The Autoxidation and Cleavage of Poly(vinyl alcohol) with *tert*-Butyl Hydroperoxide in the Presence of Various Metal Acetylacetonates and Cobalt Salts

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ABSTRACT: The catalytic effect of 12 acetylacetonates, Al(III), Ce(III), Co(II), Co(III), Cr(III), Cu(II), Fe(II), Fe(III), Mn(II), Mn(III), Ni(II), and V(III), on the cleavage and autoxidation of poly(vinyl alcohol) in the presence of *tert*-butyl hydroperoxide at 42° in dimethyl sulfoxide and water is reported. Peroxide decomposition and uv spectral changes are also reported. The effect of varying ligands on the cobalt(II) species in the above reactions was observed by measuring rates of cleavage and autoxidation of poly(vinyl alcohol) and peroxide decomposition in the presence of CoF_2, $CoCl_2$, $CoBr_2$, CoI_2, $Co(NO_3)_2$, and cobalt(II) phthalocyanine. The results are discussed in the light of other studies attempting to compare metal activity.

In previous reports,[1] the autoxidation and cleavage of poly(vinyl alcohol) in the presence of cobalt(II) and -(III) acetylacetonate and *tert*-butyl hydroperoxide in water and dimethyl sulfoxide were described. In this report the role of other metal acetylacetonates in the same systems is presented. In addition the effect of varying the ligand is described.

Other studies have compared metal acetylacetonates in a variety of reactions including peroxide decomposition,[2,3] hydrocarbon autoxidation,[2–5] amine oxidation,[6] olefin epoxidation,[7] and free radical polymerization.[4,8] Although there is no definite correlation between relative reactivities of the metals for the reactions studied the behavior of the metals falls generally into two broad categories: reactive metals which have more than one oxidation state readily available (e.g., Cu, Co, V, Fe, Cr) and unreactive metals which are more resistant to oxidation–reduction processes (e.g., Al, Zn, Zr). This study shows that this broad generalization is once again exhibited and suggests that some of the difficulty in correlating metal activity from system to system may arise from the effect of the medium, the ligand, or both.

Experimental Section

Chemicals. The metal acetylacetonates (McKenzie Chemical Corp.) were purified by recrystallization from acetone, except cobalt(II) acetylacetonate which was recrystallized from benzene. Cobalt(II) fluoride, cobalt(III) fluoride, cobalt(II) nitrate, cobalt(II) bromide, cobalt(II) iodide, and cobalt(II) phthalocyanine were obtained from Pfaltz and Bauer Co. Poly(vinyl alcohol) (K&K Laboratories) of viscosity average mol wt 9.1×10^4 g/mol (measured in dimethyl sulfoxide) was used for this work.

NMR Measurements. A Varian A-60 spectrometer was used to detect the broadening of the OO–H peak of *tert*-butyl hydroperoxide. Carbon tetrachloride solutions were 10^{-3} *M* in metal acetylacetonate and 0.96 *M* in *tert*-butyl hydroperoxide. The unperturbed line width was 5 cycles.

Kinetics. Procedures for oxygen uptake measurements, *tert*-butyl hydroperoxide decomposition, uv spectral measurements, and poly(vinyl alcohol) cleavage measurements have been described previously.[1,9] Extinction coefficients measured in chloroform for metal acetylacetonates were taken from Cotton and Holm.[10] Table I lists extinction coefficients in dimethyl sulfoxide, water, and chloroform.

Results and Discussion

Table II presents the initial rates of poly(vinyl alcohol) autoxidation, the initial rates of *tert*-butyl hydroperoxide decomposition, the ratio of the uv absorbance at λ_{max} after 2×10^5 sec to the initial absorbance of the metal acetylacetonates, and the initial cleavage rates of poly(vinyl alcohol) all at 42° in both dimethyl sulfoxide and water. Table III presents the relative NMR broadening of the OO–*H* signal of *tert*-butyl hydroperoxide in carbon tetrachloride in the presence of metal acetylacetonates. Table IV presents the rates of poly(vinyl alcohol) cleavage, oxygen uptake by poly(vinyl alcohol) solutions, and *tert*-butyl hydroperoxide decomposition in the presence of various cobalt salts.

