Metal ions can also act as potent *inhibitors* of autoxidation,[14, 28-30] by means of reactions **12** and **13** in Scheme 1.1. Reaction **12** commonly occurs for Mn^{2+} and Co^{2+} metal salts and this reaction can completely suppress autoxidation when the concentration of metal ions is higher than the hydroperoxide concentration.[14, 15] Particularly for manganese(II) complexes, reaction **12** is one of the causes for the induction time that is often observed for metal-catalysed autoxidation reactions. To eliminate this induction time, the $[Mn^{2+}]/[ROOH]_0$ ratio has to be less than one.[31] Higher valent metals might be able to inhibit autoxidation (at low oxygen concentration) by scavenging carbon radicals, reaction **13** in scheme 1.1. Cu^{2+} and Fe^{3+} ions have been shown to readily reduce certain carbon radicals.[32, 33]

An extensive treatment of the general kinetics of metal-catalysed autoxidation will not be given here, but the interested reader is referred to an excellent review by Reich and Stivala.[34]

1.2.2 The autoxidation of alkyd paint

1.2.2.1 General considerations

Several aspects of alkyd paint autoxidation are typical for the alkyd system:

- Autoxidation occurs in an apolar environment
- Oxidations take place at the fatty acid tail of the alkyd resin
- Oxidation leads to cross-link formation.

These different aspects are highlighted in the following sections.

1.2.2.2 Autoxidation in apolar media: metal-hydroperoxide complex formation

Autoxidation drying starts when all solvent is evaporated. Consequently, autoxidation takes place in a mixture of pure alkyd resin and pigments, which is very likely a significantly apolar environment. This has some consequences for the autoxidation reactions, *i.e.* ionization processes will be suppressed and metal salts will not dissociate into ions.[9] The most notable consequence for autoxidation of the alkyd system is that the Haber-Weiss reactions **3** and **4** do not occur in apolar media. Hydroperoxides are decomposed following metal-hydroperoxide complex formation, as shown in scheme 1.3.[9, 10, 14, 35, 36] This has some far-reaching implications for metal catalysis, since reaction **4b** in scheme 1.3 has been reported to be very slow for simple metal salts.[10]

$$ROOH + M^{n+} \rightleftharpoons [(ROOH)M]^{n+} \qquad \textbf{3a}$$

$$[(ROOH)M]^{n+} \rightarrow RO^{\bullet} + [(M^{(n+1)+}(OH^{-})]^{n+} \qquad \textbf{3b}$$

$$ROOH + M^{(n+1)+} \rightleftharpoons [(ROOH)M]^{(n+1)+} \qquad \textbf{4a}$$

$$[(ROOH)M]^{(n+1)+} \rightarrow ROO^{\bullet} + M^{n+} + H^{+} \qquad \textbf{4b}$$

Scheme 1.3: Metal–hydroperoxide complex formation in media of low polarity

Thus, reduction of the higher valence state metal is proposed not to be accomplished by hydroperoxides, but rather by easily oxidizable autoxidation products such as aldehydes and alcohols or directly by the substrate (reaction **6** in scheme 1.1).[10, 22] Metal-hydroperoxide complex formation is also thought to account for the very sudden conversion of catalyst into inhibitor upon steadily increasing the metal concentration.[14] In apolar media, metal salts will form a complex with a hydroperoxide as long as the hydroperoxide is available. Metal ions that are not coordinated can participate in the inhibiting reaction **12** in scheme 1.1, and thus sudden inhibition of autoxidation occurs if the metal concentration becomes higher than the hydroperoxide concentration.[14, 30, 31]

1.2.2.3 Fatty acid autoxidation

The fatty acid tail of the alkyd resin (Fig 1.1) is where autoxidation takes place. Fatty acids are important biomolecules, and are present in lipids as their triester with glycerol. Consequently, a considerable amount of research has been performed on elucidation of their autoxidation mechanism, since lipid autoxidation is known to be the cause of vital issues such as food spoilage, tissue injuries and degenerative diseases.[7, 27]

