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Effect of [Mn(acac)$_3$] and its combination with 2,2′-bipyridine on the autoxidation and oligomerisation of ethyl linoleate

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Abstract

In this study we investigated the autoxidation and oligomerisation of ethyl linoleate (EL) catalysed by [Mn(III)(acac)$_3$] (acac = 2,4-pentanedionate) and its combination with 2,2-bipyridine (bpy), in comparison with the EL catalysed by Co(II) 2-ethylhexanoate (Co-EH). EL is a model compound for the alkyd resin in alkyd paints, Co-EH is a common drying catalyst for alkyd paints, and [Mn(acac)$_3$] and the [Mn(acac)$_3$]/bpy combination are potential new drying catalysts. The autoxidation of EL was studied through time-resolved Raman spectroscopy, oxygen uptake measurements, and peroxide amount determination. To follow the oligomerisation of EL in time, size exclusion chromatography was used. Head-space GC-MS measurements were performed to determine the amounts of hexanal and pentanal that were formed as volatile byproducts during the autoxidation of EL. The autoxidation rates of EL in the presence of Co-EH and [Mn(acac)$_3$]/bpy were found to be similar, while the rate in the presence of [Mn(acac)$_3$] was slower. The extent of EL oligomerisation was much higher for [Mn(acac)$_3$] compared to the other catalysts. Different mechanisms are proposed for the mode of action for each of the catalysts: Co-EH is primarily a hydroperoxide decomposition catalyst, as is [Mn(acac)$_3$], only less active. The [Mn(acac)$_3$]/bpy combination probably forms the very reactive complexes [Mn(III)(acac)$_2$(bpy)]$^+$ and [Mn(II)(acac)$_2$(bpy)], which are responsible for a very high autoxidation rate, but also for significant degradation of the formed EL oligomers via β-scission reactions due to the promotion of alkoxy radical formation.

Keywords: Polymer chemistry; Polymer physical chemistry

1. Introduction

It is well known that the chemical drying of alkyd-based paints occurs through oxidation of unsaturated fatty acid ester side chains in the alkyd resin (Scheme 1) [1–4], followed by decomposition of the formed hydroperoxides. The decomposition of these hydroperoxides is accelerated by the added metal catalysts, so-called 'driers', which enhance the overall alkyd paint drying rate. Currently, cobalt carboxylates (e.g. cobalt(II) 2-ethylhexanoate) are the most effective, commercially available catalysts for the oxidative drying of alkyd paints [5]. Nevertheless, cobalt compounds are suspected to be *carcinogenic* to tissues and lungs [6,7]. Due to this fact, it is desirable to replace the cobalt complexes used in paint systems with environmentally friendlier alternatives.

The commercially available manganese-based drying catalysts for alkyd paints are manganese carboxylates. Their catalytic activity is, however, much lower than that of cobalt carboxylates. As a consequence, alkyd-based paints containing Mn carboxylates usually suffer from slow drying that leads to undesirable final film properties [5]. Recently, a high catalytic activity of *tris*(acetylacetonato) manganese(III), [Mn(acac)$_3$], was reported for the autoxidation of ethyl linoleate (EL) [8], a model compound for alkyd resins [9,10]. It was also found that the autoxidation of EL catalysed by [Mn(acac)$_3$] was accelerated significantly by the addition of 2,2′-bipyridine (bpy) [8].

In the present study, the catalytic activity of [Mn(acac)$_3$]

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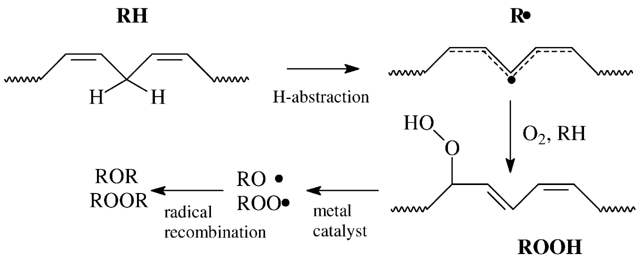

Scheme 1. Oxidation reactions of EL.

and its combination with bpy for the autoxidation of EL was further examined, in comparison with the catalytic activity of cobalt(II) 2-ethylhexanoate.

2. Experimental

2.1. Materials

Technical grade ethyl linoleate (EL), containing 73% EL, 19% ethyl oleate, 6% ethyl palmitate, and 2% ethyl stearate as determined by GC-MS, and Mn(III) acetylacetonate, [Mn(acac)$_3$], were obtained from Fluka. 2,2′-bipyridine (bpy) and Co(II) 2-ethylhexanoate (Co-EH, 65% w/w solution in white spirit) were obtained from Sigma-Aldrich. Chemicals were used as received unless stated otherwise.

