Manganese Complexes as Drying Catalysts for Alkyd Paints

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Methods for studying the drying of alkyd paint using ethyl linoleate as a model compound.†

Abstract:
In this chapter, the use of Fourier Transform Infrared Spectroscopy and Size Exclusion Chromatography to monitor the autoxidation of ethyl linoleate as a function of time is discussed. The experimental setup for each technique is described in detail. Two methods for determining the hydroperoxide concentration in ethyl linoleate reaction mixtures are also discussed and the experimental details given. One of these methods 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.
It is concluded that the oxidation of ethyl linoleate monitored by all described techniques in concert provides a very suitable high-throughput screening model reaction for the selection of new drying catalysts for alkyd paint.

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2.1 Introduction

2.1.1 General

In paint industry, only the bulk parameters of complex "real paint" mixtures are studied. With specialized equipment information is obtained about, for example, the drying time of a paint formulation and the hardness or the whiteness of the resulting paint film. However, a different approach is necessary if the understanding of paint chemistry at the molecular level is desired. An actual paint system is too complex to reach any detailed conclusions concerning the chemical mechanisms behind (metal-accelerated) alkyd paint drying. This chapter describes the experimental techniques that have been used to study the drying of alkyd paint using a model compound and to screen different metal complexes for their capability to enhance the drying rate.

2.1.2 Modeling alkyd paint

In order to avoid using complex paint mixtures, compounds can be used that model certain aspects of the mixture. Since in alkyd paint drying most chemistry takes place at the unsaturated fatty acid tails of the binder compound (see Chapter 1, Fig 1.1), the entire binder resin can be modeled by using compounds that structurally or chemically resemble this fatty acid chain. Simple dienes such as 4,7-heptadiene,[1] 3,6-nonadiene,[2] and 2,5-undecadiene,[3] as well as methyl or ethyl esters of the unsaturated fatty acids linoleic, linolenic and ricinoic acid [4-7] have been used as model compounds for the alkyd resins (see also Chapter 1). An advantage besides having a much simpler system to study is that when model compound mixtures become "dried" (cross-linked, see Chapter 1) they remain liquid and consequently are much more easily analysed with standard analysis techniques. In the present study the ethyl ester of the fatty acid linoleic acid has been used: ethyl linoleate (EL), see Figure 2.1.

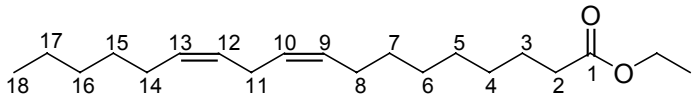

Figure 2.1: ethyl ester of (*Z,Z*)-9,12-octadecadienoic acid; ethyl linoleate

2.2 Analytical techniques to monitor the autoxidation of ethyl linoleate

2.2.1 General

A wide range of analytical techniques has been used to study the autoxidation of alkyd paint model compounds, such as ^{13}C-NMR,[2-5] GC,[5] HPLC,[1-3] FTIR,[6, 8-10] SEC,[4, 5] and SIMS.[7]

To quickly screen different metal complexes for their ability to enhance the "drying" of EL, the two most useful parameters to measure are: 1) the rate of the autoxidation reaction and 2) the extent of the cross-linking that takes place. The EL autoxidation rate could be called a measure of how fast the "paint" dries and the extent of the cross-linking is a measure of how well it dries and how "hard" the formed "paint-

layer" is. Thus, time-resolved Fourier transform infrared (FTIR) is used to study the kinetics of EL oxidation and size exclusion chromatography (SEC) is used to measure the extent of the cross-linking. In the following sections each technique will be discussed.

2.2.2 Time-resolved FTIR experiments

2.2.2.1 Description of a typical experiment

The kinetics of fatty acid oxidation can be studied by time-resolved FTIR spectroscopy [11, 12] The *cis* **H-C**=CH stretching vibration at 3010 cm^{-1} [13] is especially suitable to follow the disappearance of the substrate in time. In the first step of the reaction a hydrogen atom is abstracted from the reactive methylene group of the *cis*, *cis*-1,4-diene moiety. After rearrangement of the resulting pentadienyl radical and reaction with dioxygen (see also Chapter 1, section 1.2.2.2, Scheme 1.4), a hydroperoxide is formed and one of the *cis* **H-C**=CH hydrogens has now become a hydrogen on a secondary carbon atom (see Figure 2.2). The decrease of the infrared vibration due to the