The fatty acids in an alkyd resin are polyunsaturated fatty acids, commonly linolenic acid, (α-linolenic acid = 9*Z*,12*Z*,15*Z*-octadecatrienoic acid and γ-linolenic acid = 6*Z*,9*Z*,12*Z*-octadecatrienoic acid) which is a major constituent of linseed oil,[37] or linoleic acid (9*Z*,12*Z*-octadecadienoic acid) which is a major constituent of, for example, sunflower oil and soya oil. The high susceptibility of non-conjugated polyunsaturated fatty acids (or lipids) for autoxidation comes from the presence of *bis*-allylic hydrogen atoms, which have a relatively low bond dissociation energy of 75 kcal/mol (see Fig 1.2) and can therefore be easily abstracted, resulting in radical chain initiation and thus autoxidation.[27, 38, 39] Abstraction of one of the *bis*-allylic hydrogen atoms results in the formation of a radical species. This radical species is stabilised by delocalisation due to the local pentanediene structure. Molecular oxygen reacts extremely rapid with this pentanedienyl radical species to form a peroxy radical which has the double bonds dominantly conjugated, since this is the most stable structure.[7] The peroxyl radical can then participate in a host of reactions, as was outlined in section 1.2.1 and scheme 1.1, but in the early stages of autoxidation the dominant reaction will be to abstract a hydrogen atom from another lipid molecule to form a hydroperoxide and propagate the radical chain (reaction **8** in scheme 1.1). Scheme 1.4 shows the initial autoxidation reactions for a fatty acid pentanediene substructure, forming a hydroperoxide. Figure 1.3 shows the total time course of fatty acid autoxidation: the fatty acid concentration will rapidly decrease as hydroperoxides are formed. The hydroperoxide concentration will go through a maximum when hydroperoxide formation is surpassed by hydroperoxide decomposition.

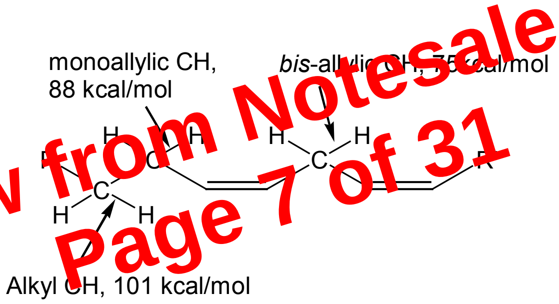
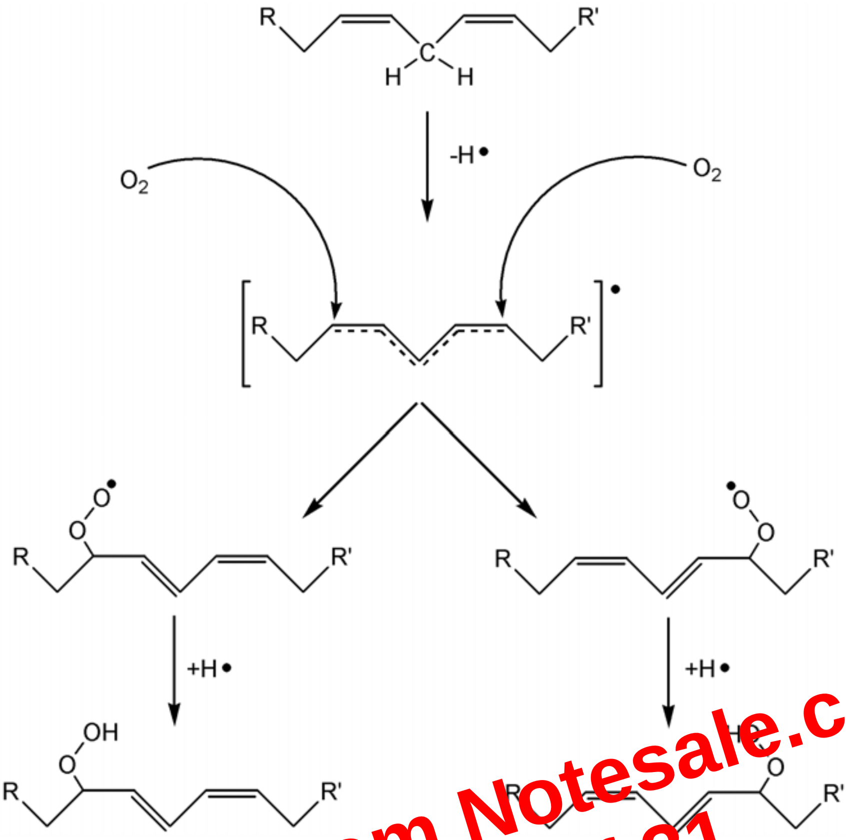


