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Characterization of the reaction of cobalt(II) acetate, dioxygen and acetic acid, and its significance in autoxidation reactions

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Abstract

When cobalt(II) acetate is added to an oxygenated solution of acetic acid at reflux, a reaction occurs producing cobalt(III) acetate, carbon dioxide, carbon monoxide, methane, methyl acetate and water. Evidence is presented that this reaction is initiated by a trace amount of adventitious peroxide in acetic acid and is then is propagated via a free radical chain reaction. A balanced set of reactions is given which are consistent with the products observed. It is suggested that this is the initiation step in cobalt-catalyzed autoxidations in acetic acid. Of the first row metal acetates from calcium to zinc, only cobalt(II) acetate undergoes this reaction. It is shown that cobalt is, by far, the most active autoxidation catalyst toward *p*-toluic acid in acetic acid. The author concludes that the $Co(OAc)_2/O_2/$HOAc reaction is one of the reasons for cobalt's unique character as an autoxidation catalyst in carboxylic solvents.

Introduction

Cobalt, as a soluble salt either alone or in combination with other components, is the most commonly used autoxidation catalyst in the industrial oxidation of hydrocarbons. Thus butane, naphtha and propylene can be oxidized to acetic acid, pentenes to methyl isobutyl ketone, cyclohexane to a cyclohexanone and cyclohexanol mixture [1] and toluene, *m*-xylene, *p*-xylene and pseudocumene [2] to their corresponding aromatic acids (benzoic, isophthalic, terephthalic and trimellitic acids respectively). The most common solvents for these processes are aliphatic acids, usually acetic acid. For example, this is the solvent used for catalysts composed of transition metals combined with bromine [3]. Usually the $Co(OAc)_2/Mn(OAc)_2/HBr$ combination is used*. The author has a file containing 351 reactions in which 269 different reactants have been oxygenaged using transition metal/bromide catalysts in acetic acid**. This paper addresses the question of why cobalt-containing catalysts are used in conjunction with acetic acid as the solvent.

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*The process associated with this catalyst is often called the Amoco Mid-Century Process. See [18] for details.

**This has been assembled in a proprietary database in the Molecular Design Ltd software called REACCS (Reaction Access System).

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The model used for autoxidation reactions is the free radical chain mechanism. This mechanism involves the initial formation of an organic radical (initiation step), a propagation of the organic radical using dioxygen to produce a peroxide, and termination steps in which the radicals re-combine [4]. Organic radicals of hydrocarbons are highly unstable and can spontaneously form only above 400 °C [5]. Since most autoxidation reactions occur far below this temperature, one needs to explain how they form in the initiation step. It will be shown that placing cobalt(II) acetate in acetic acid with dioxygen can produce radical species. This reaction is hereafter signified as the $Co(OAc)_2/O_2/HOAc$ reaction in the rest of this paper.

There are two related reports on the reaction of metal acetates with aliphatic acids and dioxygen. Van Helden *et al.* [6] report that manganese/dioxygen does not decompose butyric acid but that cobalt does; 20–30% of the butyric acid was decomposed in 24 h by cobalt. It is not clear whether the reagents were metal(II) or metal(III) acetates or a combination of the two. The latter are strong oxidants in aliphatic acids and the decomposition would be expected*, while the metal(II) acetates have virtually no oxidizing characteristics. Levy [7] reports than when manganese(II) acetate tetrahydrate is heated with dioxygen (air) to 95 °C with long-chain fatty acids, manganese(III) is formed. He reports that this reaction does not occur in acetic acid, however. This reaction will be discussed further later.

Experimental

The metal acetates, often obtained as hydrates, were used as received, as was the EM brand glacial acetic acid. Cobalt(III) acetate was prepared via ozonolysis of cobalt(II) acetate in an acetic acid/acetic anhydride mixture [8]. It contained 24.0% cobalt, of which 23.5% was cobalt(III) (via iodometric titration). Manganese(III) acetate was prepared as described previously [9].