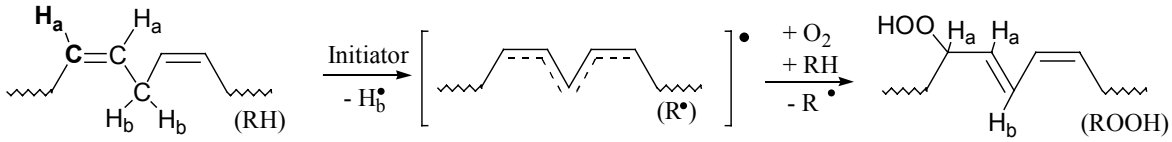

Figure 2.2: The *cis* H_a-C=CH hydrogen of a 1,4-pentadiene unit in a fatty acid disappears in the first step of the autoxidation, due to abstraction of a H_b atom and rearrangement of the resulting pentadienyl radical.

disappearance of this *cis* **H-C**=CH hydrogen can thus be associated directly to the first step of the autoxidation reaction.

To follow the autoxidation of EL in time, an FTIR spectrum is recorded (automatically) every 5 minutes, Figure 2.3 shows (part of) several representative spectra of an oxidation experiment. For each spectrum, integration is carried out for the area

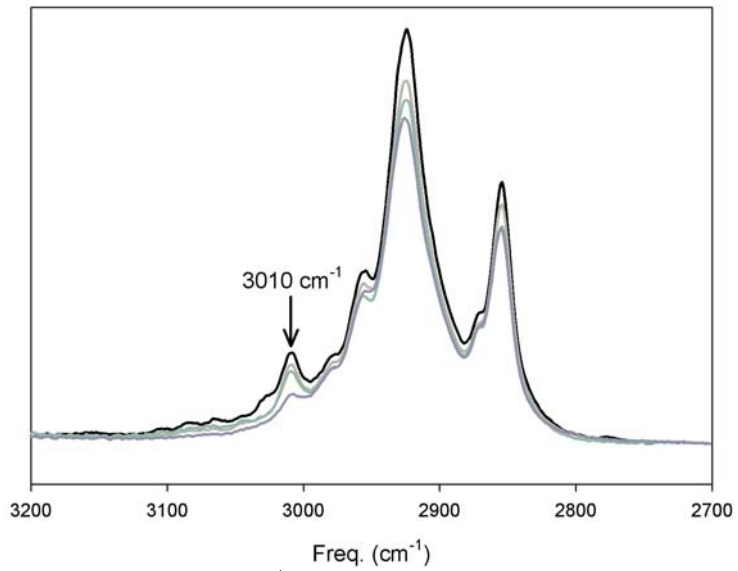

Figure 2.3: 2700 – 3200 cm^{-1} region of the FTIR spectra of EL at increasing reaction times during an autoxidation reaction. The peak at 3010 cm^{-1} decreases as the autoxidation reaction proceeds.

between 2992 and 3025 cm^{-1}. As a result a table is obtained with the integral of the 3010 cm^{-1} peak at different times. The logarithmic plot of these data gives a straight line and thus, in first approximation, the oxidation of EL follows pseudo first-order kinetics. From the slope of this graph the first-order reaction rate of $H^{\bullet}$ radical abstraction can be determined. In some cases an induction time occurs, which can vary from several minutes to many hours. The occurrence of an induction time can have several reasons, but the most important factors are the concentration of hydroperoxides in EL at the start of an autoxidation reaction (see section 2.3) relative to the catalyst concentration and the metal complex that is used as a drying catalyst. Figure 2.4 shows an example of an EL autoxidation experiment: the plot of the peak-integral ratio A_t/A_0 of the 3010 cm^{-1} peak vs oxidation time. In section 2.4.1 a more detailed description is given of the experimental setup and a typical autoxidation experiment.

