Manganese Complexes as Drying Catalysts for Alkyd Paints
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Summary, general discussion and outlook.

7.1 Summary

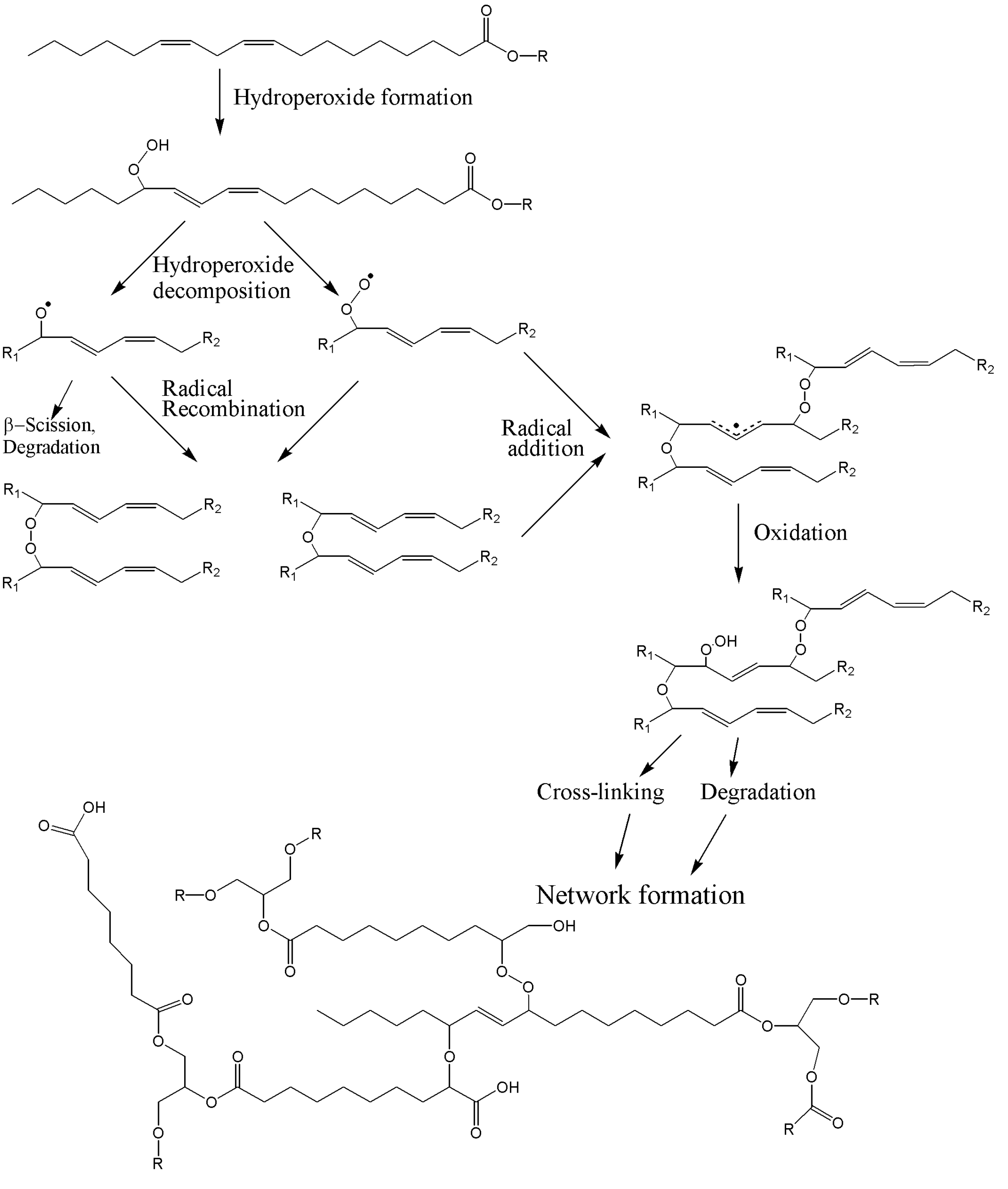
7.1.1 The chemistry of alkyd (paint) drying