The $M(OAc)_n/O_2/HOAc$ reactions (where n is the oxidation state of the metal) at ~100 °C and ambient pressure were performed in glass cylindrical flasks, fitted on the bottom, with glass frits, with a capacity of ~200 ml. The gases were passed through the glass frit, through the reactor, and then through water and dry-ice cooled condensers. The gases were continuously analyzed via a Beckman model 715 oxygen analyzer and periodically via GC. The concentration of the metals was varied in the experiments by incremental additions of the metal acetate. The incremental additions were made ~60 min apart, with the GC analyses of the vent gases occurring ~50 min later. The experiments at higher temperature and pressure were performed in a 1 liter titanium-clad autoclave fitted with a condenser, a research control valve and then a series of dry ice traps. The vent gases

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*There are numerous stoichiometric oxidations of hydrocarbons in which cobalt(III) and manganese(III) acetates are used. See examples in [4].

were analyzed continuously for dioxygen (as described above) and for carbon dioxide and carbon monoxide via Beckman IR analyzers.

The composition of the vent gases was analyzed for carbon dioxide, carbon monoxide, nitrogen, oxygen and argon using a HP5880 GC instrument with a Porapak QS 50/80, 1/8 inch o.d. 20 foot column. The temperature was ramped from -50 to 220 °C at 30 °C min^{-1}.

The UV–VIS spectra were measured with a HP8451A diode array spectrometer with the accompanying software to perform the multicomponent analysis. Analysis of Co(II)–Co(III) mixtures were performed over the 350–800 nm region. The analysis for cobalt(III) acetate is more accurate than for cobalt(II) because of its greater molar absorptivity and because there are regions in the spectrum where only cobalt(III) absorbs. Because of this the Co(II) concentration was normally calculated knowing the original cobalt(II) acetate placed in the reactor and subtracting the cobalt(III) concentration as determined by UV–VIS.

Results and discussion

Characterization of the reaction of cobalt(II) acetate and dioxygen in acetic acid

A reaction occurs when air is first bubbled through acetic acid and then cobalt(II) acetate tetrahydrate is added. Examples 1–8 in Table 1 give typical results when the vent gases of the $Co(OAc)_2/O_2/HOAc$ reaction are analyzed via GC. The vent dioxygen concentration is less than that of the air being added to the reactor, hence oxygen is being consumed. The vent gases also contain carbon dioxide, carbon monoxide and often methane. Carbon monoxide is a minor product of the reaction, with CO_2/CO ratios typically ranging from 17–48. At a constant flow rate of air into the reactor, the oxygen consumption increases as the cobalt concentration increases (see examples 1–4 and 5–8 of Table 1 and Fig. 1). Similarly, increases in carbon dioxide, carbon monoxide and methane occur. Less methane, relative to carbon dioxide, is seen as the flow rate of air increases (compare examples 1–4 to 5–8). The CO_2/O_2 ratio in Table 1 is the value of carbon dioxide being formed divided by the dioxygen being consumed. These values range from 1.1 to 1.7.

The UV–VIS spectrum that results from the $Co(OAc)_2/O_2/HOAc$ reaction is consistent with a mixture of cobalt(II) and cobalt(III) acetates. The visible spectrum of authentic cobalt(II) acetate tetrahydrate and cobalt(III) acetate (prepared by ozonolysis) is illustrated in Fig. 2. The large differences in band shape and molar absorptivities of these two species make the multicomponent analysis for a mixture of the two quite accurate, *i.e.* even a small amount of cobalt(III) in the presence of substantial amounts of cobalt(II) is readily detected. If cobalt(II) acetate in acetic acid is placed in air at the reflux temperature of acetic acid (~114 °C), the visible spectrum given in Fig. 3 is obtained. Experimental conditions are given in example 9 of Table 1. The increase in absorbance at ~350 and 650 nm is attributed to the

TABLE 1

Analysis of the reactor vent gases in the $Co(OAc)_2/O_2/HOAc$ reaction[a]

