The Complex Synergy of Water in Metal/Bromide Autoxidations. Part II. Effect of Water and Catalyst on the Aerobic Oxidation of Benzaldehydes and the Effect of Water on the Elementary Catalytic Pathways

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Received: June 10, 2004; Accepted: January 17, 2005

Abstract: All of the rates of the elementary steps in the Co/Br and Co/Mn/Br homogeneous, liquid-phase catalyzed reactions decrease with increasing water concentration in acetic acid. The step-wise replacement of the acetic acid ligands by water ligands in the coordination sphere of the catalyst metals may be responsible for this behavior. The non-catalyzed and metal-catalyzed (Co, Co/Mn/Br and Co/Mn) aerobic oxidations of benzaldehyde and 4-methylbenzaldehyde are reported. The non-catalyzed autoxidations are quite vigorous reactions in acetic acid/water mixtures but by-products from the Baeyer–Villiger reaction, the thermal decomposition of the peroxy acid, and over-oxidation to carbon dioxide limit the yield to the aromatic carboxylic acids. As the concentration of a Co or Co/Mn/Br catalyst increases these by-products are first reduced and then eliminated probably due to the very fast, selective reaction of $[Co(II)]_2$ with the peroxy acid. A Co/Mn catalyst completely inhibits the autoxidation of the benzaldehydes. There is a gradual change in the yield of terephthaldicarboxaldehyde from 4-methylbenzaldehyde with increasing Co/Mn/Br concentration suggesting that the non-catalyzed steps are being replaced by catalyzed ones. The autoxidation of heptaldehyde generates about 500 times more carbon monoxide than does benzaldehyde using a Co/Mn/Br catalyst and gives only a 50% yield to heptanoic acid consistent with excessive amounts of decarbonylation with aliphatic aldehydes.

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

Introduction

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. These catalysts have been used to produce hundreds of different carboxylic acids in high yield, typically 80–98%, and purity, often 98–99.5%. This method is used in the commercial production of terephthalic acid from *p*-xylene[1] which is a component of polyethyleneterephthalate (PET).

This paper is a continuation of a study on the effect of water on metal/bromide-catalyzed autoxidations.[2] Previously it was shown that for methylaromatic compounds with sufficiently strong electron-withdrawing substitutents (4-methyl-, 4-carboxy-, 4-chlorotoluene) that good yields in benzoic acid can be achieved only if the reaction contains a sufficient amount of water present in the acetic acid. Although water inhibits autoxidations in acetic acid, it is necessary to have it present otherwise all of the active ionic bromide becomes inactive benzyl bromide ($PhCH_2Br$). If one initially starts with anhydrous acetic acid, the Co/Mn/Br catalyst becomes a Co/Mn catalyst due to benzyl bromide formation and the reaction ceases with resultant poor yields. The complex synergy caused by water on the inorganic by-products, such as manganese(IV) formation, and organic by-products, such as insoluble metal carboxylic acid compounds, was previously outlined.[2] These effects make it quite difficult to predict the outcome of autoxidations in an acetic acid/water solvent especially because water is usually one of the products from the reaction itself.

In this study we have chosen to study benzaldehyde and *p*-methylbenzaldehyde for the following reasons. Benzaldehydes do not form benzylic bromides so that this complication, see above, is absent. Secondly, benzaldehydes spontaneously react with oxygen in the acetic acid solvent in the absence of any added catalyst.[3b] Methylaromatic compounds themselves cannot be autoxidized, without catalysts, even at high temperatures

  DOI: 10.1002/adsc.200404169

and pressures.[4] So it is possible to study a non-catalyzed autoxidation with and without water present in the acetic acid solvent. Thirdly, by addition of selected catalysts, one can observe the activity and selectivity changes that occur due to the metal-catalyzed pathways. Finally, 4-methylbenzaldehyde was chosen because it is one of the main intermediates in the commercial *p*-xylene to terephthalic acid process.[1] The chemistry and mechanism of cobalt-catalyzed[5] and metal/bromide-catalyzed[3] autoxidation of benzaldehydes has been extensively studied.

In addition, the effect of water on the elementary steps of a Co/Mn/Br catalyst have been assembled from literature reports. All of the diverse rates have been put on a common basis and it is found that all these stoichiometric, elementary reactions are also retarded by the presence of water in the acetic acid.

Results and Discussion

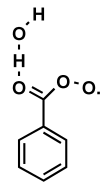
Chemistry of Oxidation of Benzaldehydes and their By-Products

In Figure 1 the free-radical chain mechanism (RFCM) for benzaldehyde is shown. The important product of the FRCM is the peroxy acid, a powerful two-electron oxidant. Initiation can occur thermally, photochemically,[5] and *via* adventitious peroxide.[4] The oxidizability of benzaldehydes, which is defined as $k_p/(2k_t)^{1/2}$ where k_p is the propagation rate constant and k_t is the termination rate constant, is orders of magnitude higher than for methylbenzenes and benzyl alcohols.[7]

The pertinent chemistry leading to the products and by-products quantitatively measured in this work is given in Figure 2. The peroxy acid, the primary product of the FRCM, undergoes three competitive reactions – reactions 1, 2, 3 on Figure 2. Reaction 1, the thermal decomposition of the peroxy acid, is slow and unselective as compared to the two-electron oxidation of Co(II) to Co(III).[8] Reaction 2 with 3-chloroperoxybenzoic acid at 60 °C in 10 wt % water/acetic acid has a half-life of 0.0023 s and is 400,000 times faster than reaction 1. Reaction 2 is also very selective producing the carboxylic acid in 100% yield as compared to reaction 1 which gave an 89% yield and a 4.8% yield to the decarboxylation product, chlorobenzene. So one can anticipate in the oxidation of the benzaldehyde discussed below that the presence of Co(II) will reduce the amount of carbon dioxide, from reaction 8, and the formation of benzene, reaction 12. The Baeyer–Villiger reaction, reaction 3 also competes for the peroxy acid. From the experimental data below it will be shown that the formation of the aryl formate *via* reaction 5 is eliminated with very low concentrations of Co(II), hence reaction 3 is also slower than reaction 2.