2.2. Instrumentation and procedures

2.2.1. Raman spectroscopy

The autoxidation of EL was followed by Raman spectroscopy on a Dilor-Jobin Yvon-Horiba confocal dispersive Raman spectrometer (633 nm excitation wavelength, 1000 μm pinhole, and 8 mW laser intensity) with an Olympus MX40 microscope. EL containing 0.07 wt% (based on EL; the same for below) of different catalysts was deposited (∼200 μm) onto glass slides for in situ Raman analysis. In the experiments involving bpy, 3 molar equiv. of bpy were added relative to [Mn(acac)$_3$].

2.2.2. Oxygen uptake

A Fibox fiber-optic oxygen meter (Precision Sensing GmbH) was used to measure the oxygen uptake of EL in the presence of various catalysts. The oxygen meter consists of an oxygen sensor probe (PSt3). The tip of the probe is coated with a Pt(II) indicator dye embedded in a silicone matrix, which is connected to a LED (excitation wavelength: 505 nm) through a fiber optic cable, a photomultiplier detector (PMT). A PT 100 type temperature sensor is used for temperature compensation (details can be found at http://www.presens.de).

For the oxygen uptake measurement at room temperature (∼21 °C), 4 g of EL, premixed with a catalyst (0.07 wt%), was placed into a 6-L sealed container filled with air at a normal atmospheric pressure, equipped with oxygen and temperature sensors inside. When [Mn(acac)$_3$] was used, it was first dissolved in a small amount of toluene. The consumed oxygen concentration was expressed as mol oxygen per mol of EL.

2.2.3. Peroxide value

An American Oil Chemists' Society (AOCS)-approved method for determining peroxide value (PV) was used with some modifications [11]. EL (40 g) was mixed with a catalyst (0.07 wt%) and placed in a Petri dish (∼20 cm radius) for oxidation at room temperature (21 °C, 50% RH). About 2 g of EL was withdrawn from Petri dishes for PV measurements. Samples were dissolved in 30 mL of a mixture of glacial acetic acid/chloroform (3:2 v/v). 0.5 mL of saturated potassium iodide solution (in excess) was added followed by the addition of 30 mL of deionised water and 0.5 mL of starch dispersion (5 g/L). The solution was titrated with sodium thiosulfate solution (0.02 N), until the yellow/brown colour fully disappeared. The results were corrected with a blank sample that did not contain EL. Duplicate measurements were performed for each sample and average values were taken. The accuracy of the method was checked by the titration of H_2O_2 and cumene hydroperoxide, and it was found that the difference between experimental values and theoretical values was less than 2%.

2.2.4. Size exclusion chromatography

The oligomerisation of EL was followed by size exclusion chromatography (SEC) on a Waters GPC instrument equipped with a Waters model 510 pump and a model 410 differential refractometer (40 °C); THF was used as the eluent. Samples were withdrawn from Petri dishes (see Section 2.2.3) and dissolved in THF (1 mg/mL).

2.2.5. Head-space gas chromatography-mass spectrometry (GC-MS)

EL (1 g) was first mixed with different catalysts (0.07 wt%). An aliquot of 10 mg was placed in a 20 mL head-space vial for each measurement, followed by the addition of 1 μL of cyclohexane solution (0.37 M in xylene) as an internal standard. Vials were then sealed with silicon rubber Teflon® caps using a crimper. EL was oxidized in the sealed vials in the presence of catalysts. Several vials were prepared and, at different time intervals, volatile byproducts were determined on a Thermoquest CE 2000 series trace GC-MS equipped with static head-space autosampler (HS 2000 model). Trace GC was equipped with a capillary column (based on silica, length 60 m×0.25 mm, 0.25 μm thickness, Alltech). Helium was used as a carrier gas, and ionisation mode of the trace MS was electron impact (EI+). All of the intricate operations of establishing an equilibrium in static head-space analysis was performed by the HS 2000 robotic autosampler through a local controller using Windows®-based software. After reaching equilibration, the heated gas-tight head-space syringe (45 °C) was moved over the incubator by a turret and a sample was withdrawn. The turret was turned to the position over the inlet, and the injection was made. The syringe was then automatically cleaned with a purged carrier gas (He). For the programmable temperature vaporisation (PTV) injector method, the base temperature was 43 °C with a split flow of 50 mL/min. The transfer temperature to the column was 325 °C. The GC column was programmed with an initial hold of 4 min at 45 °C and then the temperature was raised to 330 °C at a rate of 10 °C/min. Peak areas for the volatiles (e.g. hexanal, pentanal) were integrated and normalised with the peak area of cyclohexane using characteristic mass ranges. The amounts of hexanal and pentanal formed during the oxidation of EL were calculated by using pure compounds of hexanal, pentanal, and cyclohexane as references. The typical experimental error for the GC-MS analysis was found to be 6%.

3. Results

3.1. Variation of the double bonds in EL followed by Raman spectroscopy

The variation of the double bonds in EL was followed in time by Raman spectroscopy, for the autoxidation with different catalysts. Over the course of an autoxidation experiment, the non-conjugated *cis* double bonds in the pentadiene moiety in EL first become *trans*,*cis*-conjugated (see Scheme 1) and eventually, isolated *trans* [12]. Raman spectroscopy proved to be a very suitable technique to detect the changes in the various types of double bonds [13–15], due to their high Raman absorbance. Conjugated (1599, 1634 cm^{-1}), non-conjugated *cis*-C=C (1655 cm^{-1}), and isolated *trans*-C=C (1670 cm^{-1}) bonds could be easily differentiated [14].

