

The Complex Synergy of Water in the Metal/Bromide Autoxidation of Hydrocarbons Caused by Benzylic Bromide Formation

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Abstract: One of the most active and selective catalysts in homogeneous liquid phase oxidation using molecular oxygen (O_2) is a mixture of cobalt, manganese and bromide salts in acetic acid. It has been used to produce hundreds of different carboxylic acids in high yield and purity including the commercial production of terephthalic acid from *p*-xylene. Water is normally a by-product in these reactions and it is shown here that its concentration is an important reaction variable. In anhydrous acetic acid, with reagents with sufficiently strong electron-withdrawing substituents (toluene, 4-carboxytoluene, 4-chlorotoluene), all of the active bromide becomes inactive *via* benzylic bromide formation. The Co/Mn/Br catalyst is therefore converted to a Co/Mn catalyst which is dubbed 'catalyst failure' because of its undesirable characteristics of lower activity, decreased selectivity especially towards over-oxidation

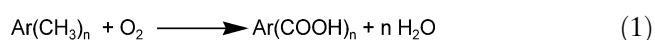
and color formation. For 4-chlorotoluene, increasing the water concentration to 5 weight % *initially* decreases the rate of reaction but eventually is more active and selective because the oxidation and hydrolysis of the benzylic bromide allows for sufficient active catalytic bromide. It is shown that benzylic bromides do not 'promote' the reaction and that both oxidation and solvolysis of the benzylic bromide occurs during autoxidation. During polymethylbenzene oxidation, benzylic bromide formation occurs only with the most reactive methyl group. The complex factors during metal/bromide autoxidation – some favored by increased water concentration and others detrimental – are outlined.

Keywords: autoxidation; bromide; catalytic hydrocarbon oxidation; C–H activation; cobalt; manganese; oxygen

Introduction

The high reactivity and selectivity of metal/bromide catalysts for the homogeneous liquid-phase air oxidation of hydrocarbons has been industrially exploited since the 1960s for the large-scale production of aromatic acids, such as terephthalic acid. Literally hundreds of different hydrocarbons have been shown to produce oxygenates by this method and at least 30 different combinations of metals with bromide have been shown to have often different and unique catalytic behavior.^[1,9,18] This has been summarized in detail.^[1]

Water forms as the product of the autoxidation of hydrocarbons. For methyl aromatic compounds one mole of water is produced for every methyl group oxidized (where Ar is an aromatic ring such as benzene, naphthalene, biphenyl, etc.):



In homogeneous liquid-phase reactions, invariably the hydrocarbon and solvent 'overoxidize' to produce carbon dioxide, carbon monoxide and additional water.^[1] In metal-catalyzed autoxidations there are reports in which increasing water concentration decreases the overall rate of reaction^[1–3] and others in which the rate initially increases with concentration then decreases.^[4–6] In metal/bromide systems, the decrease in rate is very general since it occurs for a number of different reactants (*p*-xylene, *m*-xylene, 2,2-bis(tolyl)hexafluoropropane, and *p*-nitrotoluene^[2]), and different catalysts (Mn/Br, Co/Br, Ni/Mn/Br, Co/Mn/Br, Mn/Zr/Br, Ni/Mn/Zr/Br, Co/Mn/Br/Zr).^[1]

The general statement that high water concentrations during autoxidation in acetic acid solvent are detrimental is not true. As will be described, there are reagents of specific reactivity where higher water concentrations are necessary to produce high yields such as with 4-chlorotoluene. The effect of water is quite subtle. There are more phenomena – some which are favored by low water concentration and others that are favored by high

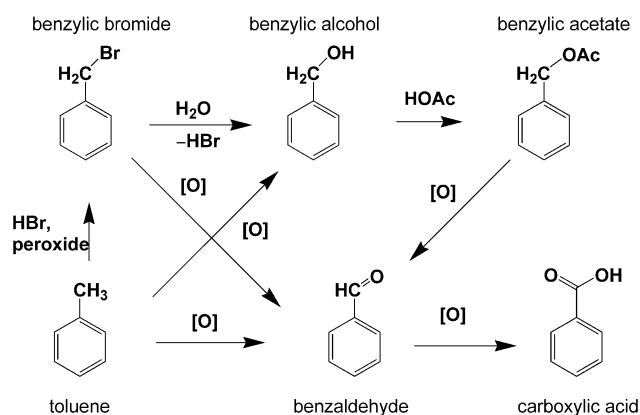


Figure 1. General description of the autoxidation of toluene or substituted toluenes using metal/bromide catalysts.

concentrations – which are beyond the scope of a single paper. The phenomena are briefly mentioned in the conclusion of this paper and will be more fully detailed in a subsequent paper.

The presence of benzylic bromides during the autoxidation of hydrocarbons is well-known.^[1] They form with a variety of catalysts (Mn/Br, Ce/Br, Co/Br, Co/Ce/Br, Co/Mn/Br, Co/Mn/Ce/Br, Co/Mn/Zr/Br) and a variety of different alkylbenzenes.^[1,7,8,9] The mechanism of benzylic bromide disappearance during autoxidation has generally been ascribed to oxidation^[7,8] although hydrolysis of the benzylic bromide to benzyl alcohol and hydrobromic acid has also been proposed.^[9] The hydrolysis of alkyl bromides to produce hydrobromic acid from bromoform,^[10] acetylene tetrabromide,^[11] and even bromobenzene^[12] are commonly used as sources of ionic bromide in metal/bromide-catalyzed reactions including the industrial manufacture of terephthalic acid from water.