The phenols can be formed either through the decarboxylation and subsequent oxidation of the aryl radical, reactions 8 and 10, or from the hydrolysis of the phenyl or tolyl formates, reaction 9. The phenols are oxidized to quinones, reaction 11. The structures of the quinones have been characterized.[5f] Phenols are very effective inhibitors of autoxidation and quinones are known to autoretard these reactions.[10] The inhibition caused by the phenols is thought to be due to the reaction of peroxy radicals, formed in the propagation step (Figure 1), with the phenol. Quinones are easily oxidized to carbon dioxide[1], reaction 13. The phenyl formate itself will not inhibit the reaction because the formate functionality will mask the phenolic antioxidant properties as is well-established for phenyl acetates.[1]

There are other known mechanisms for the deactivation of benzaldehydes such as hydrogen bonding of water to the transient peroxy radicals:



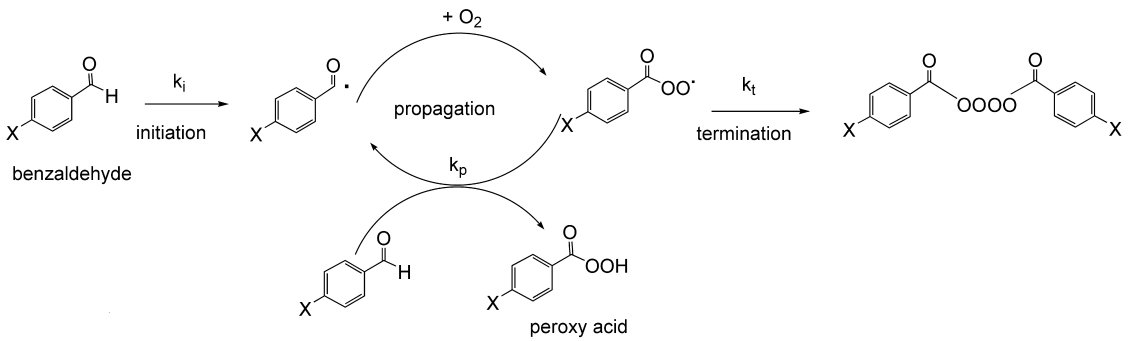


Figure 1. Free-radical chain mechanism for the formation of the peroxy acid from benzaldehydes (X = H, CH_3).

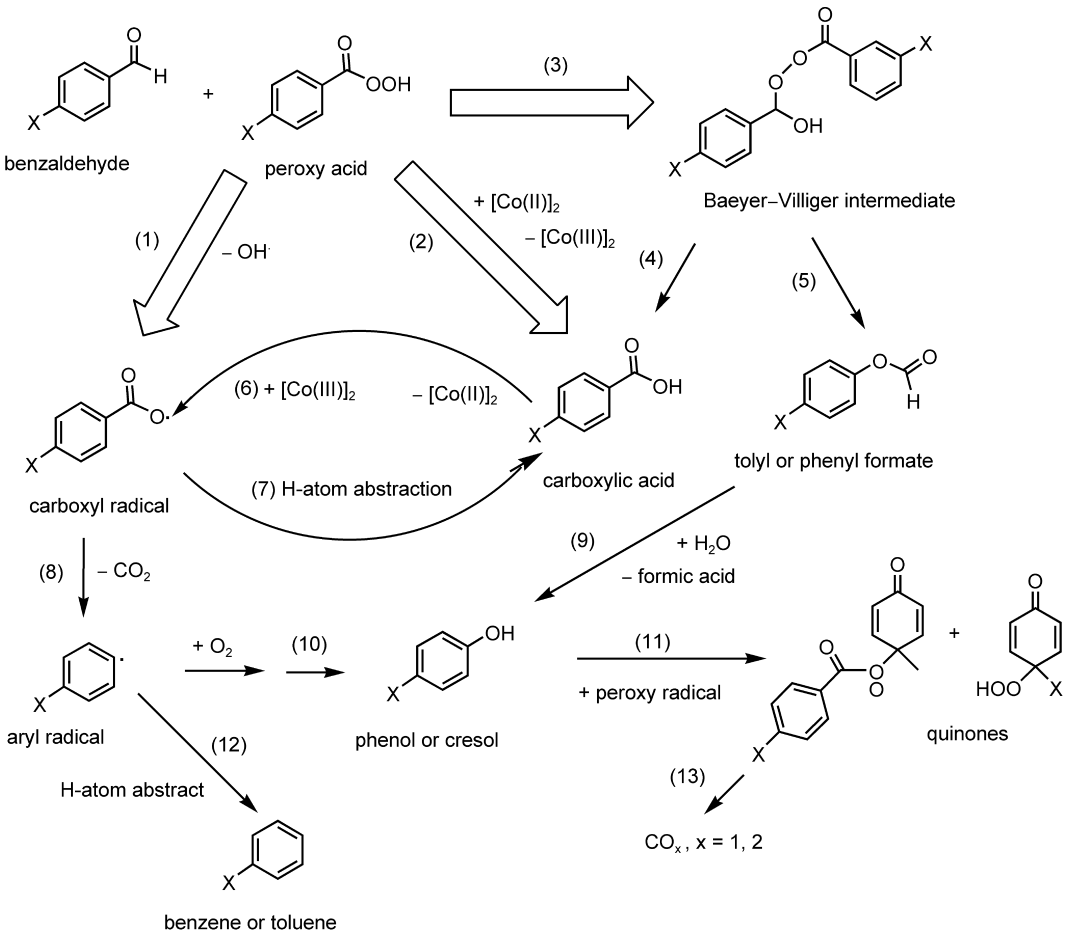


Figure 2. Chemistry leading to product and by-product formation during the oxidation of benzaldehydes (X = H, CH_3).

which have been well-documented in the literature.[11,12,13] The relative importance of this mechanism to phenol inhibition is unknown.

Characteristics of Incomplete Oxidations of Benzaldehydes

Incomplete reactions occurred when the rate of oxygen uptake in the experiment fell to zero while the conversion of the aldehyde was $<98\%$. A typical example is given in Figure 3.

Incomplete reactions occurred when the catalyst was absent or in low concentrations, see examples 1–3 in Table 1 for benzaldehyde and examples 1–4 in Table 2 for 4-methylbenzaldehyde. The changes in the yields of phenyl formate and phenol are given in Figure 4 for the oxidation of benzaldehyde in 5% water. There is an increase in the phenol and phenyl formate concentrations until the reaction terminates. Then there is a discontinuity in the rate at which phenol increases and the phenyl formate decreases. After the reaction terminates, the rate of disappearance of the phenyl formate is matched by the rate of increase of the phenol. This behavior was seen in all of the incomplete reactions. The interpretation of these changes is that during the reaction both phenyl formate and phenol concentrations increase as expected *via* reactions 5 and 9. At a sufficiently high concentration, the phenol terminates the reaction due to its anti-oxidant properties. After termination of

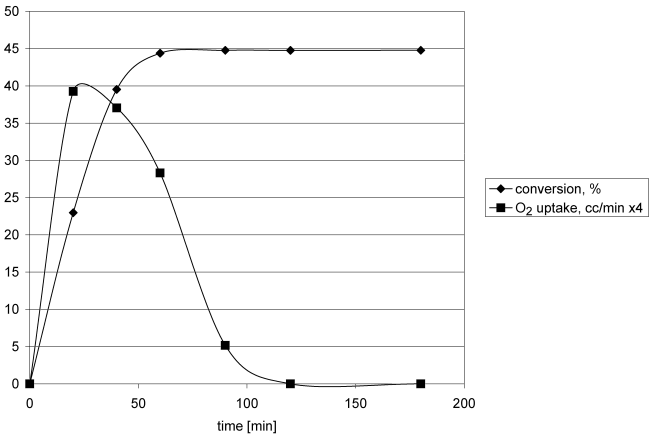


Figure 3. Autoxidation of 4-methylbenzaldehyde in 5% water with no catalyst. Example 2 in Table 2.