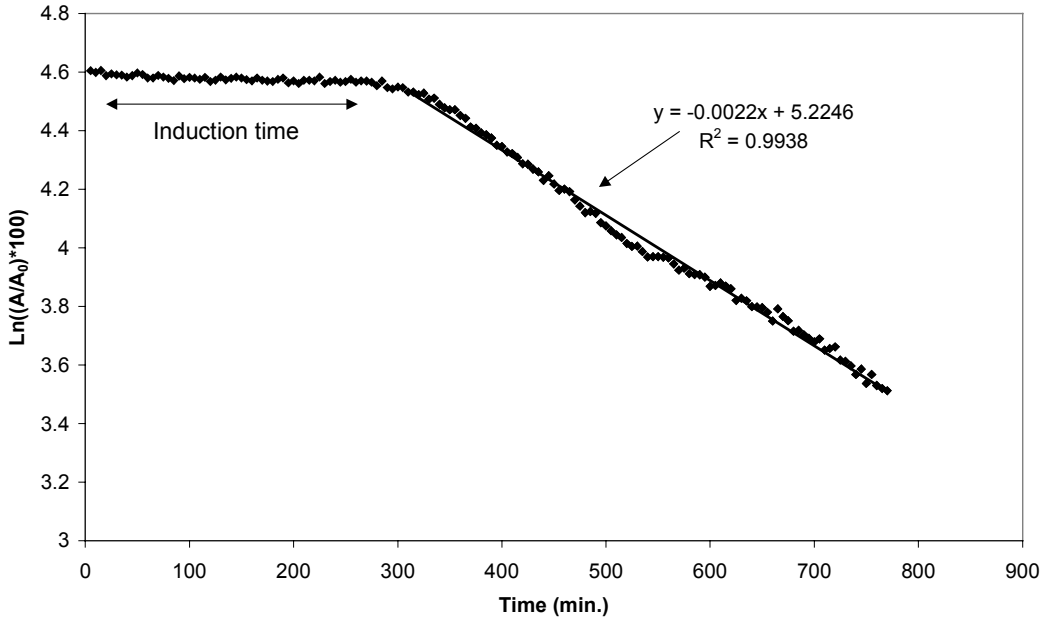

Figure 2.4: Logarithmic plot of the IR 3010 cm^{-1} peak area integrals vs time. In this particular example an induction time of 300 min. occurs, after which the reaction proceeds with a rate constant $k = 22\times10^{-4} min^{-1}$.

2.2.2.2 Optimal substrate/catalyst ratio

Since the metal-catalyzed autoxidation of EL is a radical reaction an optimal catalyst concentration is expected, as with higher concentrations saturation would occur. To determine the optimal concentration for the screening of different metal catalysts a series of measurements with different concentrations of Co Nuodex[14] has been performed. The curve as obtained from a plot of the reaction rate constants for different molar ratios Co/EL indeed shows saturation behavior. Using cobalt concentrations in a molar ratio of Co/EL higher than 4×10^{-3} does not result in a significant increase of the reaction rate, see Figure 2.5. Therefore, for all FTIR experiments discussed in this thesis a molar catalyst/EL ratio of 2.5×10^{-3} (EL/catalyst = 1/400) has been used. At this ratio the reaction rate is still dependent on the metal concentration, but is not too sensitive to small experimental errors as compared to very low metal concentrations.

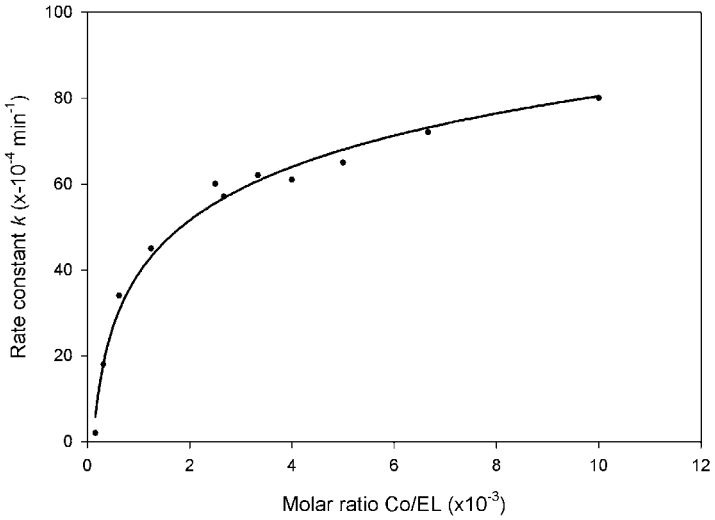

Figure 2.5: The effect of the molar Co/EL ratio on the reaction rate.