Results and Discussion

The Effect of Water on 4-Chlorotoluene and 4-Carboxytoluene (*p*-Toluic Acid) Oxidations

The sequence of reactions that occurs during the metal/bromide autoxidation of toluenes is given in Figure 1. The effect of water concentration on the *maximum rate* of oxygen uptake of the two reagents used in this study is given in Figure 2 and experiments 1 and 2 in Table 1. These reactions are complicated by benzylic bromides formation, see below. The effect of water is substantial with the rate essentially being reduced by one-half when the water is increased from 0 to 5 weight % and then again when increased from 5 to 10 weight %. A 2 M solution of toluene completely oxidized to benzoic acid will generate about 4 weight % water in acetic acid.

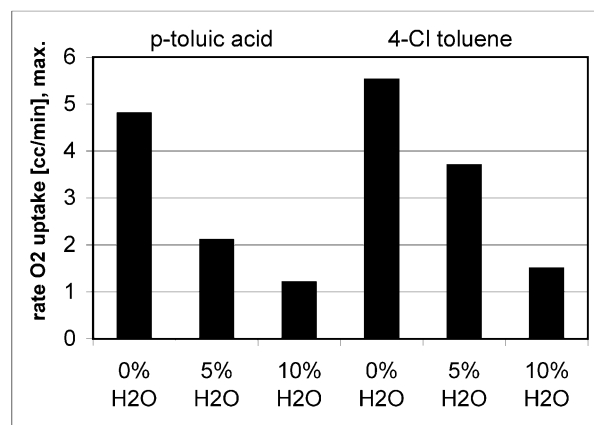


Figure 2. Effect of water on the Co/Mn/Br-catalyzed aerobic oxidation of *p*-carboxytoluene (*p*-toluic acid) and 4-chlorotoluene.

Commercial processes operate at approximately 5–20 weight % water in the reactors.

Comparison of the Autoxidation of Chlorotoluene in 0 and 5 weight % Water in Acetic Acid, Experiments 3 and 4

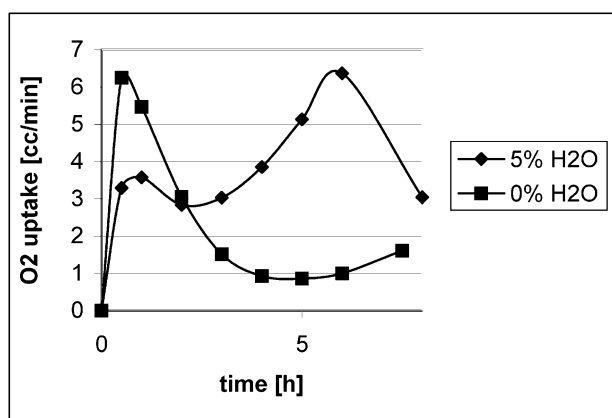
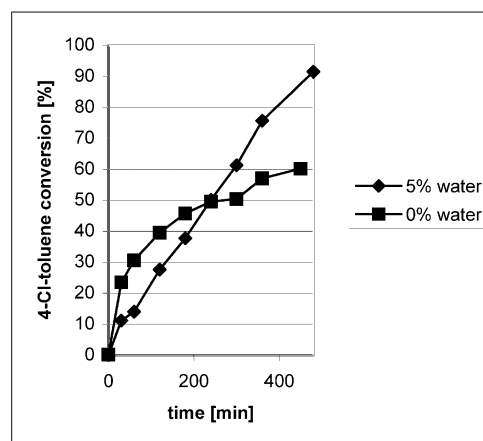
Figure 3 illustrates the effect of the batch reaction of 4-chlorotoluene with a Co/Mn/Br catalyst. At a initial water concentration of 5 weight %, the rate of oxygen uptake as a function of time is typical – the initial activity is due to the oxidation of the methyl group and the latter maximum to formation of the more reactive benzaldehyde. What was surprising was the oxygen uptake when anhydrous acetic acid was initially used. The initial rate of oxygen uptake was higher in anhydrous acetic acid – as expected since 5% water in acetic acid depresses the rate of oxidation (Figure 2) – but then quickly decreased to a rate less than in 5% water. From the total oxygen uptake it was obvious that the reaction was not complete. This is confirmed with the conversion of the 4-chlorotoluene, see Figure 4. The initial rate of conversion is higher in anhydrous acetic acid but the final conversion is only 60% – in contrast to that in 5% water, where the final conversion is higher than 90%. The rate of formation of the intermediate 4-chlorobenzaldehyde is also consistent with still substantial amounts of the unreacted benzaldehyde at the end of the experiment, see Figure 5. (The 4-Cl-benzoic acid yield is not reported because the acid is quite insoluble at room temperature and only the soluble compounds were measured by GC). The benzaldehyde yield in the presence of water is slightly higher than when starting with anhydrous acetic acid.

A striking observation that indicates that something is drastically different in anhydrous acetic acid is that the color of the solution was becoming opaque in anhydrous

Table 1. Initial conditions of the aerobic oxidation experiments.

