



# The effect of zirconium in metal/bromide catalysts on the autoxidation of *p*-xylene

## Part II. Alternative metals to zirconium and the effect of zirconium on manganese(IV) dioxide formation and precipitation with pyromellitic acid

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### Abstract

Metals, such as Fe, V, Ti, Hf, have the same properties as Zr(IV), i.e. the ability to activate a Co/Mn/Br catalyst and to enhance the rate of benzaldehyde formation. There is a perfect correlation with the  $pK$  of hydrolysis, a measure of Lewis acidity, and the degree of activation of the metals. The data is consistent with the activation mechanism being a Lewis acid catalyzed dehydration of the benzyl peroxides. Certain metals, including zirconium, inhibit the formation of the undesirable black, insoluble  $MnO_2$ , during Co/Mn/Br catalyzed autoxidations. In general, the increasing ability of a metal to avoid  $MnO_2$  formation is correlated to increasing  $Z^2/r$  values ( $Z$  is the formal valence state and  $r$  the ionic radius). It is proposed that the metal can avoid  $MnO_2$  formation by decreasing the precursor concentration of  $Mn-OH_2$ . The solid  $MnO_2$  produced during an autoxidation can produce radicals derived from *p*-xylene which further react to form undesirable dimeric by-products. The presence of Zr(IV) or Hf(IV) kinetically and thermodynamically inhibit the precipitation of the Co(II) and Mn(II) pyromellitic acid (PMA) complexes. The phenomena of activation, prevention of Mn(IV) formation, and solubilization in the presence of select carboxylic acids all occur when the metal has high Lewis acidity. This is consistent with the ability of Zr and Hf to preferentially complex with the acid. Mechanisms are suggested for the above phenomena which illustrates the intimate role that the solvent, acetic acid, performs in these autoxidations.

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### 1. Introduction

The activating and selectivity changes of zirconium salt addition to metal/bromide catalysts is described

in part I of this series [1]. One of the primary methods to incorporate molecular oxygen into hydrocarbons to give oxygenates is the highly selective and active metal/bromide catalysts. Over 251 reagents, ranging from alkylaromatics, heterocyclics, organometallics, and aliphatics, have been converted to alcohols, acetates, ketones, aldehydes, and carboxylic acids. Over 30 different metal/bromide combinations have been

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utilized using, most often, acetic acid as the solvent [2]. Two difficulties that can occur with this methodology is the formation of highly insoluble manganese(IV) dioxide and the precipitation of the catalyst metals with certain aromatic carboxylic acids particularly pyromellitic acid (PMA).

Sixteen of the reported 30 metal/bromide catalysts contain the element manganese. These are homogeneous, liquid-phase systems that require soluble forms of the catalyst [2]. UV-Vis studies have established that the working oxidation states for manganese are Mn(II)–Mn(III) [3]. It is known that under specific circumstances, such as at high water concentration or high reagent oxygen concentration [4,5], that a soluble form of manganese(IV) can form which subsequently reacts with water to form the highly insoluble, manganese(IV) dioxide. This can be a problem in commercial processes such as in the production of terephthalic acid from *p*-xylene using a Co/Mn/Br catalyst. A majority of the terephthalic acid precipitates during the oxidation reaction and if manganese(IV) dioxide does form, then a mixture of the black manganese dioxide with the white terephthalic acid produces a ‘grey’ product with high manganese content. Additionally loss of the catalytically active form of manganese will result in a reduced activity because there is a strong synergistic interaction between Co and Mn. The loss of manganese also increases the rate of carbon monoxide and carbon dioxide formation because the rapid reaction of Mn(II) with Co(III) lowers the steady-state concentration of the Co(III). Co(III) is known to rapidly decarboxylate carboxylic acids.

The formation of aromatic acids during autoxidation can cause a number of phenomena such as activation or deactivation, elimination of the induction period, and precipitation of the catalyst metals [2]. Catalyst metals precipitation can occur during the oxidation of 1,2,3-trimethylbenzene (hemimellitene), 1,2,4-trimethylbenzene (pseudocumene) and 1,2,4,5-tetramethylbenzene (durene) because of the formation of 1,2,3-tricarboxybenzene (hemimellitic acid), 1,2,4-tricarboxybenzene (trimellitic acid) and 1,2,4,5-tetracarboxybenzene (pyromellitic acid), respectively [2]. Pyromellitic acid forms insoluble cobalt and manganese salts which can precipitate during the oxidation reaction and *prematurely* terminate the reaction and subsequently result in low pyromellitic acid yields. The precipitation can be avoided by (a)

increasing the water concentration, (b) by decreasing the pH and (c) by increasing the bromide concentration [6]. We report here for the first time that certain metals, zirconium and hafnium can also be used to decrease precipitation of these metals.

## 2. Experimental

The reactor, procedures, and calculations have been previously described [7]. The different sources of zirconium were obtained from Aldrich. The cobalt and manganese salts were the (+II) acetate tetrahydrates. The bromide source was sodium bromide. Other compounds used as received from commercial sources were yttrium(III), neodymium(III), chromium(III), antimony(III), iron(III) acetates, molybdenum(VI) dichlorodioxide, tungsten(VI) ethoxide, niobium(V) ethoxide, vanadium(IV) oxide bis(2,4-pentandioate), titanium(IV) ethoxide, hafnium(IV) tetrachloride.

### 2.1. Procedure for the observation of manganese(IV) dioxide formation

A typical experiment consisted of the addition of cobalt(II) acetate tetrahydrate (0.249 g, 1.00 mmol) and manganese(II) acetate tetrahydrate (0.245 g, 1.00 mmol) to 100 cm<sup>3</sup> of 30.0 wt.% water/acetic acid and the mixture heated to reflux. 3-Chloroperoxybenzoic acid (0.769 g, 77% purity, 0.349 mmol) was dissolved in 10.01 g of acetic acid at room temperature, and 1.018 g of this solution added to the refluxing Co and Mn solution. *Note:* it is important to use a freshly prepared solution of 3-chloroperoxybenzoic acid since the latter slowly decomposes in acetic acid. There is a flash of green color (formation of Co(III)) which then turned dark (formation of Mn(III) and Mn(IV)). After 5 min a black precipitate was present. After 15 min at reflux, the solution is cooled and the black solids filtered off, air dried and analyzed. The black solids consisted of 30.6 wt.% Mn and 0.70% Co. 14% of the Mn and 3.0% of the Co precipitated. Repetition of these experiments in the presence of different substances is given in Table 3. Analysis of the combined solids from eight different experiments with Co/Mn/Zr present gave 47.1% manganese and 0.31% Zr. Calculated Mn content of MnO<sub>2</sub>·1.5H<sub>2</sub>O is 49.1%.

*Procedure for the precipitation of catalyst metals with pyromellitic acid:* The metal acetates were dissolved in 100 g of a 10 wt.% water/acetic acid solution and heated to reflux for 30 min. After 30 min at reflux, PMA was added to each of the above solutions at a PMA/(Co + Mn) ratio of 0.45 mol/mol. The solution was then cooled to room temperature, filtered the next day, and filtrate analyzed for metals via inductively coupled plasma (ICP). Results are given in Table 4 and Fig. 8.

