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Fast Autoxidation of Ethyl Linoleate Catalyzed by [Mn(acac)$_3$] and Bipyridine: A Possible Drying Catalyst for Alkyd Paints

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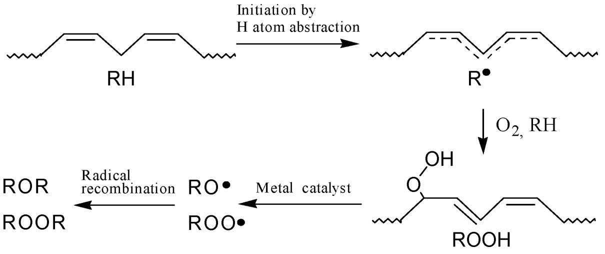
It has been found that [Mn(acac)$_3$], by functioning both as a radical initiator and a hydroperoxide decomposition catalyst, has a very high activity in the autoxidation of ethyl linoleate (EL), a model compound for the binder molecule in household alkyd paint. Adding 1 equiv of bipyridine (bpy) to a reaction mixture of EL and [Mn(acac)$_3$] significantly enhances the autoxidation rate. The redox properties of [Mn(acac)$_3$] and [Mn(acac)$_2$(bpy)] have been compared with cyclic voltammetry; the observed peak potentials show that addition of bpy facilitates reduction of Mn(III) to Mn(II), which may explain the increase in autoxidation activity.

The drying of alkyd paint is an autoxidation process: the alkyd resin binder molecules in the paint react with dioxygen, forming a cross-linked network and thus a hard coating. Binder molecules typically are polyesters containing fatty acid side chains. The autoxidation of these fatty acid side chains can be regarded as a lipid peroxidation process, resulting in hydroperoxide species (ROOH).[1] Cross-linking of the oxidized fatty acid chains occurs by metal catalyzed decomposition of the formed hydroperoxides into alkoxy and peroxy radicals. These radicals can then recombine to form ether, peroxo, and, to a lesser extent, carbon−carbon bonds.[2] Scheme 1 schematically shows the course of the drying reactions.

Cobalt salts are the most widely used drying catalysts for oxidative air-drying alkyd paint. It is generally accepted that the most important function of the cobalt catalyst is to decompose the formed fatty acid hydroperoxides into radicals, according to the well-known Haber−Weiss mechanism, see Scheme 2.[3,4]

Scheme 1. Oxidation and Crosslinking Reactions of the C_9-C_{13} Pentadiene Unit in Linoleate, the Fatty Acid Part of Common Alkyd Resin Binder Molecules



Scheme 2. Haber−Weiss Reactions for Metal Catalyzed Peroxide Decomposition

$$\mathrm{ROOH + M(II) \longrightarrow RO^{\cdot} + M(III) + OH^{-}} \quad (1)$$

$$\mathrm{ROOH + M(III) \longrightarrow ROO^{\cdot} + M(II) + H^{+}} \quad (2)$$

Recently, several reports have been published describing the possible carcinogenity of cobalt and cobalt salts.[5,6] This has initiated a search to find alternatives for cobalt complexes as drying catalysts in alkyd paint. Some commercial paint formulations contain manganese carboxylates as primary driers instead of cobalt. These do not show the same drying activity as cobalt, however.[4]

Because of the complex nature of real alkyd mixtures, a model reaction using ethyl linoleate (EL) has been developed for rapid screening of new possible catalysts; the different activities can be compared using FT-IR and size exclusion chromatography.[7,8] The rate of the consumption of EL can be followed by plotting the natural logarithm of the percentage decrease of the peak integral of the 3010 cm^{-1} peak in the FT-IR spectrum, as was described by Vandevoort et al.[9]

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Table 1. Oxidation Rates and Induction Times for the Oxidation of EL[a]

	induction time (min)	rate constant k (10^{-3} min^{-1})
Co nuodex[b]	0	3
Mn nuodex[b]	>700	2
[Mn(acac)$_3$]	<100	1
[Mn(acac)$_3$] + 1 equiv bpy	30	4
[Mn(acac)$_3$] + 2 equiv bpy	50	4
[Mn(acac)$_3$] + 3 equiv bpy	45	5
[Mn(acac)$_2$(bpy)]	430	2

[a] EL was purified by eluting over Al_2O_3 before use. No peroxides could be detected in purified EL.[10] Molar ratio catalyst/EL = 1/400, reaction in neat EL at room temperature. Due to the radical nature of the reactions, the average experimental error is about 2%. [b] Co Nuodex and Mn nuodex are paint driers commonly used in commercial paints.[11]