Autoxidation and *tert*-Butyl Hydroperoxide Decomposition. The effect of different metals on the autoxidation of poly(vinyl alcohol) has been examined in dimethyl sulfoxide and aqueous solution at metal concentrations of 2×10^{-5} *M* and relatively high peroxide concentrations, 0.66 *M* (Table II). Rates are generally higher in dimethyl sulfoxide than in water for most of the examples in which reaction could be run in both media.

The effect of the metal in autoxidation must be related in some way to its ability to decompose *tert*-butyl hydroperoxide. Possible factors which might affect peroxide decomposition for different metals are reduction potential,[5] peroxide–metal interactions (Table III), the ease with which the metal is deactivated,[11] and the ability of the metal to complex with radicals thereby acting as a chain inhibitor.[12] During the autoxidation reaction other factors such as metal substrate reactions, metal oxygen reactions, and products could influence autoxidation rates, while not necessarily altering *tert*-butyl hydroperoxide decomposition rates in vacuo.

Peroxide decomposition experiments were carried out with solutions of lower *tert*-butyl hydroperoxide concentration than those employed in autoxidation (0.016 *M*) but with similar metal concentrations. Under these conditions radical induced decomposition of the peroxide is not as important as with higher peroxide concentrations and the main decomposition reaction is expected to be from metal peroxide interactions. At low metal concentrations radical–metal interactions are not expected to be significant.

Those metal acetylacetonates with higher reduction potential values (e.g., Co(II), Co(III), and Cr(III)) are more active and better catalysts than those with lower values (e.g., Al(III)).[5] Some species (e.g., Mn(II) and (III)) do not indicate a great deal of catalytic activity even though they would be expected to on the basis of their reduction potential values. This may be related to solubility (aggregation),[13] deactivation of the metal,[11] or to the ability of manganese(II) to act as an inhibitor in the autoxidation reaction.[11] The effectiveness of copper(II) acetylacetonate has been observed for hydroperoxide decomposition.[2,3]

In relation to autoxidation the relative reactivity of metal acetylacetonate is Co(III), Cu(II) > Co(II), Cr(III), Ni(II) > V(III) > Mn(III) > Fe(II) > Fe(III) > Mn(II), Al(III) in dimethyl sulfoxide solution and Co(III), Co(II) > Cu(II), Fe(III), Ni(II) > V(III) in aqueous solution. This

Table I
Extinction Coefficients and Wavelengths of Maximum Absorption for Metal Acetylacetonates in Dimethyl Sulfoxide, Water, and Chloroform

	Extinction coefficient, l./(mol cm)	Maximum absorption, l./cm(λ_{max})		
	Literature value ($CHCl_3$)[10]	DMSO	H_2O	Literature value ($CHCl_3$)[10]
Al(III)	42,800	N.D.[c]	N.D.	288
Co(II)	16,200[a]	292	290	292
Co(III)	34,000[b]	256	254	258
Cr(III)	15,800	340	N.S.[d]	336
Cu(II)	20,100	295	290	296
Mn(II)	20,500	282	N.S.	276
Mn(III)	24,000	280	N.S.	274
Fe(II)	N.D.	295	N.S.	N.D.
Fe(III)	29,600	283	N.S.	274
Ni(II)	23,700	302	280	294
V(III)	19,600	289	276	280

[a] A Beer's law plot in water gives a value of 16,300 and in DMSO a value of 13,100. [b] A Beer's law plot in water gives a value of 20,800 and in DMSO a value of 38,100. [c] N.D. = no data. [d] N.S. = not soluble in water.