### 3. Results and discussion

#### 3.1. Effectiveness of metals to activate a Co/Mn/Br catalyst

The effectiveness of Zr to activate autoxidation catalysts have led others, as well as us, to evaluate other potential metals. For the Co/M catalyzed autoxidation of *p*-xylene, it was found that zirconium activated the cobalt system, as well as a number of other metals including rare earths like neodymium and gadolinium [8]. Another set of workers found that Zr and Hf had a strong activation effect while Th had a moderate effect [9,10]. For the Co/methyl ethyl ketone (MEK) catalyzed autoxidation of *p*-xylene, Zr but also neo-

dymium and aluminum were claimed to activate the rate of reaction [11]. It was found during the autoxidation of cyclohexane with a Co catalyst that only Zr and Hf activated the Co catalyst [12]. In this study, the evaluation of different metals using a Co/Mn/Br catalyst with *p*-xylene are given in Table 1. The table is arranged in order of increasing degree of activation. Besides zirconium, Fe(III), V(IV), Ti(IV) and Hf(IV) also activate the autoxidation. When used in the same concentration as Zr(IV), the metals are in the order Hf(IV) = Zr(IV) > Ti(IV) > V(IV) > Fe(III). Hafnium and zirconium are being compared as their chloride salts. A better choice would have been to compare their acetates since this is the anion characteristic of the solvent, acetic acid. The hafnium(IV) acetate is not available, however. The acetate of Zr(IV) appears to be more active than the tetrachloride salt. Invariably, where activation is seen, also a higher value of the aldehyde/(alcohol + acetate) ratio is also seen. This suggests a common mechanism of activation and this is consistent with the Lewis acid benzyl peroxide dehydration theory of activation as previously discussed in Part I of this series [1].

If our interpretation is correct [1], activation would require a Lewis acidity higher than Co(II) and Mn(II), the ability of the activator metal to form a polynuclear complex, and the same mechanism with the associated

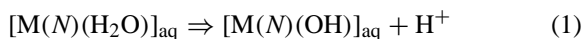
Table 1  
Activity and aldehyde/alcohol ratio of Co/Mn/M/Br catalysts

M in Co/Mn/M/Br (1)	Metal, M (mol/mol)	$d(O_2)/dt$ (cm <sup>3</sup> /min)	$d(pX)/dt$ ( $\times 10^5$ , s <sup>-1</sup> )	Degree of activation	Ratio <sup>a</sup>	pK hydrolysis
Ce(III)	0.115	1.30 (0.14)	2.16 (0.13)	0.77	2.4	Ce(IV), -1.1
Nd(III)	0.082	1.65 (0.26)	2.41 (0.19)	0.86	2.4	8.0
W(IV) (3)	0.0010, 0.005	1.38 (0.17)	2.53 (0.29)	0.90	2.2	Not available
Y(III)	0.0871	1.38 (0.17)	2.53 (0.29)	0.90	2.2	7.8
Cr(III)	0.0983	1.05 (0.10)	2.63 (0.11)	0.94	2.1	3.66
Mo(IV) (2)	0.080, 0.14	1.61 (0.26)	2.67 (0.15)	0.95	2.5	Not available
No metal (2)	0.0	2.49 (0.08)	2.81 (0.18)	1.00	2.1	-
Sb(III)	0.0978	1.06 (0.05)	2.92 (0.27)	1.04	2.2	Not available
Nb(V)	0.082	1.53 (0.29)	2.97 (0.34)	1.06	2.4	Not available
Fe(III)	0.151	1.40 (0.14)	3.03 (0.23)	1.08	3.0	3.05
V(IV) (5)	0.023–0.21	2.87 (0.35)	3.48 (0.29)	1.24	4.3	V(V), 3.2
Ti(IV) (2)	0.096, 0.91	1.88 (0.21)	3.83 (0.45)	1.36	3.1	Not available
Hf(IV) (as Cl <sup>-</sup> )	0.096	6.10 (0.32)	9.81 (0.81)	3.49	5.9	0.25
Zr(IV) (as Cl <sup>-</sup> )	0.096	5.88 (0.15)	10.1 (0.09)	3.70	5.7	-0.3
Zr(IV) (5) (as OAc <sup>-</sup> )	0.058–0.47	7.38 (0.54)	12.3 (1.6)	4.36	4.8	-0.3

[Co] = 0.0100 M, Co/Mn = Br/(Co + Mn) = 1.0 mol/mol. Arranged with increasing degree of activation. Numbers in parentheses in first column are number of experiments.

<sup>a</sup> Aldehyde/(alcohol + acetate) ratio at 30% conversion.

favorable kinetics. One can consider two measures of the Lewis acidity for the metal. One is the theoretical value of  $Z^2/r$  where  $Z$  is the formal valence state of the metal and  $r$  is the ionic radius. For a bond of 100% ionic character, it would be a measure of the M–O bond strength. As the values become larger, the bond becomes more covalent and the relationship is less certain. Another measure of Lewis acidity is the hydrolysis constant, where  $N$  is the formal valence of metal  $M$ :



The hydrolysis  $pK$  values reported in Table 1 have been critically evaluated [27]. Hydrolysis constants are dependent not only on the Lewis acidity, but on the coordination number and type of metal–oxygen bonds, i.e. M–OH and M=O, for example. Both of these measures of Lewis acidity become less certain as the formal valence of the metal increases since M=O bonds become more prevalent at the higher values, for example V(IV)=O and V(V)(=O)<sub>2</sub>.

Fig. 1 gives the very satisfying correlation of the  $pK$  of the metals with the degree of activation observed when a metal,  $M$ , was added to the Co/Mn/Br catalyst. One would not necessarily expect this correlation with the transition metals. They have variable valence states and can subsequently interfere with the Co, Mn, Br redox cascade as shown in Fig. 2. Since Co(III) and Mn(III) are the active catalytic species, any metal

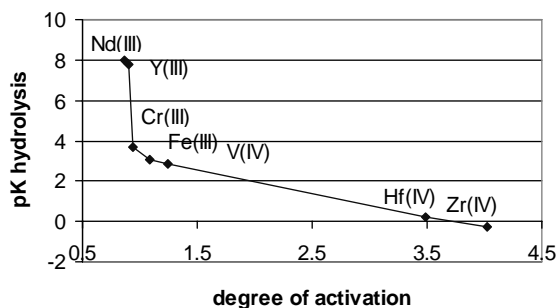


Fig. 1. Correlation of the degree of activation due to the addition of the given metal to a Co/Mn/Br catalyst with the  $pK$  of the hydrolysis constant of the metal. Not shown is Ce(IV), see text.

that can readily and rapidly reduce Co(III) or Mn(III) would deactivate the catalyst. The one point *not shown* in Fig. 1 is that for Ce(IV) which does not correlate. Its  $pK$  is  $-1.1$  which makes it a very strong Lewis acid which, barring other factors, should have strongly activated the system. This has not been observed. This is understandable because of the known rate constants of reactions:

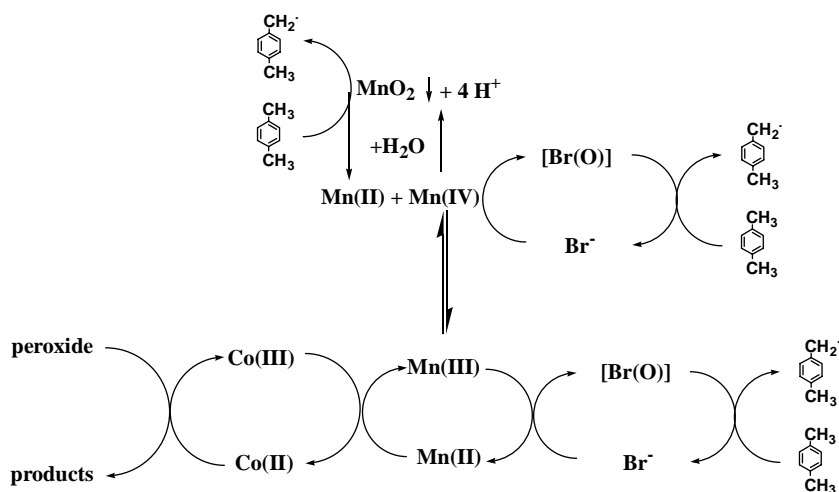
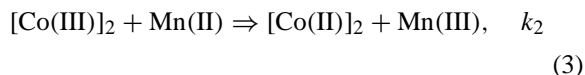
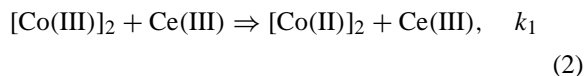


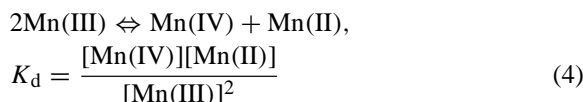
Fig. 2. Suggested chemistry of Mn(IV) dioxides precipitation occurring during the autoxidation of *p*-xylene using a Co/Mn/Br catalyst.

where  $k_1/k_2$  is 2.7 [1]. Hence, the Co prefers to react with Ce rather than Mn and a Co/Ce/Br catalyst results. The Co/Ce/Br is known to be less active than the Co/Mn/Br catalyst. The Co/Mn/Br catalyst is 2.0 (towards toluene) and 1.7 (towards *p*-xylene) more active than the Co/Ce/Br catalyst [1].

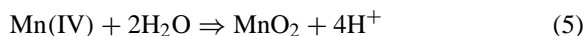
### 3.2. The reduction of MnO<sub>2</sub> formation in the presence of Zr and other metals

#### 3.2.1. Known chemistry and experimental results

The known chemistry is summarized in Fig. 2. Mn(III) spontaneously disproportionates in water (0.56 V, −12 kcal/mol) and in acetic acid/water mixtures (ligands omitted for clarity):



The equilibrium constants for this reaction in acetic acid/water solutions have been measured via ESR [13] presumably at room temperature and are reproduced in Table 2 along with the calculated equilibrium concentration of soluble Mn(IV). The equilibrium concentration of Mn(IV) increases with water concentration. The soluble Mn(IV) reacts with water to form the highly insoluble, black MnO<sub>2</sub>:



The chemistry on Fig. 2 has been performed by addition of 3-chloroperoxybenzoic acid (MCPBA) to a mixture of Co(II) and Mn(II) in a refluxing acetic acid/water mixture. The amount of 3-chloroperoxybenzoic acid is limited to a MCPBA/Co ratio of 0.35/1.0 mol/mol because the steady-state concentration of these peracids are believed to be low during an autoxidation. MCPBA is a two-electron

oxidant hence the initial Mn(III) concentration was 0.0070 M. The use of 3-chloroperoxybenzoic acid as one of the oxidants of Co(II) is justified because it is structurally similar to the 4-methylperoxybenzoic acid and 4-carboxyperoxybenzoic acid that form during the autoxidation of *p*-xylene.

The addition of 3-chloroperoxybenzoic acid to the initially pink solution results in the rapid formation of a green color due to Co(III) formation which then reacts with Mn(II) to form brown Mn(III). If the solution contains 30 wt.% water, the solution turns dark and solids form due to manganese(IV) dioxide formation. MnO<sub>2</sub> is not seen at lesser water concentration of 20 or 10%. Apparently, the equilibrium concentration of Mn(IV) is too small at these lower water concentrations so that no solid MnO<sub>2</sub> forms. One apparently is observing at reflux temperature a similar change to what has been observed at room temperature where the equilibrium value of Mn(IV) increases with water concentration, Table 2.

One would expect a reduction or elimination of Mn(IV) formation with the addition of sodium bromide, see Fig. 2, since the bromide can react with Mn(III) which would be in competition with the Mn(IV). Indeed this is seen. At Br/Co ratios of 1.0, 2.0, and 3.0 precipitation is seen, but *not* when the Br/Co ratio is 4.0. This is consistent with the formation of MnO<sub>2</sub> during commercial production of terephthalic acid since it occurs when the Br/(Co + Mn) ratio is too low [5]. Table 3 summarizes a set of experiments where different Zr(IV) compounds are added to the Co/Mn mixture and then 3-chloroperoxybenzoic acid is added. No MnO<sub>2</sub> precipitation is seen if sufficiently high Zr concentration is used. A number of other metals also can reduce Mn(IV) formation. If one defines the effectiveness of a metal salt, M, to prevent MnO<sub>2</sub> formation as the lowest M/Co ratio observed *without* MnO<sub>2</sub> formation, then one has: V > Ti > Hf > Ce > Zr > Cr = Fe. Metal salts that are ineffective at M/Co ratios of 1.0 are Na, Al, Ca, Cu, Zn, La, Nd. In continuous [5] and batch autoxidation [4] of *p*-xylene it has been observed that Ce, Fe, and Cr diminish the propensity for MnO<sub>2</sub> formation which is the same as seen here. It appears that the results of the highly complex chemistry occurring during the autoxidation of *p*-xylene can be accurately duplicated in a simple beaker experiment.

Table 2

Calculated equilibrium values of Mn(IV) from the disproportionation of Mn(III) in acetic acid/water mixtures

Water (vol.%)	Water (M)	$K_d$ ( $\times 10^6$ )	Mn as Mn(IV) (%)
1.0	0.56	7.60	2.7
4.7	2.61	8.00	2.8
9.1	5.06	30.0	5.2
16	8.89	800	22

$K_d$  from [13].