2.2.3 Size exclusion chromatography

In the metal-catalyzed autoxidation of EL cross-links are formed, predominantly due to radical termination reactions. These cross-links consist of ether, peroxy, and carbon-carbon bonds.[5, 7] Due to cross-link formation, dimers, trimers and even oligomers of EL are formed while the autoxidation reaction proceeds, as is schematically depicted in Figure 2.6. Taking samples of an autoxidation reaction mixture at increasing reaction times and measuring them with SEC gives insight in the rate of formation of the different cross-linked species. In Figure 2.7 several chromatograms are shown which have been

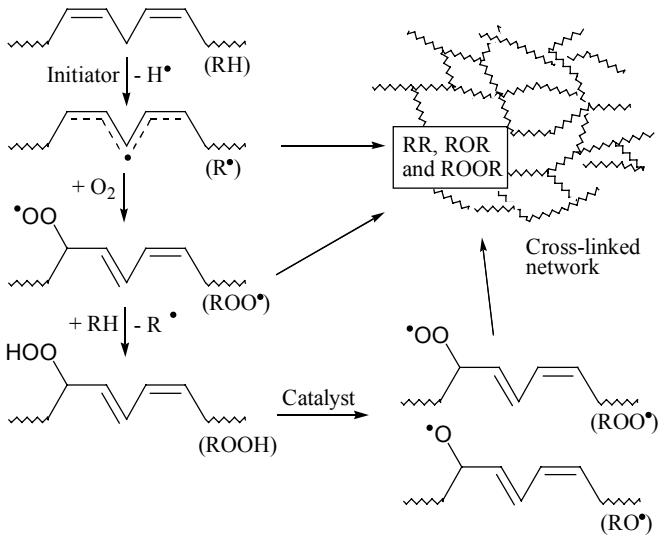

Figure 2.6: The metal catalyst decomposes hydroperoxides to form alkoxy and peroxy radicals. These radicals terminate with each other and carbon radicals to form RR, ROR and ROOR cross-links.

obtained at different times during an autoxidation reaction. The EL peak decreases in time as EL-hydroperoxides are formed. The hydroperoxide peak will first increase and then decrease, as hydroperoxides are decomposed to form cross-linked species. The intensity of the peaks due to these cross-linked species increase over time: first dimers are visible, then trimers and given enough reaction time, higher oligomers are detected. The experimental details will be discussed in section 2.4.2.

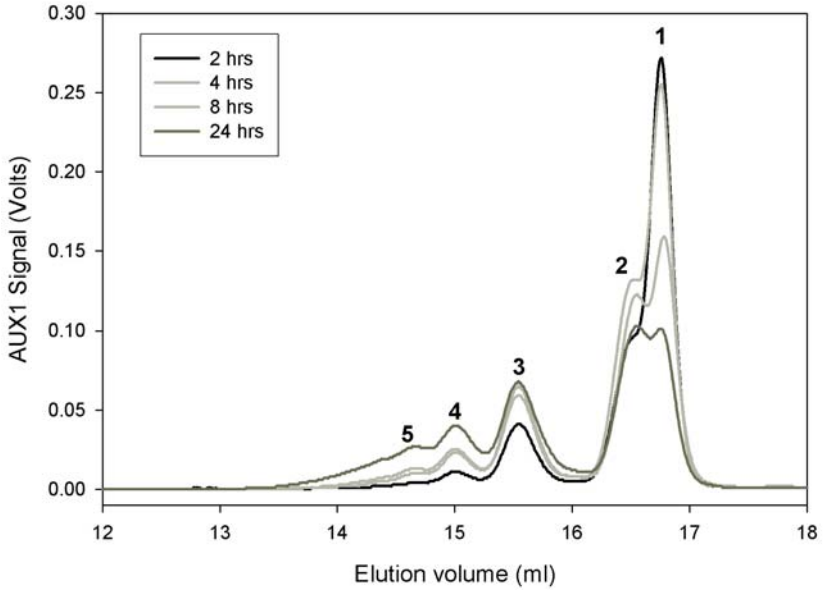

Figure 2.7: Several size exclusion chromatograms; samples taken after 2, 4, 8 and 24 hours reaction time of an autoxidation reaction mixture of EL with a metal complex drying catalyst. Peak assignments: 1: EL 2: EL-hydroperoxide 3: dimers 4: trimers 5: oligomers

2.3 Determination of the hydroperoxide concentration in ethyl linoleate

2.3.1 General

During storage the hydroperoxide concentration in EL will slowly increase due to various reactions with dioxygen from the air. Since hydroperoxides have a direct influence on the metal-catalyzed autoxidation (see chapter 1, section 1.2) in most cases it is desirable to remove all hydroperoxides from EL prior to use in an oxidation experiment. In the remainder of this thesis, whenever "purified EL" is mentioned, it is meant "EL from which all peroxides have been removed". Hydroperoxides are removed from EL by eluting it over a basic Al_2O_3 column. In section 2.4.1 the experimental procedure used for removing hydroperoxides from EL is described. To determine the hydroperoxide content in EL before and after purification, an HPLC method was used.