the reaction the phenyl formate concentration declines as it hydrolyzes to the phenol, reaction 9. Experimentally in examples 1, 2, 3 in Table 1 the reaction terminated when the phenol concentration was 5–13 mM and for the 4 examples in Table 2 the range was 6–50 mM. In the reactions where no phenol or significantly less amounts are observed high conversions are invariably seen, see Tables 1, 2. Thus the incomplete reactions appeared to be caused by excessive hydrolysis of the phenyl or *p*-tolyl formate to their corresponding phenols. The same conclusion has been made by others.[5f,3b] Previously it has been shown that addition of phenol, at the same concentrations observed here, during the Co/Mn/Br autoxidation of toluene can either terminate or decrease the rate of oxidation.[14] Addition of phenol results in a deep red coloration of the solution due to the quinones that form.[14]

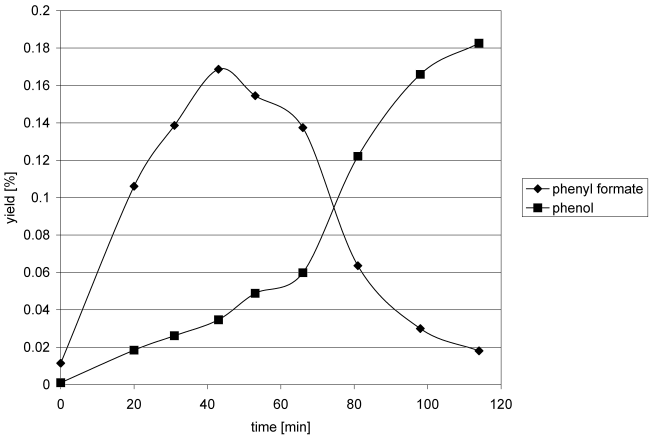


Figure 4. Changes in phenyl formate and phenol during the autoxidation of benzaldehyde in 5% water with no catalyst. Experiment 2 in Table 1

Table 1. Initial conditions and product formation during the autoxidation of benzaldehyde (initial concentration: 0.79 M).

Entry	Water [wt %]	Catalyst[a]	Co [mM]	$k \times 10^4$ [s^{-1}] (std. dev.)[c]	$CO_2 + CO$ [mmol]	Conversion [%]	Yields [% based on benzaldehyde][b]			
							benzene	phenyl formate	phenol	benzoic acid
1	0.00	none	0.0	4.19(0.13)	88	94	0.864	3.04	0.063	88
2	5.00	none	0.0	3.00(0.25)	160	88	0.714	0.102	0.082	84
3	5.00	Co/Mn/Br	0.157	3.00(0.08)	79	80	0.071	0.0073	0.049	78
4	5.00	Co/Mn/Br	0.629	3.60(0.29)	8.9	100	0.003	0.00	0.000	99
5	5.00	Co/Mn/Br	2.65	4.29(0.63)	9.5	99	0.000	0.00	0.000	99

[a] Mole ratios $Co/Mn = Br/(Co + Mn) = 1.0$.
[b] The maximum yield observed in the experiment. Carbon dioxide and carbon monoxide values were obtained by numerical integration assuming the perfect gas law applies. Benzene yields are higher than stated due to losses from the reactor due to the flow of air through the reactor.
[c] Rate of disappearance of benzaldehyde

Table 2. Initial conditions and product formation during the autoxidation of 4-methylbenzaldehyde (initial concentration: 0.79 M).

Entry	Water [wt %]	Catalyst[a]	Co [mM]	$k \times 10^4$ [s^{-1}] (std. dev.)[c]	$CO_2 + CO$ [mmol]	Conversion [%]	Yields [% based on 4-methylbenzaldehyde][b]			
							toluene	tolyl formate	*p*-cresol	terephthalaldehyde
1	0.00	none	0.0	2.09(0.22)	33	67	0.75	10.5	0.17	0.21
2	5.00	none	0.00	1.70(0.26)	84	46	0.78	1.5	0.63	0.29
3	5.00	Co/Mn/Br	0.63	1.66(0.08)	150	81	0.20	4.0	0.09	0.29
4	5.00	Co/Mn/Br	1.26	1.51(0.15)	79	73	0.14	0.03	0.04	1.29
5	5.00	Co/Mn/Br	2.51	2.07(0.15)	14	99	0.32	0.02	0.02	2.03
6	5.00	Co/Mn/Br	5.02	2.08(0.05)	15	98	0.0	0.000	0.01	2.49
7	5.00	Co/Mn/Br	5.02	1.81(0.16)	8.3	97	0.0	0.000	0.00	2.90
8	5.00	Co/Mn/Br	10.0	2.31(0.22)	4.5	98	0.0	0.004	0.00	2.66
9	5.00	Co/Mn/Br	10.0	2.25(0.15)	5.0	98	0.0	0.000	0.00	2.10
10	5.00	Co	10.0	4.22(0.80)	11	99	0.071	0.005	0.00	0.17
11	5.00	Co/Mn	10.0	0	0.0	0	0.0	0.000	0.00	

[a] Mole ratios are $Co/Mn = Br/(Co + Mn) = 1.00$.
[b] The maximum yield observed in the experiment. Carbon dioxide and carbon monoxide values were obtained by numerical integration assuming the perfect gas law applies. Toluene yields are higher than stated due to losses from the reactor due to the flow of air through the reactor.
[c] Rate of disappearance of 4-methylbenzaldehyde.

Affect of Water on the Non-Catalyzed Autoxidation of Benzaldehydes

As expected the tolyl and phenyl formates hydrolyze much faster in 5% water/acetic acid than in anhydrous acetic acid. One can measure the rate of hydrolysis from the rate of *p*-tolyl or phenyl formate disappearance after the reaction terminates when only the hydrolysis reaction is occurring. The measured first order rate constant for the hydrolysis of *p*-tolyl formate in anhydrous acetic acid was 5.8 (0.6) $\times 10^{-4}$ min^{-1} (values in parentheses are standard deviations). In 5% water/acetic acid, the rate of hydrolysis is 0.011 (0.003) min^{-1} for the phenyl formate and 0.010 (0.001) min^{-1} for tolyl formate. Thus the 5% water enhanced the rate of hydrolysis by a factor of 19.

Yields to the phenyl formates in anhydrous acetic acid are much higher than in 5% water/acetic acid, see Figure 5. At the same conversion, 20 times more of the phenyl formate forms in 0% water than in 5% water. For tolyl formate the ratio is about 7. The water is apparently suppressing the occurrence of the Baeyer–Villiger rearrangement to the phenyl formates because if the rates were the same, the much greater hydrolysis rate of that occurs in 5% water would have inhibited the reaction much sooner, i.e., the observed conversions would have been much less. *p*-Cresol and phenol do also arise from the thermal decomposition of the peroxy acid *via* reactions 1, 8, and 10. Since benzene comes from the same reaction sequence (reaction 12, Figure 2) and the benzene yields are essentially the same in both 0 and 5% water (Table 1), the contribution of the phenols from this source should be about the same. Hence the data are consistent with the formation of the aryl formate being suppressed by the presence of water.