In the absence of a catalyst, the peaks in EL due to double bonds did not change even after 130 h [14]. In the presence of Co-EH, as is illustrated in Fig. 1a, the C=C-related peaks of EL showed significant changes within 1 h. After 1 h of oxidation, the non-conjugated *cis*-C=C peak (1655 cm^{-1}) and the *cis*-C=CH rock peak (1265 cm^{-1}) started to decrease while the conjugated-C=C (1599, 1634 cm^{-1}) peaks started to form. After a few hours of reaction, the amount of the conjugated-C=C bonds reached maximum levels. After that, both the non-conjugated *cis*-C=C and conjugated-C=C peaks of EL decreased substantially, eventually resulting in low amounts of C=C bonds (including isolated *trans*-C=C at 1670 cm^{-1} and some conjugated-C=C) after 100 h.

The C=C related peaks of EL in the presence of [Mn(acac)$_3$] showed similar variations (Fig. 1b), however, the conversion appeared to be at a much lower rate compared to that in the presence of Co-EH. For instance, after 21 h of oxidation, the intensity of the non-conjugated *cis*-C=C (1655 cm^{-1}) peak was still relatively high.

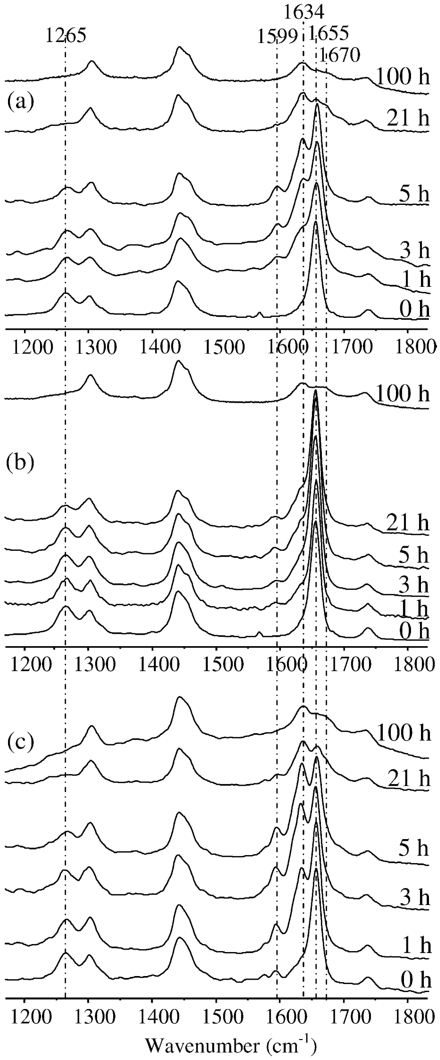

Fig. 1. Raman spectra (1200–1800 cm^{-1}) during the oxidation of EL in the presence of (a) Co(II)-2-ethylhexanoate, (b) [Mn(acac)$_3$], and (c) [Mn(acac)$_3$]/bpy.

The catalytic capability of [Mn(acac)$_3$] is greatly enhanced by the addition of bpy, which has been shown previously by FT-IR [8]. As is shown in Fig. 1c, conjugated-C=C Raman peaks (1599, 1634 cm^{-1}) of EL already formed after 1 h when bpy was added, while *cis*-C=C related peaks decreased. The time-evolution of the double bond peaks appeared to proceed in a very similar manner compared to the Co-EH-catalysed system. Careful examinations reveal that in the early stage of oxidation (1–3 h), the intensity of conjugated peaks was slightly higher for the [Mn(acac)$_3$]/bpy system than for the Co-EH catalyst, indicating an even faster reaction in the presence of [Mn(acac)$_3$]/bpy.

3.2. Oxygen uptake during EL oxidation

In Fig. 2, the O$_2$ uptake results are shown for EL without

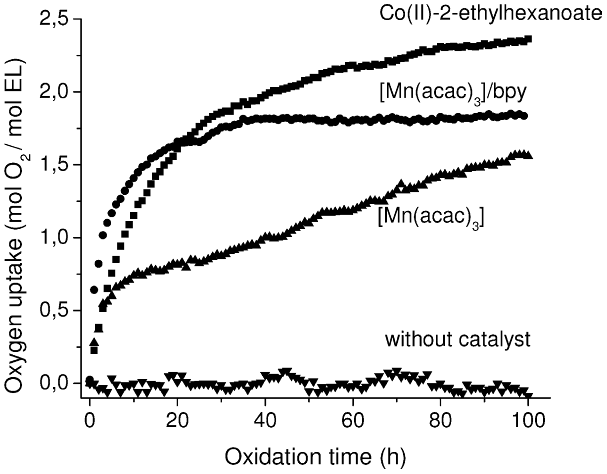

Fig. 2. O_2 uptake during the EL oxidation in the presence of various catalysts.