Table 3

Observation of manganese(IV) dioxide formation by addition of 3-chloroperoxybenzoic acid to a Co(II)/Mn(II) mixture in 30 wt.% water/acetic acid

Compounds	MnO <sub>2</sub> Pptn observed, M (mol)/Co (mol) = R <sub>1</sub>	MnO <sub>2</sub> Pptn not observed, M (mol)/Co (mol) = R <sub>2</sub>	Effectiveness factor	Z <sup>2</sup> /r values from [28]
VO(acac) <sub>2</sub>	0.008	0.017, 0.033, 0.072, 0.132, 0.287, 0.513	2.2	V(V), 42.4
Ti(IV)O(acac) <sub>2</sub>	0.029	0.065, 0.127	1.3	25.4
Hf(IV) ethylhexano- <i>t</i> -butoxide	0.065	0.130	1.0	20.5
Ce(III) acetate	0.130	0.92, 0.51, 0.24	0.73	Ce(IV), 17.0
Zr(IV) butoxide	0.140	0.88, 0.52, 0.27	0.67	20.3
Cr(III) acetate	0.180	1.5, 0.73, 0.38	0.55	10.7
Zr(IV) carbonate	0.220	0.80, 0.39	0.53	20.3
Fe(II) acetate	0.240	1.0, 0.50	0.43	Fe(III), 12.2
Zr(IV) acetate	0.240	1.0, 0.50	0.43	20.3
Nb(V) ethoxide	0.500	1.00	0.12	36.2
Ni(II) acetate	0.990		0	5.80
Al(III) acetate	1.00		0	17.3
Ca(II) acetate	1.00		0	12.9
Cu(II) acetate	1.00		0	5.56
La(III) acetate	1.00		0	7.89
Na(I) acetate	1.00		0	1.03
Zn(II) acetate	1.00		0	5.41
Nd(III) acetate	1.00		0	8.65

### 3.2.2. Definition of the effectiveness factor for Mn(IV) precipitation and its correlation with Z<sup>2</sup>/r

One can express the effectiveness of a given metal to avoid MnO<sub>2</sub> semi-quantitatively as follows. The experiments were designed to locate a range of metal concentrations, M, that when added to a 0.01 M solution of cobalt and manganese would avoid the precipitation of manganese dioxide. The lowest value of M/Co (mol/mol) where black solids are not seen is defined as R<sub>1</sub>, and the highest value where solids are seen is R<sub>2</sub>. Since the 'true' breakeven ratio occurs somewhere between these values, the average of R<sub>1</sub> and R<sub>2</sub> was used. The effectiveness factor is then defined as

$$F_{\text{effective}} = \log \left( \frac{1}{R_{\text{average}}} \right)$$

When solids were observed at the highest concentration used (a M/Co ratio of 1.00), a R value of 0.00 was assigned, see Table 3.

The correlation of the effectiveness factor with Z<sup>2</sup>/r (Z is charge on metal ion and r is its ionic radius) is given in Fig. 3. Ignoring outlying points for Al(III) and Nb(V) and assuming a linear relationship one obtains

for 14 pts:

$$F_{\text{effectiveness}} = 0.0583(4) \left( \frac{Z^2}{r} \right) - 0.278(68),$$

where R<sup>2</sup> = 0.946

The correlation suggests that finding a metal salt that will prevent manganese(IV) dioxide formation is a matter of using a metal salt with a Z<sup>2</sup>/r higher than 9. In the correlation one needs to make some assumptions. For the oxidation state of cerium, Ce(IV) was chosen rather than Ce(III) because it is known that

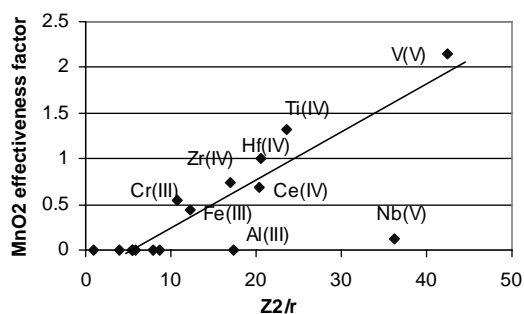


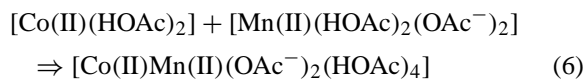
Fig. 3. Relationship between the effectiveness factor for MnO<sub>2</sub> and Z<sup>2</sup>/r (Z = valence state of metal, r = ionic radius).



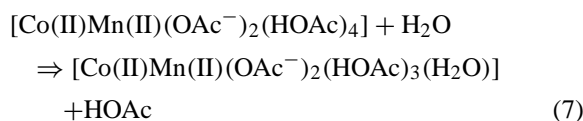
Co(III) reacts more rapidly with cerium(III) than does Co(III) with Mn(II) (see above). Therefore, Ce(III) would be initially oxidized to Ce(IV). The initial vanadium compound used was V(IV)(acac)<sub>2</sub>O. We have chosen to use V(V) because this is the more stable oxidation state in the presence of air. The major exceptions in the correlation is niobium(VI) and aluminum(III). This may be for kinetic reasons in which the time to form the necessary Mn–metal complex may be too slow. Three different Zr compounds with different ligand fields do give slightly different effectiveness factors ranging from 0.43 to 0.67 which may be due to variation in the rate of Mn–Zr formation.

### 3.2.3. Proposed mechanism of MnO<sub>2</sub> formation

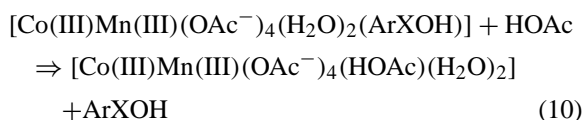
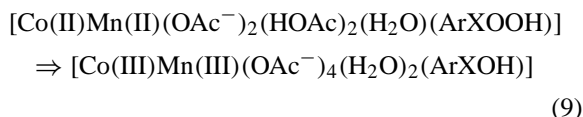
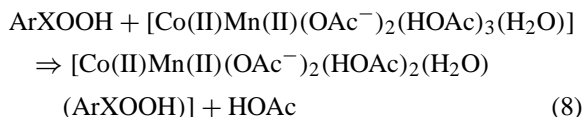
A suggested mechanism for manganese(IV) dioxide formation, consistent with experimental observations would be as follows. One has a choice of starting with a one electron oxidant, such as the peroxy radical, ArCH<sub>2</sub>OO• or a two-electron oxidant such as a benzylic peroxide, ArCH<sub>2</sub>OOH, or peracid, ArC(=O)OOH. Since the oxidation of Mn(II) to Mn(IV) is a two-step change the two-electron oxidant was used. The use of a single-electron oxidant would be less kinetically favorable since it would require a bi-molecular interaction of the peroxy radical with the metal. It is known that peracids and peroxides *prefer* to react with Co(II) or Mn(II) via dimeric polynuclear, rather than monomeric compounds [14,15] and the reaction of the peracid is much faster with the cobalt than the manganese [3,15]. The mechanism therefore starts with the formation of a dinuclear [Co(II)Mn(II)] complex in which the cobalt is first oxidized. Using the notation introduced previously [1] where only the ligands necessary for the mechanism are placed in the coordination sphere:



Water, which is necessary for the MnO<sub>2</sub> formation is placed into the coordination sphere at this point because the rate of ligand exchange is probably faster for Co(II) and Mn(II) than for Mn(III) and Co(III):

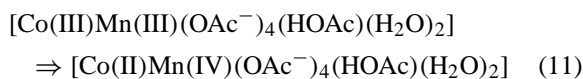


Oxidation then occurs with either the peracid or peroxide (ArXOOH; X=CH<sub>2</sub> or (=O)) in which the peroxide is first incorporated into the coordination and displaces the weak, labile HOAc ligand:

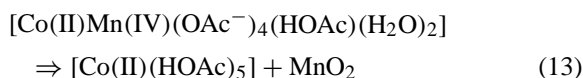


Reaction 9 could occur in a concerted manner as shown in Fig. 4. One starts with acetic acid bonded via the carbonyl oxygen consistent with that found for solid acetic acid compounds [31]. The benzyl hydroperoxide enters the coordination sphere and coordinates to the Co–Mn cluster. Simultaneous electron transfer and proton transfer from the acetic acid to the peroxide yields the water and benzylic alcohol. The acetic acid ligands become acetate ligands.

