



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

Part I. Activation and changes in benzaldehyde intermediate formation

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Abstract

The changes in activity and intermediate formation by the addition of zirconium to a Co/Mn/Br and Co/Ce/Br catalyzed aerobic *p*-xylene oxidation as a function of catalyst concentration, Co/Mn ratio, and Zr concentration are presented. There is a maximum activity increase at an optimum Co/Mn/Br concentration. As the degree of activation caused by Zr increases so does the ratio of the rate of benzaldehyde/rate of benzyl alcohol formation. While the most active Co/Mn/Br catalyst is at a 5/1 Co/Mn ratio, the most active Co/Mn/Zr/Br catalyst is at a 1/1 ratio. The coordination chemistry in acetic acid/water systems is summarized. The experimental data is rationalized by postulating that the benzyl hydroperoxide is dehydrated in the coordination sphere of the metals to give benzaldehyde and water, that the strong Lewis acidity of Zr(IV) is responsible for the changes in activity and selectivity, and that it occurs through a polynuclear Co/Mn/Zr coordination compound.

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1. Introduction

Homogeneous, liquid phase aerobic oxidation is a highly productive method to produce oxygenates. The mechanism is a catalyst modified free-radical chain mechanism [1]. Two of the dominate industrial processes using this methodology are cyclohexane to adipic acid, for use in nylon, and *p*-xylene to terephthalic acid, used in polyester manufacture [2,3]. Finding more active, but especially more selective, catalysts,

is therefore important and the patent literature describes many such attempts [4]. One of the fascinating observations in this area is the addition of a soluble form of zirconium to an already active catalyst system which can greatly enhance the activity and in some instances, change its selectivity. Zirconium is especially interesting because (1) it does not have a catalytic activity when used alone, (2) it is a non-transition metal, i.e. does not have variable oxidation states or unpaired electronic spin, (3) its maximum increase in activity is at low Zr/(total catalyst metals) ratio, typically 0.2 mol/mol. Addition of Zr to Co, Mn/Br, Ni/Mn/Br, and Co/Mn/Br catalysts results in increases by factors of 5.0, 8.3, 2.3, and 3.0, respectively [5–7].

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The first report on the use of Zr in homogeneous autoxidation is with Co/Zr catalysts in 1967 [8] which was followed by detailed kinetic studies [5,9]. Subsequent studies illustrated the activating effect of Zr on Co/Br [10], Mn/Br [11], Ni/Mn/Br [11], and Co/Mn/Br catalysts [4,12–16]. The activating effect of Zr appears to be general to all substrates—both aliphatic and alkylaromatic. Substrates used include various methylaromatic compounds [4–8], cyclohexane [17], hydroxymethylfurfural [15], and polymers such as polystyrene, polyethylene, etc. [16]. The latter is used for recycling of used plastics. The first report of a selectivity enhancement by Zr has been reported [15]. The aerobic oxidation of toluene using a Co/Zr/Br catalyst has been reported [10] using $ZrCl_4$ as the initial source of Zr. Unfortunately, the results are clouded by the fact that substantial amounts of the bromine existed, in variable amounts, as the benzylic bromide. Benzylic bromide is known to be a catalytically inactive form [18] and the activity of metal/bromide catalysts are known to be very dependent upon the activity of the bromide/metal(s) ratio [4] hence it can have a confounding effect. Additionally, the chloride from the $ZrCl_4$ catalyst will undergo a slow displacement reaction of the bromine from the benzylic bromide [18]. The patent literature teaches that Zr/metal ratios of about 1.0 produce excessive ‘over-oxidation’ to carbon oxides (carbon dioxide and carbon monoxide) [12] which can be avoided by using the much lower ratio of 0.01–0.05 [13].

Parts I and II of these papers are the first detailed report of the effect of Zr on Co/Mn/Br and Co/Ce/Br catalysts. The effect of varying the Zr concentration, the Co/Mn/Br concentration, the Co/Mn ratio on the rate of *p*-xylene disappearance, on the rate of oxygen uptake, and on the distribution of intermediate benzylic alcohols and benzaldehydes is presented. The latter effect is quite striking and has led to the new hypothesis that Zr functions as a strong Lewis acid which enhances the rate of dehydration of the intermediate peroxide. Evidence is given in Part II that Zr is not unique and other metals behave similarly. It is shown that increasing Lewis acidity of the metals gives increased catalytic activity. The presence of Zr (and other metals) also change the chemistry during autoxidation in other subtle and desirable ways. The propensity for Mn(IV) dioxide formation and precip-

itation of the catalyst metals by aromatic acids such as pyromellitic acid during aerobic oxidation are both also decreased.

2. Experimental

The reactor, procedures, and calculations have been previously described [15]. All data was obtained at 95 °C at ambient atmospheric pressure of air (20.9% O_2). The source of zirconium in all of the experiments is the Aldrich ‘zirconium acetate’ solution which, upon analysis, contained 17.8 wt.% Zr (via ICP), 4.36% acetic acid (via GC) and 72.8% water (via Karl Fischer). The cobalt and manganese salts were the (+II) acetate tetrahydrates. The bromide source was sodium bromide.

An HP6890 Gas Chromatograph equipped with a FID detector was used to identify the reaction products. The column was a 25 m HP-FFAP with 0.32 mm i.d. and 0.5 μ m film thickness. The initial temperature is 50 °C for 5 min. The GC is then ramped at 5 °C/min to 220 °C and held for 1 min at that temperature. The products of the oxidation of *p*-xylene were confirmed by GC/MS.

One measure of the activity of the reaction is measured by the first-order disappearance of the *p*-xylene concentration. Five to six liquid samples were removed and analyzed via GC during the 5–6 h experiments. Errors in the rate constants are from: (1) loss of *p*-xylene (bp 138 °C) from the reactor because of the flow of air through the solution. The rate of *p*-xylene loss from the reaction was measured and contributes to less than a 4% error in the slowest reactions and a 0.4% error in the fastest ones; (2) *p*-toluic acid formation becomes important at *p*-xylene conversions higher than 30%. The rate of dioxygen uptake, which remains fairly constant, was averaged over the time of the experiment.