any catalyst as well as in the presence of the catalysts Co-EH, [Mn(acac)$_3$], and [Mn(acac)$_3$]/bpy. In the absence of a catalyst, virtually no oxygen was taken up by EL for the entire duration of the experiment (100 h). In the presence of Co-EH, a significant amount of O_2 was taken up by the system, up to about 2.35 mol/mol EL after 100 h. A noticeably smaller amount of O_2 (1.55 mol/mol EL) was consumed when [Mn(acac)$_3$] was used as a catalyst. The uptake of O_2 by EL was enhanced when bpy was combined with [Mn(acac)$_3$]: not only was a larger amount of oxygen (1.85 mol/mol EL) taken up than in the presence of [Mn(acac)$_3$], also the rate of O_2 uptake was considerably higher. Interestingly, a plateau level for the O_2 consumption was reached after about 35 h when [Mn(acac)$_3$]/bpy was used, whereas in the case of [Mn(acac)$_3$] and Co-EH no plateau has yet been reached even after 100-h oxidation.

3.3. The time-evolution of peroxides in EL oxidation

Hydroperoxides (ROOHs) have a crucial role during the autoxidation reactions of alkyds. ROOHs are formed and then decomposed to form free radicals (i.e. R•, RO•, ROO•) and these radicals are recombined to form R–R, R–O–R, R–O–O–R cross-links [1–5]. These free radicals can also directly add to (preferably conjugated) double bonds [14,16]. The sequential formation and decomposition of ROOHs can be greatly enhanced by an appropriate catalyst. An effective catalyst accelerates both the formation of ROOHs and the decomposition of the formed ROOHs. Hydroperoxides can also be formed and then be decomposed thermally (in the absence of a metal catalyst), however, this process is very slow at room temperature [17].

The concentration of peroxides was monitored in time for the autoxidation of EL in the presence of the various catalysts, and the results are shown in Fig. 3. The peroxide value for the unreacted EL, straight from the bottle received from the supplier, was determined to be 4 mmol/mol EL. In the presence of Co-EH the amount of peroxides reached about 50 mmol/mol in 5 h. As the oxidation of EL proceeded, the amount of peroxides increased continuously and reached a maximum value of 170 mmol/mol in about 30 h. Then, the peroxide value decreased rapidly to a level of approximately 40 mmol/mol. These observations are in accordance with EL-oxidation studies reported by Mallegol et al. [2,17]

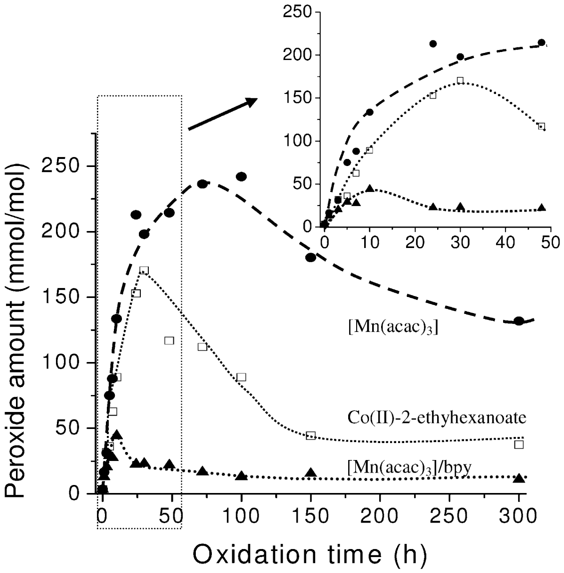

Fig. 3. The evolution of peroxide amounts during the oxidation of EL in the presence of various catalysts. Lines are added to aid the eye.

In the presence of [Mn(acac)$_3$], a much higher concentration of peroxides (240 mmol/mol) was reached after a much longer reaction time of 100 h. The rate of decrease of the peroxide value after attaining the maximum was also much less than for the oxidation with Co-EH. Even after 300 h a significant amount of peroxides of 130 mmol/mol still remained.

When bpy was added to [Mn(acac)$_3$], a totally different scenario was observed (Fig. 3). The concentration of peroxides was, at all times, much lower than was observed for the other two cases: a maximum value was reached of about 45 mmol/mol in just 10 h of reaction time. The amount of peroxides then decreased to a very low level of 10 mmol/mol over the course of the experiment (up to 300 h).

3.4. Oligomerisation during EL oxidation

The oxidation reactions of EL generally lead to the formation of oligomers, which is pivotal for the drying and hardening of real alkyd coatings. In Fig. 4, the SEC chromatograms are shown of EL after various periods of oxidation catalysed by Co-EH, [Mn(acac)$_3$], and [Mn(acac)$_3$]/bpy.