Exam.	[Metal] (M)	Air flow (ml min^{-1})	Vent O_2 (%)	Vent CO (%)	Vent CH_4 (%)	Vent CO_2 (%)	CO_2/O_2 (mol/mol (h))	CO_2/CO (mol/mol)
1	0.017	24	20.554	0.000	0.000	0.161	1.5	–
2	0.029	24	20.428	0.013	0.003	0.397	1.7	31
3	0.038	24	20.331	0.019	0.004	0.492	1.5	26
4[c]	0.046	24	20.327	0.020	0.003	0.498	1.5	25
5	0.10	10	19.773	0.020	0.093	1.2	1.4	–
6	0.18	14	17.983	0.073	0.485	3.57	1.3	48
7	0.26	10	17.303	0.155	0.601	4.28	1.7	27
8	0.34	9.6	16.544	0.229	0.835	5.09	1.3	22
9[d]	0.12	10	19.081	0.103	0.053	1.80	1.1	17
10[e]	0.12	10	20.643	N.D.[b]	N.D.	0.042	–	–
11[f]	0.12	19	20.739	N.D.	N.D.	0.044	–	–
12	0.080	24	19.214	0.082	0.884	1.95	1.4	24
13[g]	0.080	24	20.657	N.D.	N.D.	0.041	–	–

[a] Obtained at refluxing acetic acid (113–114 °C), initial volume of acetic acid 100 ml. Composition of air, measured by GC, and averaged over the time these experiments were performed, was 20.656% O_2 and 0.044% CO_2.

[b] N.D. = none detected.

[c] UV–VIS analysis gives [Co(III)] = 0.00038 M.

[d] UV–VIS analysis gives [Co(III)] = 0.0024 M

[e] 0.0053 M phenol was added. No Co(III) detected via UV–VIS analysis. Compare with example 9 in which phenol was not added.

[f] Contains an equimolar amount of manganese(II) acetate.

[g] After 0.080 M of NaBr was added to example 12.

[h] Defined as the carbon dioxide formed (vent CO_2, %) divided by the dioxygen consumed (20.656 – vent dioxygen, %).

presence of cobalt(III). If one does a multicomponent analysis (assuming the presence of $Co(OAc)_2$ and $Co(OAc)_3$ only) one obtains a cobalt(III) concentration of 0.0024 M when starting with a cobalt(II) acetate concentration of 0.12 M. Hence 2.0% of the cobalt existing in solution is cobalt(III) acetate. Figure 3 also gives the difference between the calculated and observed spectrum. The fit is excellent, considering that different forms of cobalt(III) exist which have slightly different spectra [10].

A confirmation of the presence of cobalt(III) is its spontaneous reaction with manganese(II) acetate. Manganese(II) acetate rapidly reacts with cobalt(III) in acetic acid:

$$Co(OAc)_3 + Mn(OAc)_2 \longrightarrow Co(OAc)_2 + Mn(OAc)_3 \qquad (1)$$

The visible spectra of manganese(II) and manganese(III) acetates are significantly different from those of Co(II) and Co(III) acetates (see Fig. 2). Therefore, a substantial change should be observed in the spectrum when $Mn(OAc)_2$ is added to a solution prepared from the $Co(OAc)_2/O_2/HOAc$