3. Results

3.1. Organic chemistry of metal/bromide catalyzed autoxidation of methylaromatic compounds

The reaction network and the relative activities of the intermediates during the aerobic Co/Mn/Br

3.2. Kinetic data as function of Co/Mn/Br and Zr concentration

All of the kinetic data in this paper use 20.9% dioxygen in nitrogen (air) at ambient atmospheric pressure at 95 °C. Initial *p*-xylene concentration was always 0.943 M, the Co/Mn ratio and Br/(Co + Mn) ratio are 1.00 mol/mol unless otherwise specified. The water concentration in the acetic acid is 5.55 M (10.0 wt.%). The reasons for the presence of water are: (1) the confounding effect of benzylic bromide (α -bromo-*p*-xylene and α -*p*-toluic acid; XPhCH₂Br, X = CH₃ and COOH), due to their catalytic inactivity, is largely eliminated because water greatly increases its rate of solvolysis. The α -bromo-*p*-xylene was monitored in all the reactions via GC. Their rate of formation is proportional to the rate of peroxide formation hence they were present only in the most active reactions in 10–15% yield (on a NaBr basis); (2) industrial processes using these metal/bromide catalysts operate at approximately this water concentration because (a) water is a product of the reaction and (b) only a limited amount of water can be eliminated during acetic acid recycle due to the acetic acid/water azeotrope.

The activity of the Co/Mn/Br catalyst system, as measured by the rate of *p*-xylene disappearance, is first order above a cobalt concentration of 0.0025 M with the calculated coefficient being 0.984 at four different catalyst concentrations (ranging from 0.0025 to 0.020 M). Fig. 2 illustrates the activation of a Co/Mn/Br catalyst as a function of zirconium and Co/Mn/Br concentration. One observes:

1. An enhancement in rate is seen at cobalt concentrations as low as 0.00125 M.
2. At sufficiently high Co concentrations, approaching 0.0200 M, zirconium does not have an activating effect.
3. Increasing zirconium concentration at a constant cobalt concentration results in increasing activity but most of this activity increase is seen at or below a Zr/Co ratio of around 0.20 mol/mol.
4. The maximum activity of a Co/Mn/Zr/Br catalyst can be duplicated by a Co/Mn/Br catalyst but the latter at a higher concentration. For example, a Co/Mn/Zr/Br catalyst at a [Co] = 0.0050 and a Zr/Co ratio of 0.15 has a rate of $12.3 \times 10^{-5} \text{ s}^{-1}$

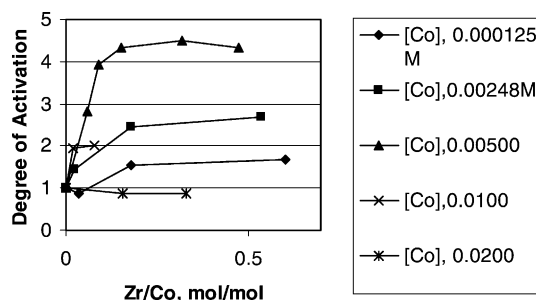


Fig. 3. Degree of activation by Zr of a Co/Mn/Br catalyst as a function of Zr/Co ratio.

while a Co/Mn/Br catalyst at [Co] = 0.020 has a rate $12.9 \times 10^{-5} \text{ s}^{-1}$. Co/Mn ratio and Br/(Co+Mn) ratio are 1.00 mol/mol.

5. The *degree of activation* is defined as the rate constant of a Co/Mn/Zr/Br catalyst divided by the rate of a Co/Mn/Br catalyst both at the same Co/Mn/Br concentration, i.e. $k_{\text{with Zr}}/k_{\text{without Zr}}$. It reflects the change in activity upon the addition of Zr to a Co/Mn/Br catalyst. The degree of activation occurs at an optimum cobalt concentration, see Figs. 3 and 4.

Another measure of the activity of the system is by the rate of oxygen uptake. This is shown in Fig. 5 which should be compared to Fig. 2. In general, one can draw similar conclusions as above but one must recognize that the presence of zirconium changes the *selectivity* of the reaction. The strong activation in the presence of Zr increases the benzaldehyde yield but not the benzyl alcohol yield, see below. *p*-Xylene reacts with 0.5 mol of dioxygen to form

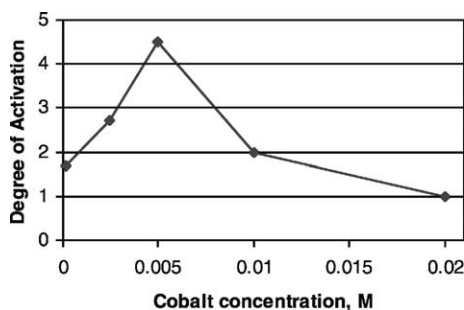


Fig. 4. Degree of activation of a Co/Mn/Br catalyst by zirconium as a function of the Co concentration, Zr/Co = 0.17 mol/mol.

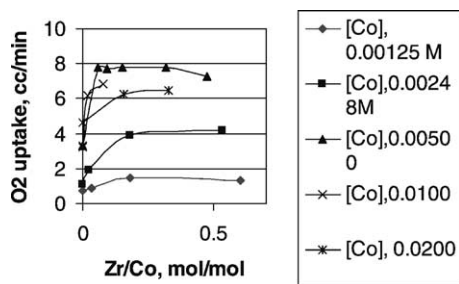


Fig. 5. Rate of oxygen uptake as a function of cobalt concentration and Zr/Co ratio (mol/mol).

4-methylbenzyl alcohol and with 1.0 mol of dioxygen to form 4-methylbenzaldehyde:



As a consequence, the rate of *p*-xylene disappearance at 0.0050 and 0.020 M Co is similar while the rate of oxygen uptake is significantly higher for 0.0050 M Co than 0.020 M Co. This is because Zr has strongly activated the system at 0.0050 and has favored the benzaldehyde formation which reacts with twice as much dioxygen as does benzyl alcohol.

It has been previously reported for Co/Zr catalysts that insoluble forms of zirconium are not active [5,9]. A soluble form of zirconium is required to see an effect. We observe the same effect since when Zr(IV) oxide was used as the source of zirconium rather than the acetate, the degree of activation was 1.3 as compared to 4.4 at a [Co] = 0.0050 and Zr/Co = 0.18 mol/mol.

