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Selective aerobic oxidation of *para*-xylene in sub- and supercritical water. Part 1. Comparison with *ortho*-xylene and the role of the catalyst

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The selective, continuous, aerobic oxidations of *para*-xylene (pX) and *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' due to the internal, concerted attack of the peroxides with the oX methyl group. This mechanism forms the phthalide directly from *o*-tolualdehyde (oTOL) which is consistent with the observation that *ortho*-toluic acid (OTA) is much lower in oX than *para*-toluic acid, 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 *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,^{1,2} (b) more generally, aromatic acids can be obtained from oxidation of alkylaromatic compounds,³ (c) the simultaneous oxidation of mixtures of xylenes is feasible⁴ and (d) increased Brønsted acidity, increased bromide concentration, and the addition of aromatic acids can all substantially reduce the precipitation of manganese oxides that can occur when MnBr₂ is used as a catalyst.⁵ In this paper, we compare the results of oxidizing *ortho*and *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,⁶ describes our successful attempts to find better catalysts and their optimization.

Research activity has been growing in the field of SCW ($T_c = 374 \, ^{\circ}$ C, $p_c = 221 \, \text{bar}$) or more generally in high-temperature water because of the unusual properties of H₂O under these conditions.⁷ A wide range of chemical reactions have been studied where SCW plays the role of a solvent and/or reactant and/or catalyst.⁷⁻¹² Research on the homogeneously catalysed oxidation of methylaromatics in HTW and SCW was first reported by Holliday *et al.*¹³ and subsequently by others.^{1-4,14-21}

The aerobic oxidation of pX to TA is carried out industrially using acetic acid as the solvent. Despite its extraordinary efficiency (99% selectivity, >95% yield), the process still has some drawbacks.²² The crude TA contains ~0.3% of 4carboxybenzaldehyde (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.²³ Moreover, solvent degradation generates the greenhouse gas CO₂ and the ozone-depleting agent CH₃Br. Finally, re-use of the solvent necessitates an energy-consuming

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distillation step to remove the H_2O 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.²² 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 *p*- and *o*-toluic acid have been reviewed and summarized²⁴ but there is only a small amount of literature which directly compares results from oX and pX even in acetic acid.²⁵⁻²⁷ Oxidation of oX in SCW has been reported previously,^{4,5} but without any data for formation of CO₂. Recently, we studied catalyst stability in the oxidation of oX in SCW⁶ and, although we have noticed differences between the isomers of xylene,^{2,4} this paper is the first time that we have studied these differences systematically.

Method

A simplified schematic of our tubular continuous flow reactor³ 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.⁶



Fig. 1 Simplified scheme of the continuous reactor used in this work. O_2 is generated from aqueous H_2O_2 by high temperature decomposition in a pre-heater, PH.³ The mixture O_2/H_2O , 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.²⁸

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).

$$Y_{\rm A} = 100 \frac{[\rm A]}{[\rm X]} \tag{1}$$

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. $[X] = (F_X \rho_X)/(F_{total} M_X)$, where F_X , F_{total} are the flow rates of the xylene and the total flow after quench; ρ_X and M_X are the density and molar mass of the xylene, respectively. CO₂ yield was calculated from the carbonate concentration obtained from titration by eqn (2), with [BA] being subtracted to avoid counting the CO₂ molecules arising from decarboxylation.

$$Y_{\rm CO_2} = 100 \frac{[\rm CO_3^{2-}] - [\rm BA]}{8[\rm X]}$$
(2)

Finally we define "burn" as Y_{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, CoBr₂, and MnBr₂ by itself or with either HBr or benzoic acid added to increase the solubility of the catalyst.⁵ 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 *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.²⁹ Fig. 2 also shows that the CO₂ 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 CO₂ 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 reactivities³⁰ and our previous work¹⁻⁵ 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 [\Box] 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 [HBr] = 2.57 mM. ^b [HBr] = 5.13 mM. ^c [HBr] = 10.3 mM. ^d [HBr] = 20.5 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