The rate of formation of carbon dioxide is very high in both 0 and 5% water/acetic acid with the rate being about twice as high in 5% water than in 0% water. Carbon dioxide can form in a number of different reactions

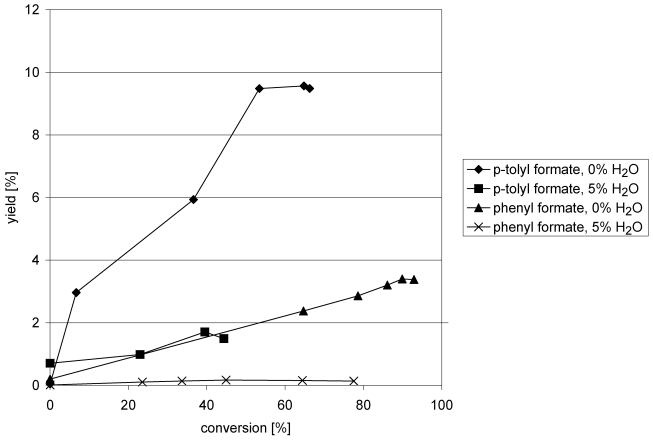


Figure 5. Affect of water on the formation of phenyl formate and *p*-tolyl formate.

emanating from both the benzaldehyde and the acetic acid solvent. The higher rate of carbon dioxide formation in 5% water ***may be*** due to a more rapid rate of *p*-cresol formation as discussed above. The *p*-cresol is rapidly oxidized to the quinones which are oxidized to the carbon oxides, see reactions 11 and 13 of Figure 2. The lower conversions of the benzaldehydes and higher concentrations of the phenols in 5% water than in 0% for both benzaldehyde and *p*-tolylaldehyde, see Tables 1 and 2, are consistent with this interpretation. Addition of phenol to a Co/Mn/Br-catalyzed autoxidation of toluene is accompanied by a high rate of carbon dioxide formation.[14]

Effect of Catalyst Addition on the Selectivity of Benzaldehyde Oxidation

Addition of 10.0 mM cobalt(II) acetate more than doubled the rate of autoxidation of *p*-tolylaldehyde, compare examples 2 and 10 in Table 2. Moreover, it was no longer an incomplete reaction with the conversion quickly going to 99% as compared to only 46% without cobalt present. Most significantly however, is that all the by-products are significantly reduced – the carbon dioxide from 84 to 11 mmol, toluene from 0.78 to 0.071%, toyl formate from 1.5 to 0.005%, and the *p*-cresol from 0.63 to 0.0% The reason for this can be seen in Figure 2. When cobalt is added the peroxy acid preferentially reacts with $[Co(II)]_2$ thus greatly reducing the thermal decomposition of the peroxy acid, reaction 1, as well as nearly completely by-passing the formation of the Baeyer–Villiger intermediate, reaction 3. During the autoxidation, 68% of the cobalt is in its Co(III) oxidation state, as evidenced by its deep green color and previous UV-VIS studies.[14] Cobalt(III) is known to decarboxylate aromatic acids,[15,16] hence reactions 6, 8 and 12 continue and toluene is still observed. An important conclusion is that at 10.0 mM Co, the reaction of the peroxy acid is nearly completely metal-catalyzed and the undesirable reactions to by-products, emanating from reactions 1 and 3, nearly completely eliminated.

At the same cobalt concentration as used above (10.0 mM), the Co/Mn/Br completely eliminates the last vestiges of toluene seen in a Co catalyst, as well as reducing the carbon dioxide yield by 50%, see Figure 6 and examples 9 and 10 in Table 2. The reason for this can be seen in Figure 7. As previously discussed, there is a rapid reaction of the Co(III) with Mn(II), with a half-life of 0.0008 s at 60 °C, which reduces the steady-state concentration of cobalt(III) in solution.[8] Mn(III) decomposes acetic acid at a rate of 56 less than Co(III) hence one expects to see less carbon dioxide formation *via* decarboxylation.[14] Additionally, the steady-state concentrations of both Co(III) and Mn(III) are significantly less for the Co/Mn/Br catalyst than for the Co catalyst due to their reaction with bromide.[14] One con-

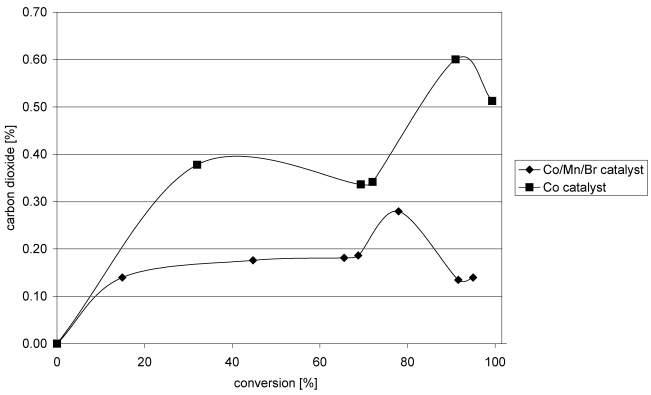


Figure 6. Comparison of the rate of formation of carbon dioxide during the autoxidation of *p*-tolylaldehyde with Co and Co/Mn/Br catalysts; [cobalt] = 10.0 mM.

cludes that the rate of decarboxylation due to the steady-state concentration of Co(III) is much less with a Co/Mn/Br catalyst. Therefore one expects the further reduction of toluene and carbon dioxide formation which is observed.

The reduction in by-products occurs at very low catalyst concentrations, see Tables 2 and 3. Even at 0.16 mM cobalt (9 ppm), there is a 50% reduction in carbon dioxide formation, a 90% reduction in benzene, and a 75% reduction in the phenyl formate, see examples 2 and 3 in Table 1. Further increases in catalyst concentration continue to reduce the by-product formation, see Tables 1 and 2. At 5.0 mM cobalt, the presence of benzene, phenyl formate and phenol are virtually eliminated, see examples 2–9 of Table 2. The Co/Mn/Br catalyst only modestly improves the activity for the benzaldehydes. The maximum activity improvement is only 43% for benzaldehyde and 36% for 4-methylbenzaldehyde. The efficacy of the Co/Mn/Br catalyst with benzaldehydes lies in its promotion of the selectivity of the reaction, i.e., greatly reducing the rate of by-product formation rather than its activity.