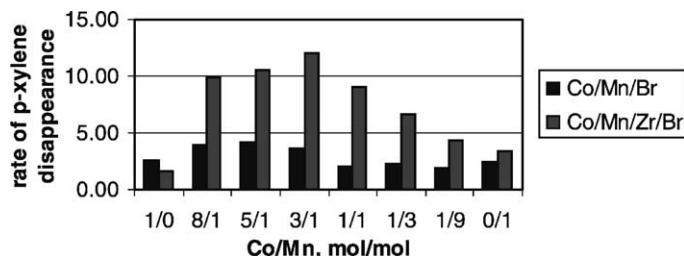


Fig. 6. Comparison of the rates of *p*-xylene disappearance (s⁻¹) as a function of the Co/Mn ratio. Co + Mn = 10.0 mM, Br/(Co + Mn) = 1.00 mol/mol, 10 wt.% in acetic acid.

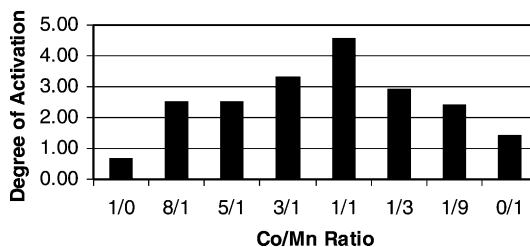


Fig. 7. Degree of activation, $k_{\text{with Zr}}/k_{\text{without Zr}}$, as a function of Co/Mn ratio. Co + Mn = 10.0 mM, Br/(Co + Mn) = 1.00 mol/mol.

3.3. Activity of the catalyst as a function of the Co/Mn ratio and the Influence of Zr on the ratio

Under these experimental conditions, Zr does not activate the Co/Br catalyst but does activate the Mn/Br catalyst. Maximum rate of reaction occurs at a Co/Mn ratio of 5/1 (mol/mol) without Zr and 3/1 (mol/mol) with Zr, see Fig. 6. Most striking however, is the degree of activation that occurs as a function of the Co/Mn ratio, see Fig. 7. The maximum degree of activation now occurs at a 1/1 Co/Mn ratio.

3.4. Effect of addition of Zr to a Co/Mn/Br catalyst on formation of organic intermediates

The effect of Zr on yields is shown in Fig. 8 where two experiments are compared with and without Zr. The alcohol yield is nearly identical in both experiments but the benzaldehyde yield is considerably higher with Zr present. Thus, Zr activation is associated with a significant increase in the yield of the aldehyde. The major *selectivity* change that occurs when Zr is added to the Co/Mn/Br catalyst is that the rate of benzaldehyde formation is favored over

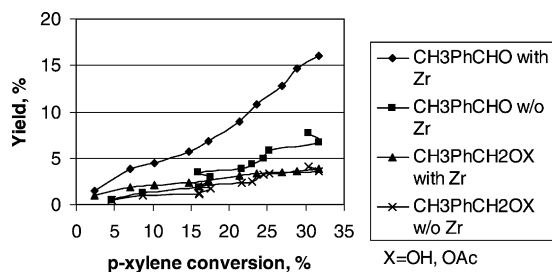


Fig. 8. Intermediate formation during the Co/Mn/Br catalyzed autoxidation of *p*-xylene. [Co] = 0.0050 M, Zr/Co = 0.017 mol/mol.

benzyl alcohol formation. Thus, the pathway k_2 in Fig. 1 becomes more important relative to pathway k_1 .

A way of expressing this is by plotting the ratio of (*p*-tolualdehyde yield)/(4-methylbenzyl alcohol yield + 4-methylbenzyl acetate yield) as a function of conversion, see Fig. 9. The benzyl alcohol formed is acetylated by the solvent acetic acid to form the more stable 4-methylbenzyl acetate, associated with rate constant k_4 on Fig. 1. The acetate normally constitutes only a small fraction, 5–15% of the total of the alcohol and acetate under the experimental conditions used here. This is because the rate of acetylation is $4.1 (0.53) \times 10^{-5} \text{ s}^{-1}$ (half-life 4.7 h) under these experimental conditions while the time of each kinetic experiment is 4–6 h. The amount of acetate formation from the time of removal from the reactor to the measurement on the GC instrument is very small since the measured half-life of acetylation at room temperature is 1280 h.

One finds that if Zr addition to a Co/Mn/Br catalyst results in activation that the aldehyde/(alcohol +

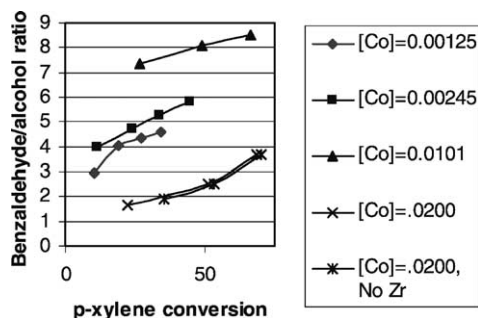


Fig. 9. Effect of Zr on benzaldehyde/alcohol ratio as a function of Co/Mn/Br concentration. Zr/Co = 0.17 mol/mol unless otherwise stated.

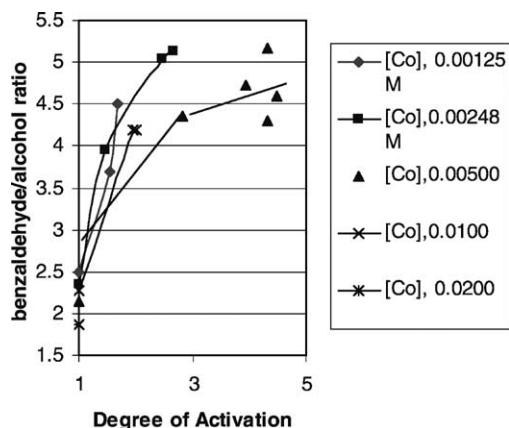


Fig. 10. Correlation of degree of activation caused by zirconium with benzaldehyde/alcohol ratio. Benzaldehyde/alcohol ratio is at a *p*-xylene conversion of 30%.

acetate) ratio increases but if activation doesn't occur, then the ratio does not decrease. This can be seen in Fig. 9. The highest degree of activation occurs with Zr is at a Co concentration of 0.0100 M. This reaction has the highest benzaldehyde/alcohol ratio. Co concentrations of 0.00125 and 0.00245 M have intermediate degrees of activation which also have intermediate benzaldehyde/alcohol ratios. At a Co concentration of 0.020 M, no activation with Zr addition occurs and no increase in the benzaldehyde/alcohol ratio is observed. This can be most clearly seen when one obtains the aldehyde/alcohol ratio, interpolated to a *p*-xylene conversion of 30%, and plots it versus the degree of activation, see Fig. 10. In general, the greater degree of activation is associated with the higher benzaldehyde/alcohol ratio. When Zr was added to Co/Mn/Br catalysts at different Co/Mn ratios, one again finds that