Entry	Catalyst species	[Metal]/mM	[Br]/mM	Yield, mol (%)			Selectivity (%)					
				$\overline{\text{CO}_2}$	TA or OA	Burn	TA or OA	Toluic acid	CBA	HMBA or phthalide	TOL	BA
1	None	0.0	0.00	14.3	0.6	23.8	8.4	73.3	4.7	1.8	9.9	1.9
2				14.6	16.0	0.91	46.3	1.8	20.1	28.1	1.2	2.6
3	HBr	0.0	2.57	26.6	3.7	7.19	19.1	65.1	3.9	2.0	4.3	5.7
4				11.8	36.2	0.33	60.3	2.2	11.0	23.7	0.0	2.7
5	HBr	0.0	5.13	29.8	8.0	3.73	30.8	52.2	7.1	2.0	0.6	7.2
6				13.7	44.2	0.31	69.1	2.9	6.6	18.5	0.0	2.9
7	HBr	0.0	10.3	32.4	15.8	2.05	59.9	27.3	2.2	0.2	0.6	9.8
8				15.2	58.6	0.26	94.1	0.7	0.7	1.1	0.0	3.4
9	HBr	0.0	20.5	33.7	19.1	1.76	68.1	21.0	0.2	0.0	1.3	7.4
10				23.4	55.6	0.42	97.6	0.0	0.0	0.0	0.0	2.4
11	CoBr ₂	2.57	5.13	14.8	6.3	2.35	19.4	56.4	15.8	2.6	3.0	2.8
12	-			12.4	33.9	0.37	58.1	3.3	15.2	19.3	0.8	3.2
13	MnBr ₂	2.57	5.13	18.4	36.1	0.51	51.3	34.9	6.3	1.4	0.0	6.0
14				13.4	55.0	0.24	75.2	3.2	7.0	12.5	0.0	2.1
15	$MnBr_2 + HBr^a$	2.57	7.70	14.3	22.7	0.63	39.5	44.9	8.1	3.8	0.0	3.7
16	-			11.1	56.7	0.20	79.9	4.3	3.3	11.0	0.0	1.5
17	$MnBr_2 + BA^b$	2.57	5.13	17.5	35.6	0.49	48.7	36.2	7.0	1.8	0.0	6.3
18	-			13.1	52.4	0.25	75.0	2.6	5.0	16.0	0.0	1.4

2. $MnBr_2$ 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 $MnBr_2$ as the catalyst.^{1-5,14-17,20-21} However, addition of HBr to $MnBr_2$ reduces the yield of TA compared to that obtained with $MnBr_2$ 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 CO_2 :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



Scheme 1 Suggested sequence of formation of intermediates during the aerobic oxidation of (a) pX to TA and (b) oX to OA.

Table1. HBr also reduces the burn, even though the total yield of CO_2 increases; see Fig. 3.

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[•], can be easily generated by thermal decomposition of the organic peroxides, ROOH \rightarrow RO[•] + OH[•], 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.³¹ Elegant pulse radiolysis experiments on SCW have shown that OH[•] radicals react with aromatics at close to diffusion controlled rates.^{33,34} Therefore the lifetime of OH[•] 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[•] 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[•] with the aromatic ring.

$$Br^- + OH^- \rightarrow Br^+ + OH^-$$
 (3)



Fig. 3 Comparison of uncatalyzed and HBr catalyzed autoxidation of pX (black symbols) and oX (white symbols) as a function of the concentration of HBr. (\blacksquare, \Box) Diacid yield, (\bullet, \bigcirc) toluic acid yield, $(\bullet, \bigtriangleup)$ burn, (\bullet, \diamondsuit) ratio Y_{BA}/Y_{DiAcid} .

Table 2Rate constants for the reaction of OH' with selected species in
aqueous solution at room temperature 31

Reacting species	Reaction product	pН	Rate constant/L $mol^{-1} s^{-1}$
Br ⁻	BrOH ⁻	1	$\begin{array}{c} 1.1 \times 10^{10} \\ 8 \times 10^5 \\ 2.9 \times 10^7 \\ 7.0 \times 10^9 \\ 6.7 \times 10^9 \end{array}$
Co(II)	Co(III)OH	7	
Mn(II)	Mn(III)OH	6.7	
pX	HOPh(CH ₃) ₂	~7	
oX	HOPh(CH ₃) ₂	~7	

$$Br' + PhCH_3 \rightarrow HBr + PhCH_2'$$
 (4)

Thus the reaction of Br⁻ can decrease the concentration of OH[•] 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 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 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 CO₂ 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 uncatalyzed reaction. Since thermal cracking of aliphatic hydrocarbons starts at ~400 °C,³⁵ 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:

 $PhCH_3 \rightarrow PhCH_2^{\bullet}$ (benzylic radical) + H[•] (5)

Propagation steps:

$$PhCH_2 + O_2 \rightarrow PhCH_2OO (peroxy radical)$$
 (6)

$$PhCH_2OO' + PhCH_3 \rightarrow PhCH_2OOH \text{ (benzylic} \\ hydroperoxide) + PhCH_2 \text{.}$$
(7)

Rationalization of results from metal-catalyzed oxidation of \ensuremath{pX} and \ensuremath{oX}