#	[Reagent], M	Catalyst	Catalyst M	[H ₂ O], wt %
1	<i>p</i> -toluic acid, 0.75	Co/Mn/Br	0.01/0.01/0.02	0.0, 5.0, 10.0
2	4-chlorotoluene, 0.80	Co/Mn/Br	0.01/0.01/0.02	0.0, 5.0, 10.0
3,4	4-chlorotoluene, 0.80	Co/Mn/Br	0.01/0.01/0.02	0.0, 5.0
5	1,2,4-trimethylbenzene, 0.83	Co/Mn/Br Br as BPTA	0.01/0.01/0.02	10.0
6	1,2,4-trimethylbenzene, 0.83	Co/Mn	0.04/0.002	10.0
7	1,2,4-trimethylbenzene, 0.83	Co/Mn/Br	0.01/0.01/0.02	10.0
8	<i>p</i> -toluic acid	Co/Mn/Br	0.005/0.005/0.01	0.0
9	toluene, 0.65	Co/Mn/Zr/Br	0.02/0.02/0.001/0.04	0.0
10	<i>p</i> -tolualdehyde	Co/Mn/Br	0.0025/0.0025	0.0
11	<i>p</i> -tolualdehyde	Co/Mn/Br HBr added at 124 min	0.0025/0.0025/0.0050	0.0
12	1,2,4-trimethylbenzene	Co/Mn/Br + BPTA	0.01/0.01/0.02 + 0.02	10.0
13	1,2,4-trimethylbenzene, 0.83 <i>p</i> -toluic acid, 0.37	Co/Mn/Br	0.01/0.01/0.02	10.0

All performed at 95 °C except #9 at 75 °C.

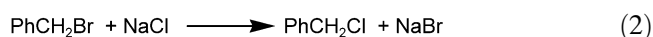
**Figure 3.** Effect of water on the rate of molecular oxygen uptake during the Co/Mn/Br-catalyzed aerobic oxidation of 4-chlorotoluene.**Figure 4.** Effect of water on the conversion during the Co/Mn/Br-catalyzed aerobic oxidation of 4-chlorotoluene.

acetic acid while the normal light pink color was observed in 5% water throughout the reaction. The absorbances of the samples were taken at 450 nm as a function of time, see Figure 6. The samples were diluted prior to measurement and Beer's law was assumed to be valid. Finally, the rate of carbon dioxide generation was exceptionally high when the solution began to turn opaque, see Figure 7. The carbon dioxide selectivity is defined as the rate of carbon dioxide formation/rate of oxygen uptake $\times 100$.

Inactivity of Benzylic Bromides as a Catalyst

A decrease in catalytic activity attributed to benzylic bromide formation has been reported during the autoxidation of toluene.^[7,9,13] Also, the addition of the

chloride ion, which does not promote metal-catalyzed reactions,^[1] to a Co/Mn/Br catalyst has been shown to enhance the rate of autoxidation by forming additional ionic bromide *via* the displacement reaction:



These experiments suggest that either benzylic bromide is a weaker 'promoter' during autoxidation or does not have any catalytic activity whatsoever. An experiment was designed to demonstrate whether or not benzylic bromides have catalytic properties.

Homogeneous cobalt(II) catalysts at 0.01 M are very slow to initiate with methylbenzenes at 95 °C, often taking 2–3 h for significant activity to occur.^[14] Cobalt/manganese catalysts are even less active because any

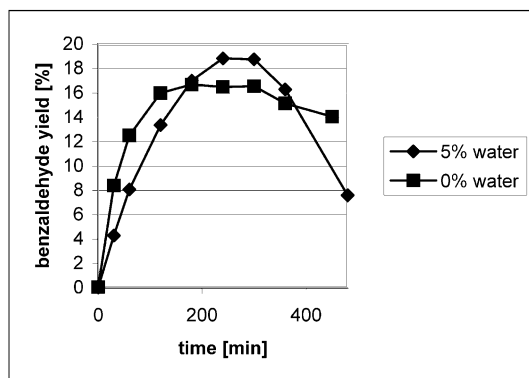


Figure 5. Effect of water on the benzaldehyde yield during the Co/Mn/Br-catalyzed aerobic oxidation of 4-chlorotoluene.

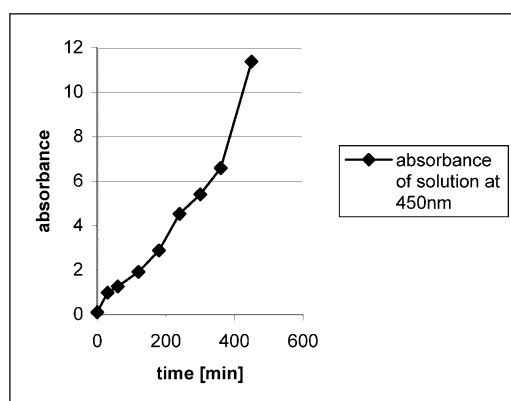
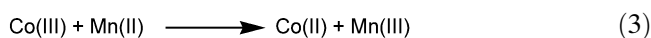


Figure 6. Absorbance during the Co/Mn/Br-catalyzed aerobic oxidation of 4-chlorotoluene with 0% initial water concentration.