Hydroperoxides are also important intermediates in the autoxidation reaction. Therefore, it is valuable to determine the hydroperoxide level in an autoxidation reaction mixture at different reaction times. For this purpose, a spectrophotometric method was used. Both methods are described in the following sections.

2.3.2 Determination of the hydroperoxide concentration in EL.

To check whether the used purification methods are sufficient, the hydroperoxide contents of unpurified and purified EL were determined using a method described by Nakamura *et al*.[15] This method is based on the stoichiometric oxidation of triphenylphosphane (TP) to triphenylphosphane oxide (TPO) by hydroperoxides present in a given sample. The concentration of formed TPO can then be determined by reverse phase HPLC using an UV detector at 220 nm. All hydroperoxides are quantitatively reduced within 30 minutes, and the detection limit for TPO at 220 nm is lower than 10 pmol.

In Figure 2.8 two chromatograms are shown, one obtained after reaction of TP with unpurified EL, and one from a blank experiment: using only TP in CH_3CN. It is difficult to keep a TP solution completely TPO-free, since in solution TP is rather easily oxidized to TPO by dioxygen from the air. Therefore, when an experiment is run to determine the amount of peroxides in a sample, a blank experiment using the same TP solution should always be recorded simultaneously. The peak surface of the TPO peak from the blank experiment is subtracted from the TPO peak of the reaction mixture. A calibration curve is used to convert the obtained peak surface to the TPO concentration of the reaction mixture, and thus the hydroperoxide concentration is obtained. The amount of hydroperoxides in a fresh bottle of EL 70% (as obtained from Fluka) was determined to be 0.2 mol%, which is equivalent to a peroxide value of 6.48 mmol hydroperoxide/kg EL. This number is quite significant, especially since in a standard EL autoxidation experiment with a metal complex (see section 2.4.1) a molar ratio of metal/EL of 1/400 (0.25mol%) is typically used, which makes the metal-to-hydroperoxide ratio almost 1:1. Purifying EL by eluting it over Al_2O_3 and then reacting it with TP does not result in an

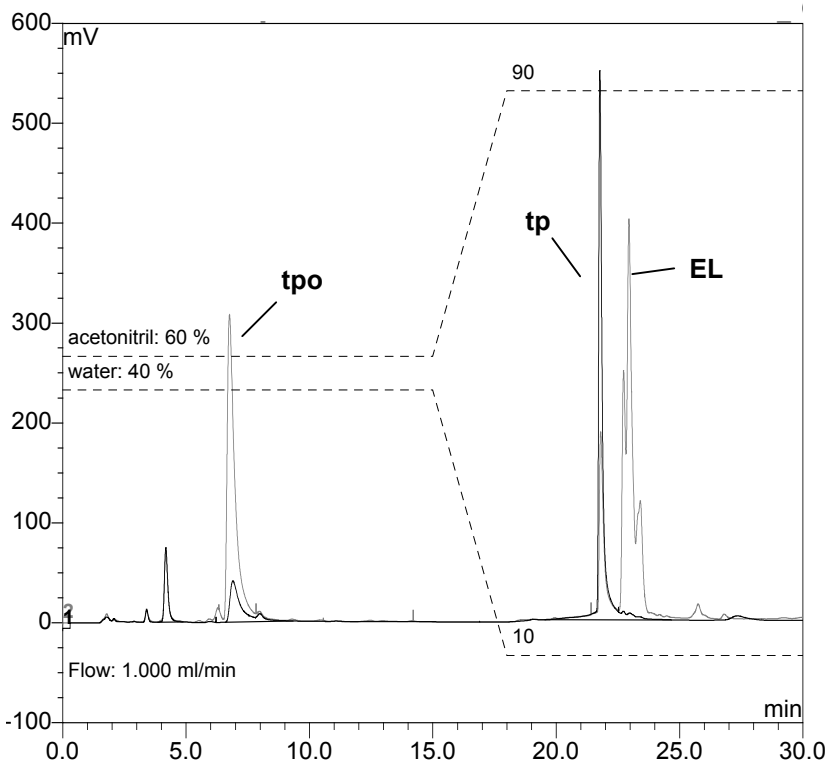

Figure 2.4: HPLC of the reaction mixture of TP with EL 70% (thin gray line) in CH_3CN, using an UV detector at 220 nm. The black line is the result of a blank experiment, only TP in CH_3CN

increase of the TPO peak in the reaction mixture as compared to a blank experiment. The removal of hydroperoxides from EL by Al_2O_3 is thus effectively quantitative. The experimental setup and conditions are described in section 2.4.3.1

