fig. 2 also shows that the CO\(_2\) yield in SCW is always higher when using pX, except for the uncatalyzed reaction where it is similar to oX. However, even in the uncatalyzed reaction, the OA yield is much higher than that of pX; so the burn will be much lower for oX. This suggests that the intrinsic amount of CO\(_2\) being generated by pX is always higher than that of oX (even for the uncatalyzed reaction).

Scheme 1 shows the various intermediates expected for the oxidation of pX and oX, and their sequence. The sequence of formation of intermediates for pX in acetic acid is well established as well as their relative reactivities and our previous work\(^5\) has shown that the sequence is likely to be the same in SCW. Table 1 summarizes the observed selectivity of the main intermediates as well as the yields of diacid and CO\(_2\) and the overall burn. Together, Fig. 2 and Table 1 indicate the following:

1. HBr catalyses both the formation of diacids and yield of CO\(_2\). However, HBr is far more effective at catalyzing the formation of OA than of TA (see also Fig. 3) and it increases the yield of CO\(_2\) from pX more than from oX.
Fig. 2  Summary of the yields of dicarboxylic acid (OA or TA) and CO2 obtained from the oxidation of \( [\square] \) oX and \( [\blacksquare] \) pX in SCW at 380 °C and 230 bar with a number of different catalysts. For detail, see Table 1. The data clearly show that under all circumstances oX produces more dicarboxylic acid than does pX, and almost always less CO2 than pX. Note that the % scale for CO2 is expanded compared to the diacid.a \([\text{HBr}] = 2.57 \text{ mM}\). b \([\text{HBr}] = 5.13 \text{ mM}\). c \([\text{HBr}] = 10.3 \text{ mM}\). d \([\text{HBr}] = 20.5 \text{ mM}\).

Table 1  Comparison of the yields and selectivities of the autoxidation of pX (in bold) and oX (italics) in SCW at 380 °C and 230 bar

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst species</th>
<th>[Metal]/mM</th>
<th>[Br]/mM</th>
<th>Yield, mol (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO2</td>
<td>TA or OA</td>
<td>Burn</td>
<td>CO2</td>
<td>TA or OA</td>
</tr>
<tr>
<td>1</td>
<td>None</td>
<td>0.0</td>
<td>0.00</td>
<td>14.3 0.6</td>
<td>23.8</td>
</tr>
<tr>
<td>2</td>
<td>HBr</td>
<td>0.0</td>
<td>2.57</td>
<td>14.6 16.0</td>
<td>0.91</td>
</tr>
<tr>
<td>3</td>
<td>HBr</td>
<td>0.0</td>
<td>5.13</td>
<td>26.6 3.7</td>
<td>7.19</td>
</tr>
<tr>
<td>4</td>
<td>HBr</td>
<td>0.0</td>
<td>5.13</td>
<td>11.8 36.2</td>
<td>0.33</td>
</tr>
<tr>
<td>4</td>
<td>HBr</td>
<td>0.0</td>
<td>5.13</td>
<td>29.8 8.0</td>
<td>3.73</td>
</tr>
<tr>
<td>7</td>
<td>HBr</td>
<td>0.0</td>
<td>10.3</td>
<td>32.4 15.8</td>
<td>2.05</td>
</tr>
<tr>
<td>8</td>
<td>HBr</td>
<td>0.0</td>
<td>20.5</td>
<td>15.2 58.6</td>
<td>0.26</td>
</tr>
<tr>
<td>9</td>
<td>HBr</td>
<td>0.0</td>
<td>20.5</td>
<td>33.7 19.1</td>
<td>1.76</td>
</tr>
<tr>
<td>10</td>
<td>HBr</td>
<td>0.0</td>
<td>20.5</td>
<td>23.4 55.6</td>
<td>0.42</td>
</tr>
<tr>
<td>11</td>
<td>CoBr₂</td>
<td>2.57</td>
<td>5.13</td>
<td>14.8 6.3</td>
<td>2.35</td>
</tr>
<tr>
<td>12</td>
<td>MnBr₂</td>
<td>2.57</td>
<td>5.13</td>
<td>12.4 33.9</td>
<td>0.37</td>
</tr>
<tr>
<td>13</td>
<td>MnBr₂</td>
<td>2.57</td>
<td>5.13</td>
<td>18.4 36.1</td>
<td>0.51</td>
</tr>
<tr>
<td>14</td>
<td>MnBr₂</td>
<td>2.57</td>
<td>5.13</td>
<td>13.4 55.0</td>
<td>0.24</td>
</tr>
<tr>
<td>15</td>
<td>MnBr₂ + HBr</td>
<td>2.57</td>
<td>7.70</td>
<td>14.3 22.7</td>
<td>0.63</td>
</tr>
<tr>
<td>16</td>
<td>MnBr₂ + HBr</td>
<td>2.57</td>
<td>7.70</td>
<td>11.1 56.7</td>
<td>0.20</td>
</tr>
<tr>
<td>17</td>
<td>MnBr₂ + BA</td>
<td>2.57</td>
<td>5.13</td>
<td>17.5 35.6</td>
<td>0.49</td>
</tr>
<tr>
<td>18</td>
<td>MnBr₂ + BA</td>
<td>2.57</td>
<td>5.13</td>
<td>13.1 52.4</td>
<td>0.25</td>
</tr>
</tbody>
</table>