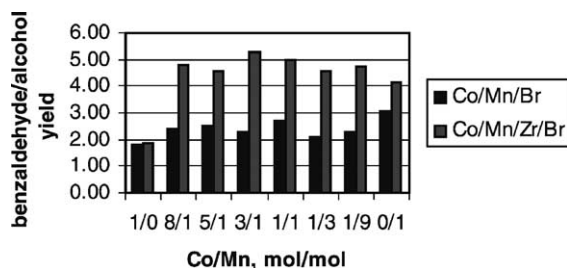


Fig. 11. Benzaldehyde/alcohol ratio as a function of Co/Mn ratio with and without Zr in a Co/Mn/Br catalyst. Co + Mn = 10.0 mM, Br/(Co + Mn) = 1.00 mol/mol.

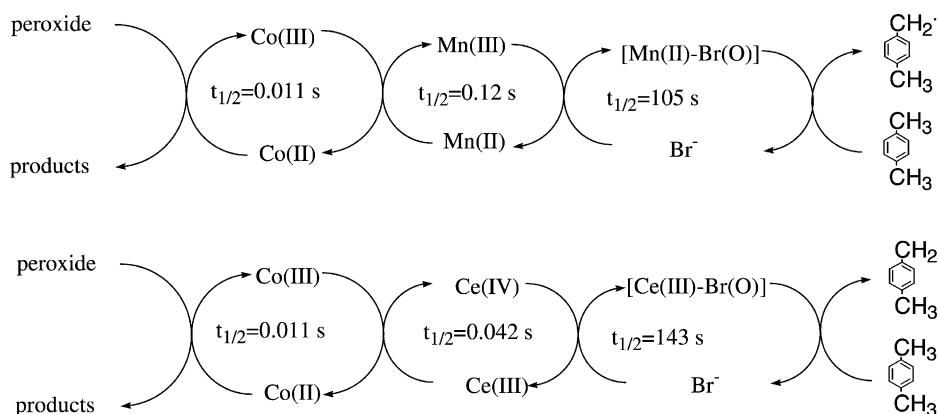


Fig. 12. Measured kinetics of the redox cascades of the Co/Mn/Br and Co/Ce/Br catalysts. MCPBA is *m*-chloroperbenzoic acid. MCPBA is *m*-chlorobenzoic acid. Rates at 23 °C, [MCPBA] = 0.00050 M, all other species at 0.010 M.

Table 1

Activity and benzaldehyde/alcohol ratios of Co/Mn/Br, Co/Ce/Br and Co/Ce/Zr/Br catalysts with *p*-xylene in 10% water/acetic acid

Catalyst	Concentration (M)	d(O ₂)/dt (cc/min)	d(PX)/dt (×10 ⁵ s ⁻¹)	Degree of activation	Benzaldehyde/alcohol at 30% conversion
Co/Br	0.01/0.01	0.95	2.56 (0.23)	–	1.8
Mn/Br	0.01/0.01	1.30	3.32 (0.15)	–	3.0
Co/Mn/Zr/Br	0.005/0.005/0.0011/0.01	6.20	9.07 (0.97)	4.56	5.0
Co/Mn/Br	0.005/0.005/0.01	1.39	1.99 (0.13)	–	2.7
Co/Mn/Br	0.010/0.010/0.020	3.2 (0.1)	5.12 (0.14)	–	2.4
Co/Ce/Br	0.010/0.011/0.020	1.1 (0.2)	2.56 (0.31)	–	1.3
Co/Ce/Zr/Br	0.010/0.011/0.0093/0.020	1.9 (0.1)	4.04 (0.36)	1.56	2.1

only when activation occurs does the aldehyde/alcohol ratio change, see Fig. 11. At a Co/Mn ratio of 1/0 where no activation due to Zr is observed, no change in the ratio is observed.

3.5. Effect of addition of Zr to a Co/Ce/Br catalyst

The catalytic chemistry and some of the properties of the Co/Ce/Br have been previously reported

Table 2

Some characteristics of Co/Mn/Br and Co/Ce/Br catalysts

Catalyst	Activity, d(toluene)/dt (×10 ³ s ⁻¹)	ρ in Hammett equation	Synergy factor ^a	Carbon dioxide selectivity ^b
Co	–	–1.81	–	29
Co/Br	1.57	–0.851	–	3.1
Mn/Br	1.43	–	–	4.4
Ce/Br	0.86	–	–	4.2
Co/Mn/Br	5.60	–1.28	1.86	1.4
Co/Mn/Zr/Br	12 ^c	–1.33	1.30 ^d	–
Co/Ce/Br	3.22	–1.38	1.32	2.3
Co/Ce/Zr/Br	5.0 ^c	–	–	2.9

^a For example, the synergy factor for the Co/Mn/Br catalyst is $R_{\text{Co/Mn/Br}}/(R_{\text{Co}} + R_{\text{Mn}} + R_{\text{Br}} + R_{\text{Co/Br}} + R_{\text{Mn/Br}})$, where R is the rate of disappearance of toluene.

^b Defined as rate of carbon dioxide formation/rate of oxygen uptake × 100.

^c Assumes that degree of activation observed in this work for *p*-xylene is the same for toluene.