No reaction occurs when a catalyst composed solely of Co(II) and Mn(II) acetates is used, see example 11 in Table 2. This reaction was performed to confirm that, when all of the active hydrobromic acid is converted to a benzylic bromide during a Co/Mn/Br-catalyzed reaction, the resultant Co/Mn catalyst would be inactive. It has been previously observed that when all of the hydrobromic acid becomes benzylic bromide the reaction terminates.[2] We confirm here the lack of reactivity of the Co/Mn catalyst. This is particularly striking since the oxidizability of benzaldehyde is 340 times that of toluene.[7]

On the Synthesis of Carboxylic Acids from Benzaldehydes in Acetic Acid

High yields of carboxylic acids from non-catalyzed reactions are not possible at 95 °C in acetic acid due to significant yields of the aryl formates (3% for benzaldehyde and 10.5% for 4-tolylbenzaldehyde) and because of the hydrolysis of aryl formates to phenols, whose antioxidant behavior terminates the reactions before they are complete. It ***may be*** possible to obtain higher conversions by addition of acetic anhydride to the acetic acid or use acetic anhydride by itself as the solvent. This would avoid hydrolysis of the phenyl formate to phenol and hence the premature termination of the reaction. This would not eliminate yield losses due to the Baeyer–Villiger rearrangement to the phenyl formate, however. Thus, without a catalyzed system in acetic acid, high yield conversions of benzaldehydes to carboxylic acids do not appear feasible.

At catalyst concentrations of 0.0063 M and above, benzaldehyde gives essentially quantitative yields of benzoic acid, see Table 1. This is consistent with report-

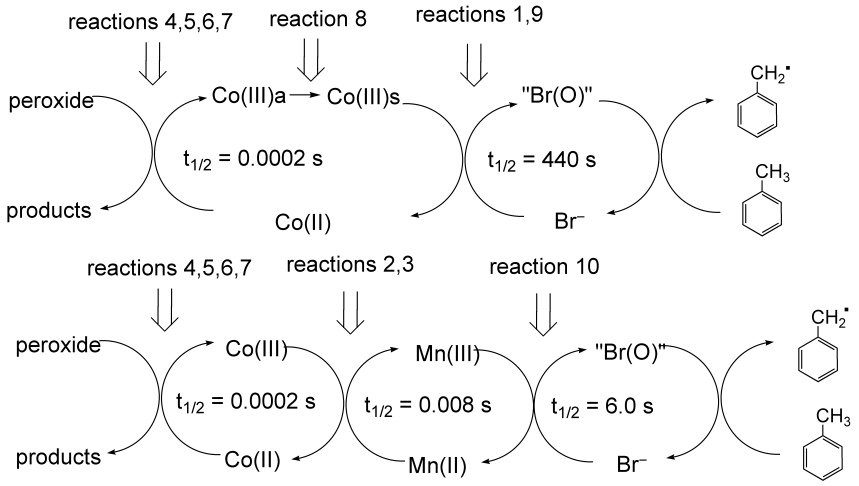


Figure 7. Elementary reactions for Co/Br and Co/Mn/Br catalysts. Reaction #'s refer to those on Table 3. Half-lives are at 60 °C in 10 wt % water/acetic acid.[20]

ed yields from the literature of 90–96% for other benzaldehydes using metal/bromide catalysts.[1] As discussed above, this is because the peroxybenzoic acid is predominately reacting with $[Co(II)]_2$ to give the carboxylic acid in one single step, reaction 2, and largely eliminating the less-selective thermal decomposition of the peroxy acid, reaction 1, and the Baeyer–Villiger reaction, reaction 3. At sufficiently high catalyst concentrations the aryl formate and phenols are analytically undetectable as are all the other by-products except for carbon dioxide and carbon monoxide. For the yields given in Table 1, all the carbon oxides were assumed to come from the unselective oxidation of the benzaldehyde. Quantitative yields of *p*-toluic acid are not seen because the *p*-toluic acid is further oxidized to 4-carboxybenzaldehyde and terephthalic acid before the *p*-tolylaldehyde conversion is 100%. The oxidation of *p*-methylbenzaldehyde to terephthalic acid is reported to give a 96 mol % yield.[1]

Separation of the carboxylic acid product and catalyst is generally not a problem using acetic acid/water mixtures as a solvent. Most aromatic carboxylic acids have a limited solubility in acetic acid and they often precipitate during the reaction (such as terephthalic acid), or upon cooling to room temperature, or upon partial evaporation of the solvent.[1] The traces of residual catalyst in the solid carboxylic product are easily removed by a simple water rinse. In commercial processes a very high degree of direct recycle of the catalyst and solvent is practiced, i.e., the reactions have so few by-products that the solvent containing the catalyst can be used repeatedly in subsequent reactions.

Evidence for Changes in Mechanism for Different Catalysts

Most catalyzed autoxidations obey the Hammett relationship: $\log(k/k_o) = (\text{rho}) \times (\text{sigma})$, where rho is a constant for a given set of conditions and sigma is a constant characteristic of the substitutent on the ring. Changes in rho signify a change in the mechanism of the reaction. The value of rho is -1.81 for a Co-catalyzed and -1.28 for a Co/Mn/Br-catalyzed autoxidation.[18] This reflects the different transition states of radical formation *via* Co(III) in a Co catalyst and a reduced bromide species in the Co/Mn/Br catalyst. The latter is thought to be either a metal-bromine(0) complex or an $HBr_2^{\cdot}$ species.[21] The negative value of rho indicates that the rate of reaction will decrease with electron-withdrawing groups on the ring.

As previously discussed,[1] different values of rho for different catalysts signify changes in selectivity. The larger value of rho will be more selective because changes in the substitutents on the ring will result in larger differences in the rates of reaction. For example, if one wanted to prepare *p*-toluic acid from *p*-xylene, one might chose a Co catalyst rather than a Co/Mn/Br catalyst. The reason for this is that the difference in reactivity of *p*-xylene and *p*-toluic acid using a rho value of -1.81 for a Co catalyst is calculated to be 43. A similar calculation using a Co/Mn/Br catalyst with a rho of -1.28 is 17. Indeed, this is seen for the Co- and Co/Mn/Br-catalyzed oxidation of 4-methylbenzaldehyde, see Figure 8. For the Co-catalyzed oxidation of 4-methylbenzaldehyde the reaction proceeds to 100% conversion, i.e., to nearly quantitative yields of *p*-toluic acid and then the reaction terminates (the oxygen uptake is 0.0 within experimental error). The Co/Mn/Br-catalyzed reaction, however, continues and eventually forms 1,4-dicarboxybenzene (terephthalic acid) which is highly insoluble at 95 °C and precipitates from solution as a white powder. No precipitation was seen with the Co-catalyzed reaction.