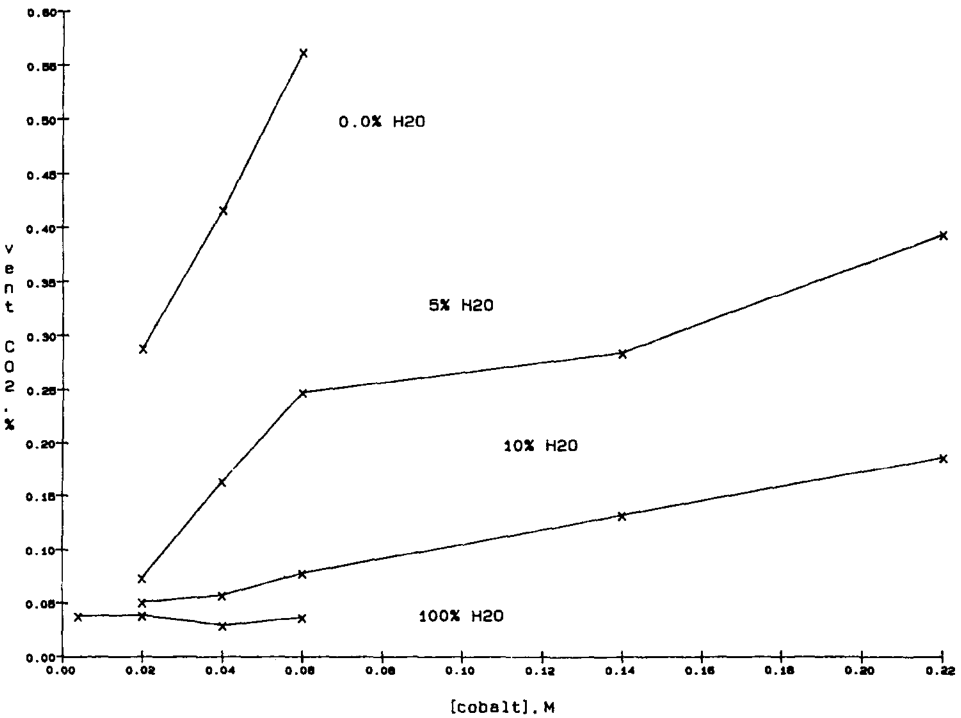

Fig. 1. Effect of water and cobalt concentration on the Co/O_2/HOAc reaction. Air flow rate of 25 ml min^{-1} through 100 ml of acetic acid.

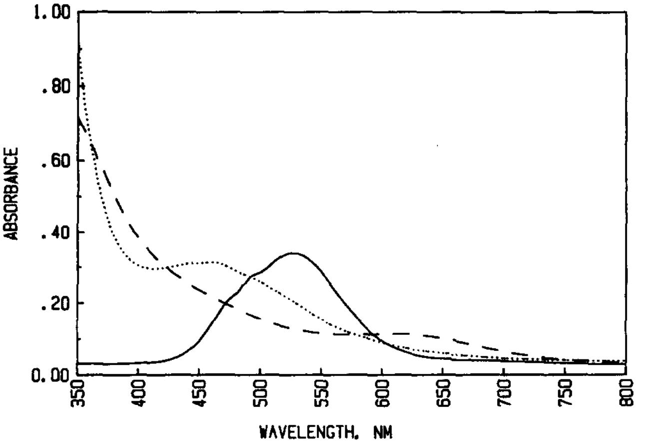

Fig. 2. UV–VIS difference between authentic cobalt(II), cobalt(III) and manganese(III) acetate. Co(II) $(OAc)_2$, 0.0201 M (——); Co(III) $(OAc)_3$, 0.000444 M (– – –); Mn$(OAc)_3$, 0.00100 M (·····).

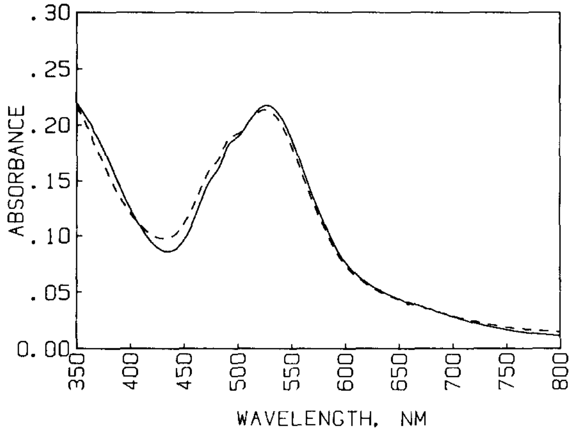

Fig. 3. UV–VIS of a solution after the Co/O_2/HOAc reaction (——) and the multicomponent fit assuming $Co(OAc)_2$ and $Co(OAc)_3$ are present (– – –).