* MnBr₂ + HBr in 1 : 1 molar ratio; ratio Br : metals is 3 : 1. BA concentration is 45.5 mM.

2. MnBr₂ is a good catalyst for the formation both of TA and of OA, which is to be expected since most of the studies of pX oxidation in SCW have focused on MnBr₂ as the catalyst.\(^{1-5,14-17,20-21}\) However, addition of HBr to MnBr₂ reduces the yield of TA compared to that obtained with MnBr₂ alone.

3. Benzoic acid (BA) always forms during the autoxidation of xylenes. The selectivity to BA was higher for pX than for oX in seven of the nine different catalyst solutions used in this paper. A maximum value of 9.8% is seen in entry 7 of Table 1. The ratio of BA to diacid yield is greater for pX oxidation than oX oxidation. This is analogous to burn, defined as CO₂:diacid ratio. See Fig. 3.

4. Under the same catalytic conditions, the proportion of intermediates with two methyl groups totally or partially oxidized is always higher for oX than pX; i.e. by inspection of Table 1 one can see that the sum of selectivities for the diacid, CBA, and 4HMBA (or phthalide) is higher than those of TOL and the toluic acid for the oxidation of oX.

5. The observed amounts of phthalide are high, reaching almost 30% in some cases. This strongly suggests that the second pathway to OA is significant, see reaction 11 of Scheme 1.

6. The selectivity to o-toluic acid is always significantly lower than that to p-toluic acid. However the selectivity to p-toluic acid decreases markedly as the concentration of HBr is increased; see...
Discussion

Considering the industrial importance of avoiding decarboxylation and burn in the oxidation of methyl aromatics in general and of pX in particular, the main question that needs to be resolved is: what are the mechanisms mainly responsible for these undesirable phenomena? The differences between the oxidations of oX and pX can give us a clue. The higher yields of OA than TA as well as the lower burn, point to factors which might favour oX oxidation over pX and these factors are probably related to an inhibition in SCW of the decarboxylation and burn of oX compared to pX.

The hydroxyl radical, OH\(^\cdot\), can be easily generated by thermal decomposition of the organic peroxides, ROOH \(\rightarrow\) RO\(^\cdot\) + OH\(^\cdot\), at several points in the oxidation pathways from xylene to diacid. The hydroxyl radical is a powerful oxidant that reacts unselectively with organic substrates. It prefers to react with the benzylic ring rather than the methyl group of xylenes\(^{31,32}\) which leads to formation of phenol, a strong anti-oxidant, followed by its total destruction to carbon dioxide.\(^{33}\) Elegant pulse radiolysis experiments on SCW have shown that OH\(^\cdot\) radicals react with aromatics at close to diffusion controlled rates.\(^{33,34}\) Therefore the lifetime of OH\(^\cdot\) is far too short to be detected in our experiments. Nevertheless many of the observations described in this paper can be rationalized by effects that decrease the concentration of the unselective hydroxyl radical and by the behavior of the Mn(II) catalyst.

Rationalization of the HBr catalyzed reactions

One of the factors leading to the increased selectivity in the presence HBr is that OH\(^\cdot\) can react very rapidly with Br\(^-\), see Table 2, to give Br\(^+\) which can then propagate the reaction selectively unlike the indiscriminate reaction of OH\(^\cdot\) with the aromatic ring.

\[
Br^- + OH^\cdot \rightarrow Br^+ + OH^- \tag{3}
\]

Thus the reaction of Br\(^+\) can decrease the concentration of OH\(^\cdot\) and hence increase the overall rate of reaction, the yield to the desired diacid, and decrease the rate of CO\(_2\) formation.