Co(III) that is generated is rapidly reduced (half-life of 0.0056 sec at 60 °C in 10% water/acetic acid) by the reaction:



In contrast, addition of bromide to a cobalt catalyst *immediately initiates* the reaction and the activity is increased by a factor of 3.8.^[14] A further synergistic interaction occurs when manganese is added to a cobalt/bromide catalyst as its activity is increased from 3.8 to 16.^[15] Thus an experiment which will confirm whether or not a benzylic bromide ‘promotes’ an autoxidation would be to initially use a cobalt/manganese catalyst with a benzylic bromide. One would want a benzylic bromide that does not hydrolyze readily under the experimental conditions used. α -Br-*p*-toluic (BPTA) acid was chosen because the measured solvolysis of BPTA has a 1st order rate constant of $8.0 \times 10^{-6} \text{ s}^{-1}$ with a

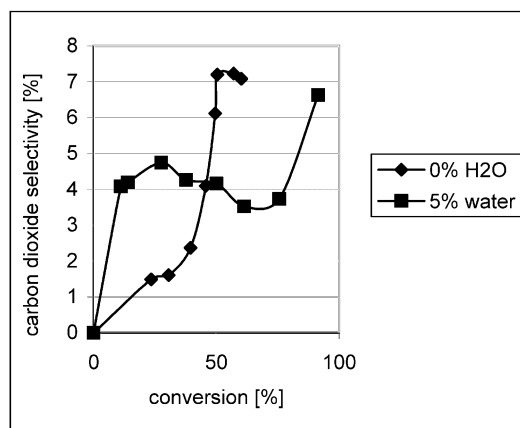
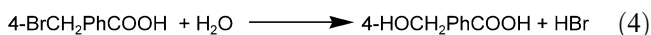


Figure 7. Effect of water on the carbon dioxide selectivity during the Co/Mn/Br-catalyzed aerobic oxidation of 4-chlorotoluene.

half-life of 24 h at 95 °C in 10% water/acetic acid. The reaction is:



The reagent chosen is 1,2,4-trimethylbenzene because it is 5 times more reactive than 4-chlorotoluene, see Table 2, hence more easily initiated.

The experimental result, #5 in Table 1, is that when 1,2,4-trimethylbenzene was mixed with a Co/Mn catalyst, no recordable oxygen uptake occurred for two hours, see Figure 8. Repeating the experiment with a Co/Mn/Br catalyst (0.01/0.01/0.02 M) results in an immediate high rate of oxygen uptake, see Figure 8, and a rate of disappearance of the reagent of $6.95 \times 10^{-5} \text{ s}^{-1}$. The calculated amount of hydrobromic acid provided by solvolysis of α -Br-*p*-toluic acid is only 0.0005 M during this time period. It is concluded that benzylic bromide has virtually no activity or promotional effect in metal-catalyzed autoxidations. After 2 h, the oxygen uptake slowly increased as sufficient hydrobromic acid was supplied by hydrolysis of the BPTA to initiate the reaction.

Rationalization of the Observations During the Autoxidation of Chlorotoluene at 0 and 5% water/acetic mixtures

The above empirical observations become understandable when the yield of the benzylic bromide of 4-chlorotoluene was measured – where the yield is of benzylic bromide it is based on the amount of sodium bromide added to the reaction, see Figure 9. At 120 min reaction time, 95% of the bromide is benzylic bromide and at 180 min 100% of the bromide has been converted to the catalytically inactive benzylic bromide. One has

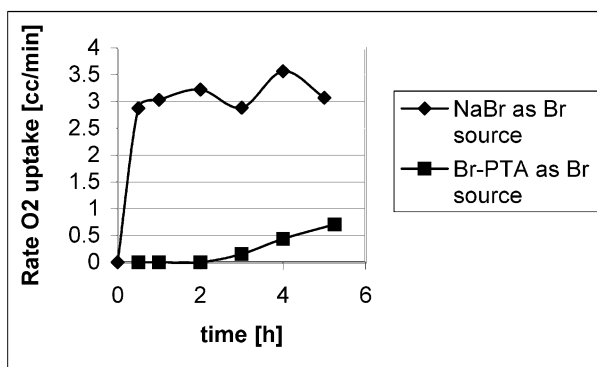


Figure 8. Effect of different bromine sources on the rate of oxygen uptake during the Co/Mn/Br-catalyzed aerobic oxidation of 1,2,4-trimethylbenzene. Br-PTA is α -bromo-*p*-toluic acid.

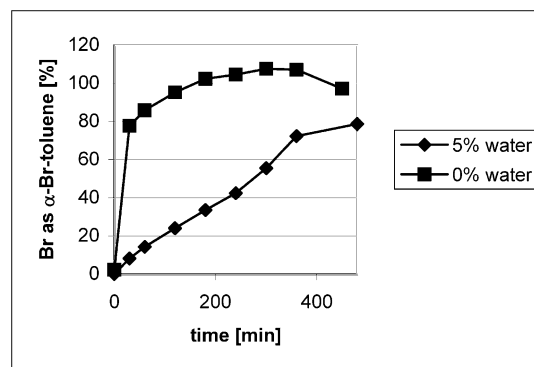
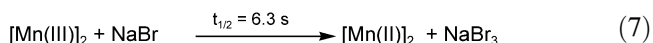
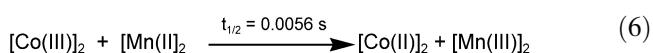
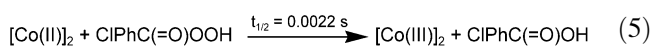


Figure 9. Effect of water on the benzylic bromide formation during the Co/Mn/Br-catalyzed aerobic oxidation of 4-chlorotoluene.

essentially gone from a more active Co/Mn/Br catalyst to a much less active Co/Mn catalyst. For example, in a Co/Mn-catalyzed autoxidation of 1,2,4-trimethylbenzene the rate of disappearance of the reagent is $2.31(0.49) \times 10^{-6} \text{ s}^{-1}$ while with a Co/Mn/Br catalyst, the rate is $6.9(0.036) \times 10^{-5} \text{ s}^{-1}$ or 30 times more reactive, experiments 6 and 7.