2.3.3 Determination of hydroperoxide content in a reaction mixture.

To determine the hydroperoxide content in an EL autoxidation reaction mixture, a spectrophotometric method was used. Although this method is less sensitive than the HPLC technique described in the previous section, it is faster and easier to use when working with a larger number of samples. The method is based on rapid peroxide-mediated oxidation of Fe^{2+} to Fe^{3+} under acidic conditions, and is nicknamed the "FOX assay" after "Ferrous Oxidation Xylenol orange".[16] The concentration of Fe^{3+} in the presence of xylenol orange can be determined by the characteristic absorbance of the Fe^{3+}-xylenol orange complex at 550 nm in the UV-Vis spectrum. Calibration with the hydroperoxide of interest allows for an accurate determination of the hydroperoxide content of any given sample.

In figure 2.5 two UV-Vis spectra are depicted: one spectrum is a blank experiment, (only a methanol solution containing iron(II) and xylenol orange) and the other spectrum is of the same solution containing also a 10 µl sample from an EL autoxidation reaction. The peak which develops around 550 nm is due to the iron(III)-xylenol orange complex. The difference in absorption at 550 nm between the blank and the sample spectrum can be used to calculate the hydroperoxide concentration. A blank experiment is necessary since the iron(II) in the assay solution may slowly oxidise to iron(III) in air. Consequently, some Fe^{3+}-xylenol orange complex formation does not result from reaction with hydroperoxides. The inset in Figure 2.5 shows the formation of

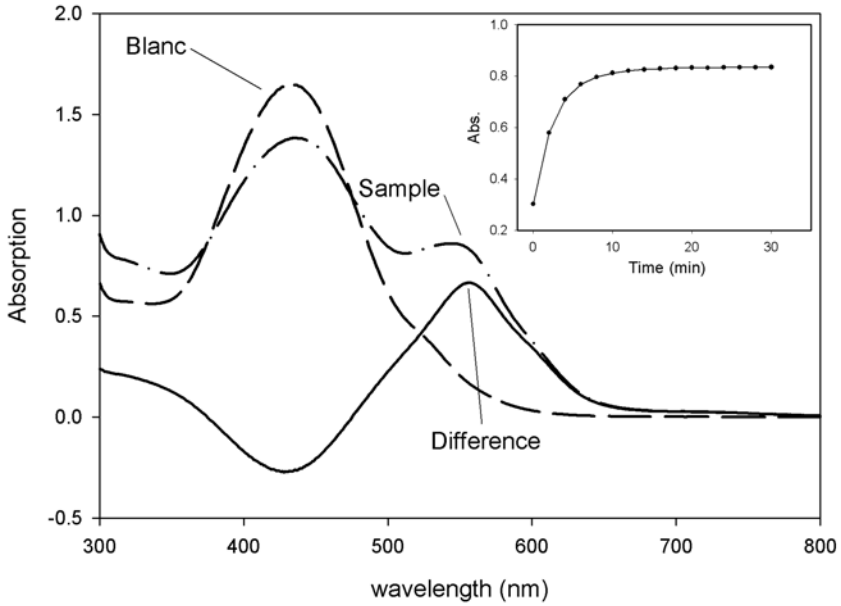

Figure 2.5: UV-Vis spectra of acidic methanol solutions of an iron(II) salt and xylenol orange (FOX-assay), with (sample) and without (blank) a reaction mixture sample added. The absorption peak at 550 nm is due to the formation of an Fe^{3+}-Xylenol orange complex. The increase in adsorption due to the formation of the Fe^{3+} complex can be determined by the difference spectrum between the sample and blank spectra. The inset shows the increase in the 550 nm peak vs time after the reaction mixture sample has been added to the blank.

the Fe^{3+}-xylenol orange complex after addition of the reaction mixture sample, by plotting the increase of the 550 nm peak vs time. All hydroperoxides have reacted within 15 minutes. The experimental details of the FOX assay are described in section 2.4.3.2.

2.4 Experimental

2.4.1 A standard autoxidation experiment followed by FTIR

Technical grade ethyl linoleate (consisting of 70% EL, 16% ethyl oleate (EO), 9% ethyl palmitate (EP) and 5% ethyl stearate (ES))[17] obtained from Fluka is used. Fourier transform infrared spectroscopy is carried out with a BRUKER IFS 113v FT-IR spectrometer equipped with a Specac ATR measuring cell (ZnSe crystal, angle of incidence 45°), using the reflectance technique (4000-600 cm^{-1}, resolution 2 cm^{-1}). For the time-resolved measurements the kinetic mode of the software Win-IR *pro* is used. Spectra are recorded automatically every 5 minutes for the duration of the experiment in an attenuated total reflection (ATR) mode and an integration of the peak at 3010 cm^{-1} (between 2992 cm^{-1} and 3025 cm^{-1}) is performed for each scan. As a result an output file is obtained, containing a table of the integrals of this peak at different times. This file can be further processed with standard spreadsheet programs.