Oxidation of oX

One of our key observations has been the relatively large amounts of phthalide that are formed in the oxidation of oX. We suggest that this is the result of a second pathway to the formation of OA in SCW, see reaction 11 of Scheme 1. In particular, we propose that oTOL can be converted directly to

Table 2. Rate constants for the reaction of OH\(^\cdot\) with selected species in aqueous solution at room temperature\(^{31}\)

<table>
<thead>
<tr>
<th>Reacting species</th>
<th>Reaction product</th>
<th>pH</th>
<th>Rate constant/L mol(^{-1}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br(^-)</td>
<td>BrOH(^-)</td>
<td>1</td>
<td>(1.1 \times 10^{10})</td>
</tr>
<tr>
<td>Co(II)</td>
<td>Co(III)OH</td>
<td>7</td>
<td>(8 \times 10^{9})</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>Mn(III)OH</td>
<td>6.7</td>
<td>(2.9 \times 10^{9})</td>
</tr>
<tr>
<td>pX</td>
<td>HOPh(CH(_3))(_2)</td>
<td>-7</td>
<td>(7.0 \times 10^{9})</td>
</tr>
<tr>
<td>oX</td>
<td>HOPh(CH(_3))(_2)</td>
<td>-7</td>
<td>(6.7 \times 10^{9})</td>
</tr>
</tbody>
</table>

\[
Br^- + PhCH\(_3\) \rightarrow HBr + PhCH\(_2\)^+ \tag{4}
\]
phthalide via reaction 11 in Scheme 1. In detail, we believe that reaction 11 could proceed by the peroxyacid of oX reacting with the adjacent methyl group in a concerted fashion to form phthalide, as shown in Scheme 2.

![Scheme 2](image)

Scheme 2  Suggested pathway from oTOL to phthalide.

In this pathway, the formation of o-toluic acid from oTOL (reaction 2, Scheme 1b) can be skipped by direct formation of phthalide from oTOL. This could explain why less o-toluic acid is observed in SCW from oxidation of oX than p-toluic acid from pX. Furthermore, the intramolecular transfer of OH$^-$ in Scheme 2 avoids formation of free OH$^-$ and therefore reduces the steady-state concentration of OH$^-$ in oX oxidations. This pathway could also occur with the primary hydroperoxide of the oX in an analogous way. Since transfer of OH$^-$ also oxidizes the adjacent methyl group, it increases the overall reaction rate while simultaneously reducing unwanted burn via unselective attack by OH$^-$ on the C−H bonds of the aromatic ring. Since no analogue of Scheme 2 is possible for pX, more ring attack would be expected in pX reactions. Thus, especially in the uncatalysed reactions of pX, one would expect (a) a lower yield of TA and (b) a higher rate of CO$_2$ formation due to ring degradation, precisely what is observed experimentally.

The steps in Scheme 2 occur in the later stages of the oxidation and there must be an additional initiation step of the uncatalysed reaction. Since thermal cracking of aliphatic hydrocarbons starts at ~400 °C, there should be sufficient thermal energy at 380 °C to dissociate a benzylic C−H bond of xylene in preference to the stronger bond of the aromatic carbons, reaction (5). This preferential dissociation will lead to selective autoxidation of a methylaromatic even without a catalyst.

Initiation step:

$$\text{PhCH}_3 \rightarrow \text{PhCH}_3^\cdot \quad \text{(benzylic radical) \ + \ H}^+ \quad \text{(5)}$$

Propagation steps:

$$\text{PhCH}_3^\cdot + \text{O}_2 \rightarrow \text{PhCH}_3\text{OO}^\cdot \quad \text{(peroxy radical)} \quad \text{(6)}$$

$$\text{PhCH}_3\text{OO}^\cdot + \text{PhCH}_3 \rightarrow \text{PhCH}_3\text{OOH} \quad \text{(benzylic hydroperoxide)} \ + \text{PhCH}_3^\cdot \quad \text{(7)}$$

Rationalization of results from metal-catalyzed oxidation of pX and oX

It can be seen from Table 1 that, during the oxidation of both xlenes, the MnBr$_2$ catalyst gives substantially higher diacid yields than does HBr, at the same total Br$^-$ concentration. One effect of Mn(III) is to reduce the steady state concentration of OH$^-$ by reacting selectively with the benzylic hydroperoxides:

$$\text{Mn(III) + CH}_3\text{PhCH}_3\text{OOH} \rightarrow \text{Mn(III)(OH)} \ + \ \text{CH}_3\text{PhCH}_3\text{O}^\cdot \quad \text{(8)}$$