After oxidation of EL for 8 h catalysed by Co-EH, dimers (the peak at an elution time of 15.7 min), trimers (at 15 min)

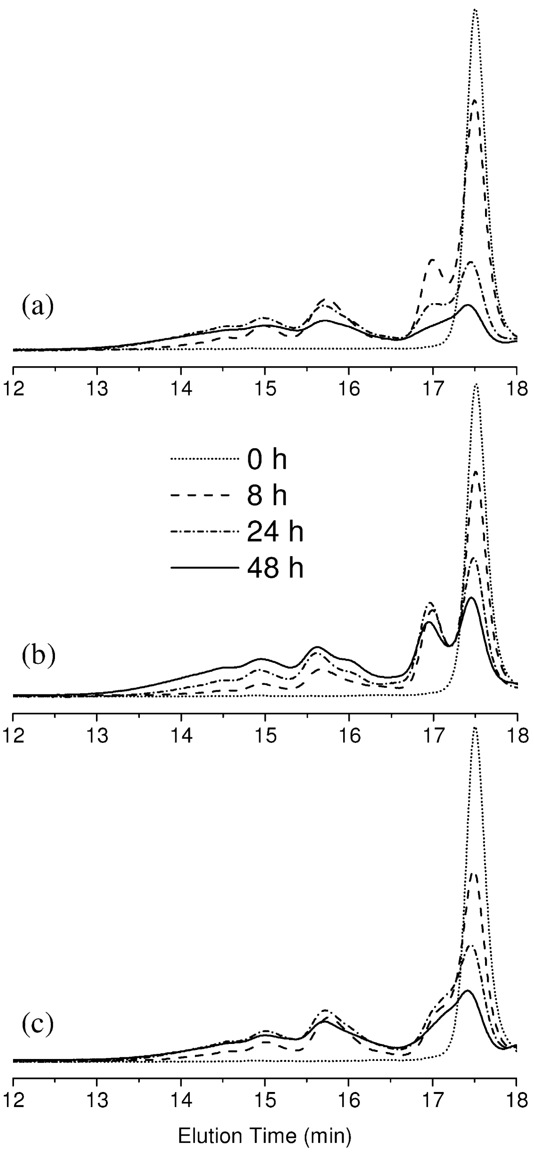

Fig. 4. Size exclusion chromatograms of EL after different periods of oxidation in the presence of various catalysts: (a) Co(II)-2-ethylhexanoate, (b) [Mn(acac)$_3$], and (c) [Mn(acac)$_3$]/bpy.

and higher oligomers (13–14.5 min) could be readily observed (Fig. 4a). As the oxidation proceeded for 24 h, more trimers and higher oligomers were formed as the dimer peak slightly decreased [10]. After 48 h, both the dimer and trimer peaks have decreased relative to their levels after 24 h, probably due to the formation of higher oligomers and due to oxidative degradation of the fatty acid chains (see also the GC-MS results in the next section). The EL peak did not disappear completely even after 48 h, which is most likely due to the presence of about 8% of non-reactive saturated esters and the presence of 19% of the less reactive ethyl oleate [10,14,18] in the technical grade EL. The peak appearing at 17 min is due to EL hydroperoxides [1,19,20] and other oxygen-containing EL derivatives (for example, epoxide species) [1]. The amount of hydroperoxides first increased and then significantly decreased over the course of the reaction (Fig. 4a), in agreement with the results obtained for the peroxide value determination.

In the oxidation of EL with [Mn(acac)$_3$], the same observations can be made after 8 h as for the oxidation with Co-EH: dimers and trimers were formed although to a lesser extent than for the Co-EH catalysed reaction. In contrast to the oxidation with Co-EH, however, the amount of (higher) oligomers only increased with prolonged reaction times, indicating little degradation of the oligomerised EL. The peak due to hydroperoxides remains significant for the entire duration of the experiment (48 h), again in agreement with the results obtained for the peroxide value determination for the oxidation with [Mn(acac)$_3$]. The peak due to the EL-monomer also remains considerable, which is in perfect agreement with the difference in EL oxidation rates as were found for Co-EH and [Mn(acac)$_3$], using FT-IR [8].

In the oligomerisation of EL with [Mn(acac)$_3$] and bpy, the same trends in the formation of dimer, trimer and higher oligomers can be seen as for the oxidation with Co-EH (Fig. 4c). Here, the peroxide peak is rather low in intensity at all times, in accordance with the observations made in the peroxide value determination (Fig. 3).