An internal electron transfer oxidizes the Mn(III) to Mn(IV):



The Mn(IV)–H<sub>2</sub>O bond will be stronger than the Mn(III)–H<sub>2</sub>O bond due to its enhanced Lewis acidity (i.e. Z<sup>2</sup>/r ratio), hence solvolysis of the water molecule will be enhanced when Mn(IV) is formed. The formation of MnO<sub>2</sub> can be viewed starting with two water molecules attached to the Mn(IV). The water molecules then simply protonate four acetate groups associated with the cobalt and manganese to give the desired products. See reaction 13, for a balanced equation and Fig. 5 for an intimate mechanism.



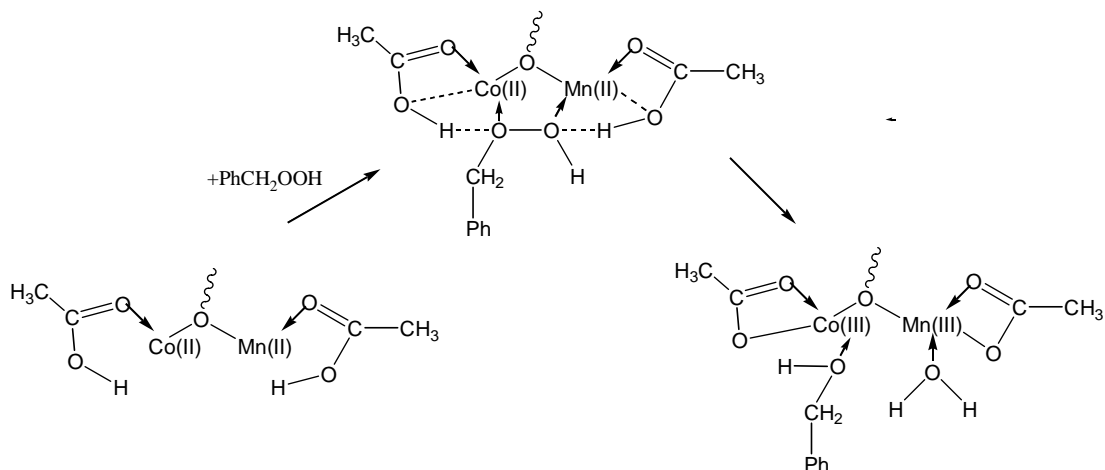
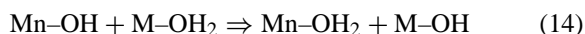


Fig. 4. Suggested concerted mechanism for the oxidation of a di-nuclear metal complex with benzyl peroxide. Two acetic acid ligands protonate the benzyl hydroperoxide with simultaneous electron transfer to the peroxide.

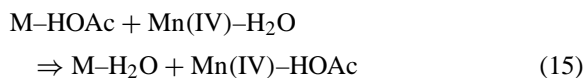
The mechanism rationalizes the increased tendency for  $\text{MnO}_2$  formation with increasing water concentration by the presence of reaction 7.

Using the above mechanism one can understand why a given metal can diminish the formation of  $\text{MnO}_2$  and why it is more effective with metals with higher  $Z^2/r$  values. There is evidence that acetic acid/water mixtures consist of micro-phases—one which is predominately acetic acid and the other aqueous [16,17]. If one assumed an aqueous solvent system with the intermediate  $\text{Mn(IV)-OH}$  species

leading to  $\text{MnO}_2$  precipitation, one can write:



In an acetic acid/water system one has:



Both of these reactions express a competition for the precursor to  $\text{MnO}_2$  formation. One desires a metal which would drive the reactions 14 and 15 to the right.

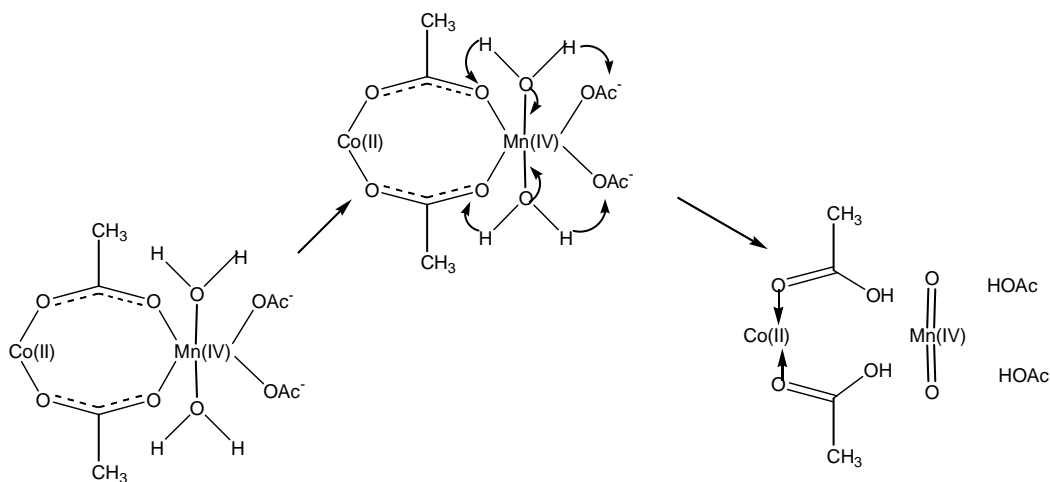
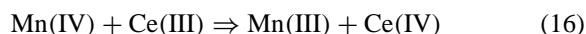


Fig. 5. Suggested formation of  $\text{MnO}_2$  from soluble  $\text{Mn(IV)}$ . Simultaneous protonation of the acetates by water with electron transfer to the  $\text{Mn-O}$  bond.



Assuming a bond with largely ionic character, both of these reactions will be favored to the right by a higher  $Z^2/r$  for metal M because of the increase in M–O bond strength. In reaction 14, the stronger the M–O bond will result in an increased weakening of the O–H bond, hence protonation of the Mn–OH will occur more easily to give Mn–OH<sub>2</sub>. For reaction 15, the M–water bond is stronger than the metal–HOAc bond, hence as metal M has increasingly higher  $Z^2/r$  ratio, it will increasingly favor the bonding of the water to it. The  $Z^2/r$  value of Mn(IV) is 27. By far, the most effective metal in avoiding manganese(IV) oxide formation is V(V) which has a  $Z^2/r$  value of 42. The next two most effective metals are Ti and Hf which have values of 24 and 21, respectively. This explanation is undoubtedly too simple, because metals with high charge have significant covalent character. Also the coordination number and the other ligands in the coordination sphere will affect the strength of interaction of the ligands of interest.