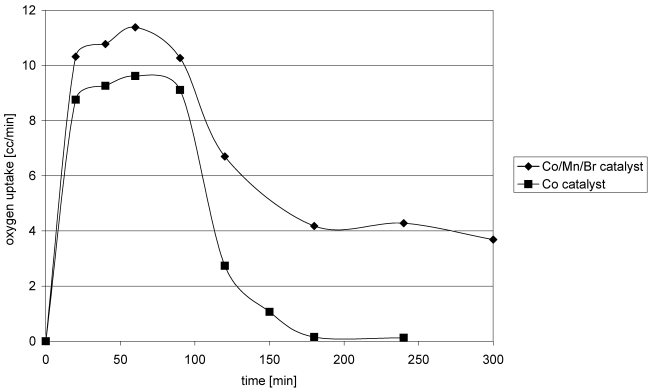


Figure 8. Rates of reaction of Co- and Co/Mn/Br-catalyzed autoxidation of 4-methylbenzaldehyde.

The same phenomenon discussed in the previous paragraph is seen in the terephthaldicarboxaldehyde $[1,4\text{-}C_6H_4(CHO)_2]$ yield. The electron-withdrawing character of the aldehyde group (sigma = 0.45) is similar to that of the carboxylic acid group (sigma = 0.52), hence the calculated differences in reactivity for the Co and Co/Mn/Br catalysts will be similar to that calculated above. This is indeed found since the maximum terephthaldicarboxaldehyde yield is 0.17% for the Co catalyst and 2.1% for the Co/Mn/Br catalyst, see Table 2. The Co catalyst favors the oxidation of the methyl group in 4-methylbenzaldehyde more than the Co/Mn/Br catalyst does.

The differences in terephthaldicarboxyaldehyde yield for the Co and Co/Mn/Br are the result of a change in mechanism of the reactions in the FRCM. In Figure 9 the change in terephthaldicarboxyaldehyde yield is given in the non-catalyzed reaction and then as a function of the Co/Mn/Br catalyst concentration. One observes a gradual increase in the terephthaldicarboxaldehyde yield. We interpret this change as evidence for the non-catalyzed pathways becoming dominated by the catalyzed ones. This is the first illustration of this kind in liquid-phase autoxidation that the author is aware of.

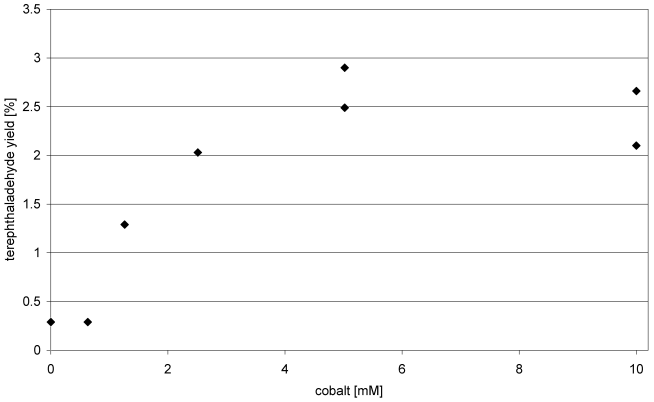


Figure 9. Changes in terephthaldicarboxyaldehyde yield as a function of Co/Mn/Br catalyst concentration.

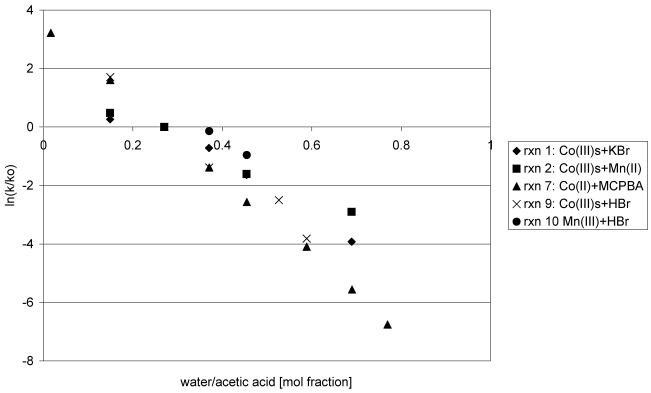


Figure 10. Rates of elementary reactions in Co/Br and Co/Mn/Br Catalysts as a function of water in acetic acid. Reaction numbers refer to those in Table 3 and Figure 7.

The Importance of Decarbonylation in Co/Mn/Br Autoxidations

Very little carbon monoxide, generally less than 0.01%, is formed during the reaction of benzaldehydes described above. This is indicative that decarbonylation, i.e., $PhCO^{\bullet} \Rightarrow Ph^{\bullet} + CO$, is not important in aromatic aldehyde autoxidations. Previously it has been shown that metal-catalyzed (Co, Mn, Ni) autoxidation of aliphatic aldehydes does not proceed in high yield to the carboxylic acid ($<10\%$)[19] due to high rates of decarbonylation. We autoxidized heptaldehyde using a Co/Mn/Br catalyst in the same manner as described here for 4-methylbenzaldehyde to determine if high yields of heptanoic acid could be obtained, i.e., that the Co/Mn/Br catalyst may be more effective than Co, Mn, or Ni catalysts. Unfortunately, metal/bromide catalysts do not improve the yield, at least for heptaldehyde. The vent carbon monoxide concentration was as high as 5% with a maximum yield of heptanoic acid of only 50% Assuming all of the vent carbon monoxide is due to decarbonylation, it is $5/0.01 = 500$ times higher for heptaldehyde than with the benzaldehydes studied here. Hexanoic acid, one of the products of decarbonylation, was formed in 20% yield. Thus the Co/Mn/Br catalyst does not give high yields to carboxylic acids with aliphatic aldehydes but does so with benzaldehydes.

Effect of Water on the Elementary Catalytic Steps in Metal/Bromide Catalysts

There are at least 30 different reported metal/bromide catalysts using the elements Ca, Ce, Co, Cu, Fe, Hf, Mn, Mo, Ni, Ru, Si, Te, U, V, Zn, Zr. The 'redox cascades' which give the elementary catalytic steps for the Co/Br, Co/Mn/Br and Co/Ce/Br catalysts have been previously reported.[8,20] Those for Co/Br and Co/Mn/Br are given in Figure 7. For a Co/Br catalyst the cobalt is initially oxidized with a peroxide to Co(III). Initially this peroxide is adventitious peroxide formed in the acetic acid solvent,[4] reactions 4–6, or a peroxy acid, reaction 7. The initially formed cobalt [Co(III)a] predominately re-arranges to a less active form [Co(III)s][9] before it reacts with the bromide ion to form a reduced bromide species, reactions 1 and 9. For the Co/Mn/Br catalyst the initially formed Co(III) next reacts with Mn(II), reactions 2 and 3, and then with the bromide ion, reaction 10. This reduced bromide species reacts with the hydrocarbon, toluene in Figure 7, to form the benzylic radical which further propagates the reaction.