From the literature reviewed in Chapter 1 a clear picture can be drawn of the reactions involved in the drying of a fatty acid ester, drying oil, or alkyd paint-binder resin. Based on these data, a scheme can be drawn (Scheme 7.1) that summarises the different steps of the formation of a dried paint network.[1] In all cases the first step is hydroperoxide formation, with concomitant formation of conjugated double bonds in the case of fatty acids that contain the pentadienyl moiety. A metal complex, also called "drier", catalyses hydroperoxide decomposition, which results in the formation of peroxy and alkoxy radicals. Through recombination of these radicals, ether and peroxide crosslinked dimers are formed. The species with conjugated double bonds are prone to radical addition reactions and thus in the later stages of drying this is the most important route to cross-link formation. Alkoxy radicals give rise to β-scission reactions which leads to degradation of the network and results in the formation of numerous oxidation products such as epoxides, aldehydes and ketones, most of which will be oxidised further to alcohols and carboxylic acids. Over time, all unsaturation disappears, as do the peroxide cross-links. What most likely remains is a network of predominantly carboxylic acid C_9 chains, linked via ester bonds and ether cross-links.

7.1.2 The screening of new drying catalysts using a model system

Early research into paint-drier chemistry has mostly been on a trial-and-error basis, seemingly with the motive that if a drier dries paint, no further attention is needed. Only a few publications go into detail on the mechanisms of drier action.[2-4] Replacement of the toxic cobalt salts as driers in alkyd paint is crucial, however, since environmental regulations are becoming increasingly stringent. Development of new driers not based on cobalt is thus of the utmost importance. Many water-borne coatings also require new and improved drier systems, as do high-solids paints.

In Chapter 2, the experimental methods and techniques are described which can be used to quickly screen different coordination compounds as potential new paint driers.[4] The fatty acid ester ethyl linoleate (EL) has been used as a model compound for the binder in a real alkyd. To quickly screen different metal complexes for their ability to enhance the "drying" of EL, two essential parameters to measure are: (1) the rate of the autoxidation reaction and (2) the extent of the cross-linking that takes place. Thus, time-resolved Fourier transform infrared (FTIR) has been used to study the kinetics of EL oxidation and size exclusion chromatography (SEC) has been used to measure the extent of the cross-linking.



Scheme 7.1: Schematic representation of the formation of a cross-linked network characteristic for a dried oil, or dried alkyd paint. Hydroperoxide formation and decomposition leads to formation of alkoxy and peroxy radicals. Recombination and addition reactions lead to the formation of ether and peroxy cross-links. Further oxidation reactions mainly result in, eventually, carboxylic acid formation and degradation of the network.

Commercial EL always contains a certain amount of hydroperoxides (about 0.2 mol%, see Chapter 2). These hydroperoxides were found to have a large influence on especially the induction time that is often observed in autoxidation reactions (see the FTIR results described in Chapter 3). To measure the hydroperoxide concentration in EL, two techniques have been used (described in Chapter 2). One of these techniques is based upon the oxidation of triphenylphosphane (TP) to triphenylphosphane oxide (TPO) by hydroperoxides and subsequent detection of TPO by HPLC and UV. The other method is based on the oxidation of iron(II) to iron(III) in a xylenol-orange containing solution, followed by measuring the absorption due to the formed Fe^{3+}-xylenol orange complex in the UV-Vis spectrum. By eluting the EL over pure Al_2O_3, all hydroperoxides are removed, as was confirmed by the HPLC method. All measurements described in this thesis have been performed with EL that is purified from hydroperoxides (termed "purified EL"). The use of purified EL greatly increased the reproducibility of the oxidation experiments.

The oxidation and oligomerisation reactions of ethyl linoleate as monitored with time-resolved FT-IR spectroscopy and size exclusion chromatography were found to be very suitable as screening model reactions for finding new drying catalysts for alkyd paint.