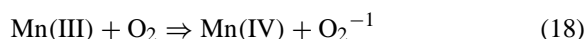
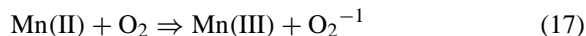
A possible mechanism could be that the metals reduce the Mn(IV) as it forms such as:



This is probably not true because the non-transition metals Zr(IV) and Hf(IV) are incapable of redox reactions yet they are effective at interfering with MnO<sub>2</sub> precipitation.

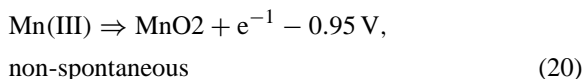
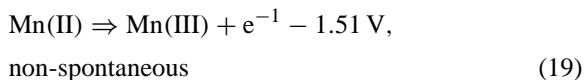
### 3.2.4. On the 'direct' oxidation of metals using dioxygen

It has been shown that the propensity of MnO<sub>2</sub> precipitation increased with higher reagent molecular oxygen concentration during the autoxidation of *p*-xylene and that the MnO<sub>2</sub> formation could be reduced by the presence of iron and chromium. It was therefore proposed [4] that a direct oxidation of Mn(II) or Mn(III) occurs:

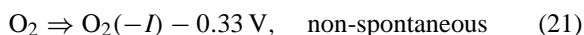


This type of 'direct' oxidation has also recently been proposed by others [30]. Both of these reactions are however highly non-spontaneous (positive free energy) for the following reasons. Mn(III) and Mn(IV) are both good stoichiometric oxidants as evidenced by

their non-spontaneous oxidation to their higher oxidation states:



What is often not recognized is the initial reduction of dioxygen is non-spontaneous, i.e. dioxygen has very little oxidizing power:



Clearly, direct oxidation of Mn(II) to Mn(III) or Mn(III) to Mn(IV) by dioxygen is therefore not feasible. The strong oxidizing power of oxygen is unleashed after the initial one electron reduction through the formation of peroxy species. In autoxidation this is through the reaction of the organic radicals, R•, with dioxygen, to give the peroxy radicals, ROO•. The increased propensity of MnO<sub>2</sub> with higher oxygen concentration is probably being caused by a secondary effect such as a higher percentage of inactive benzylic bromides during reaction.

### 3.2.5. Selectivity of *p*-xylene oxidation during MnO<sub>2</sub> precipitation

Both Mn(III) and Mn(IV) are known oxidants for alkylaromatic compounds and their mechanisms (electron transfer, hydride transfer, and hydrogen atom transfer) are known to be dependent upon the manganese ligand field [18]. Solid manganese(IV) oxide is a common reagent for the oxidation of organic substrates [13]. For example benzyl alcohol reacts with MnO<sub>2</sub> via a free radical mechanism to give benzaldehyde and Mn(II) [19]. This is a reaction whereby insoluble MnO<sub>2</sub> is converted back to a soluble form of active manganese, Mn(II), during autoxidation, see Fig. 2. We have reacted solid MnO<sub>2</sub>, the latter generated by the reaction of MCPBA with cobalt and manganese as described above, to *p*-xylene in 10% water/acetic acid *under nitrogen*. The observed products, via GC, are *p*-tolualdehyde, 4-methylbenzyl alcohol, and 4-methylbenzyl acetate. In addition two compounds with mass = 210 amu were identified by GC/MS as being consistent with the structure of 4,4'-dimethylbibenzyl

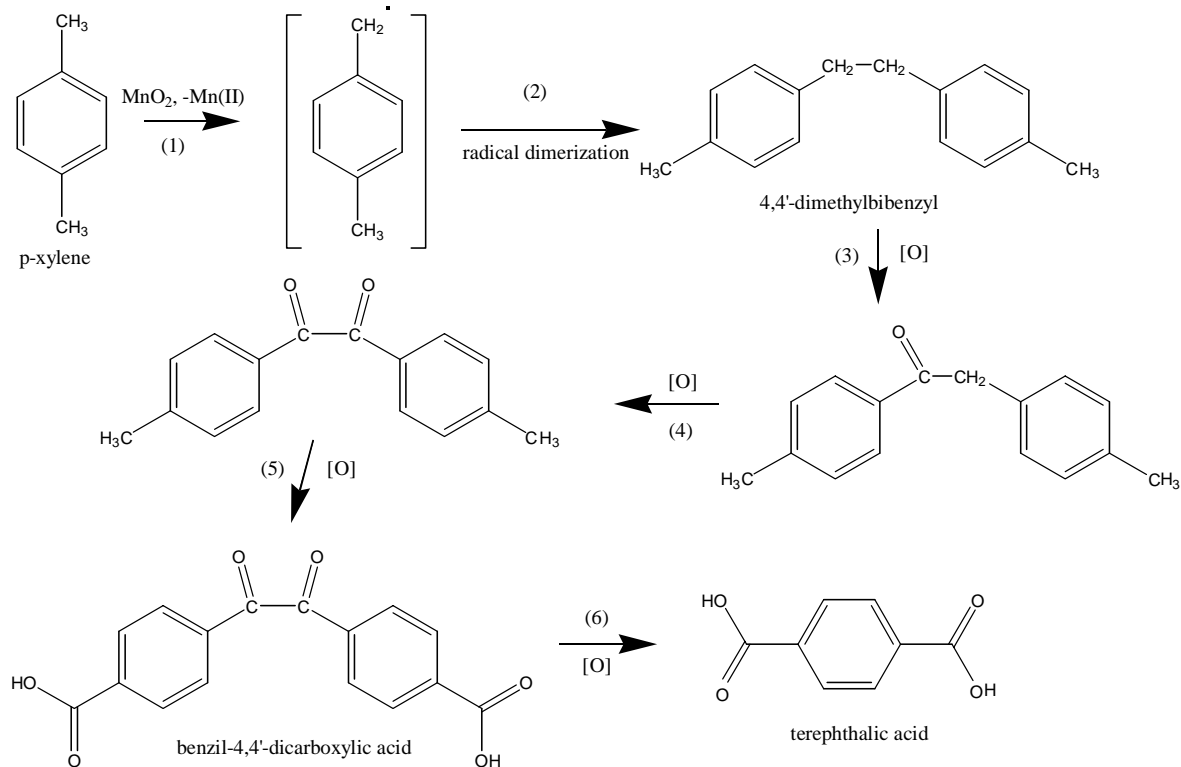


Fig. 6. Formation of 4,4'-dimethylbibenzyl from manganese(IV) dioxide with *p*-xylene under  $\text{N}_2$  and their expected subsequent products via aerobic oxidation.

and 2,5,4'-trimethyldiphenylmethane. Both products can form from the *transient 4-methylbenzyl radical*, see Figs. 6 and 7, and subsequently oxidized to known undesirable, yellow compounds [20]. The 4,4'-dimethylbibenzyl during subsequent oxidation leads first to 4,4'-dimethylbenzil (Fig. 6), since the bond dissociation energies of the methylene group is 364 kJ/mol as compared to 373 kJ/mol for the methyl group [21]. Subsequent oxidation leads to the oxidation of the methyl group to carboxylic acids and to the formation of the yellow benzil-4,4'-dicarboxylic acid. The benzil is known to cleave during further oxidation to terephthalic acid [2]. The formation of 2,5,4'-trimethyldiphenylmethane leads to the yellow anthraquinone-2,6-dicarboxylic acid and white tricarboxybenzophenone. The mechanism is shown in a simplified form in Fig. 7. The radical ring addition reactions are discussed in [22]. The fluorene carbons are preferentially oxidized to the methyl groups since the

bond dissociation energy of the former is 333 kJ/mol as compared to the methyl group of 373 kJ/mol [21].