And also by the oxidation of Mn(II) by the OH radical, see Table 2:

$$\text{Mn(II) + OH}^\cdot \rightarrow \text{Mn(III) + OH}^- \quad \text{(9)}$$

Assuming that the relative redox potentials are the same at 380 °C as they are in ambient water, reaction (9) should be thermodynamically favoured since the standard reduction potential of OH$^-/OH^-$ is 2.7 V in ambient water$^{31}$ compared to 1.5 V for Mn(III)/Mn(II).$^{36}$

The MnBr$_2$ catalyst gives higher yields of both OA and TA than does CoBr$_2$ as well as lower burn. One reason for this may be the fact that Co(II) reacts with the OH radical 36 times slower than Mn(II), see Table 2. The higher activity of MnBr$_2$ has been reported for pX oxidation in HTW and SCW$^{16}$ but the comparison has not previously been made for oX.

Table 1 shows that addition of HBr to the MnBr$_2$ catalyst decreases the TA yield but slightly increases the OA yield. This may be the result of competing effects; addition of HBr increases the concentration of Br$^-$, which might accelerate selective oxidation, but also lowers the pH which could promote burn.$^{24}$

Mechanisms for decarboxylation and burn of aromatic acids

Savage and coworkers have reported the relative rates of thermal decarboxylation in water at various temperatures as OA > TA > BA.$^{37}$ But even for OA, the process is slow compared to the residence times in our reactor, e.g. 73% of OA decarboxylates to BA in 1 h at 300 °C. Therefore, thermal decarboxylation is unlikely to be responsible for the large amounts of CO$_2$ observed in our reactions, particularly because the yield of BA is much lower than that of CO$_2$. On the other hand, if the peroxy acid intermediates discussed above do not react via intramolecular transfer of OH$^-$, they will not only liberate OH$^-$ but will also open up pathways leading to decarboxylation and ultimately burn,$^{34}$ for both oX and pX, see Scheme 3.

There is also the possibility that the metal ions could catalyse the decarboxylation (Scheme 3, reaction 4). We have previously pointed out similarities between the mechanism of the metal catalyst in acetic acid and SCW.$^1$ It is known that, in acetic acid, transition metals have a role as redox catalysts recycling Br(−1) to Br(0), Scheme 4. Metals with a weak ligand-field environment also have sufficient energy for decarboxylation of aromatic carboxylic acids e.g. Co(III), Mn(III), Ce(IV), Ag(II), Cu(II).$^{39–43}$

Catalytic decarboxylation may occur when a carboxylic acid enters the coordination sphere of the metal while it is in its lower oxidation state. The metal is oxidized in the redox cycle in Scheme 4 but then the acid decarboxylates releasing a proton and deactivates the catalyst by reducing the metal ion back to its lower oxidation state without oxidation of Br(−1). In an oxidative environment, as well as CO$_2$, the products of decarboxylation are phenols and quinones which are also known to strongly retard the rate of reaction.$^{44}$ However, the fact that there is such a marked difference in burn between oX and pX in the absence of catalyst or with HBr, i.e. without metals present, suggests that reactions of OH$^-$ are more significant than metal-catalyzed decarboxylation and burn in SCW.

We have included CO in because we detected CO in a number of experiments. However, the amount was low compared to CO$_2$, <10%, and there did not appear to be any significant difference between the relative amounts of CO generated from oX and pX.
Scheme 3 Formation of benzoic acid and carbon dioxide. $R = -\text{CH}_3$ or $-\text{COOH}$.

Scheme 4 Catalytic decarboxylation in metal/bromide autoxidations. There is some evidence\textsuperscript{39–43} that the carboxylic acid is in the coordination sphere of the metal during the decarboxylation.

Comparison between oxidation in acetic acid and SCW

Large differences in yields and intermediates are found when $oX$ and $pX$ are oxidized in acetic acid.\textsuperscript{25–27} However these differences are quite different from those observed in SCW. Deliberate spiking of selected aromatics into a $\text{Co/Mn/Br}$ autoxidation in acetic acid has demonstrated that OA undergoes catalytic decarboxylation much more readily than TA and this results in a much stronger deactivation.\textsuperscript{26} It has been reported that the initial rate of oxidation for $oX$ is greater than $pX$ in the $\text{Co/Mn/Br}$ catalyzed oxidation in acetic acid but the rates reverse themselves in the second half of the reaction.\textsuperscript{26} when high concentration of OA strongly deactivates the reaction. In the $\text{Co/Br}$ catalyzed oxidation of $\text{ortho-}$ and $\text{para-}$toluic acid in acetic acid, at low initial toluic acid concentrations, the rate of oxidation of $o$-toluic is faster than $p$-toluic acid but, at higher concentrations, the opposite is observed.\textsuperscript{25} This is expected since higher concentration of OA form at higher concentration of $o$-toluic acid, hence more strongly deactivating the system.