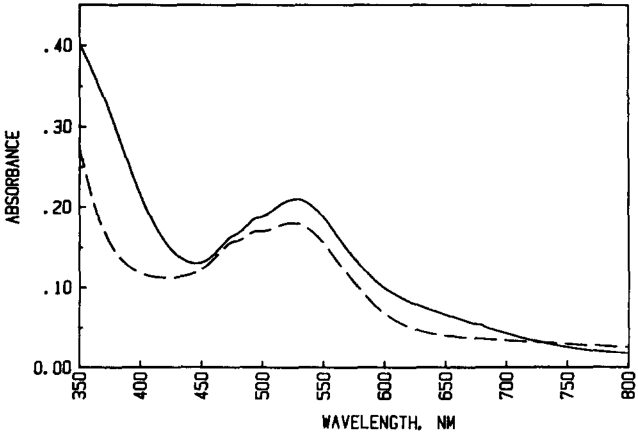

Fig. 4. UV–VIS of a solution after the Co/O_2/HOAc reaction (——) and after $Mn(OAc)_2$ addition (– – –).

reaction. The reaction conditions are given in example 9. The solution was first removed from the reactor and then the $Mn(OAc)_2$ added to it. Addition of manganese(II) acetate (approximately equimolar to the cobalt(III) that had formed) results in a significant UV–VIS spectral change, see Fig. 4. The UV–VIS multicomponent analysis gives a reduction of the [Co(III)] from 0.0024 to 0.00074 M and the [Mn(III)] increasing from 0.0 to 0.0014 M. This is consistent with eqn. (1).

Cobalt(III) acetate in acetic acid rapidly oxidizes the bromide ion to dibromine. The presence of cobalt(III) was further confirmed by first reacting a solution from the $Co(OAc)_2$/O_2/HOAc reaction with a known excess amount of sodium bromide and then precipitating the remaining bromide ion with silver nitrate. The solution from the $Co(OAc)_2$/O_2/HOAc reaction was prepared as given in example 12 (Table 1). It was found that 0.89% of the cobalt present was present as cobalt(III) acetate. For comparison, the UV–VIS analysis of example 4 gives 0.84% cobalt(III).

Water and methyl acetate are products of the $Co(OAc)_2/O_2/HOAc$ reaction. In an autoclave experiment, 400 l of air was passed through 500 ml of a 0.024 M cobalt solution at 300 psi. The average vent dioxygen value was 17.6% (air is 20.9%), the average CO value was 0.22% and the average CO_2 value was 3.3% during the experiment. The measured moles of water (Karl-Fisher), methyl acetate (via GC) and carbon dioxide (via GC and subsequent numerical integration) were 0.66, 0.26 and 0.62 moles.

Evidence for the presence of a free radical chain reaction was obtained by performing the $Co(OAc)_2/O_2/HOAc$ reaction in the presence of phenol (see Example 10, Table 1). This example should be compared to example 9 which was performed identically but with no phenol present. The presence of phenol completely inhibited the reaction, *i.e.* no oxygen uptake is observed nor any carbon dioxide, carbon monoxide or methane formation. Furthermore, a UV–VIS multicomponent analysis of example 10 showed no cobalt(III) formation. The addition of sodium bromide (compare Example 12 to 13) and the presence of manganese(II) acetate with cobalt(II) (see Example 11) also inhibits the reaction. The inhibition due to manganese(II) and sodium bromide suggests that they interfere with the chain carrier in the chain reaction.

Indirect evidence was obtained for the presence of adventitious peroxide which is proposed in reaction (2). This is indicated by the fact that the above reaction sequence is not observed at 112 °C if the cobalt(II) acetate is first placed in the acetic acid under nitrogen for 114 min and then exposed to a flow of air. This is explained as follows. If the cobalt acetate were placed first in a nitrogen atmosphere, then reactions (2) and (3) would occur but the reactions in the propagation step, reactions (4)–(8) would not since the latter are propagated by dioxygen. The $RO^{\cdot}$ and methyl radicals would quickly react and form non-peroxidic species. Since the half-life of $Co(OAc)_3$ is 10 min at 100 °C*, 114 min at 112 °C should be sufficient time (11 half-lives) to reduce cobalt(III) to an amount unable to sustain the propagation reactions (rxns (4)–(8)).