### 3.3. The solubilization of Co(II)/Mn(II)/pyromellitic acid (PMA; 1,2,4,5-tetracarboxybenzene) complexes by the addition of Zr(IV) and Hf(IV)

The activity of metal/bromide catalyzed autoxidations are dependent upon the catalyst metals being soluble in solution. It is known that PMA can precipitate metals during autoxidation of durene and limit the yields of PMA [6]. Therefore, it is of interest to find a catalyst system where the solubility of Co and Mn can be enhanced.

The results of addition of PMA to a refluxing Co(II)/Mn(II) mixture and their subsequent filtration at room temperature are given in Table 4. The results are shown in graphically in Fig. 8. In all cases the PMA/(Co + Mn) ratio is 0.45 mol/mol. One can

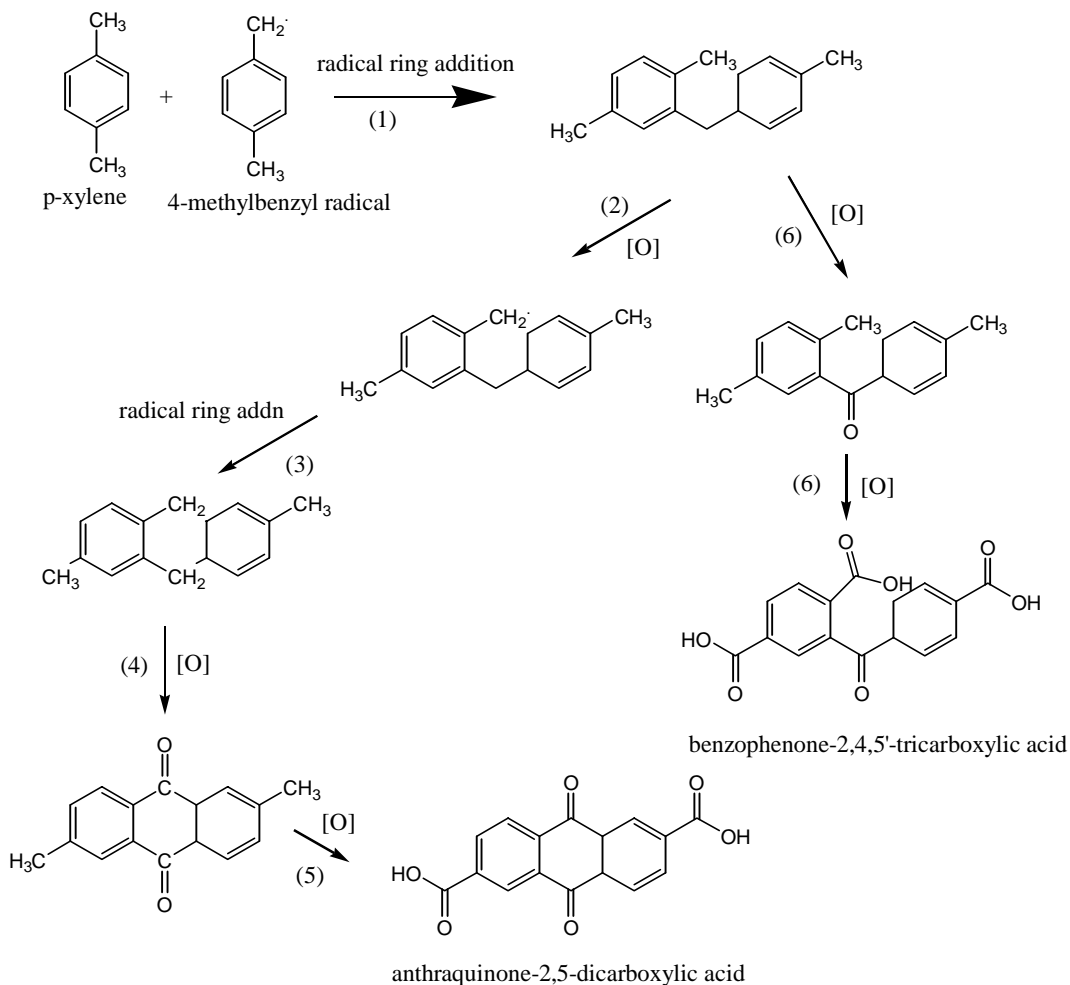


Fig. 7. Formation of 2,4,5'-trimethyldiphenylmethane and their expected products via aerobic oxidation.

Table 4

Concentration of metals in solution (molal) after addition of pyromellitic acid (PMA)/(Co + Mn) = 0.45 mol/mol) in 10 wt.% water/acetic acid solution<sup>a</sup>

Examples		Co (m)	Mn (m)	Zr (m)	Hf (m)	Observations
1	Co/Mn/Br	0.00407	0.00131	0.00000	0.00000	Immediate blue ppt
2	Co/Mn/Zr/Br	0.00407	0.00209	0.00065	0.00000	Blue ppt after 1 min
3	Co/Mn/Zr/Br	0.00424	0.00255	0.00126	0.00000	Blue ppt
4	Co/Mn/Hf/Br	0.00390	0.00264	0.00000	0.00081	Blue ppt after 10 min
5	Co/Mn/Hf/Br	0.00441	0.00410	0.00000	0.00106	Blue ppt
6	Co/Mn/Zr/Hf/Br	0.00407	0.00228	0.00030	0.00024	Blue ppt
7	Zr	–	–	Not measured	–	No pptn
8	Hf	–	–	–	Not measured	No pptn

<sup>a</sup> Initial concentrations for Co, Mn, PMA are 0.0050, 0.0050 and 0.0045 m, respectively. Initial concentration of Zr(IV) in examples 2, 3, 6 and 7 are 0.00059, 0.00116, 0.00029 and 0.00058 m, respectively. Initial concentration of Hf(IV) in examples 4, 5, 6 and 8 are 0.0057, 0.00119, 0.00027 and 0.0054 m, respectively.