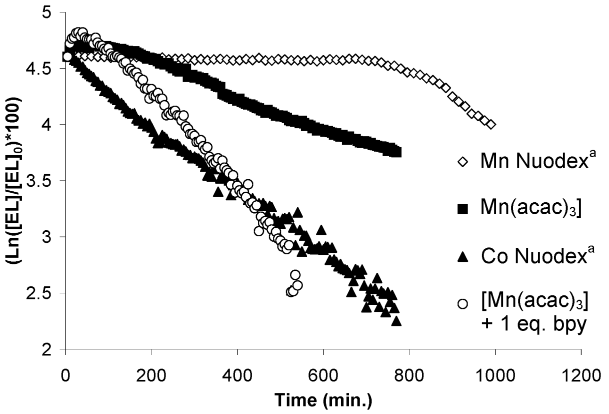
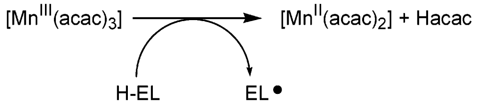


Figure 1. Time dependent integral plots of the 3010 cm^{-1} IR peak of purified EL, reaction with different autoxidation catalysts. Superscript a designates paint driers commonly used in commercial paints.[11]

Scheme 3. Radical Initiation by [Mn(acac)$_3$] through Hydrogen Atom Abstraction of the Activated Methylene Group in Ethyl Linoleate



In the course of our experiments to find new drying catalysts based on manganese complexes, it was found that [Mn(acac)$_3$] is an excellent autoxidation catalyst for EL.

Large variations in induction times are observed, however, when unpurified EL is used as the substrate. Unpurified EL contains hydroperoxides in varying amounts, due to slow air-oxidation during storage. The presence of hydroperoxides directly influences the reaction rate and induction time. When purified EL is used (all peroxides removed), the induction time for the commercially used manganese catalyst Mn Nuodex[11] increases from 400 to over 700 min (Table 1). Short induction times (varying between 0 and 100 min) are observed, however, when manganese(III) acetylacetonate is used as an oxidation catalyst. The higher oxidation activity (activity meaning the effectiveness with which EL is consumed in a certain amount of time) for [Mn(acac)$_3$] compared to that of Mn Nuodex can be attributed mostly to the large induction time for Mn Nuodex.

When the EL oxidation rate for [Mn(acac)$_3$] is compared with the rates for Mn and Co Nuodex,[11] it is clear that although [Mn(acac)$_3$] shows a slightly lower rate than Co Nuodex, its overall activity is far superior to that of Mn Nuodex (Figure 1).

Addition of 1 equiv of bipyridine to a reaction mixture of [Mn(acac)$_3$] and EL increases the rate of oxidation of EL significantly, surpassing even that of the cobalt drier. Adding more than 1 equiv does not enhance the rate any further, though (Table 1).

Mn(III) is well-known as a radical initiator, mostly as [Mn(OAc)$_3$] in acetic acid, at elevated temperatures and often with radical-chain starters as for example NHPI added.[3,12,13] [Mn(acac)$_3$] in combination with cocatalysts such as acetic acid[14,15] or benzyl bromide[16] is also known to act as a radical initiator, in the radical polymerization of various substrates. The induction time in the oxidation of EL is a measure of the ability of the catalyst to initiate the autoxidation radical-chain reaction, and thus, from the short induction time it seems that [Mn(acac)$_3$] is able to initiate the radical autoxidation of EL directly and at room temperature, even in absence of any acids, halides, peroxides, or other easily oxidizable radical chain starters. A tentative mechanism for the autoxidation initiation is depicted in Scheme 3. Radical initiation is proposed to occur via a hydrogen atom abstraction pathway, in analogy with a mechanism for the oxidation of 1,4-cyclohexadiene by tris(hexafluoroacetylacetonato)-manganese(III) as described by Bryant et al.[17] H-atom transfer from EL to [Mn^{III}(acac)$_3$] results in [Mn^{II}(acac)$_2$], a free acetylacetone ligand and an ethyl linoleate radical (EL$^{\bullet}$). This ethyl linoleate radical reacts immediately with dioxygen to form a peroxy radical, which can form a hydroperoxide by again abstraction of an H$^{\bullet}$ from another EL molecule. Currently, we are focusing our efforts on verifying this tentative initiation mechanism, since H-atom abstraction by [Mn(acac)$_3$] at room temperature has, to the best of our knowledge, not been described before.

Once the radical-chain reaction is started, the ELOOH concentration will quickly build up. Both [Mn^{III}(acac)$_3$] and [Mn^{II}(acac)$_2$] can catalytically decompose hydroperoxides,[18] and thus, both redox states of the catalyst are active in the autoxidation reactions. Manganese(III) will be active both in the initiation and in the peroxide decomposition step and manganese(II) only in the peroxide decomposition step.