7.1.3 [Mn(III)(acac)$_3$] and [Mn(II)(acac)$_2$(bpy)] as potential paint drying catalysts

[Mn(III)(acac)$_3$] was found to be a good catalyst for the autoxidation and oligomerisation of EL, as is described in Chapter 3.[5, 6] [Mn(III)(acac)$_3$] was also found to function as a very good drying catalyst in a real alkyd system, better than conventional manganese driers and comparable to, or even better than a cobalt combination drier.[7] The system [Mn(III)(acac)$_3$] with bpy added has a very high activity for the oxidation of EL. *In-situ* formation of the species [Mn(II)(acac)$_2$(bpy)] and [Mn(III)(acac)$_2$(bpy)]$^+$ and the high reactivities of these two species with ROOH and EL, respectively, have been proposed as an explanation for the observed high oxidation rate. In the oxidation of EL by the [Mn(acac)$_3$]/bpy catalyst less oligomerisation and a higher amount of volatile products is observed as compared to other catalysts. This difference is attributed to a proposed tendency of the [Mn(acac)$_3$]/bpy catalyst to generate predominantly alkoxy radicals in hydroperoxide decomposition. In real alkyd systems, the addition of bpy to [Mn(III)(acac)$_3$] is therefore not advantageous, which is also evident from the longer drying times that have been observed for [Mn(III)(acac)$_3$]/bpy in a real alkyd system, as compared to the drying times for [Mn(III)(acac)$_3$].

The compound [Mn(II)(acac)$_2$(bpy)] was found to have the rather rare trigonal prismatic coordination geometry in the solid state.[8] In Chapter 6, the solution and solid state structures of [Mn(II)(acac)$_2$(bpy)], as studied by EPR spectroscopy, magnetic susceptibility measurements and XRD have been presented. The complex has the trigonal prismatic geometry only in the solid state. Density functional theory (DFT) calculations have been used to address the question of the preference for a specific coordination geometry in the related Mn(II) complexes [Mn(II)(acac)$_2$(bpy)] (trigonal prismatic) and [Mn(II)(acac)$_2$(phen)] (distorted octahedral). Based on the very small energy differences for the calculated trigonal prismatic and octahedral structures it has been concluded that crystal packing effects must contribute significantly in determining the trigonal prismatic structure for [Mn(II)(acac)$_2$(bpy)].

7.1.4 Tripodal ligand complexes

In Chapter 4 the preparation of new manganese and iron complexes with the general formula [M(tripod)L]$_n$ (n = 1, 2) is described, where M = Fe(III), Mn(III) or Mn(II), "tripod" is a mono- or dianionic tetradentate tripodal ligand and L is a β-diketonate, an acetate, or a chloride ligand. The complexes have been characterised by X-ray crystallography and/or infrared spectroscopy, UV-Vis spectroscopy, cyclic voltammetry and elemental analysis. The general motivation for using tripodal ligands in this work is that such large, tetradentate ligands usually form very stable complexes with manganese and iron. Furthermore, the synthesis of these ligands is straightforward, and many variations on ligand structure are easily made. The tripodal ligands that have been prepared all have at least one, but more often two (subsituted) phenol groups. Consequently, these ligands can coordinate as mono- or dianions. The complexes that have been prepared all have two features in common: they are all mixed-ligand complexes and all the complexes have *anionic* ligands. The reason for using anionic ligands is that the resulting complexes should preferentially be non-charged, since this will increase their solubility in apolar solvents. Most of the synthesised complexes are manganese(III) or iron(III) coordination compounds with one tripodal ligand and one β-diketonate ligand, but some other complexes which have an anionic ligand such as chloride, 8-oxyquinoline or acetate instead of the β-diketonate have also been prepared. β-diketonates were chosen as the "secondary" ligand because good autoxidation results were obtained with simple, homoleptic manganese β-diketonate complexes (as described in Chapter 3).