Proposed reaction sequence for the $Co(OAc)_2/O_2/HOAc$ reaction

The experimental observations given in the previous section can be rationalized by the following set of balanced reactions:

Initiation:

$$Co(OAc)_2 + ROOH(trace) + HOAc \longrightarrow Co(OAc)_3 + RO^{\cdot} + H_2O \qquad (2)$$

$$Co(OAc)_3 \longrightarrow Co(OAc)_2 + CH_3^{\cdot} + CO_2 \qquad (3)$$

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*This was measured in our laboratory using the cobalt(III) acetate prepared via ozonolysis. The form of cobalt acetate obtained in the $Co(OAc)_2/O_2/HOAc$ reaction is probably different [10] and hence the actual half-life somewhat different than stated.

Propagation:

$$CH_3^{\bullet} + O_2 \longrightarrow CH_3OO^{\bullet} \tag{4}$$

$$Co(OAc)_2 + CH_3OO^{\bullet} + HOAc \longrightarrow Co(OAc)_3 + \underset{\text{methyl hydroperoxide}}{CH_3OOH} \tag{5}$$

$$Co(OAc)_2 + CH_3OOH + HOAc \longrightarrow Co(OAc)_3 + CH_3O^{\bullet} + H_2O \tag{6}$$

$$Co(OAc)_3 \longrightarrow Co(OAc)_2 + CH_3^{\bullet} + CO_2 \tag{7}$$

$$Co(OAc)_2 + CH_3O^{\bullet} + HOAc \longrightarrow Co(OAc)_3 + CH_3OH \tag{8}$$

The sum of reactions (4)–(8) is:

$$2Co(OAc)_2 + 3HOAc + O_2 \longrightarrow 2Co(OAc)_3 + CH_3OH + H_2O + CO_2 \tag{9}$$

The UV–VIS spectra of cobalt(II) and cobalt(III) acetates in acetic acid–water mixtures indicate that they are octahedral coordination compounds. They are simplified to $Co(OAc)_2$ and $Co(OAc)_3$ in the above reaction sequence. The scheme above is similar to that proposed by Levy [7], which is based on chemistry proposed by Anderson and Kochi [11].

Reaction (9) rationalizes the observed oxygen uptake, cobalt(III) formation, methyl acetate (from the reaction of methanol with the solvent), water and carbon dioxide formation. Furthermore, the observed amounts of water and carbon dioxide are the same as was experimentally observed in the autoclave experiment. Although carbon dioxide is made both in the initiation step and in the propagation step, with reasonably long chain lengths (over 100), the amounts of water and carbon dioxide would be expected to be the same. The experimentally observed methyl acetate in the filtrate of the autoclave experiment does not equal the amount predicted in reaction (9). It was typically found that a substantial amount of methyl acetate is volatilized during the reaction and lost via the vent gases.

The observed methane is strongly indicative of transient methyl radicals which react with hydrogen atom donors. The decrease in methane formation with increasing flow rate of air is consistent with the increased availability of dioxygen which promotes reaction (4). The addition of sodium bromide and manganese(II) acetate rapidly quenches the reaction, since they rapidly reduce the cobalt(III) acetate thus terminating the chain reaction.

The products formed in the propagation step should be consistent with those reported for the decomposition of authentic cobalt(III) acetate in acetic acid. Heiba *et al.* [12] report that carbon dioxide and methane are the main products when cobalt(III) acetate is decomposed in an inert atmosphere. We have confirmed this observation. Hendriks *et al.* [13] report the formation of carbon dioxide and methyl acetate when cobalt(III) acetate is decomposed in air. We have found that decomposition of cobalt(III) acetate in air gives the expected oxygen uptake and the formation of carbon dioxide, see Table 2. The formation of the minor amounts of carbon monoxide are not rationalized in the above reaction sequence but are observed with similar CO_2/CO ratios during the decomposition of authentic cobalt(III) acetate.