A Co/Mn/Br catalyst has a redox cascade in which Co(II) is rapidly oxidized to Co(III) *via* the peroxy acid, ClPhC(=O)OOH . This then rapidly oxidizes Mn(II) to Mn(III) which in turn oxidizes the Br(–I) to Br(0) at 60°C ^[16] (ligands omitted for simplicity):



The active catalytic species may be a metal(II)-bromine(0) compound or HBr_2 .^[17] As a result the steady state concentrations of cobalt and manganese remain largely in their lower oxidation states.^[14] With a Co/Mn catalyst, reactions 5 and 6 will occur but not 7, hence high steady states of Mn(III) are expected to occur. In the presence of water disproportionation of the Mn(III) can also occur:^[18]



The colors of these species in acetic acid and acetic acid/water solutions are given in Table 3. Authentic samples of these metals in their different oxidation states can be generated from reactions 5, 6 and 7 although reaction 8 is more complex.^[19] The color of the solutions during the oxidation reactions are consistent with the conversion of a Co/Mn/Br catalyst to a Co/Mn catalyst. In experiment 3, when 4-chlorotoluene is reacted in anhydrous acetic acid, the initial color was an intense blue due to the tetrahedral Co(II) species present. [The solution is

Table 2. Reactivity and the rates of solvolysis of benzylic bromides in 10 weight % water and 95°C correlated with ‘catalyst failure’. Reactivity and rates of solvolysis predicted by Hammett relationships.

Substituent	Reactivity (relative to toluene)	PhCH_2Br Solvolysis, $t_{1/2}$ [h]	Catalyst failure?
4-OCH ₃	5.61	0.12	
3,4-OCH ₃	5.02	0.15	no
1,2,4-CH ₃	3.94	0.24	no
4-CH ₃	1.98	0.94	no
4-C(CH ₃) ₃	1.78	1.2	
3-CH ₃	1.25	2.4	
H	1.00	3.7	yes
4-Cl	0.78	6.0	yes
4-Br	0.72	7.2	
4-COOH	0.40	24	yes
4-C(=O)OCH ₃	0.35	31	
4-CN	0.23	69	
4-NO ₂	0.17	123	

actually composed mostly of octahedral Co(II) species but the small amount of tetrahedral that exists accounts for the majority of the absorbance.] As the reaction proceeds, the color turns to a deep brown color characteristic of Mn(III). Manganese(IV) will not form in significant quantities at these low water concentrations. In experiment 4 when 4-chlorotoluene is oxidized with a high initial water concentration, the solution has a pale blue color throughout the reaction which is indicative of very low Co(III) and Mn(III) concentrations and is basically due to octahedral cobalt(II) species.

Use of the molar absorptivities in Table 3 at 450 nm and assuming that *all* of the metal present is oxidized to these higher oxidation states results in a calculated absorbance less than that observed in the experiment. The observed absorption at 450 nm, Figure 6, cannot be just due to Co(III), Mn(III) and Mn(IV), i.e., there must be some other absorbing species. The probable cause is radical coupling associated with the organic reagents and subsequent oxidation which are known to produce highly colored species.^[18]

The disappearance of benzylic bromides during these reactions is due both to the oxidation and hydrolysis of the benzylic bromides, see below. The lower steady state concentrations of the benzylic bromide during the oxidation of 4-chlorotoluene in the presence of 5 weight % water, Figure 9, would be expected from the rate of hydrolysis alone since the half-lives of α -bromotoluene decrease from 14 to 3.7 to 1.1 h at 5, 10 and 20 weight % water/acetic acid, respectively, at 95 °C.^[9]

The high rate of carbon dioxide formation is expected from the high steady state concentrations of Co(III) and Mn(III), see Figure 7, since both Co(III) and Mn(III) are strong oxidants that readily decarboxylate acids. A Co catalyst has high steady state concentrations of Co(III) giving it an intense green color. When bromide is added to a Co catalyst, the color instantly changes from deep green to pale blue. Similarly, the rate of carbon dioxide is greatly reduced, by a factor 5.9.^[14] (The rise of

the carbon dioxide selectivity at the end of a Co/Mn/Br-catalyzed reaction in 5 weight % water seen in Figure 7 is normal. At the end of the experiment, the substrate is used up and the operating catalyst starts to attack the acetic acid solvent. This occurs for only a short period of time. The number is also magnified because the rate of reaction is very slow and the carbon dioxide selectively is a ratio of rate of carbon dioxide formed divided by the total rate of oxygen uptake.)

When a Co/Mn/Br catalyst is converted to a Co/Mn catalyst due to all of the active ionic bromide being converted to benzylic bromide, the resultant catalyst is much less active, much less selective, and imparts a deep coloration to the system. Consequently, we have dubbed this phenomena 'catalyst failure' because it converts to the characteristics of a non-metal/bromide catalyst.

Catalyst Failure for 4-Carboxytoluene (*p*-Toluic Acid, PTA) and Toluene

Similar to 4-chlorotoluene in anhydrous acetic acid, the reaction of 4-carboxytoluene (*p*-toluic acid) also terminates due to α -Br-*p*-toluic acid formation, see experiment 8 and Figure 10. The slightly greater than 100% yields shown in Figures 9 and 10 are probably due to experimental error since the calculations are based on small GC areas. The changes were mimicked by the oxygen uptake (not shown). The autoxidation of toluene with the highly active Co/Mn/Zr/Br catalyst^[20] in anhydrous acetic acid at 75 °C also terminates prematurely due to benzylic bromide formation, experiment 9, see Figure 11.