3.5. Formation of volatile byproducts during EL oxidation

The characteristic odour of air drying alkyd paints is due to the formation of volatile aldehydes, typically hexanal and pentanal. These aldehydes are formed through β-scission reactions of alkoxy radicals [21], as schematically illustrated in Fig. 5. The amount of hexanal and pentanal formed

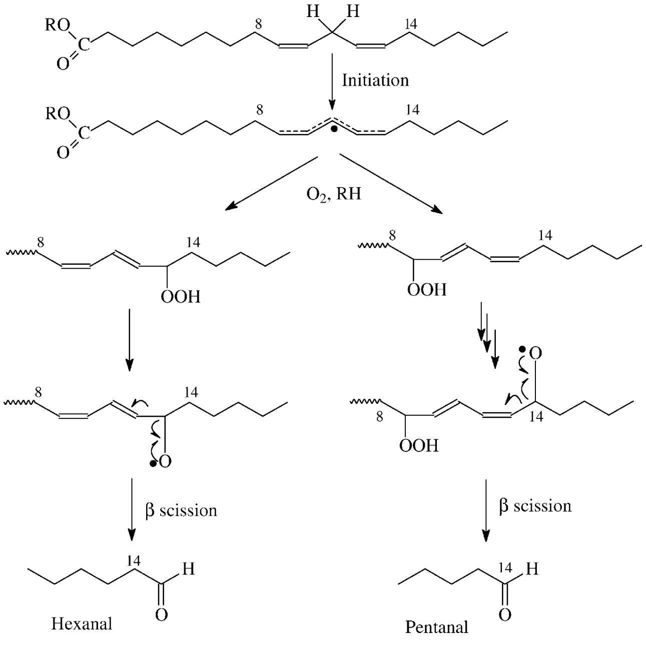

Fig. 5. Schematic illustration on the formation of by-products hexanal and pentanal via β-scission.

during the oxidation of EL in the presence of different catalysts was quantified by head-space GC-MS, as shown in Fig. 6. In the reaction catalysed by Co-EH, the amount of hexanal and pentanal increased steadily over the course of the reaction (105 h), reaching 16.6 and 0.4 mmol/mol EL, respectively. During the first 50 h of the oxidation with the [Mn(acac)$_3$]/bpy system much more hexanal was generated than when Co-EH was used (Fig. 6a). However, after 100 h the hexanal levels for both catalysts were found to be similar. The amount of pentanal that was generated with the [Mn(acac)$_3$]/bpy catalyst was significantly higher. In the oxidation with only [Mn(acac)$_3$] as a catalyst, lower amounts of both hexanal and pentanal were formed compared to the reactions with Co-EH or [Mn(acac)$_3$]/bpy.

4. Discussion

The Raman results and the FTIR results of our previous report [8] have shown that [Mn(acac)$_3$] can oxidise EL at a reasonable rate, although this rate is lower than for the oxidation with Co-EH. The addition of bpy to [Mn(acac)$_3$] enhances the oxidation rate considerably. In the Raman spectra for the [Mn(acac)$_3$]/bpy system, at $t=0$ there is already a small peak visible due to conjugation (1599 cm^{-1}) of double bonds, a clear sign that the oxidation reaction has already started. The Raman spectra and the rate of oxygen uptake for the catalysts Co-EH and [Mn(acac)$_3$]/bpy clearly show that the rate of oxidation of EL is higher for the [Mn(acac)$_3$]/bpy system, a result which is in agreement with FTIR data reported previously [8]. From the data of the peroxide amounts it becomes clear that the high oxidation activity for the [Mn(acac)$_3$]/bpy system might be attributed to its extremely efficient capability of hydroperoxide decomposition.

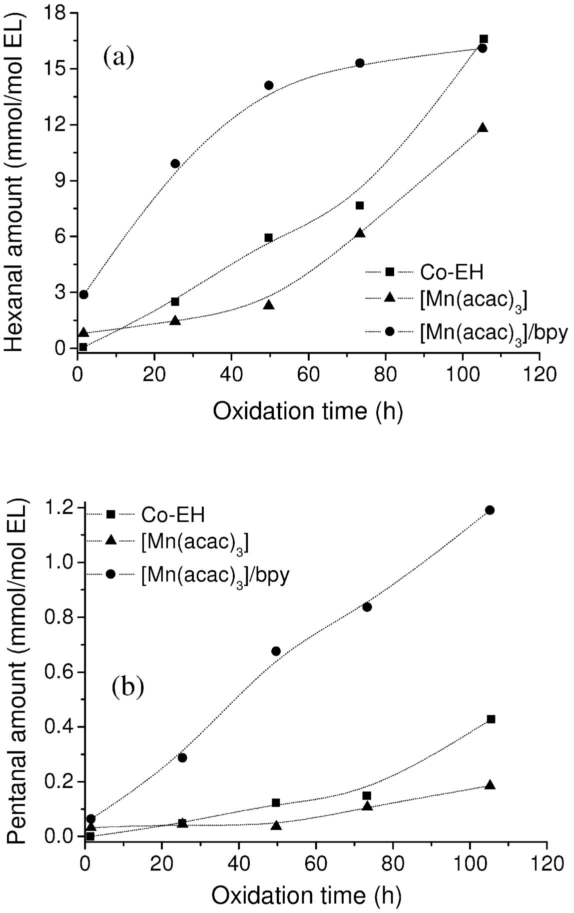

Fig. 6. The formation of volatile byproducts (a) hexanal and (b) pentanal during the oxidation of EL in the presence of different catalysts. Lines are added to aid the eye.