TABLE 2

Vent gas composition when cobalt(III) acetate is heated in acetic acid in the presence of air[a]

Time (min)	Vent O_2 (%)	Vent CO_2 (%)	Vent CO) (%)	CO_2/CO
0	20.9	0.03	0.000	
5	20.5			
10	20.0			
15	19.5			
20	19.4			
22	19.4	2.74	0.083	33.01
50	19.5			
80	19.8	1.32	0.103	12.82
155	20.4			
195	20.5	0.37	0.038	9.74
305	20.8			

[a] Initial conditions: 4.05 mmol $Co(OAc)_3$ in 100 ml acetic acid at 95 °C with an air flow rate of 19.5 ml min^{-1}.

Significance of the Co/O_2/HOAC reaction

In the autoxidation of hydrocarbons, the initiation step requires the formation of a radical of the hydrocarbon, RH:

$$RH \longrightarrow R^{\cdot} + \text{products} \qquad (10)$$

or

$$RH + O_2 \longrightarrow ROOH \qquad (11)$$

Benson and Nangia have stated, "Perhaps the most elusive feature of the oxidation reaction has been the initiation reaction, the step by which the reaction gets started. Below 450 °C there is usually no homogeneous, radical reaction which can account for the initiation of the oxidative chain cycle" [14]. The problem lies in the kinetic and thermodynamic prohibitions of reaction (10). Because of this problem, Benson and Nangia [14] suggest that the initiation step involves an ionic pathway rather than free radical, while Skibida [15] suggests the formation of superoxo–metal complexes followed by their reaction with the hydrocarbon RH. In fact, these elementary reactions may account for the trace amount of peroxide proposed in reaction (2).

For the very important class of cobalt-catalyzed oxygenations using acetic acid or other carboxylic acids as solvent, it is quite reasonable that the Co/O_2/HOAc reaction takes advantage of the adventitious peroxide. Starting with the trace amount of peroxide, reactions (2)–(8) result in relatively high concentrations of radicals and Co(III) acetate. Both cobalt(III) acetate [16] and the highly energetic methyl radical* are known to generate the $R^{\cdot}$ radical

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*See [17]. The statement made in this reference that methyl radicals are not involved in homogeneously catalyzed reactions is clearly incorrect.

required in reaction (10). The author commonly uses cobalt(III) acetate to initiate (if necessary) the oxidation of a variety of alkylaromatic compounds in their laboratory. The methyl radical would not be a very efficient initiator, however, because of its lack of selectivity. The methyl radical would not be good for the initiation of *p*-xylene, for example, because it could easily react with the acetic acid solvent as well as the methyl group on the aromatic ring. The fact that bromide ion inhibits the $Co(OAc)_2/O_2/HOAc$ reaction suggests that in transition metal/bromide-type catalysts this reaction is not as important as in reactions where only cobalt is used. The cobalt(III) produced in the reaction very rapidly reacts with the bromide to form the extraordinarily active and selective cobalt(II)–bromine(0) complex [18].

It has implicitly been assumed thus far that hydrocarbons would not autoxidize without the presence of cobalt. The results in Table 3 show that placing toluene in an autoclave under high air pressures and temperatures does not result in a significant oxidation, while addition of cobalt acetate or a cobalt acetate/hydrogen bromide mixture results in vigorous reactions. No carbon dioxide or carbon monoxide gases are detected in the reaction without metals, so their absence is consistent with the lack of toluene autoxidation. Perhaps a trace of benzaldehyde was observed. There is a report that a very weak reaction occurs with toluene in acetic acid [19], however, we did not observe it.

Consistency of the proposed initiation reaction sequence with the autoxidation of hydrocarbons

As indicated in the introduction, cobalt is usually used in the autoxidation of hydrocarbons. Manganese is sometimes used but with more easily oxidizable substances such as acetaldehyde, butyraldehyde, cyclohexanol and cyclohexanone [1]. We have previously reported, using *p*-toluic acid as a feedstock, that cobalt is the only the first row transition metal acetate (Ti, V, Cr, Mn, Fe, Co, Ni, Cu) that catalyzes a significant rate of oxygen uptake [20]. This data is reproduced in Table 4 as well as results we have obtained with Co/