All experiments were performed in a climate-controlled compartment at room temperature (20 °C). All peroxides are removed from EL just prior to an experiment. To accomplish this experiment a small column of basic Al_2O_3, approximately 4 cm in length, is prepared in a Pasteur's pipette plugged with a piece of cotton wool. The desired amount of neat EL is passed over this column using air pressure. The EL obtained this way is peroxide free, as was checked with the HPLC method described in section 2.3.2.

In a typical oxidation reaction, approximately 1 mg of solid metal complex is weighed into a small flask and dissolved in 200 µl of toluene or CH_2Cl_2. Other co-catalysts or additives may now be added to this mixture. Then, EL is added, depending on the molar quantity of metal complex, making the molar metal-to-EL ratio 1/400 (see section 2.2.2.1). Of this mixture, 125 µl is then transferred to the FT-IR cell, resulting in a layer of a thickness of no more than 0.3 mm; this will prevent oxygen diffusion from becoming rate limiting.

2.4.2 A standard autoxidation experiment followed with SEC

Size Exclusion Chromatography (SEC) was performed using an HPLC-system containing a Dionex P580 pump, a Gina50 autosampler and a Wyatt optilab differential refractometer with two mixed_E columns of Polymerlabs. The reaction mixture for a SEC measurement is prepared in the same way as for an FTIR experiment (see the previous section), only for a SEC experiment the EL was not purified.

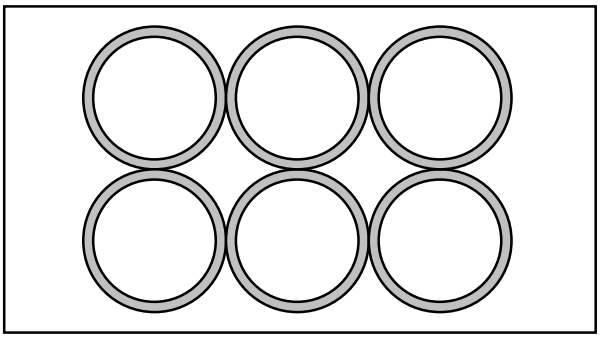

Figure 2.6: Sketch of the sample holder array used to do autoxidation experiments followed with SEC. Six glass rings with a thickness of 0.5 mm and an inner diameter of 2 cm are glued to a 11.5 × 7 cm glass plate, forming six small containers.

A sample holder array was used which was specially constructed for

this experiment; it consists of six glass rings glued to a glass plate, see figure 2.6. Each ring forms a flat cylindrical container, which can hold a thin layer of sample. A thin layer reaction mixture is used to mimic the reaction conditions of a common paint mixture applied to a surface.

At the start of an experiment, 98 µl of the prepared reaction mixture is transferred to each of the six containers. The layer thickness in each sample holder does not exceed 0.32 mm, thereby preventing oxygen diffusion from becoming a rate-limiting step in the oxidation reaction.[11] To follow the cross-link formation in time, an 18 µl sample is taken from the reaction mixture in a sample holder, dissolved in 1.5 ml of $CHCl_3$ and injected into the HPLC. Typically samples are taken after 2, 4, 6, 8 and 24 hours. Only one sample is taken from each single sample holder, to keep the reaction conditions for the entire experiment as constant as possible.

2.4.3 Determination of the hydroperoxide concentration in EL

2.4.3.1 HPLC method

TP and TPO were obtained from Acros and were re-crystallized from cyclohexane before use. CH_3CN is distilled from CaH_2 and stored on 3 Å molecular sieves under argon before use. TP and TPO were separated by reverse-phase HPLC on a column of Spherisorb ODS-2 (5µm, 5.4 mm ∅ X 300 mm) using CH_3CN/H_2O (first 15 min 60/40, then 90/10, v/v) as the eluent with a flow rate of 1 ml/min. The signals were detected using the UV absorption at 220 nm with a Gilson 119 UV/Vis detector.

The following experiment is an example and the concentrations of the reagents used are based on an estimated hydroperoxide concentration in the sample of 0.1 mol%. A TPO calibration curve is made by measuring five different solutions of TPO in CH_3CN with concentrations in the range of 0.1 to 1 mM.