Scheme 2 shows the set of radical reactions that are often proposed for hydroperoxide (ROOH) build-up in metal-catalysed autoxidation reactions [3]. The hydroperoxide concentration, at a given time, depends on the ratio of the rates for hydroperoxide decomposition vs hydroperoxide formation [22]. According to the reactions in Scheme 2, the higher the rate for reactions **4** and **5**, the lower the hydroperoxide concentration will be. It appears that the [Mn(acac)$_3$]/bpy catalyst is able to decompose ROOH almost as soon as it is formed, thus attaining a very low ROOH concentration. In Scheme 3, a tentative overview is given for the metal-catalysed peroxide decomposition reactions for each catalyst used in the present study. The cobalt catalyst is mainly a robust peroxide decomposition catalyst, where the rate for reaction **6** will probably be comparable to the rate for reaction **7**. It is clear from Fig. 3, where the ROOH concentration decreases steadily after the maximum has been reached, that the cobalt catalyst retains its decomposition activity for at least 150 h. The oxygen uptake data for the Co-EH-catalysed EL show that significant over-oxidation of EL takes place (oxygen uptake higher than 1 mol O$_2$/mol EL). The most common pathways for over-oxidation are: (1) through radical addition to conjugated double bond systems, generating a new carbon-centred radical which can again react with dioxygen [16], or (2) via oxidation of the products generated by a β-scission reaction of an alkoxyl radical. The head-space GC-MS data for the Co-EH-catalyzed EL shows that increasing hexanal and pentanal formation takes place, a sure sign for β-scission reactions. The degradation of the oligomers linked by a peroxy bond is also discernible in the SEC chromatogram for the Co-EH catalysed oxidation, where the peaks due to dimers, trimers and higher oligomers noticeably decrease over the course of the reaction.

Reactions **8** and **9** in Scheme 3 are the proposed ROOH decomposition reactions for the catalyst [Mn(acac)$_3$].

$\mathrm{RH + initiator \rightarrow R^{\bullet}}$ **1**
$\mathrm{R^{\bullet} + O_2 \rightarrow ROO^{\bullet}}$ **2**
$\mathrm{ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}}$ **3**
$\mathrm{ROOH + M^{n+} \rightarrow RO^{\bullet} + {}^{-}OH + M^{(n+1)+}}$ **4**
$\mathrm{ROOH + M^{(n+1)+} \rightarrow ROO^{\bullet} + H^{+} + M^{n+}}$ **5**

Scheme 2. General autoxidation reactions catalysed by a metal (M)-based catalyst.

Co-EH catalyst

$\mathrm{Co^{II} + ROOH \rightarrow RO^{\bullet} + [Co^{III}(OH)^{-}]}$ **6**
$\mathrm{[Co^{III}(OH)^{-}] + ROOH \rightarrow Co^{II} + ROO^{\bullet} + H_2O}$ **7**

[Mn(acac)$_3$] catalyst

$\mathrm{[Mn^{III}(acac)_3] + ROOH \rightarrow [Mn^{II}(acac)_2(Hacac)] + ROO^{\bullet}}$ **8**
$\mathrm{[Mn^{II}(acac)_2(Hacac)] + ROOH \rightarrow [Mn^{III}(acac)_3] + RO^{\bullet} + H_2O}$ **9**
$\mathrm{[Mn^{III}(acac)_3] + RH \rightarrow [Mn^{II}(acac)_2(Hacac)] + R^{\bullet}}$ **10**

[Mn(acac)$_3$]/bpy catalyst

$\mathrm{[Mn^{II}(acac)_2(Hacac)] + bpy \rightarrow [Mn^{II}(acac)_2bpy] + Hacac}$ **11**
$\mathrm{[[Mn^{II}(acac)_2bpy] + ROOH \rightarrow [Mn^{III}(acac)_2bpy]^{+}(OH)^{-} + RO^{\bullet}}$ **12**
$\mathrm{[Mn^{III}(acac)_2bpy]^{+}(OH)^{-} + ROOH \rightarrow [Mn^{II}(acac)_2bpy] + ROO^{\bullet} + H_2O}$ **13**
$\mathrm{[Mn^{III}(acac)_2bpy]^{+}(OH)^{-} + RH \rightarrow [Mn^{II}(acac)_2bpy] + R^{\bullet} + H_2O}$ **14**

Scheme 3. Proposed sets of reactions for each of the catalyst systems.