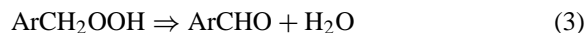
^d $R_{\text{Co/Mn/Zr/Br}}/(R_{\text{Co}} + R_{\text{Mn}} + R_{\text{Br}} + R_{\text{Zr}} + R_{\text{Co/Mn/Br}} + R_{\text{Co/Zr/Br}} + R_{\text{Mn/Zr/Br}})$ calculated for *p*-xylene as substrate.

and compared to the Co/Mn/Br catalyst [22]. The Co/Ce/Br catalyst is similar to Co/Mn/Br in its redox cascade chemistry, Fig. 12 [22,40]. A summary of the previously reported characteristics of selected Co/Ce/Br catalysts [22] combined with those from this study is given in Tables 1 and 2. There is a synergistic interaction of Co and Ce in a Co/Ce/Br catalyst just as there is for Co and Mn in a Co/Mn/Br catalyst. The Co/Ce/Br and Co/Ce/Zr/Br catalysts are somewhat less active than the Co/Mn/Br and Co/Mn/Zr/Br catalysts toward *p*-xylene just as previously found for toluene. The rate of carbon dioxide and carbon monoxide formation is significantly decreased whenever either Mn or Ce is added to a Co/Br catalyst. The rate of carbon oxide formation is somewhat higher with the addition of Zr to a Co/Ce/Br catalyst but still superior to Co, Co/Br, and Ce/Br catalysts. Just as with the addition of Zr to a Co/Mn/Br catalyst, the benzaldehyde/alcohol ratio increases when Zr is added to a Co/Ce/Br catalyst, see Table 2. The yield to 4-methylbenzyl alcohol is higher in a Co/Ce/Br catalyst than in a Co/Mn/Br catalyst as previously reported [23] although the differences are small.

4. Discussion

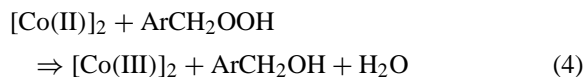
4.1. Promotion of metal/bromide catalysts by Zr(IV) through a benzyl peroxide dehydration mechanism

Scott [24] studied the reaction of the benzyl hydroperoxide with Co(II) and Co(III) acetate in acetic acid at 25 °C under conditions that closely simulate those during autoxidation. His conclusion, based on product yields and kinetic analysis, is that Co(II) primarily reacts with the peroxide via a dehydration mechanism to the benzaldehyde:



Reaction (3) by-passes benzyl alcohol formation—it is a pathway directly from the *p*-xylene to the 4-methylbenzaldehyde as shown in reaction (2) in Fig. 1. The reaction of Co(II) with benzyl peroxide gives the dehydration product benzaldehyde (84% yield) with a small amount of the benzyl alcohol (16%). The latter can be formed via oxidation of the

Co(II) to Co(III) and is consistent with his kinetic analysis:



Furthermore, Scott provides experimental evidence for the conclusion “Co(III) acetate appears to promote the reaction of Co(II) acetate with benzyl hydroperoxide but without increasing the Co(III) concentration”. No chemical explanation was given by Scott why this would be true. We propose that the dehydration is a Lewis acid effect and that the promoting effect of Co(III) is due to the latter’s higher Lewis acidity than Co(II). Starting initially with Co(II) and the benzyl peroxide, the initial reaction is a competing reaction between Co(II) dehydration and oxidation, reactions (3) and (4). Once some of the Co(II) is oxidized to Co(III), the dehydration via Co(III) proceeds faster and the dehydration mechanism dominates. This also rationalizes why Zr(IV) can promote these reactions. The Lewis acidity is $\text{Zr(IV)} > \text{Co(III)} > \text{Mn(III)} > \text{Co(II)} > \text{Mn(II)}$, see Table 3. During a Co/Mn/Br catalyzed autoxidation, the Co(III) and Mn(III) steady state concentration always remains very low (less than 1% of the total cobalt [25]) and hence little promoting action of Co(III) and Mn(III) is possible. The presence of Zr(IV) with Co/Mn/Br will be expected to increase the rate by promoting the benzylic peroxide to the benzaldehyde and subsequently increase the benzaldehyde/alcohol ratio. This is also consistent with experimental observations. The rationalization of the experimental results requires a more detailed description of the coordination chemistry which is presented in the next section.

Table 3
Lewis acidity as given by the ionic Z^2/r values of selected metals

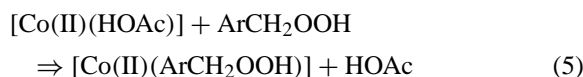
Element	Formal valence	Ionic radius ^a	Z^2/r
Mn(II)	2	0.80	5.0
Co(II)	2	0.73	5.5
Ce(III)	3	1.07	8.4
Mn(III)	3	0.66	14
Co(III)	3	0.63	14
Ce(IV)	4	0.94	17
Zr(IV)	4	0.79	20

^a Ionic radii from [41].

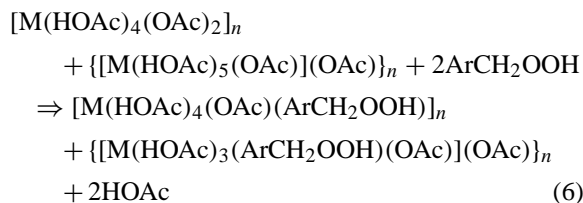
4.2. Coordination chemistry model for the metal-catalyzed dehydration of the benzyl hydroperoxide

Virtually all metal catalyzed autoxidations utilizing Co, Mn, Ce, V, Ni, Zr, Ce and Br combinations use carboxylic acids solvents either wholly or partially with acetic acid being the most common [4]. The structures of Co and Mn in acetic acid/water is quite complex and not easy to describe [26]. This is because of ion-pair formation, the metals exist with variable polynuclearity, the ligands are labile and because water competes readily for the other ligands in the system [26]. Because of this complexity, the coordination chemistry will be simplified by denoting *only* the mechanistically required metals and ligands in the coordination sphere. The coordination sphere is denoted by square brackets [].

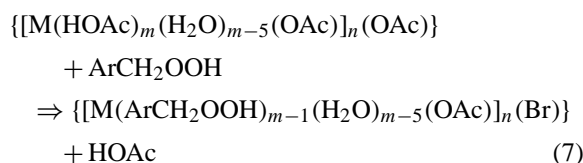
For example, the incorporation of a benzylic peroxide into the coordination sphere will be described by



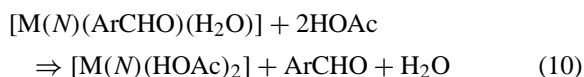
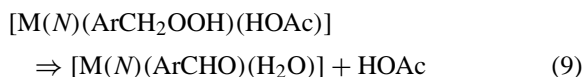
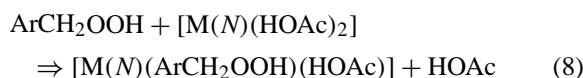
rather than by the more detailed description [26] in anhydrous acetic acid (where { } denotes an ion-pair):



or in hydrous acetic acid:



Using this simplified notation one has for the dehydration of the peroxide, where *N* is the oxidation state of the metal, M:



The model should be consistent with the following observations and principles:

1. A stable Co/Mn/Zr/Br catalyst, during autoxidation has predominately Co(II) and Mn(II), much smaller steady state amounts of Co(III) and Mn(III) and all of the zirconium as Zr(IV). Conditions do exist, at low catalyst concentrations or if an excessive amount of the bromide becomes benzylic bromide [10,18,21,27] that ‘catalyst failure’ is observed, i.e. the solutions become deep green or brown, significant amounts of Co(III) and Mn(III) form, and the rate of carbon oxide liberation is much higher. Importantly, the observance of ‘catalyst failure’ was not seen in the experiments described here.
2. NMR studies in acetic acid/water solutions reveal that the acetic acid–metal bond (metal = Co(II), Mn(II)) is thermodynamically very weak (5.9 kcal/mol) and the rate of ligand exchange very fast [26]. Therefore the benzyl hydroperoxide ligand enters the metal coordination sphere via acetic acid displacement rather than by displacement of other available ligands such as water or anions of carboxylate acids. This is consistent with the X-ray crystal structure of Mn(III) acetate where the metal–oxygen bond length of the acetic acid ligand is 0.3 Å longer than the mean value of the other Mn–O distances, the latter which are bridging acetate ligands [28]. There is considerable evidence that the key intermediates during autoxidation enter the coordination sphere of the metals. Published thermodynamic and kinetic data for the displacement of acetic acid by *p*-xylene, *p*-toluic acid, water, peracids, benzaldehyde, and alkyl peroxy radicals with cobalt acetate as the initial salt in acetic acid are summarized in Table 4. It will be therefore assumed that much of the chemistry occurs within the coordination sphere.
3. Water is always present during autoxidation in acetic acid because it is the product of most oxidation reactions and is also produced by the ‘over-oxidation’ of the acetic acid solvent. Even

Table 4

Thermodynamic and kinetic data on the incorporation of pertinent ligands into the coordination sphere of cobalt

Reaction	Method, solvent	Results	Reference
$[\text{Co(II)(HOAc)(OAc)}_2\text{Br}] + \text{L}$ $\Rightarrow [\text{Co(II)L(OAc)}_2\text{Br}] + \text{HOAc}$	NMR, HOAc	$K(p\text{-xylene}) = 1.03$, $K(p\text{-toluic acid}) = 1.68$	[29]
$[\text{Co(III)(HOAc)}] + \text{H}_2\text{O}$ $\Rightarrow [\text{Co(III)(H}_2\text{O)}] + \text{HOAc}$	HOAc	$K = 2.50$, $k_{\text{forward}} = 0.050/\text{M s}$	[30]
$[\text{Co(III)(HOAc)}] + \text{RCO}_3\text{H}$ $\Rightarrow [\text{Co(III)(RCO}_3\text{H)}] + \text{HOAc}$	HOAc	Range of $k = 11\text{--}32/\text{M min}$ for 10 different peracids	[31]
$[\text{Co(III)(HOAc)}] + \text{PhCHO}$ $\Rightarrow [\text{Co(III)(PhCHO)}] + \text{HOAc}$	UV-Vis, ion migration, HOAc	$K = \text{large}$	[30]
$[\text{Co(III)(HOAc)(RCHO)}] + \text{H}_2\text{O}$ $\Leftrightarrow [\text{Co(III)(RCHO)(H}_2\text{O)}]$ + HOAc	HOAc		[30]
$[\text{Co(III)(HOAc)(RCHO)}] + \text{H}_2\text{O}$ $\Leftrightarrow [\text{Co(III)(RCHO)(H}_2\text{O)}]$ + HOAc	HOAc		[30]
$[\text{Co(II)}] + \text{R}^\bullet \Rightarrow [\text{Co(II)R}^\bullet]$	ESR, benzene	$\text{R}^\bullet = t\text{-butylperoxy radical}$	[32]

in the presence of substantial amounts of water, the M(II)–HOAc (M = Co and Mn) bond persists. For example, in 10 wt.% water (5.55 M), 18% of the cobalt(II) species would have two acetic acid molecules bonded to it and 38% would have one acetic acid molecule [26].

- The intimate mechanism of dehydration is suggested in Fig. 13. The catalytic effect is two-fold. The coordination of the peroxide bond with the metal weakens the O–O bond. Secondly, the metal will geometrically position the benzyl hydroperoxide so that after the proton transfer occurs, both the water and benzaldehyde will bond to the metal. One would expect the O–O bond to be increasingly weakened in the order Zr(IV) > Co(III) > Mn(III) > Co(II) > Mn(II). since these are ‘hard’ metals which favor ionic bonding. The strength of the peroxide-metal bond will increase in this order.
- The phenomena reported in this and the subsequent paper are consistent with the formation of a polynuclear compound of Zr with Co(II) and/or Mn(II).

A mechanism consistent with the activating effect of Zr is shown in Fig. 14. The entry of the benzyl hydroperoxide into the polynuclear complex may be via Co(II) or Mn(II). Kinetic analysis of the Co/Zr catalyzed autoxidations have suggested a Co–O–Zr interaction [9]. There is ESR evidence for Mn–O–Zr interactions in acetic acid/water mixtures during *p*-xylene autoxidation [23]. Equilibrium studies, in anhydrous acetic acid, using Co(II), Co(III), Mn(II), Mn(III) suggest dinuclear species exist [36].

- A thermodynamic driving force for dehydration will be the formation of the metal–water bond, reaction (9). This is because the benzyl hydroperoxide, benzaldehyde, and acetic acid have significantly weaker bonds than water. Weakly basic substances such as alcohols, alkoxides and phenols, which are similar to benzyl hydroperoxide and benzaldehyde, are known to be readily displaced by water [33]. The strength of the metal–water bond is expected to increase with Lewis acidity hence

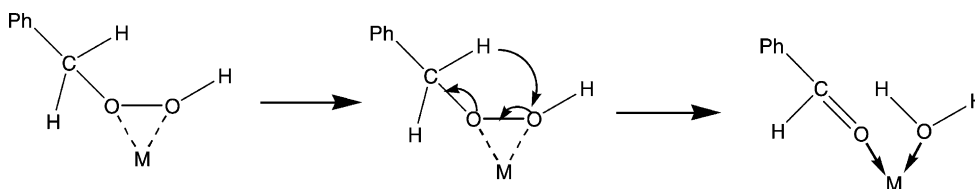


Fig. 13. Suggested mechanism of the metal catalyzed dehydration of the benzyl hydroperoxide via simultaneous proton and electron transfer.