order of reactivity in autoxidation is generally consistent with the relative reactivity of metal acetylacetonates in promoting *tert*-butyl hydroperoxide decomposition. Cobalt(III) and copper(II) acetylacetonate are the most reactive metal acetylacetonates in *tert*-butyl hydroperoxide decomposition and poly(vinyl alcohol) autoxidation. Nickel(II) acetylacetonate is more reactive in autoxidation in dimethyl sulfoxide than its ability to decompose *tert*-butyl hydroperoxide would indicate. The lack of reactivity of nickel(II) acetylacetonate in promoting hydrocarbon autoxidation has been ascribed to its tendency to form dimers.[3] In a polar solvent this tendency might not be as significant and nickel(II)–substrate reactions might be impor-

Table III
Relative Signal Broadening of OO-H[a] in CCl_4 with Metal Acetylacetonates[b]

Al(III)	+[c]	Fe(III)	+++
Co(II)	+++	Mn(III)	+
Co(III)	0[d]	Ni(II)	++
Cr(III)	+++	VO(II)	++
Cu(II)	++	Zn(II)	+

[a] *t*-BuOOH = 0.96 *M*. [b] Metal acetylacetonates are 10^{-3} *M*. [c] + represents ~20 cycles of broadening. [d] 0 or unperturbed case with 5 cycle line width on a 60 MHz instrument.

Table IV
Initial Poly(vinyl alcohol) Oxygen Absorption Rates,[a] *tert*-Butyl Hydroperoxide Decomposition Rates,[b] and Poly(vinyl alcohol) Cleavage Rates[c] in the Presence of Cobalt Salts in DMSO and Water at 42°

Cobalt salt	$-(\Delta[O_2]/\Delta t)_0 \times 10^7$, M/sec		$-(\Delta[t\text{-BuOOH}]/\Delta t)_0 \times 10^9$, M/sec		$-(\Delta M_v/\Delta t)_0 \times 10^2$, g/(mol sec)	
	DMSO	H_2O	DMSO	H_2O	DMSO	H_2O
CoF_2	0.64	0.36	4.20	1.90	1.50	0.72
$CoCl_2$	5.4	5.7	9.81	2.06	8.60	0.72
$CoBr_2$	3.2	6.3	10.2	2.80	8.50	2.50
CoI_2	3.9	6.4	11.5	2.51	9.00	0.78
CoF_3	N.D.[d]	N.D.	N.D.	N.D.	1.70	N.D.
$Co(NO_3)_2$	N.D.	N.D.	N.D.	N.D.	8.65	N.D.
CoPht[e]	14.4	N.S.[f]	18.0	N.S.	16.8	N.S.
$Co(acac)_2$	11.1	8.8	12.0	2.45	8.65	1.34
$Co(acac)_3$	13.8	11.2	11.5	2.15	4.82	0.67

[a] Oxygen atmosphere, $[M]_0 = 2.0 \times 10^{-5}$ *M*, $[PVA]_0 = 0.195$ *M* in C_2H_4O units, $[t\text{-BuOOH}]_0 = 0.66$ *M*. [b] In vacuo $[M]_0 = 2.0 \times 10^{-5}$ *M*, $[PVA]_0 = 0.240$ *M* in C_2H_4O units, $[t\text{-BuOOH}]_0 = 0.016$ *M*. [c] Ambient atmosphere, $[M]_0 = 2.0 \times 10^{-5}$ *M*, $[PVA]_0 = 0.240$ *M* in C_2H_4O units, $[t\text{-BuOOH}]_0 = 0.66$ *M*. [d] N.D. = no data. [e] Cobalt(II) phthalocyanine. [f] N.S. = not soluble.