Information on the rates of these elementary reactions 1–10 of Figure 7 as a function of water concentration in acetic acid are summarized in Table 3. Some of the data in the literature are reported in half-lives, some in relative half-lives and some in rates of oxygen uptake. One commonality is they all have been done in 0.27 water/acetic acid mol fraction (10 wt % water). One can place all the information on a common basis by assigning to the rate in 10 wt % water a value of 1.0 (called k_o) and scaling the other rates to it:

$$\ln(k/k_o) = AX_{H_2O} + B$$

where k = rate of elementary reaction k_o = rate of reaction in 10 wt % water, X_{H_2O} = mole fraction of water in acetic acid, A = slope of the line, B = intercept of line. This approach is similar to Hammett plots in organic chemistry.[22] As can be seen from Figures 10 and 11 *all of these elementary catalytic steps decrease in rate with increasing water concentration.* Moreover, except for the data of Mn(III) with HBr, reaction10, the changes are essentially linear with water concentration. The results of the linear regression analysis are given in Table 3. The slopes of the lines are also similar, i.e., the sensitivity to changes in rate as a function of water are nearly the same. It is known that the intermediate peroxy radicals in the non-catalyzed free radical chain mechanism become less reactive due to hydrogen bonding with wa-

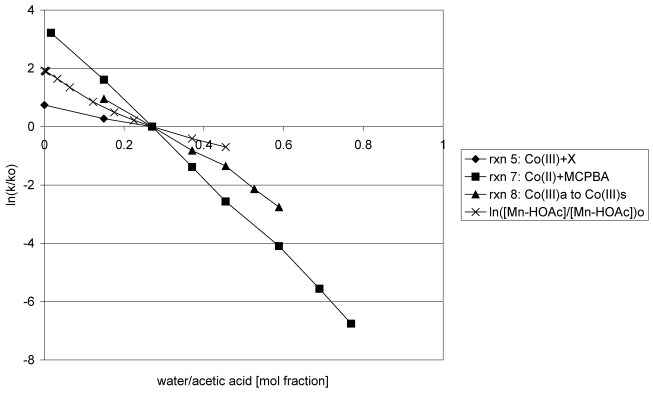


Figure 11. Rates of elementary reactions in Co/Br and Co/Mn/Br catalysts as a function of water in acetic acid. Reaction numbers refer to those in Table 3 and Figure 7.

ter.[11,12,13] We thus conclude that *both* the metal-catalyzed and non-catalyzed steps decrease in rate with increase in water concentration in acetic acid. Thus it appears that to find a catalytic system in acetic acid/water mixtures that does not decrease with increase in water concentration will be a difficult goal.

The reactions given in Figure 7 are all redox reactions except for reaction 8 which is a rearrangement of a Co(III) coordination compound. The exact reason(s) why all these reactions decrease in rate with an increase in water concentration is(are) not known. The origin of these changes *may* be due to the step-wise substitution of acetic acid and acetate in the coordination sphere by water. The rates of reaction of the elementary redox reactions may decrease because prior coordination of the peracids, peroxo radicals, bromide anion etc. may be necessary and the rate of incorporation of these species in the coordination sphere is favored by ligand substitution *via* the unusually weak and labile acetic acid ligand.[23,24] As one progresses from anhydrous to 10 wt % water, the acetic acid-metal bonds (M−HOAc), are monotonically replaced by water to form M−H_2O bonds to give mono-, di-, triaquo, etc. cobalt(II) coordination compounds.[23] To determine if these changes are significantly large, one can calculate the value of ln([Mn−HOAc]]/[Mn−HOAc]$_o$) where [Mn−HOAc] is the concentration of the Mn−HOAc bonds at an Mn(II) concentration of 0.01 M and [Mn−HOAc]$_o$ is the value in 10 wt % water using the previously reported stability constants.[23] One can see in Figure 11 that the initial slope of this change is the same as the slopes of the reactions themselves. The calculation is performed on a mononuclear octahedral manganese(II) compound. In reality the compounds may be multinuclear since it is known that, for example, the peroxybenzoic acid prefers to react with a dinuclear cobalt(II) complex.[9]

Hammett studies for Co/Mn/Br catalysts give rho values of -1.27 in anhydrous acetic acid and -0.959 in 10% water/acetic acid.[18] Assuming these differences are statistically significant, this suggests that the transition state during autoxidation is changing with water concentration and is consistent with changes in the coordination sphere of the metals from species such as $[Co(II)(HOAc)_4(OAc)]_2^{2+}$ in anhydrous acetic acid to species such as $[Co(II)(H_2O)_4(OAc)]_2^{2+}$ at higher water concentrations.[23]

Conclusions

The aerobic oxidation of benzaldehydes allows one to study the effect of water and catalyst on the free radical chain oxidation mechanism. Uncatalyzed aerobic oxidations of benzaldehyde in water/acetic acid mixtures are initially highly reactive but the reactions terminate before high yields of benzoic acids are achieved. They are also very unselective as by-products totalling 5.6% are observed due to the thermal decomposition of the peroxy acid (giving benzene, phenol) and the Baeyer–

Table 3. Summary of rates for the elementary reactions in Co/Mn/Br catalysts. Slope, standard error, and correlation coefficient are from linear regression.

Entry	Reaction	[metal]M	[substrate] M	Temp. [°C]	[water] mol fraction	Slope (std. dev.)	Reaction no., R^2	Ref.
1	Co(III)s + KBr	0.001	0.02	23	0.15–0.69	0.271 (0.033)	5, 0.958	this work
2	Co(III)s + Mn(II)	0.005	0.0125	20	0.15–0.49	–	–	[12]
3	Co(III)s + Mn(II)	0.001	0.02	23	0.15–0.69	0.347 (0.028)	5, 0.99	[12]
4	Co(II) + X[b]	0.02	solvent	113	0–0.27	0.98 (0.31)	3, 0.91	[8]
5	Co(II) + X[b]	0.04	solvent	113	0–0.27	0.83 (0.07)	3, 0.99	[8]
6	Co(II) + X[b]	0.06	solvent	113	0–0.27	0.80 (0.03)	3, 0.998	[8]
7	Co(II) + MCPBA[a]	not given	not given	0	0.016–0.764	0.174 (0.002)	8, 0.999	[12]
8	Co(III)a to Co(III)s	0.01	–	20	0.15–0.59	0.276 (0.010)	6, 0.995	[12]
9	Co(III)s + HBr	0.0005	not given	23	0.15–0.59	0.192 (0.015)	5, 0.981	[12]
10	Mn(III) + HBr	0.005	0.01	23	0.27–0.45	0.37 (0.17)	3, 0.82	this work

[a] MCPBA = 3-chloroperoxybenzoic acid.
[b] Co(II) + X is cobalt being oxidized by an unknown, 'adventitious' peroxide in the acetic acid solvent as reported in Ref.[4]

Villiger reaction (giving phenyl formate, phenol, quinones, carbon dioxide). The reason for the premature termination of the reaction is that phenol, a strong anti-oxidant, forms in sufficiently high concentrations. The cobalt present reacts very rapidly and selectively with the peroxybenzoic acid virtually eliminating both the thermal decomposition and the Baeyer–Villiger reaction. As a result no phenol forms and the reaction goes to completion and the by-products are no longer seen. A Co/Mn/Br catalyst is more selective than a Co catalyst since it further reduces carbon dioxide formation due to a lower steady-state Co(III) concentration which further reduces the decarboxylation.