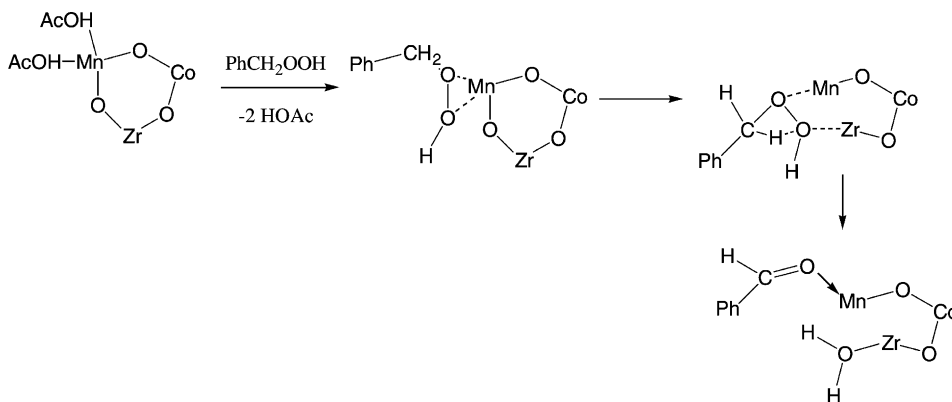


Fig. 14. Suggested mechanism of dehydration of the benzyl peroxide via a Co/Mn/Zr polynuclear complex.

Zr(IV) > Co(III) > Mn(III) > Co(II) > Mn(II) (Table 3). Therefore, the strongest thermodynamic driving force for peroxide dehydration will be Zr(IV). The change in bond energy with change in oxidation state is very substantial. For example, the Fe(II)–H₂O and Fe(III)–H₂O bond energies are 58 and 116 kcal/mol, respectively [34].

The chemistry to the benzyl alcohol and benzaldehyde is shown in Fig. 15. The initial stable species in methylaromatic autoxidation is known to be the peroxide, 4-CH₃ArCH₂OOH [35] which is formed by the chain reaction involving initiation and propagation, reactions (1)–(3) (Fig. 15). Once the reaction has initiated, the initiation is through a bromine(O)

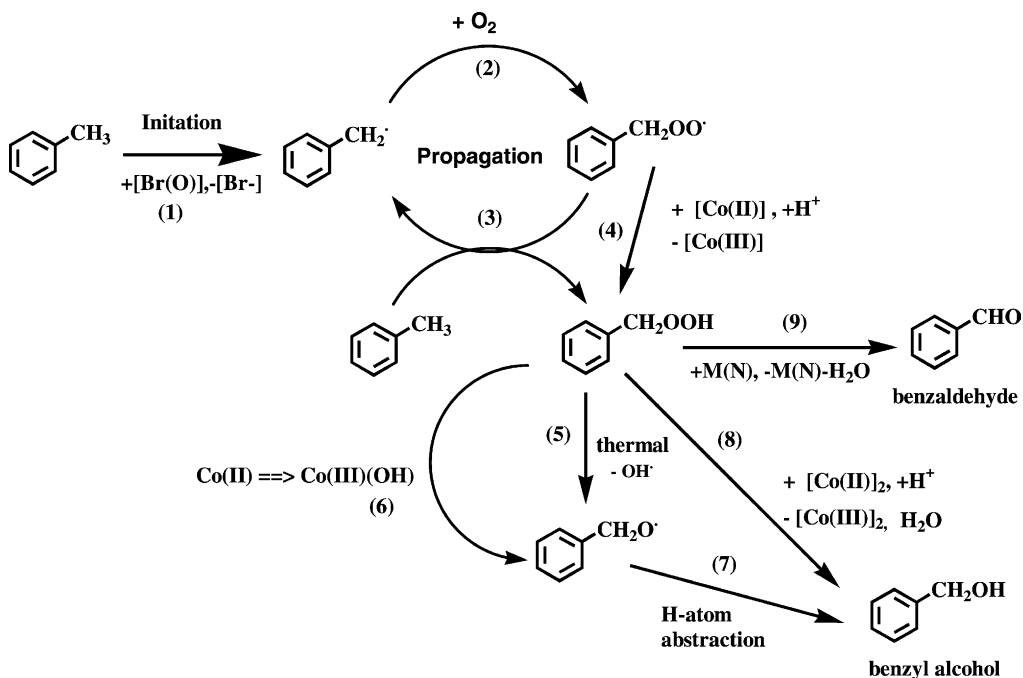


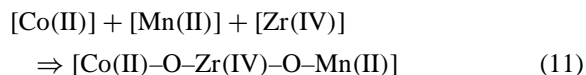
Fig. 15. Model describing formation of benzaldehyde and benzyl alcohol formation during Co/Mn/Br autoxidation of *p*-xylene.

species. The bromine(O) species may be HBr_2 [36,37] or a M-Br(O) [4,27b,38]. The formation of the benzyl peroxide is either non-catalyzed by reaction (3) or catalyzed by reaction (4), see Fig. 15 [39]. The benzyl hydroperoxide forms the aldehyde via dehydration in reaction (9) (Fig. 15). The benzyl hydroperoxide forms the benzyl alcohol via non-catalyzed via reactions (5) and (7) and by catalyzed reactions (6) and (8) in Fig. 15. The cobalt(III) formed in reactions (4), (6) and (8) go through the redox cascade shown in Fig. 12 to regenerate the initiating bromine(O) species.

4.3. Interpretation of the data by the benzyl peroxide dehydration model

The data can be rationalized by the formation of a trinuclear Co-Zr-Mn complex, noting how the concentration of this species would increase under the experimental variable change, and recognizing that the presence of Zr(IV) would significantly increase the rate of benzyl peroxide dehydration due to its high Lewis acidity.

As function of the Co/Mn ratio—the most active catalyst without Zr occurs at a Co/Mn ratio of 5/1. But *with Zr*, the highest degree of activation occurs at a Co/Mn ratio of 1/1 (Fig. 7). A straightforward explanation of this phenomena is the formation of a Co-Zr-Mn trimeric cluster which achieves a maximum equilibrium concentration at a ratio of $\text{Co/Mn} = 1.0 \text{ mol/mol}$, see reaction (11):



This is also consistent with the data on Fig. 7, where the degree of activation due to Zr is always higher with a Co/Mn/Br catalyst than in Co/Br and Mn/Br catalysts. The Co/Mn combination is more effective than Co or Mn alone.