Figure 1.2: Bond dissociation energies of the different CH bonds in fatty acids

Hydroperoxide decomposition leads to further product formation, forming cross-linked (non-volatile) species and numerous other oxygen containing products such as alcohols, ketones, aldehydes and carboxylic acids.



Scheme 1.4: Initial hydroperoxide formation in the autoxidation of the fatty acid chain of an alkyd resin binder unit.

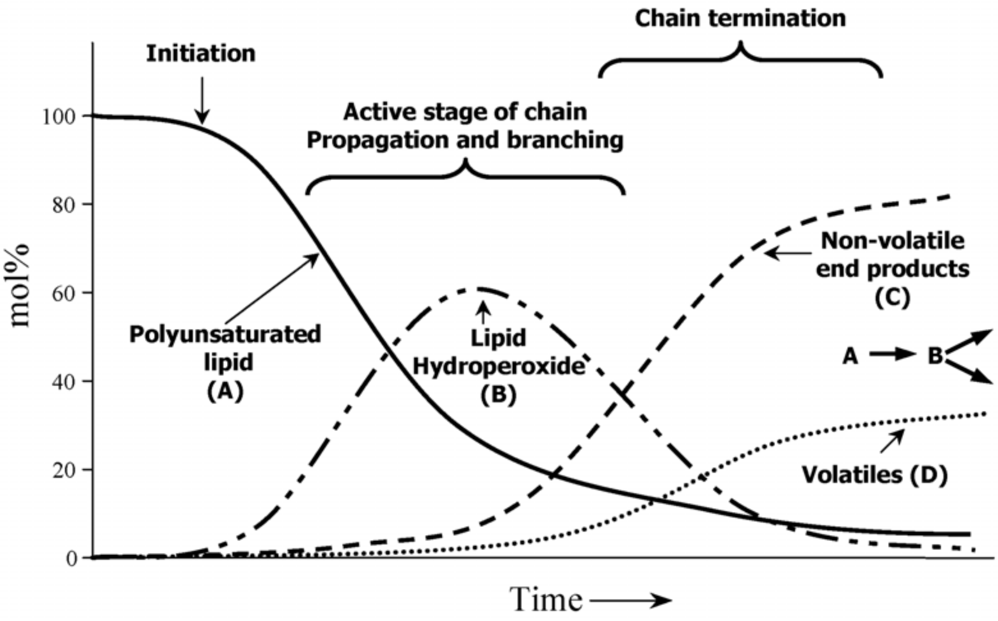
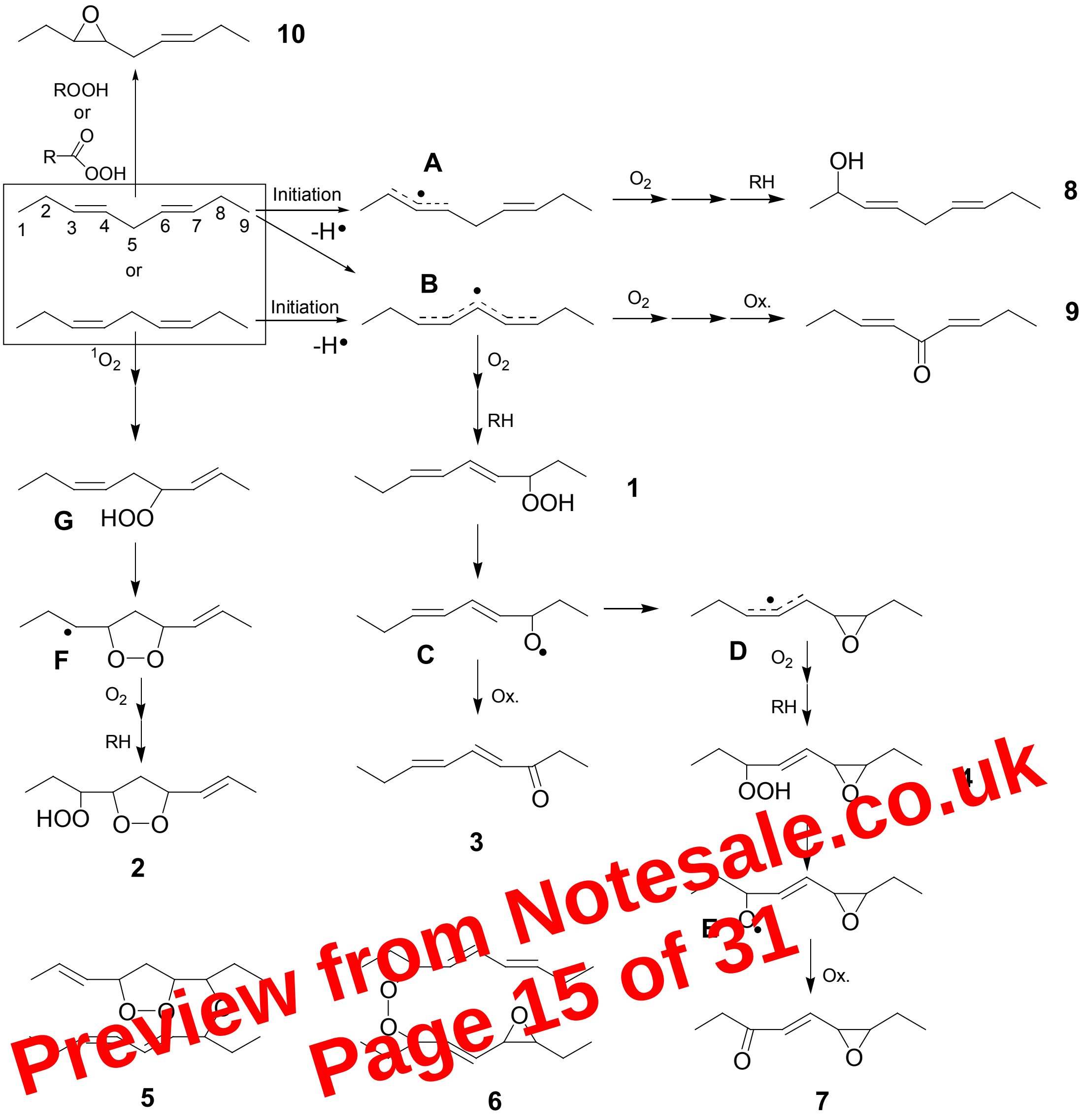
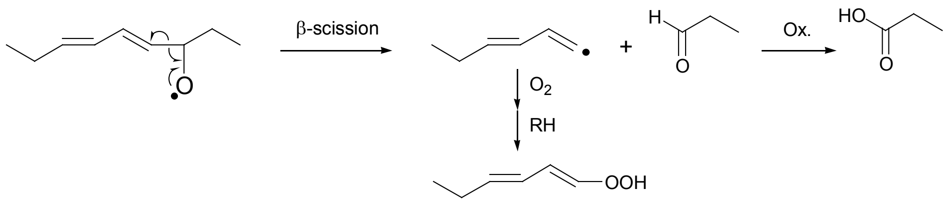