To investigate the influence of bipyridine in more detail, the complex [Mn^{II}(acac)$_2$(bpy)] was synthesized separately[19] and was tested for its autoxidation activity. As expected, a rather large induction time is observed when starting the autoxidation with this manganese(II) compound and puri-

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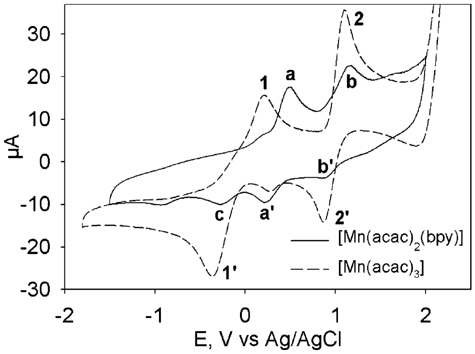

Figure 2. Cyclic voltammograms of [Mn(acac)$_3$] and [Mn(acac)$_2$(bpy)] in CH$_3$CN, [^{n}Bu$_4$N](PF$_6$) as electrolyte, scan rate 200 mV/s Selected potentials: 1/1′ 0.222/−0.373 V; a/a′ 0.50/0.203 V; 2/2′ 1.111/0.862 V; b/b′ 1.165/0.891 V; c −0.28 V.

fied EL (see Table 1). Initiation does not occur with manganese(II) complexes in the absence of peroxides, since manganese(II) is not able to oxidize the substrate under these reaction conditions. Thus, an induction time of over 400 min is observed in which either the substrate or the complex is slowly air-oxidized, after which the catalytic radical autoxidation can start. To check whether the induction time indeed results from the absence of peroxides, the oxidation experiment was also performed with unpurified EL. Then indeed no induction time is observed, and the oxidation reaction starts immediately with a rate of 4×10^{-3}min^{-1}, comparable to the rates observed for [Mn(acac)$_3$] with bpy added in situ.

In order to compare the oxidizing power of the complexes with and without bipyridine, cyclic voltammetry has been used. The cyclic voltammograms of [Mn(acac)$_3$] and [Mn(acac)$_2$(bpy)] are shown in Figure 2. The Mn(II)/Mn(III) couple (peaks 1/1′ and a/a′ in Figure 2) shifts toward more positive potential for [Mn(acac)$_2$(bpy)] as compared to [Mn(acac)$_3$]. The voltammograms of [Mn(acac)$_2$(bpy)] at different scan rates (see the Supporting Information for more details) show that the intensity of peak a′ increases with increasing scan rate. This indicates that the species [Mn^{III}(acac)$_2$(bpy)]$^+$ is unstable under these conditions and thus it is not unlikely that the more stable [Mn(acac)$_3$] complex is formed. Peak b then results from the oxidation of [Mn(acac)$_3$] and peak b′ from the reduction of [Mn^{IV}(acac)$_3$]$^+$. Indeed, the fact that the Mn(III)/(IV) transitions in the voltammograms (peaks 2,2′ and b/b′) occur nearly at the same potentials suggests also that they must both arise from the same species, i.e., [Mn(acac)$_3$]. Peak c most probably results from the reduction of [Mn(acac)$_3$] to [Mn^{II}(acac)$_3$]$^-$, as can be concluded by comparison with peak 1′. The complex [Mn^{II}(acac)$_3$]$^-$ reacts with bpy in solution to form the more stable complex [Mn^{II}(acac)$_2$(bpy)], which is supported by the absence of a (re)oxidation peak for [Mn^{II}(acac)$_3$]$^-$. The cyclic voltammogram of an in situ mixture of [Mn(acac)$_3$] with bpy is nearly identical to that of [Mn(acac)$_2$(bpy)], confirming the instability of the complexes and the rapid equilibria.

The CV data clearly show that addition of bpy results in the stabilization of the Mn(II) complex. The decrease in induction time for the catalyst [Mn(acac)$_3$] in the presence of bpy can thus be attributed to the fact that it is more easily reduced, because of the formation of the stable complex [Mn(acac)$_2$(bpy)]. The higher reaction rates observed for the system [Mn(acac)$_3$] plus bpy can also be explained by the facilitated reduction of Mn(III) to Mn(II). In autoxidation according to the Haber−Weiss reactions, the reduction of Mn(III) is always the slower reaction (reaction 2 in Scheme 2).[3] Addition of bpy thus effectively “de-bottlenecks” the autoxidation reaction, by speeding up the slower step.

In summary, it can be concluded that [Mn(acac)$_3$] is an excellent catalyst for the autoxidation of ethyl linoleate that is far superior to commercial manganese-containing paint-drying catalysts. The difference in activity could be related to the fact that [Mn(acac)$_3$] is able to initiate the autoxidation reaction. When bpy is added to [Mn(acac)$_3$], it shows even better autoxidation activity than the commercially used cobalt catalyst, making this system a potential replacement for the cobalt driers presently used in alkyd paints.

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Supporting Information Available: Experimental procedure for a standard oxidation experiment and additional CV data. This material is available free of charge via the Internet at http://pubs.acs.org.

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