The reduction of undesirable by-product formation by addition of catalyst is seen at very low catalyst concentrations (0.0001 M). The formation of the by-products continues to decrease with increases in catalyst concentration and all traces of them are eventually eliminated at around 0.002 M. There is an increase in terephthaldicarboxaldehyde yield from 4-methylbenzaldehyde with increase in catalyst concentration. Both of these phenomena illustrate the effect of non-catalyzed reaction pathways being replaced by catalyzed ones.

The presence of water apparently reduces the Baeyer–Villiger reaction to the phenyl formate so there is less yield loss to the benzoic acid. However, the water enhances the rate of phenyl formate hydrolysis to the phenol resulting in the reactions terminating earlier. Thus, as seen previously, the effect of water in metal/bromide catalyzed autoxidations is complex.

An analysis of the data available in the literature on the effect of water on *the elementary steps* in both non-catalyzed and catalyzed reactions shows that these steps are 'poisoned' by water in the acetic acid solvent, i.e., their rates of reaction decrease with increasing water concentration. It is suggested that one of the reasons for the decrease in rate is that the metal-acetic acid bonds are being replaced with metal-water ligands preventing the organic intermediate and transient species from entering the coordination sphere of the catalytic metals.

Experimental Section

The glass autoclave, procedure, calculations, and GC instrument have been previously described.[6] 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. Yields were calculated from the GC data. Unless otherwise stated, all reactions were performed at 95 °C 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* GC. At the same time, on-line gas analysis was performed for dioxygen, dinitrogen, carbon monoxide and carbon dioxide.

References

[1] W. Partenheimer, *Catal. Today* **1995**, *23*, 69.
[2] W. Partenheimer, *Adv. Synth. Catal*. **2004**, *346*, 297.
[3] a) N. G. Ariko, N. I. Mitskevich, V. A. Lashitskii, *Neftekhimiya* **1972**, *12*, 370; b) G. S. Golubev, V. N. Vleksandrov, V. V. Khomin, V. G. Nazimok, *Neftekhimiya* **1975**, *15*, 593; c) E. Marko, L. Treindl, *React. Kinet. Catal. Lett*. **1992**, *46*, 345; d) J. H. Jensen, *J. Am. Chem. Soc*. **1983**, *105*, 2639; e) M. G. Roelofs, E. Wasserman, J. H. Jensen, A. E. Nader, *J. Am. Chem. Soc*. **1983**, *105*, 6329; f) M. G. Roelofs, E. Wasserman, J. H. Jensen, A. E. Nader. *J. Am. Chem. Soc*. **1987**, *109*, 4207.
[4] W. Partenheimer, *J. Mol. Catal*. **1991**, *67*, 35.
[5] a) C. F. Hendriks, H. C. A. van Beek, P. M. Heertjes, *Ind. Eng. Chem. Prod. Res. Dev*. **1978**, *17*, 260; b) C. E. H. Bawn, J. E. Jolly, *Proc. Roy. Soc. London* **1956**, *236*, 297; c) F. Marta, E. Boga, M. Matoc, *Discuss. Faraday Soc*. **1968**, *46*, 173; d) A. M. Nemecek, C. F. Hendriks, H. C. Van Beek, M. A. DeBruyn, E. J. H. Kerckhoffs, *Ind. Eng. Chem. Prod. Res. Dev*. **1978**, *17*, 133; e) C. E. H. Bawn, *Discuss. Faraday Soc*. **1953**, *14*, 181; f) C. F. Hendriks, C. A. van Beek, P. M. Heertjes, *Ind. Eng. Chem. Prod. Res. Dev*. **1977**, *16*, 270.
[6] W. Partenheimer, V. V. Grushin, *Adv. Synth. Catal.* **2001**, *343*, 102.
[7] R. A. Sheldon, J. K. Kochi, *Metal Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**, p. 21.
[8] W. Partenheimer, R. K. Gipe, *Nature of the Co-Mn-Br Catalyst in the Methylaromatic Compounds Process: Kinetic and Thermodynamic Studies*, in *Catalytic Selective Oxidation*, (Eds.: S. T. Oyama, J. W. Hightower), American Chemical Society, Washington, D. C., **1993**.
[9] G. H. Jones, *J. Chem. Research (M)* **1981**, 2801.
[10] J. Igarashi, R. K. Jensen, J. Lustyk, S. Korce, K. U. Ingold, *J. Am. Chem. Soc*. **1992**, *114*, 7719 and 7727.
[11] K. Ukegawa, Y. Kamiya, *Bull. Chem. Soc. Jap*. **1976**, *49*, 1632.
[12] M. P. Czytko, G. K. Pub, *Ind. Eng. Chem. Prod. Res. Dev*. **1961**, *20*, 481.
[13] L. J. Csanyi, K. Jaky, *J. Catal*. **1993**, *141*, 721..
[14] W. Partenheimer, *A Chemical Model for the Amoco 'MC' Oxygenation Process to Produce Terephthalic Acid*, in: *Catalysis of Organic Reactions*, (Ed.: D. W. Blackburn), Marcel Dekker, New York, **1990**.
[15] S. S. Lande, J. K. Kochi, *J. Am. Chem. Soc*. **1968**, *90*, 5196.
[16] J. M. Anderson, J. K. Kochi. *J. Am. Chem. Soc*. **1970**, *92*, 2450.
[17] P. Roffia, P. Callini, L. Motta. *Ind. Eng.Chem. Prod. Res. Dev*. **1984**, *23*, 629.
[18] W. Partenheimer, *A Method for the Preparation of Pyromellitic Acid from Durene via Liquid Phase Oxidation*, in: *Catalysis of Organic Reactions*, (Ed.: D. W. Blackburn), Marcel Dekker, New York, **1994**.
[19] R. A. Sheldon, J. K. Kochi, *Metal Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**, p. 360.

[20] R. K. Gipe, W. Partenheimer *Catalysts by Rational Design: Prediction and Confirmation of the Properties of the Co/Ce/Br Liquid -Phase Autoxidation Catalyst Based on the Kinetic Similarity to the Co/Mn/Br Catalyst*, in: *Studies in Surface Science and Catalysis*, (Eds.: R. K. Grasselli, S. T. Oyama, A. M. Gaffney, J. E. Lyons), Elsevier, Amsterdam, **1997**, p. 1117

[21] a) P. D. Metelski, J. H. Espenson, *J. Phys. Chem. A* **2001**, *105*, 5881; b) X-D Jiao, J. H. Espenson, *Inorg. Chem.* **2000**, *39*, 1549.

[22] J. March, *Advanced Organic Chemistry*, McGraw-Hill, London, 2nd edn., **1977**, 253.

[23] W. Partenheimer, *J. Mol. Catal*. **2001**, *174*, 29.

[24] W. Partenheimer, *J. Mol. Catal.* **2003**, *206*, 105.