Re-initiation of a Catalyst Failure with Hydrobromic Acid for Toluene and *p*-Tolualdehyde (4-CH₃PhCHO)

If the termination of the reaction is due to benzylic bromide formation, then addition of HBr after a catalyst

Table 3. Visible absorption characteristics of cobalt, manganese and zirconium in acetic acid-water mixtures.

Metal	Color	Molar absorptivity
cobalt(II), tetrahedral	intense blue	550 at 600 nm ^[a]
cobalt(II), octahedral	pale pink	15 at 450 nm
cobalt(III)	intense green	320 at 450 nm
manganese(II)	colorless	- - -
manganese(III)	intense brown	239 at 450 nm
manganese(IV)	intense brown	320 at 450 nm
zirconium(IV)	colorless	- - -

^[a] For the monobromo compound, see: K. Sawada, M. Tanaka. *J. Inorg. Nucl. Chem.* **1977**, 39, 339.

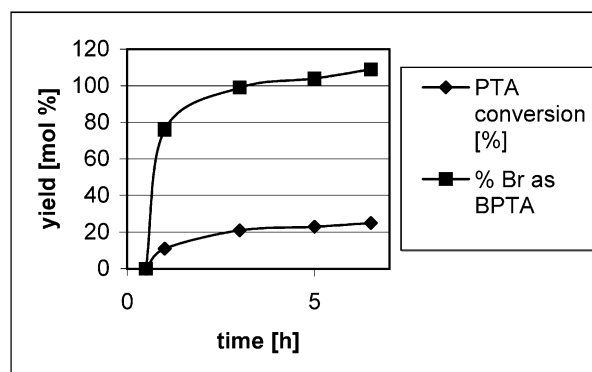


Figure 10. Effect of benzylic bromide formation on the conversion of 4-carboxytoluene during the Co/Mn/Br-catalyzed aerobic oxidation of 4-carboxytoluene.

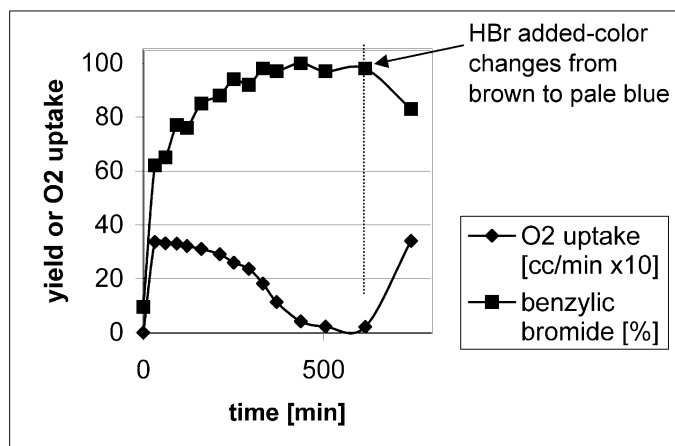


Figure 11. Effect of hydrobromic acid addition during the Co/Mn/Br-catalyzed aerobic oxidation of toluene. Additional HBr was added at 750 min.

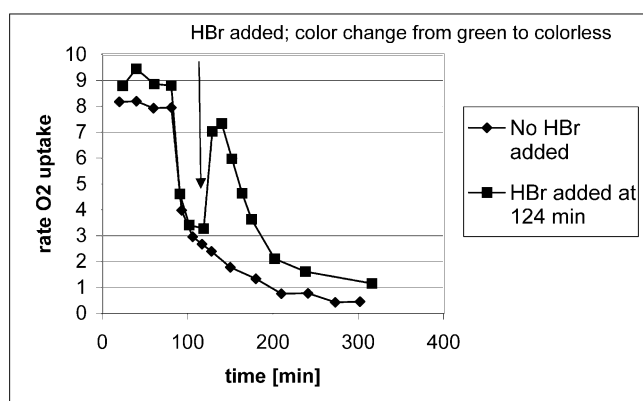


Figure 12. Effect of hydrobromic acid addition on the Co/Mn-catalyzed aerobic oxidation of *p*-tolualdehyde.

failure should result in an immediate increase in the rate of the reaction and a color change from brown back to pale blue. In the toluene experiment shown in Figure 11, addition of hydrobromic acid at 743 minutes results in immediate surge in the rate of reaction and a color change from dark brown to light pink as expected. The reaction was allowed to continue and eventually an 83 mol % yield of benzoic acid was achieved with a mass accountability of 98.8% with the other compounds being acetophenone and benzylic bromide.

One can initially start with a Co/Mn catalyst and demonstrate the same features of ‘catalyst failure’ and its rectification with an ionic bromide source using benzaldehydes as reagent. Figures 12 and 13 describe the more complex autoxidation of *p*-tolualdehyde. The oxidizability of benzaldehydes, 290, are much higher than those of toluenes, 0.014 [oxidizability is defined as $k_p/(2k_t)^{1/2}$; k_p = propagation rate constant; k_t = termination rate constant].^[21] Benzaldehydes spontaneously and vigorously autoxidize *without* any addition of

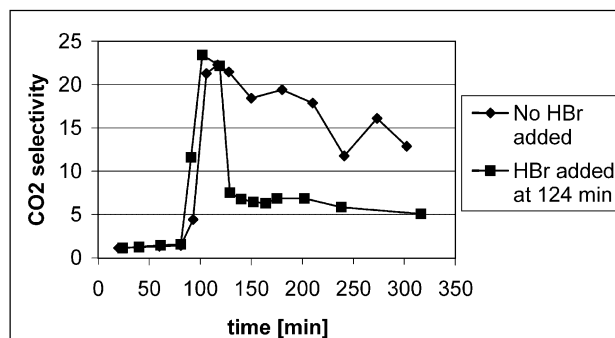


Figure 13. Effect of hydrobromic acid addition on carbon dioxide selectivity during the Co/Mn-catalyzed aerobic oxidation of *p*-tolualdehyde.