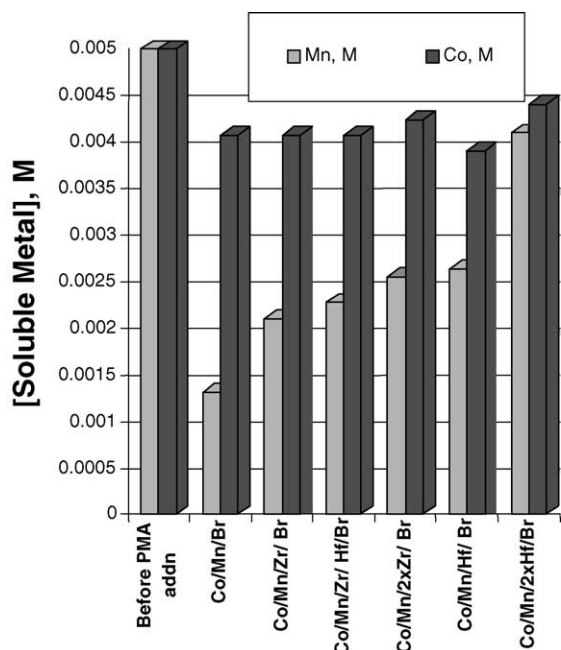


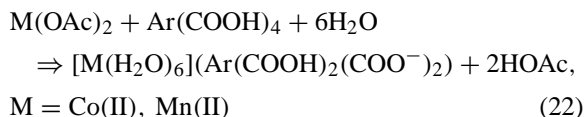
Fig. 8. Solubility of cobalt(II) and manganese(II) in the presence of zirconium(IV) and hafnium(IV) upon addition of pyromellitic acid. PMA/(Co + Mn) = 0.45 mol/mol.

summarize the observations as follows:

1. Without Zr or Hf present, within experimental error, 100% of the PMA reacts with and precipitates the Co and Mn.
2. PMA prefers to precipitate Mn(II) rather than Co(II).
3. Addition of Zr enhances the solubility of the Mn(II) and doubling the Zr concentration results in a further enhancement. The same is observed for Hf. Hafnium enhances the solubility of Mn more than an equal-molar amount of Zr.
4. One can calculate the enhancement in solubility of the manganese and cobalt due to Zr and divide it by the Zr added. This ratio of soluble PMA/Zr is 1.1 and 0.78 for the two Zr concentrations used. Similar calculations for soluble PMA/Hf is 1.8 and 2.5.
5. The presence of Zr or Hf affect the rate of Co and Mn precipitation. Initial onset of precipitation takes longer with either Zr or Hf present. The initial onset of solids formation occurs sooner with zirconium than hafnium.

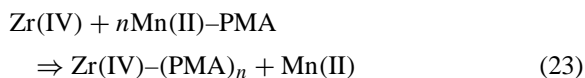
6. Zr and Hf by themselves do not precipitate with PMA nor are they precipitated in the presence of Co and Mn.

We have previously reported the X-ray crystal structure of Co(II) and Mn(II) pyromellitates [6,23]. The crystals were prepared by reacting the metal acetates with PMA in acetic acid/water mixtures. The stoichiometric reactions, based on these crystal structures, are written:



Although the crystal structures of Co and Mn are not identical there are no direct metal–carboxylic oxygen bonds in the solid state, see formulation in reaction 22. The primary coordination sphere of the metal is surrounded by an octahedral array of water molecules. There are 12 hydrogen bonds between every hydroxy group of water with every oxygen atom in the PMA anion. The solid state structures do not, of course, say anything about the structure of the metal in solution.

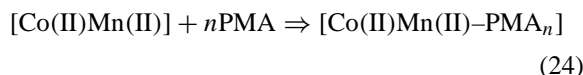
Without more available data, one can interpret the data in at least three ways: (1) the preferential complexation of PMA with the strong Lewis acid Zr(IV) or Hf(IV) rather than with Co(II) and Mn(II). These hard acids would prefer the oxygen donor ligand PMA more than Co(II) or Mn(II). This would effectively reduce the PMA concentration and result in less Co and Mn precipitation. The observed enhancement in solubility ratios calculated above would be reasonable since Zr(IV) and Hf(IV) are often eight-coordinate compounds and can therefore interact with a number of PMA molecules. This can be expressed by the equation (other ligands are omitted):



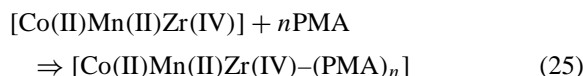
The value of  $n$  is reasonable and varies experimentally from 0.78 to 2.5. This is consistent with the stability constants for carboxylic acid complexation with metals in aqueous solutions. For example the  $\log(K)$  values for oxalate are 4.7, 3.2, and 11 for Co(II), Mn(II), and Zr(IV). Similar trends in stability constants for Co(II), Mn(II), and Th(IV), the latter which

is similar to Zr(IV), are found for malonic, oxydiacetic, and glycolic acid [29].

(2) Zr forms a polynuclear complex with Co or Mn (or both) presumably by formation of acetate bridges between the metals. This will effectively interfere with the formation of the  $M-OH_2 \cdots HO(C=O)Ar$  hydrogen bonds which eventually leads to metal precipitation. (3) A combination of the above two effects could occur where the PMA prefers to bond to the Zr (or Hf) as the PMA encounters the Zr–M ( $M = Co, Mn$ ) polynuclear complex. This could be expressed by the equation in the absence of Zr by



where PMA is bonded to the Mn(II). This changes in the presence of Zr:



The complex  $[Co(II)Mn(II)Zr(IV)-(PMA)_n]$  has the PMA bonded to the Zr(IV) and is soluble in solution.

In support of the above proposed mechanisms, polynuclear compounds of Fe(III)/Zn(II) precipitated from acetic acid solutions have been reported [24]. In aqueous solutions polynuclear cations containing Ti(IV) or Zr(IV) with Cr(III) or Al(III), and Sn(IV) with Fe(III) are known to exist [25]. It is known that binary solutions of Ti(IV) and Zr(IV) enhance the solubility of Cr(III) and Al(III) in aqueous solutions and that this enhanced solubility is due to the formation of mixed polynuclear metal/aqua/hydroxo/oxo compounds [26].

#### 4. Summary

The presence of Zr can impact the chemistry in Co/Mn/Br catalyzed autoxidations in a number of ways by (1) increasing its activity, (2) changing the relative rates of benzaldehyde to benzyl alcohol formation, (3) preventing insoluble  $MnO_2$  formation which can also affect the selectivity of the oxidation as well and (4) preventing catalyst precipitation due to carboxylic acids by increasing the solubility of

the metals. The practical impact of increasing the Co/Mn/Br catalyst activity by addition of zirconium has been discussed in part 1 of this series [1]. The latter two effects decrease the overall activity of the system by removal of the highly synergistic catalyst components from solution. Thus, Zr affects the activity both by increasing the activity of the catalyst as well as preventing activity and selectivity loss due to catalyst precipitation.

The phenomena of activation, prevention of Mn(IV) formation, and solubilization in the presence of select carboxylic acids, taken as a whole, occurs when the metal has high Lewis acidity. This is a necessary but not sufficient condition. It is not sufficient because the metal, M, may not have the necessary required ligands in the coordination sphere or proper kinetics to react with cobalt and/or manganese. There is the distinct possibility that a number of different coordination compounds of the same metal may have a widely varying effect on the Co/Mn/Br catalyst due to these thermodynamic and kinetic conditions. The effect of variation of the Co/Mn ratio with and without zirconium, see part I of this series, is most easily interpreted by formation of a Co–Zr–Mn polynuclear compound. The other phenomena reported here are not inconsistent with that proposal. Evidence for Co–Zr–Mn polynuclear compounds have been summarized in Part I.

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