Finally, in the cobalt catalyzed oxidation of $oX$ and $pX$ in acetic acid, the reaction abruptly stops when OA starts to form while with $pX$ the reaction continues to produce TA.\textsuperscript{25} The steady-state concentration of Co(III) is much higher in a cobalt catalyzed oxidation than a $\text{Co/Br}$ oxidation; hence catalytic decarboxylation is more prominent accounting for the abrupt end of the oxidation when OA starts to form.

Thus in acetic acid, OA has a much stronger negative influence on the reaction rate than TA in acetic acid but, in SCW, the opposite is observed. Catalytic decarboxylation seems to be an important mechanism for $oX$ oxidation in acetic acid; however, there must be an inhibition to this phenomenon in SCW. One can rationalize these differences by postulating that OA is the predominant species in acetic acid while in SCW, phthalic anhydride predominates which cannot undergo catalytic decarboxylation.

This hypothesis seems reasonable in view of the properties of acetic acid and water at high temperature because the dielectric constant of water decreases\textsuperscript{7} to values typical of an organic solvent. Therefore ionic and polar solutes are disfavored \textit{versus} neutral and non-polar compounds. There are some examples of SCW acting as a dehydrating medium,\textsuperscript{45,46} that would favour the formation of the cyclic condensation product such as the reaction of 1,4-butanediol to tetrahydrofuran.\textsuperscript{46} Furthermore, entropy may favour the dehydration of OA to phthalic anhydride at these elevated temperatures. Finally, carboxylic acids form strong H-bonds between them so one can think that aromatic acids are well solvated in acetic acid. By contrast, the number of hydrogen bonds decreases in SCW,\textsuperscript{7} possibly favoring the existence of the anhydride. This could have a significant industrial importance because it would allow the direct formation of phthalic anhydride, skipping the dehydration step.

Experimental

Reactions were carried out in a continuous rig similar to the one reported in reference 1 and shown in Fig. 4. The reactor was made of Hastelloy C276 pipe $\frac{1}{2}$ inch external diameter and 0.46 cm inner diameter. The length of the reactor was 34 cm. The total volumetric flow rate through the rig was 12 mL min$^{-1}$. At 380 °C the residence time in the reactor was 5.8 s. The density of pure water\textsuperscript{29} is used for these calculations. All the components are fed into the reactor \textit{via} reciprocating pumps.
Phenol concentrations are very low because it is oxidized much more rapidly than pX. Benzene is present in extremely small amounts because its formation would require the sequential decarboxylation of terephthalic acid to benzoic acid and then of benzoic acid to benzene.

CO$_2^-$ concentration was measured by titration of the sample with 0.2 N HCl. The first titre accounts for the excess OH$-\ $and the second for the protonation of CO$_2^-$ to HCO$_3^-$. The difference between these two titres was used to calculate the carbonate concentration. Further details for the experimental apparatus and can be found in the ESI of the second paper in this series.

### Conclusions

This paper reports the unexpected observation that oX is more easily oxidized to OA in supercritical water than pX, which facilitates an internal transformation of the peroxide directly to the phthalide thereby reducing the steady-state concentration of OH radical as well as lowering the steady-state concentration of the intermediate aromatic acids. Elucidating these differences has provided insights into the mechanisms of burn and decarboxylation. We have also shown that the presence of a catalyst has a significant impact on the yields and selectivities of both the desired and the undesired products. The fact that the metal can play more than one role opens up the possibility of synergistic effects in catalysts containing more than one metal. We investigate such synergies in our second paper which reports how the reaction can be improved dramatically by finding a more effective catalyst, thereby bringing the possibility of a greener process for oxidizing pX one step closer to realisation.

### Acknowledgements

We thank EPRSC, the University of Nottingham and INVISTA for financial support. We thank Graham Aird, Stuart Coote, Lucinda Dudd, Annette Matthews, Ian Pearson, John Runnacles, Peter Fields, Richard Wilson and Mark Guyler for their help.

### References