catalysts in glass reactors. Metal-catalyzed reactions are considerably less important. With a Co/Mn-catalyzed autoxidation experiment, No. 10, catalyst failure occurs at about 70 min when the rate decreases, the carbon dioxide selectivity greatly increases, and the color turns from colorless to green. The conversion of *p*-tolualdehyde is 75% at this point. When hydrobromic acid was added at 125 min, experiment 11, the rate of oxygen uptake immediately increases from 2.5 to 7.5 mL/min, the carbon dioxide selectivity decreases from 22 to 7% and the color changes from green back to colorless.

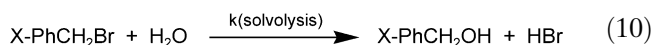
Mechanism of Benzylic Bromide Formation and Disappearance

There are different views on how benzylic bromides form during autoxidation.^[7,8] Our view is based on evidence that they form directly in the coordination sphere of the metal.^[23] Cobalt(II) metal dimers react *preferentially* with the two-electron oxidant, peroxy acids quickly and selectively,^[24] see reaction 5. In water/acetic acid mixtures, the bromide is a mixture of directly bonded bromide to the metal and ion-pairs in the coordination sphere.^[22] Hence incorporation of the methylaromatic compound into the cobalt coordination sphere and subsequent oxidation of the methylaromatic compound can lead directly to the benzylic bromide:

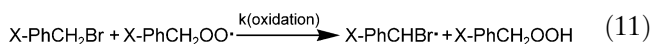


Since the formation of the benzylic bromide is a two-electron oxidation, this mechanism is particularly efficient as it occurs in one step.

The rate of its disappearance of the benzylic bromides can occur by hydrolysis:



and by oxidation. In the case of peroxy radicals one has the initial reaction:



The products of benzylic bromide oxidation are reported to be benzal bromides, benzaldehydes, benzoic acid and molecular bromide.^[7]

Evidence for Hydrolysis and Oxidation of Benzylic Bromides

In experiment 12, both HBr and α -Br-*p*-toluic acid were initially added using the highly reactive 1,2,4-trimethylbenzene as the reagent. A vigorous reaction ensued in which all of the first methyl group was consumed in 24 h. During this time the α -Br-*p*-toluic acid has been potentially exposed to 0.083 moles of peroxy radicals since the conversion of the 1,2,4-trimethylbenzene was 100% during this time. From experiment 13 we know that BPTA does *not* form under these conditions, i.e., $k(\text{formation}) = 0.0$. Thus the BPTA will disappear by oxidation and by hydrolysis:

$$k(\text{observed}) = k(\text{oxidation}) + k(\text{solvolysis}) \quad (12)$$

The observed rate of disappearance of BPTA was $1.44 \text{ e}^{-5} \text{ s}^{-1}$. The independent measurement of $k(\text{solvolysis})$ is $8.01 \text{ e}^{-6} \text{ s}^{-1}$. One then calculates the rate of oxidation of BPTA, $k(\text{oxidation})$, as $6.39 \text{ e}^{-6} \text{ s}^{-1}$ using Eq. (12). Therefore, the contribution of the overall rate of BPTA of disappearance due to oxidation is 44% and that due solvolysis is 56%. Both mechanisms of oxidation and solvolysis compete at approximately the same degree under these experimental conditions.

When would one Expect Catalyst Failure?

The rates of solvolysis of selected benzylic bromides (X-PhCH₂Br; X = 3-CH₃, 4-CH₃, H, 4-COOH) were measured in 10 weight % water at 95 °C. The Hammett plot of these data is shown in Figure 14. The rho value is $-1.93(0.29)$ which says that electron-withdrawing substituents on the benzene nucleus result in decreased rates of solvolysis. The previously published rho value for the Co/Mn/Br-catalyzed oxidation of substituted toluenes in 10 weight % water at 80 °C is $-0.95(0.16)$.^[15] Assuming the minor difference in temperature is not significant, changing substituents on the ring increases the rate of solvolysis of the benzylic bromide nearly twice as fast as the rate of oxidation, i.e., $1.93/0.97 = 2.1$. Table 2 gives the predicted half-lives of the disappearance of the benzylic bromides and their relative

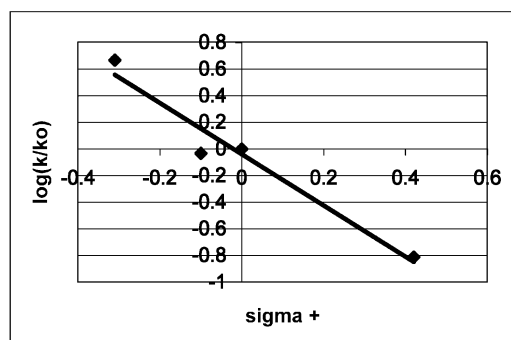


Figure 14. Hammett plot for the rate of solvolysis of selected benzylic bromides at 95 °C in 10 weight % water/acetic acid. Points from left to right are for substituents 4-CH₃, 3-CH₃, H, 4-COOH. Equation of the line is $y = -1.925x - 0.0396$ with $R^2 = 0.955$ and $\rho = -1.93(0.29)$.

reactivity of previously reported compounds^[1] in 10 weight % water. Also included in the table are the catalyst failures or lack of catalyst failure observed in this work, and in the authors experience with other reagents, at 0 weight % water. Assuming the trends observed are the same at 0% water as in 10% water, one observes that electron-withdrawing substituents result in a slower rate of benzylic bromide solvolysis as well as a slower rate of autoxidation. Since benzylic bromides react both by solvolysis and oxidation there will be an increased tendency toward catalyst failure as one moves down in Table 2. However, there will be a decreased tendency for the rate of benzylic bromide formation as one proceeds down the table as well so it is not possible to predict when catalyst failure will occur.