Increase in Zr concentration at constant Co/Mn/Br concentration—this results in increasing activity (Fig. 4) and increasing benzaldehyde/alcohol ratio, Fig. 10. The trinuclear complex concentration would be expected to increase with increasing Zr concentration (Eq. (11)) accounting for the experimental changes.

Increase in Co/Mn/Zr/Br concentration results in the ‘volcano’ type plot shown in Fig. 4—with increasing

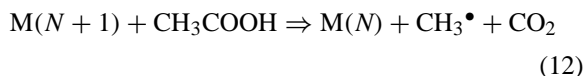
concentration, the activity increases since the trinuclear complex would be expected to increase. However, eventually as the catalyst concentration increases, the Lewis acid dehydration will occur predominately by the Co(II) and Mn(II) since they will exist in high concentrations.

Comparison of the Co/Mn/Br and Co/Ce/Br catalyst—the activity and benzaldehyde/alcohol ratio increases with the addition of Zr to a Co/Ce/Br catalyst just as occurs with Co/Mn/Br catalysts. The total Lewis acidity of a Co/Ce/Br catalyst would be expected to be somewhat higher because the value for Ce(III) is 14 while that for Mn(II) is 5.0, see Table 3. The fact that the benzaldehyde/alcohol ratio is lower for the Co/Ce/Br than the Co/Mn/Br catalyst and for the Co/Ce/Zr/Br and Co/Mn/Zr/Br catalysts cannot be rationalized using the models presented here.

4.4. Implications of the commercial use of Zr containing autoxidation catalysts

We have described how zirconium can be used to strongly activate the Co/Mn/Br catalyst *at the appropriate concentration of Co/Mn/Br*. If the catalyst concentration is too high, the effect is no longer seen.

Non-bromine autoxidation catalysts such as Co , Mn and Ce require high catalyst concentrations and operate at high steady state concentrations of the their higher oxidation states (Co(III) , Mn(III) and Ce(IV)). The high catalyst concentrations result in higher contamination of metals in the desired organic products and require a more highly efficient catalyst recycle system. The higher oxidation state produces a higher production rate of undesirable products especially carbon dioxide and carbon monoxide due to the oxidation of the carboxylic solvent, one mechanism being decarboxylation:



The oxidation of the solvent is one of the major variable costs in the commercial manufacture of aromatic acids. Addition to Zr to Co catalysts increase the steady state concentration of Co(III) [5,9,17] hence its addition may not be desirable. The addition of bromide to Co or Mn or Ce to form Co/Br , Mn/Br and Ce/Br catalysts reduce these problems because they

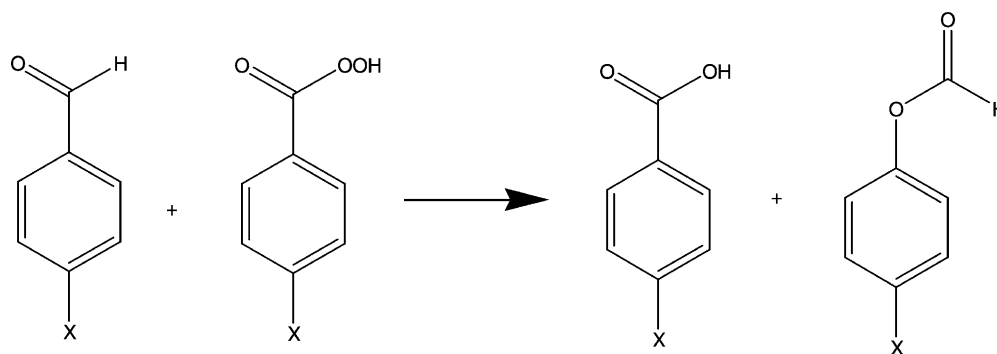


Fig. 16. Initial products from the Baeyer–Villiger rearrangement.

are more active [4] hence either lower catalyst concentrations can be used or the reactor size can be reduced. The steady state concentrations of Co(III), Mn(III) and Ce(IV) is also significantly reduced resulting in significant reductions in the rate of solvent decomposition. The addition of Mn or Ce to Co/Br to give Co/Ce/Br and Co/Mn/Br further increases the activity of the catalytic system and also results in less by-product production, see Table 2. The major disadvantage of metal/bromide systems is that the metal/bromide/acetic acid system is corrosive. This is not an insurmountable problem as titanium-clad equipment is used to counter the corrosion rate and is attested by the fact that multi-billion lb per year plants using this technology exist all over the globe.

The addition of Zr can be used to decrease catalyst concentration without sacrificing activity. But whether this is always desirable depends upon the exact experimental conditions during the aerobic oxidation. The reason being that if Zr is added to increase activity, the concentration of cobalt would decrease. However increasing Co concentration provides *selective* pathways in several ways:

1. The peroxy and alkoxy radicals can add to the aromatic ring resulting in olefins. The olefins will be rapidly oxidized and a net yield loss will result. Increasing Co concentration reduces this reaction via reaction (4) in Fig. 15. This is particularly important when the aromatic rings are highly electrophilic or have reduced aromaticity such as during the oxidation of hydroxymethylfurfural [20]
2. Increasing cobalt concentration will reduce the concentration of the highly energetic and unse-

lective hydroxy radical formed during the thermal decomposition of peroxides and peracids, see reaction (5) in Fig. 15 [25,40]. Increasing the cobalt concentration will result in an increase in reactions (6) and (8) (Fig. 15) effectively reducing the concentration of hydroxyl radicals.

3. Increasing cobalt concentration will reduce the importance of the Baeyer–Villiger reaction, see Fig. 16, since the dinuclear Co(II) reacts very rapidly and selectively with the peracid [40]. The Baeyer–Villiger reaction forms the undesirable phenyl formate which constitutes a yield loss to terephthalic acid. Even worse, however, is that the phenyl formate hydrolyzes to the phenol which it is a strong antioxidant. The phenol not only decreases the rate of reaction, but becomes further oxidized to the intensely colored, orange quinone. The latter can adversely affect the color of the desired aromatic acid. Quinones themselves have anti-oxidant properties and eventually become oxidized to carbon dioxide and carbon monoxide.

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