It can be seen from Table 1 that, during the oxidation of both xylenes, the $MnBr_2$ catalyst gives substantially higher diacid yields than does HBr, at the same total Br^- concentration. One effect of Mn(II) is to reduce the steady state concentration of OH[•] by reacting selectively with the benzylic hydroperoxides:

$$\begin{array}{l} Mn(II) + CH_{3}PhCH_{2}OOH \rightarrow Mn(III)(OH) + \\ CH_{3}PhCH_{2}O \end{array} \tag{8}$$

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

$$Mn(II) + OH^{-} \rightarrow Mn(III) + OH^{-}$$
(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 water³¹ 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 SCW¹⁶ 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 CO₂ observed in our reactions, particularly because the yield of BA is much lower than that of CO₂. 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,³⁸ 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.³ 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 metalcatalyzed 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. $R = -CH_3$ or -COOH.



Scheme 4 Catalytic decarboxylation in metal/bromide autoxidations. There is some evidence³⁹⁻⁴³ 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.²⁵⁻²⁷ However these differences

are quite different from those observed in SCW. Deliberate spiking of selected aromatics into a 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.²⁹ It has been reported that the initial rate of oxidation for oX is greater than pX in the Co/Mn/Br catalyzed oxidation in acetic acid but the rates reverse themselves in the second half of the reaction,²⁶ when high concentration of OA strongly deactivates the reaction. In the Co/Br catalyzed oxidation of ortho- and 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.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.²⁷ The steady-state concentration of Co(III) is much higher in a cobalt catalyzed oxidation than a 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 decreases⁷ to values typical of an organic solvent. Therefore ionic and polar solutes are disfavored versus neutral and non-polar compounds. There are some examples of SCW acting as a dehydrating medium,45,46 that would favour the formation of the cyclic condensation product such as the reaction of 1,4-butanediol to tetrahydrofuran.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,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 $\frac{1}{4}$ 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 water²⁸ is used for these calculations. All the components are fed into the reactor *via* reciprocating pumps.



Fig. 4 Configuration of the continuous aerobic oxidation reactor. P1–3 pressure transducers. T2–5: log temperatures. T1, T6 and T8: control temperatures.

Dioxygen was used as primary oxidant. An aqueous H_2O_2 solution was passed through a coiled pre-heater at supercritical temperature where it decomposed into a homogeneous mixture of O₂ and SCW before being driven to the reactor. The residence time in the pre-heater was long enough to achieve total decomposition of H₂O₂. The catalysts were introduced in aqueous solution. The conditions were those optimized and previously reported by us for the oxidation of *p*-xylene to terephthalic acid,1 except that the catalyst concentrations were lower than those used previously.^{2,3} This was to ensure that the catalyst was unsaturated.6 A 7.7 mM catalyst solution was fed at 4 mL min⁻¹, thus giving a catalyst concentration of 2.6 mM in the reactor. Concentration of H_2O_2 in the feed solution was 2% vol. and the flowrate was 8 mL min⁻¹. The organic flowrate was 0.06 mL min⁻¹, that is 0.5% w/w in the reactor. At the end of the reactor, the liquor was quenched with a solution of 1 M NaOH, to neutralize CO₂ in the form of carbonate and keep it in solution. NaOH also prevents precipitation of TA in pX oxidations. The quench solution flowrate was 3.5 mL min⁻¹. All the chemicals were purchased from Aldrich Ltd and used without further purification.

CAUTION: This type of oxidation is potentially extremely hazardous, and must be approached with care and a thorough safety assessment must be made. The apparatus is regularly hydrostatically pressure tested at room temperature. For safety reasons a start-up procedure must be followed: (1) water is pumped at 230 bar and room temperature at the desired flowrates; (2) the heaters are turned on; (3) once the operating temperature had been reached, the reactants are pumped. Several samples were collected for sequential periods of 5 min and analysed. Three samples taken when the system reaches steady state were analyzed and the results were averaged.

Analysis of the products was done by HPLC. A Waters Xterra reverse phase C18 column, maintained at 37 °C, was used (flow rate 0.7 mL min⁻¹, run time 15 min; UV detection at 230 nm). Solvents acetonitrile (ACN) and CH₃CO₂Na/CH₃CO₂H buffer were used. The method was as follows: isocratic method (16.7% ACN) for the first 4 min; 4–8 min, gradient method (16.7 to 40% ACN); back to isocratic method (16.7% ACN) for the last 7 min.

The analysis for phenols and benzene was not carried out routinely because they are present only in very small amounts. 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_3^{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_3^{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.⁶

Conclusions

This paper reports the unexpected observation that oX is more easily oxidized to OA in supercritical water than pX is converted to TA. In addition, the burn to CO_2 is less for oX. We attribute these differences to the presence of ortho methyl groups in oX, 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 paper⁶ 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.

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