Table II
Initial Poly(vinyl alcohol) Oxygen Absorption Rates,[a] *tert*-Butyl Hydroperoxide Decomposition Rates,[b] Uv Spectral Changes,[b] and Poly(vinyl alcohol) Cleavage Rates[c] in the Presence of Metal Acetylacetonates in DMSO and Water at 42°

	$-(\Delta[O_2]/\Delta t)_0 \times 10^7$, M/sec		$-(\Delta[t\text{-BuOOH}]/\Delta t)_0 \times 10^9$, M/sec		Uv spectral changes		$-(\Delta M_v/\Delta t)_0 \times 10^2$, g/mol/sec	
	DMSO	H_2O	DMSO	H_2O	DMSO	H_2O	DMSO	H_2O
Co(II)	11.1	11.2	12.0	2.45	0.86[e]	0.95[e]	8.65	0.67
Co(III)	13.8	11.2	11.5	2.15	0.79[e]	0.96[e]	4.82	1.34
Cr(III)	11.1	N.S.[f]	9.51	N.S.	0.58	N.S.	3.08	N.S.
Cu(II)	13.2	7.08	11.6	2.28	2.00	0.58	6.40	2.60
Mn(II)	1.36	N.S.	2.18	N.S.	1.00	N.S.	1.25	N.S.
Mn(III)	8.92	N.S.	3.40	N.S.	3.15	N.S.	2.90	N.S.
Fe(II)	5.60	N.S.	6.58	N.S.	1.00	N.S.	3.95	N.S.
Fe(III)	3.68	6.60	3.40	1.53	0.27	0.27	5.50	1.12
Ni(II)	11.0	6.60	10.2	1.01	2.16	0.39	3.00	1.14
V(III)	10.1	0.72	8.4	1.45	1.26	0.64	1.86	0.55
Ce(III)	N.D.[g]	N.S.	N.D.	N.S.	N.D.	N.S.	2.50	N.S.
Al(III)	1.05	N.D.	3.22	1.10	N.D.	N.D.	1.14	2.00
No metal	0.0	0.0	0.0	0.0			0.0	0.0

[a] Oxygen atmosphere, $[M]_0 = 2 \times 10^{-5}$ *M*, $[PVA]_0 = 0.195$ *M* in C_2H_4O units, $[t\text{-BuOOH}]_0 = 0.66$ *M*. [b] In vacuo, $[M]_0 = 2 \times 10^{-5}$ *M*, $[PVA]_0 = 0.240$ *M* in C_2H_4O units, $[t\text{-BuOOH}]_0 = 0.016$ *M*. [c] Ambient atmosphere, $[M]_0 = 2 \times 10^{-5}$ *M*, $[PVA]_0 = 0.240$ *M* in C_2H_4O units, $[t\text{-BuOOH}]_0 = 0.66$ *M*. [d] Absorbance after 2×10^5 sec/initial absorbance at λ_{max}. [e] $[Co(acac)_2 + Co(acac)_3]/[Co(acac)_n]_0$ measured at 2×10^5 sec. [f] N.S. = not soluble. [g] N.D. = no data.

tant. Aluminum(III) is unreactive in both autoxidation and *tert*-butyl hydroperoxide decomposition consistent with its reduction potential. The extent of complexation between the metal and the peroxide is qualitatively suggested by Table III which presents NMR data on the line broadening of the OO–*H* signal of *tert*-butyl hydroperoxide produced by the addition of metal acetylacetonates in carbon tetrachloride. Very inactive metals in peroxide decomposition appear to exhibit little broadening (aluminum(III) and zinc(II)), while an active metal (cobalt(II)) exhibits marked broadening.

***tert*-Butyl Hydroperoxide Decomposition and Uv Spectral Changes.** In Table II data are presented for the initial rates of *tert*-butyl hydroperoxide decomposition in the presence of several metal acetylacetonates in dimethyl sulfoxide and water. Uv data are also presented in dimethyl sulfoxide and aqueous solutions under conditions identical with those employed in the *tert*-butyl hydroperoxide decomposition. The ratio of the absorbance of the metal acetylacetonate after 2×10^5 sec to the initial absorbance of the metal acetylacetonate at the wavelength of maximum absorbance is tabulated.