Additionally, the direct activation of EL *via* reaction **10** also plays a role for [Mn(acac)$_3$], as was proposed in a previous communication [8]. The most important difference for the activity of [Mn(acac)$_3$] compared to Co-EH is the rate with which reactions **8** and especially **9** proceed (apparent from the Raman data and the rate for oxygen uptake). A lower rate for these reactions can explain the significantly higher hydroperoxide concentration that is attained through reactions **2** and **3** in Scheme 2. Additional hydroperoxides can be formed through reaction **10** in Scheme 3. The amounts of hexanal and pentanal that are formed (Fig. 6a,b) are lower but follow the same trend as observed for the Co-EH catalysed EL, also a sign that a lower rate for the ROOH decomposition reactions is probably the most important difference. Another major difference between the results for Co-EH and [Mn(acac)$_3$] is the amount of oligomers that are formed as observed in the SEC chromatograms. The levels of dimer, trimer and higher oligomers are clearly higher for the [Mn(acac)$_3$] catalyst. This observation can be explained by the high ROOH level that is generated through the cycle of reactions **2** and **3** and reaction **10**: each ROOH that is formed results in the formation of a set of conjugated double bonds, see Scheme 1. A high ROOH concentration thus implies a high concentration of conjugated double bonds which are especially prone to radical addition reactions, due to the possibility of forming a relatively stable allylic radical [16]. Consequently, each time an alkoxy or especially a peroxo radical species is formed through decomposition of a hydroperoxide, a probable reaction pathway for the radical is to react with a conjugated double bond to form a higher oligomer.

As was mentioned, the [Mn(acac)$_3$]/bpy catalyst shows a very high rate for the oxidation of EL. The high oxidation activity is ascribed to the in situ formation of the compound [Mn$^{\mathrm{II}}$(acac)$_2$(bpy)] through reactions **8** and **11** (or **10** and **11**). The involvement of this species in the oxidation of EL by [Mn(acac)$_3$]/bpy was already proposed in a previous communication [8]. The species [Mn$^{\mathrm{II}}$(acac)$_2$(bpy)] has most probably a very high rate for reaction **12**, forming species [Mn$^{\mathrm{III}}$(acac)$_2$(bpy)]$^{+}$. Cyclic voltammetry measurements have shown that this complex has a reduction wave at 0.203 V (vs Ag/AgCl in CH$_3$CN) [8]. This makes the species [Mn$^{\mathrm{III}}$(acac)$_2$(bpy)]$^{+}$ a much more potent oxidising agent than for example [Mn$^{\mathrm{III}}$(acac)$_3$], which has the corresponding reduction wave at -0.373 V (vs Ag/AgCl in CH$_3$CN). Reactions **13** and **14** in Scheme 3 will thus proceed at a much higher rate. The extremely high rate of oxygen uptake, coupled to the very low levels of detected hydroperoxides may be explained by the assumption that the oxidation will most likely be dominated by reactions **12** and **14**, once the species [Mn$^{\mathrm{II}}$(acac)$_2$(bpy)] is formed. The high amounts of hexanal and pentanal that are formed initially (Fig. 6a,b) as compared to Co-EH and [Mn(acac)$_3$], is in agreement with the notion that reaction **12** is likely very rapid. The alkoxy radicals that are formed in reaction **12** have a tendency to undergo β-scission, thus forming hexanal and pentanal. An explanation for the complete end of the uptake of oxygen once all hydroperoxides are decomposed (compare Figs. 2 and 3 after a reaction time of 35 h) could be that the complex [Mn$^{\mathrm{III}}$(acac)$_2$(bpy)]$^{+}$ can probably only rapidly abstract a C=CC**H**$_2$C=C hydrogen atom. The SEC chromatogram for the oxidation of EL catalysed by [Mn(acac)$_3$]/bpy is similar to that for the Co-EH-catalysed EL oxidation, except for the low intensity of the peak due to ROOH. A system which predominantly generates alkoxy radicals will have a lower extent of oligomerisation, since these radicals generally have more pathways to form other products of low molecular weights [21].

The cobalt(II) 2-ethylhexanoate catalyst is the most widely used oxidative drier for alkyd paints. Judging only by the oxidation rate of the alkyd model compound EL, one is tempted to say that the manganese catalyst system [Mn(acac)$_3$]/bpy would be an ideal replacement for cobalt as a drier. The results pertaining to the formation of higher oligomers show, however, that the slower catalyst [Mn(acac)$_3$] yields a much higher extent of oligomerisation. It was also found in a separate study that the catalyst [Mn(acac)$_3$] shows better drying results in an actual alkyd paint formulation than the system [Mn(acac)$_3$]/bpy [23]. In real alkyd systems, cobalt is never used as the only drier: so called ‘secondary’ and ‘auxiliary’ driers are added, sometimes to retard the activity of the cobalt drier [24]. The lower performance for [Mn(acac)$_3$]/bpy in real alkyd paint might indeed be attributed to the fact that it is *too* active: the autoxidation reactions yield predominantly alkoxy radicals, which results in less oligomerisation.

5. Conclusions

The compound [Mn(acac)$_3$] is an efficient catalyst for the oxidation and the oligomerisation of EL, which is proposed to proceed not only via hydroperoxide decomposition but also through substrate activation. The system [Mn(acac)$_3$] with bpy added has a very high activity for the oxidation of EL. In situ formation of the species [Mn$^{\mathrm{II}}$(acac)$_2$(bpy)] and

$[Mn^{III}(acac)_2(bpy)]^+$ and the high reactivities of these two species with ROOH and EL, respectively, were 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, probably due to the generation of predominantly alkoxy radicals in hydroperoxide decomposition.

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