TABLE 3

Experiments illustrating the necessity of metal catalysts in autoxidation

toluene (M)	3.26	3.26	2.17	2.17	3.26
$Co(OAc)_2$ (M)	0.0	0.066	0.040	0.040	0.066
HBr (M)	0.0	0.0	0.0	0.040	0.067
reaction temp. (°C)	121–209	117–211	160	160	147
reaction pressure (atm)	34	34	10	10	34
reaction time (min)	25	110	60	35	60
vent CO_2 (% maximum)	0.0	12	1.1	1.4	0.55
vent CO (% maximum)	0.0	2.2	0.10	0.67	0.20
yields (%)					
benzoic acid	0.0	8.1	3.3	91	89
benzaldehyde	0.06	1.1	2.7	0	0.2
benzylalcohol	0.0	0.0	0.7	0	0

TABLE 4

Activity of the metal acetate/O_2/HOAc reaction as compared to the autoxidation activity of selected metals and metal/bromide catalysts

Metal	Activity toward HOAc/O_2[a]			Activity toward *p*-toluic acid[b]	
	Conc. range (M)	Change in vent O_2 (%)	Change in vent CO_2 (%)	$M(OAc)_n$ catalyst	$M(OAc)_n$/NaBr catalyst
$Ca(OAc)_2$	0.0040–0.20	0.0	0.0	0.0	
$TiO(acac)_2$	0.0040–0.040[c]	0.0	0.0	0.0	
$VO(OAc)_2$	0.0040–0.040	0.005	0.066	0.0	0.0
$Cr(OAc)_3$	0.0040–0.040	0.014	0.065	0.0	0.0
$Mn(OAc)_2$	0.0040–0.12	0.0	0.0	0.1	0.86
$Fe(OAc)_2$	0.0040–0.12[c]	0.013	0.035	0.0	0.0
$Co(OAc)_2$	0.010–0.060	0.37	0.56	1.6	2.3
$Ni(OAc)_2$	0.0040–0.40	0.0	0.0	0.1	0.1
$Cu(OAc)_2$	0.0040–0.20	0.0	0.0	0.0	0.0
$Zn(OAc)_2$	0.0040–0.12	0.003	0.038	0.0	

[a] Obtained at an air flow rate through the reactor of 25 ml min^{-1} at reflux.

[b] At 95 °C, 45 ml min^{-1} of air, 25.0 g *p*-toluic acid, 75 ml HOAc, metal concentration 0.04 M; $Co(OAc)_2$ reactions were initiated with azobis(methylpropylnitrile); metal/bromide ratios were 1/1 mol/mol; conversion of *p*-toluic acid was less than 10% in all cases.

[c] Solution is saturated.

Br catalysts. Table 4 also describes the effect of passing air through a mixture of metal acetates (when available; TiO(acac) was used as the titanium source) in acetic acid. The metals chosen were the first row transition metals together with calcium and zinc (non-transition metals on either side of the first row). No significant effect on the vent gas composition is seen with Ca, Ti, Mn, Ni, Cu and Zn, trace effects are seen with V, Cr and Fe, and by far the strongest effect is seen with cobalt. The largest amount of carbon dioxide, by a factor of 8, is produced by cobalt.

Since the origin of the carbon dioxide is mostly from that described in reaction (7), *cobalt has the strongest ability* to decompose the acetic acid. As discussed, both the methyl radical and cobalt(III) can initiate autoxidations. We suggest this is one of the reasons cobalt is so often used in autoxidations. (Of course, cobalt's ability to rapidly decompose the peroxidic species in the initiation chain sequence, rxns (2)–(8), is also used in the normal propagation step during the oxidation of alkylaromatic hydrocarbons.)

It is well known that water inhibits the rate of autoxidations in aliphatic acids [21]. It was found that the $Co(OAc)_2/O_2$/HOAc reaction is also inhibited by water (see Fig. 1). This is expected since the overall rate of oxidation of a chain reaction is dependent upon the initiation rate constant [22]. Methyl acetate is a known byproduct in alkylaromatic Co/Mn/Br-catalyzed oxidations [23]. The initiation sequence also gives methyl acetate, which is consistent with that normally observed in autoxidations.

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