A clear correlation between the ligand sets and the electron density of the metal centre in the complexes could be made, as was shown by UV-Vis data and which was corroborated by CV measurements. The tripodal ligands are significant π-donor ligands, and electron-withdrawing or electron-donating substituents on the phenolate arms were found to have a large influence on both the position of the d-d transitions in the UV-Vis spectra and the peak potentials in the CV measurements. The "secondary" β-diketonate or acetate ligand did not have such a large effect on the electron density of the metal centre. Complexes with the same tripodal ligand but different β-diketonate ligands were found to have very similar cyclic voltammograms and a comparable energy for the observed d-d transition.

In Chapter 5, the autoxidation activity of several of the prepared tripodal ligand complexes is reported. EL autoxidation has been monitored with FTIR and the degree of oligomerisation has been determined with SEC, according to the methodology described in Chapter 2. It has been found that almost all tested complexes show the same trend in the autoxidation of EL: after a short induction time, the reaction starts at a relatively high constant rate. This rate changes to a lower rate, which is again constant and on average is *the same* for all complexes. The observation that the autoxidation rate eventually becomes the same for all complexes has been explained with the assumption that a catalytic species is formed which is structurally similar for each complex.

To gain insight in the reaction mechanisms by which complexes of the type [Mn(tripod)(β-diketonate)] react with peroxides, the reactions of [Mn(pppy)(dpm)] (pppy = 2-[bis(2-hydroxybenzyl)aminomethyl]pyridine and dpm = 2,2,6,6-tetramethyl-3,5-heptanedionate, see Chapter 4) with alkyl hydroperoxides have been studied by UV-Vis and EPR spectroscopy. Based on the results, it has been proposed that the species $[\mathrm{Mn(III)(pppy)(OH)(}^{t}\mathrm{BuOO}^{\bullet})]$ is formed. In analogy with the formation of that species, which is postulated to occur *via* a reduction to Mn(II), it has been proposed that in the direct reaction of EL with a [Mn(III)(tripod)(β-diketonate)] complex, the compound [Mn(II)(tripod)(β-diketone)] is formed. The neutral β-diketone ligand can dissociate from the complex and the [Mn(II)(tripod)] fragment that is left can form the stable catalytic species which is structurally similar for each complex.

Since almost *all* tripodal ligand complexes show very similar autoxidation and oligomerisation activity, probably all the tripodal ligand complexes are potential paint driers. However, considering other parameters such as complex solubility and complex preparation, the compound [Mn(III)(tbpppy)(dpm)] (see Chapters 4 & 5) is expected to be the most suitable as a potential alkyd paint drier.

7.2 General discussion

7.2.1 Model system vs real paint

In Chapter 1 it is stated that the aim of the research described in this thesis has been: "to find new, metal-complex-based driers for alkyd paints, which do not contain cobalt". To find a *drier* for a commercial paint is not a simple task. The results presented in Chapters 2 and 3 show that it is relatively easy to find simple compounds, such as [Mn(acac)$_3$] and [Mn(acac)$_3$] with bpy, that show autoxidation activities similar to or even better than for a cobalt catalyst. These experiments are done using a *model system*, however, and the results do not necessarily concur with those obtained in "real" paint. The results for the autoxidation of EL with [Mn(acac)$_3$]/bpy for example (described in Chapter 3) show that it is paramount to study both the autoxidation *and* the oligomerisation reactions before judging whether a complex would be a good potential paint drier. Adding bipyridine to [Mn(acac)$_3$] significantly enhances the oxidation activity, but unfortunately this also results in less oligomerisation and more degradation of the polymer network. It is important to realise, however, that in real paint primary driers based on cobalt and manganese are hardly ever used as the sole catalytically active additive. Secondary driers (see Chapter 1) are added to moderate the activity of the primary driers. In that sense, the [Mn(acac)$_3$]/bpy catalyst should be tested in real paint in the presence of secondary driers before any comparison is made with commercial cobalt combination driers.