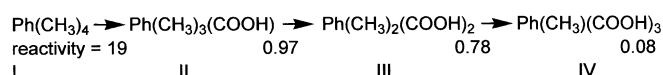
Empirically, one observes an increased tendency towards catalyst failure with more electron-withdrawing substituents.

Benzylic Bromide Formation during Nitrotoluene Oxidation

It is known that 2- and 4-nitrotoluenes are difficult to oxidize in high yield.^[1] This may be so because of their exceptionally low reactivity and high stability of the benzylic bromides, see Table 2. The low yields to the carboxylic acids that have been observed may be due to the type of catalyst failure described here. Also consistent with this analysis, is that the co-oxidation of *p*-xylene with *o*-nitrotoluene does produce high yields of *o*-nitrobenzoic acid. This is expected since the peroxides from the oxidation of the more reactive *p*-xylene can oxidize the benzylic bromide of *o*-nitrotoluene so that a sufficient amount of HBr is always present.

Benzylic Bromide Formation during the Oxidation of Polymethylbenzenes

The methyl groups in polymethylbenzenes are approximately consecutively oxidized to carboxyl groups. The reasons for this is that when the first methyl group reacts, the intermediate alcohols, benzaldehydes and carboxylic acids are electron-withdrawing groups which deactivate the other methyl groups on the ring. Thus for durene the approximate sequence is:



The relative reactivities were calculated from the Hammett equation. It is expected from their relative reactivities that increasingly stable benzylic bromides would form in this same order. The question arises is whether when a given methyl group is being oxidized (in II for example), would the more stable benzylic bromides of III form and cause a catalyst failure?

In experiment 13 1,2,4-trimethylbenzene and 4-carboxytoluene, having reactivities of 3.9 and 0.40, respectively, were reacted with air. The LC analysis of the reaction mixtures throughout the experiment did not detect any of the very stable BPTA forming. Thus, the co-oxidation of two methylbenzenes of very different reactivity will not form the more stable benzylic bromide of the less reactive compound. The rate of disappearance of 1,2,4-trimethylbenzene was 26 times faster than that of *p*-toluic acid. This is consistent with calculations using the Hammett equation.^[1]

By-Product Cascades Caused by Benzylic Bromide Formation

There is a number of complex inter-relationships in metal-catalyzed autoxidations which makes predicted outcomes very difficult. Consider what can happen as one oxidizes a methylaromatic compound:

- a) Water concentration increases which leads to:
- decreased propensity of benzylic bromide formation – a desirable condition

- decreased activity – undesirable condition
- increased propensity of manganese(IV) formation – undesirable condition
- b) As benzylic bromide formation increases
 - the Br/(Co + Mn) ratio decreases (Br is active ionic bromide)
 - results in decreased activity – undesirable condition
 - results in increased propensity for Mn(IV) formation – undesirable condition
- c) Propensity for soluble manganese(IV) formation increases
 - reduced catalytic activity due to decreased rate of initiation reaction
 - insoluble MnO₂ forms
 - Co/Mn ratio increases – catalytic activity increases^[20]
 - black particles of Mn on isolated product – undesirable condition
 - reaction of MnO₂ with reagent forms colored impurities.^[18]

Summary of the Water Effect

We have considered just one effect of water – on how it changes the steady state concentration of benzylic bromide in an oxidation reactor and the consequences of those changes. Table 4 gives a number of other factors that are also affected by water. What the *net* effect of these factors is difficult to predict. There is a delicate balance of water concentration required to avoid detrimental phenomena from occurring during an autoxidation reaction. The net effect of these factors is so difficult to predict that autoxidation, using metal and metal/bromide catalysts, will probably always be an art.

Experimental Section

The glass autoclave, procedure, calculations, and GC instrument have been previously described.^[25] The chemicals were used as received. Initial cobalt and manganese catalysts were their metal(II) acetate tetrahydrates. The reactants, intermediates, by-products, and products formed in the reactions were confirmed by GC/MS. Unless otherwise stated, all reactions were performed with a flow of air at 100 mL/min through the reactor with 100 g solvent at ambient atmospheric pressure. Periodically liquid samples were removed during reaction and analyzed *via*

Table 4. The balance of factors affected by changes in water concentration during autoxidation using metal/bromide catalysts.

Favored at low water concentration	Favored at high water concentration
reactivity of peroxy radicals of aldehydes, alcohols catalyst inhibitor conversion less Mn(IV) formed – faster reaction with bromide less Mn(IV) formed – less MnO ₂ precipitation	solvolysis of benzylic bromide with associated catalyst failure less yield loss due to aryl formate formation less phenol formation – less concentration of a strong antioxidant less carboxylic acid metal precipitation reactivity of peroxy radicals due to acetic acid H-bonding

GC. At the same time, on-line gas analysis was performed for dioxygen, carbon monoxide, carbon dioxide, and dinitrogen.

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