Some of the metals showed increased absorbance in dimethyl sulfoxide, others showed decreased absorbance; in water all the metal acetylacetonates studied which were soluble showed decreased absorbance. For the case of the cobalt acetylacetonates rapid equilibration to the Co(II) and Co(III) forms was observed regardless of which species was initially present. The total absorbance after 2×10^5 sec was less than the initial absorbance. In dimethyl sulfoxide the Co(II) species predominated; in water the Co(III) species predominated.[1]

Changes in absorbance indicate alteration of the metal oxidation state or alteration of the ligand. Although no clear correlation can be made between increased or decreased absorbance and metal reactivity, it may be seen that many of the metals which showed an increased uv absorbance with time showed a high degree of catalytic activity on peroxide decomposition. The increase in uv absorbance may be due to the increased "solubilization" of the catalyst as a result of the presence of reaction products which could decrease the extent of aggregation of the catalyst in solution.

Cleavage Reaction. The viscometrically measured initial cleavage rates of poly(vinyl alcohol) in the presence of *tert*-butyl hydroperoxide and various metal acetylacetonates are given in Table II. As observed for the autoxidation and peroxide decomposition reactions the rates in dimethyl sulfoxide are higher than in water. In a previous report[9] on the cobalt acetylacetonates it was shown that reaction occurs predominantly at 1,2-diol sites. The similar shapes of the cleavage vs. time curves obtained in this work suggest the same site of attack for all these reactions.

The effectiveness of various metal acetylacetonates in promoting the cleavage of poly(vinyl alcohol) is in the order Co(II) > Cu(II) > Fe(III) > Co(III) > Fe(II) > Cr(III) > Mn(III) > Ni(II) > V(III) > Mn(II) > Al(III) in dimethyl sulfoxide and Cu(II) > V(III), Al(III) > Co(III) > Ni(II), Fe(III) > Co(II) in water. This order of reactivity closely parallels that in *tert*-butyl hydroperoxide decomposition. The notable exception to this is cobalt(II) and -(III) acetylacetonate in aqueous solution. It is possible that cobalt(II) and -(III) acetylacetonate is inhibiting the reaction in some way, perhaps by promoting oxidation reactions, which compete with cleavage under these conditions.[12] Deactivation[3,11] of the metal catalyst may be important in the cleavage reaction.

Ligand Effects. The effects of several different cobalt salts on the autoxidation, peroxide decomposition, and cleavage reactions are presented in Table IV for both water and dimethyl sulfoxide solutions. As observed previously in varying the metal species the reactions studied are in most cases faster in DMSO than in water. It may also be noted that variations in ligand produce about as broad a spectrum of behavior as changing the metal. It was expected that variations of ligand might produce rate differences in reactions that reflect peroxide–metal interactions if the peroxide decomposition mechanism is the same in each case. The fluoride ligand is the least labile halide[14] and the one that might be least susceptible to displacement by the peroxide in complexation. The normal order of bridging efficiency in electron transfer reactions is $I^- > Br^- > Cl^- > F^-$. Cobalt(II) fluoride is significantly less active in peroxide decomposition and autoxidation than cobalt(II) chloride, bromide, and iodide in both dimethyl sulfoxide and aqueous solution. Autoxidation and peroxide decomposition rates are similar for cobalt(II) chloride, bromide, and iodide, however.

Cobalt(II) and -(III) acetylacetonate and cobalt(II) phthalocyanine are the most active catalysts in peroxide decomposition and autoxidation. On the basis of ligand exchange data, these complexes also seem to be the most stable.[15] This suggests the possibility that both ligand exchange and catalyst deactivation may be important in metal catalyzed peroxide decomposition.

Cobalt halides exhibit cleavage behavior in dimethyl sulfoxide and aqueous solution which parallels their reactivity in *tert*-butyl hydroperoxide decomposition (Table IV). The exception to this is cobalt bromide in the cleavage reaction in aqueous solution. The behavior of the bromide salt may be related to the ability of bromide ion to act as a radical chain carrier.[15]

In general there appear to be so many exceptions to attempts to correlate reaction rates (peroxide decomposition, poly(vinyl alcohol) cleavage or autoxidation) with any single set of physical properties (ligand structure, redox potential, NMR line broadening, etc.) in any fundamental way that at least the factors considered here must be taken into account in order to explain the observed orders of reactivity.

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