The tripodal ligand complexes have not yet been tested in real paints. Based on the measured autoxidation and oligomerisation activities of EL, however, it is quite likely that these complexes will also function as driers in real paint. An advantage of the large tripodal ligands that are used is that so-called loss-of-dry (drying times are longer after a certain storage time of the paint, see Chapter 1) will be minimised due to very stable complex formation. A problem for the direct application of the tripodal ligand complexes is that they are new. Therefore, investments will need to be made in terms of toxicology reports and safety regulations before the compounds are even allowed to be used in paint.

An aspect that has been excluded from study in this thesis, but which is very important when formulating paint, is colour. Manganese(III) compounds are brown, and will give light coloured paints a yellowish or brown shade. Further studies are necessary to develop paint formulations which contain the brown Mn(III) compounds, but will not show an effect on the colour of the paint. This clearly is a challenge suitable for the product development departments of the coatings industry.

7.2.2 What makes a good metal-based paint drier?

There are several different properties a metal complex has to have to make it a good paint drier. The relative importance of the different properties will be summarised in this section, from the perspective of coordination chemistry and based on the experience gained over the course of the research done for this thesis.

Three of the most important properties a complex should have are listed below:

- Solubility
- Stability
- Catalytic activity

The issue of solubility has been detailed in Chapters 1, 3, 4 and 5 and is considered to be of very high importance. A complex which does not dissolve in a paint mixture or which precipitates will not be active in paint drying. There are several strategies to make a complex soluble in the apolar environment that often constitutes an alkyd paint. The strategy followed in this thesis has been to use only uncharged complexes by using anionic ligands. Another strategy would be to use ligands with large alkyl substituents. Both these strategies have been combined in for example the complex [Mn(tbpppy)(dpm)] (Chapters 4 and 5).

Although both solubility and stability are necessary properties to make a good paint drier, the stability of a complex in solution is rated above the catalytic activity it might have. Paints are sometimes stored for weeks or months before being used. The drier must retain its potential for catalytic activity during storage. A different kind of stability is the stability of the catalytically active species that actually dries the paint. This species should be stable enough to be active for an amount of time that is sufficient to dry the paint. The catalytically active species does not have to be indefinitely stable, since when the paint binder has polymerised the oxidation reactions preferably have to stop, to avoid degradation of the paint network. A catalyst which slowly degrades (becomes inactive) while drying the paint is thus ideal.

The last important property a paint drier should have might seem trivial, but is mentioned nonetheless: it should be *catalytically* active. The autoxidation chemistry that lies at the core of alkyd paint drying implies that a compound is used that can catalytically decompose hydroperoxides to start radical chains. A complex that can start a radical chain in the absence of hydroperoxides *and* decompose hydroperoxides is preferred, since this will significantly shorten the drying time. Compare for example the autoxidation results for EL catalysed by [Mn(acac)$_3$] and Mn-EH (Chapter 3): the higher activity of [Mn(acac)$_3$] can solely be attributed to its ability to initiate radical chain reactions.

A metal complex that has all the properties discussed above has a good chance of being an active drier for alkyd paint. By tailoring the ligand system the different properties can be influenced, but the preparation of a-la-carte driers will likely remain a laborious task.

7.3 Conclusion & outlook

The results described in this thesis have shown that in principle, it is possible to replace the cobalt driers currently used in alkyd paint by manganese complexes, without a significant increase in the drying time of the paint. There are still issues (most notably colour) that need to be resolved before manganese can really replace cobalt. The task of product development lies in industry, however.

It would be interesting to try the complexes that have been studied as paint driers in oxidation reactions with other substrates. Especially the catalyst [Mn(acac)$_3$]/bpy, which is very active in the oxidation of EL. This catalyst might also be very active towards other substrates with activated C-H bonds. The same reasoning applies for the tripodal ligand complexes.

Industry will probably not use manganese driers instead of cobalt driers unless there are no other options. Unfortunately for industry, in the near future cobalt driers will probably be banned from alkyd paints by European legislation. Compounds such as [Mn(acac)$_3$] will then be a good option for replacing such cobalt driers.

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