For the hydroperoxide determination two 2-necked 50 ml round-bottom flasks are evacuated and put under argon using standard Schlenk techniques. To each flask is added 1 ml of a 0.316 mM TP solution in CH_3CN under argon. 63.6 µl EL 70% is added to one of the flasks, the other flask is used for the blank experiment.[18] Both flasks are stirred for 30 min, then, from each flask a 20 µl sample is taken and injected in the HPLC. By comparing the surface area of the TPO peak with the calibration curve the hydroperoxide concentration is determined, see section 2.3.1.

2.4.3.2 Spectrophotometric method.

The reaction setup from which samples are taken to analyze the hydroperoxide content is the same as described for SEC experiments (Section 2.4.2). Reaction samples are thus assumed to be almost pure EL and derivatives thereof.

The so-called “FOX reagent” (see section 2.4.2) is made as follows: a 250 ml 2-necked round-bottom flask is evacuated and put under argon using Schlenk techniques. To this flask are added: 90 ml of MeOH (distilled from sodium metal and kept under argon before use), 10 ml 0.25 M H_2SO_4 in H_2O, 9.8 mg ammonium iron(II) sulfate hexahydrate, 88 mg butylated hydroxytoluene (BHT = 2,6-di-*tert*-butyl-4-methylphenol) and 7.6 mg xylenol orange (= *o*-cresolsulfonephthalein-3’-3’’-bis-methyliminodiacetic acid sodium salt) The FOX reagent solution has to be stored under argon otherwise oxidation of iron(II) to iron(III)

will occur overnight. The fresh solution is light orange, and will turn red to purple to blue when more Fe^{3+} is formed. The BHT is a radical scavenging agent and is added to quench all radical reactions to prevent further oxidation once the sample has been added.

Solution UV-Vis spectra were recorded with a Varian Cary 50 spectrophotometer. The spectrophotometer baseline was recorded with the solvent (MeOH) as a blank. For each sample, spectra are recorded every 2 minutes for up to 30 minutes, to verify that all hydroperoxides have reacted. To fall within the region where the Lambert-Beer law applies, the absorption should not be above 1. Three methods were used to determine hydroperoxide content, depending on the expected concentrations of hydroperoxide in the sample. For all methods, it is sometimes necessary to shake the cuvette after 15 minutes, to make sure the color develops homogeneously.

Method 1: This method is used to determine the hydroperoxide content of pure EL. The absorption of 3 ml of the FOX reagent is measured in a stoppered quartz cuvette as a blank. To this cuvette, 10 µl of pure EL 70% is added. To dissolve all EL quickly, the mixture in the cuvette needs to be shaken vigorously. Then this sample is measured.

Method 2: The absorption of 3 ml of the FOX reagent is measured in a stoppered quartz cuvette as a blank. 10 µl of reaction sample is taken with a Finn pipette and dissolved in such an amount of MeOH that the concentration of the sample in this MeOH solution is 300× the Fe^{2+} concentration in the FOX reagent solution in the cuvette (It is assumed the sample is pure EL). Then, from this mixture 10 µl is added to the cuvette containing the FOX reagent (the concentrations of Fe^{2+} and of the reaction sample are equal in the cuvette) and the absorption is measured.

Method 3: The absorption of 1.5 ml of the FOX reagent with 1.5 ml of MeOH added is measured in a stoppered quartz cuvette as a blank. The sample preparation is the same as for method 2.

The extinction coefficient for the Fe^{3+}-xylenol orange complex used to calculate the hydroperoxide concentration in EL is 4.7×10^4. This value was obtained from literature, where pure EL-hydroperoxide was used to determine the apparent extinction coefficient with the FOX reagent.[16]

2.5 Concluding remarks

It will become clear from the remaining chapters of this thesis that the oxidation reaction of ethyl linoleate as monitored with time-resolved FT-IR spectroscopy and size exclusion chromatography is very suitable indeed as a screening model reaction for finding new drying catalysts for alkyd paint.

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[18] *Derivation of the amount of EL used: 2.5x excess of TP over the amount of peroxides in the sample: 0.316×10^{-6} mol/2.5 = 0.126×10^{-6} mol $\times$ 1000 (est. hydroperoxide conc. 0.1%) = 0.126×10^{-3} mol EL needed. (0.126×10^{-3} mol $\times$ 308.51 g/mol)/0.873 g/ml = 44.5×10^{-3} ml $\times$ 100/70 = 63.6 µl.*