Figure 1.3: time course of fatty acid (lipid) autoxidation,redrawn after Gardner.[41]



Scheme 1.6: Products of the cobalt-catalysed autoxidation of (*E,E*) or (*Z,Z*)-3,6-nonadiene. Products **1**-**10** were isolated and characterised with ^{1}H- and ^{13}C-NMR. Species **A-F** are proposed reaction intermediates. The monomeric products found with the (*Z,Z*)-isomer were also isolated starting from (*E,E*)-3,6-nonadiene.[57]

Ketones **3**, **7**, and **9** can be formed by oxidation of alkoxy radicals and epoxide **4** *via* an intramolecular addition reaction of the alkoxy radical to an adjacent double bond. The isolation of small amounts of compound **10** was evidence that direct epoxidation of isolated double bonds also occurs. The most probable routes for direct epoxidation were proposed to be *via* peracids and *via* hydroperoxides.[61] Peracids can be formed by oxidation of aldehydes. A singlet-oxygen pathway was also found to exist, since the



Scheme 1.7: Example of a β-scission reaction leading to chain breaking and formation of aldehydes and carboxylic acids.[57]

[38] W. H. Koppenol, *FEBS Lett.* **1990**, *264*, 165.
[39] F. Q. Schafer, S. Y. Qian, G. R. Buettner, *Cell. Mol. Biol.* **2000**, *46*, 657.
[40] H. Wexler, *Chem. Rev.* **1964**, *64*, 591.
[41] H. W.-S. Chan, in *Food Science and Technology* (Ed.: B. S. Schweigert), Academic Press Inc., London, **1987**.
[42] N. A. R. Falla, *J. Coat. Tech.* **1992**, *64*, 55.
[43] R. Kumarathasan, A. B. Rajkumar, N. R. Hunter, H. D. Gesser, *Prog. Lipid. Res.* **1992**, *31*, 109.
[44] J. H. Hartshorn, *J. Coat. Tech.* **1982**, *54*, 53.
[45] M. Lazzari, O. Chiantore, *Polym. Degrad. Stabil.* **1999**, *65*, 303.
[46] F. R. Vandevoort, A. A. Ismail, J. Sedman, G. Emo, *J. Am. Oil. Chem. Soc.* **1994**, *71*, 243.
[47] J. Mallegol, J. L. Gardette, J. Lemaire, *J. Am. Oil. Chem. Soc.* **1999**, *76*, 967.
[48] J. Mallegol, J. L. Gardette, J. Lemaire, *J. Am. Oil. Chem. Soc.* **2000**, *77*, 249.
[49] J. Mallegol, J. L. Gardette, J. Lemaire, *J. Am. Oil. Chem. Soc.* **2000**, *77*, 257.
[50] W. J. Muizebelt, J. C. Hubert, R. A. M. Venderbosch, *Prog. Org. Coat.* **1994**, *24*, 263.
[51] W. J. Muizebelt, M. W. F. Nielen, *J. Mass Spec.* **1996**, *31*, 545.
[52] W. J. Muizebelt, J. J. Donkerbroek, M. W. F. Nielen, J. B. Hussem, M. E. F. Biemond, R. P. Klaasen, K. H. Zabel, *J. Coat. Tech.* **1998**, *70*, 83.
[53] E. N. Frankel, *J. Am. Oil. Chem. Soc.* **1984**, *61*, 1908.
[54] H. Knoll, *Zeit. Chem.* **1978**, *18*, 302.
[55] W. J. Muizebelt, J. C. Hubert, M. W. F. Nielen, R. P. Klaasen, K. H. Zabel, *Prog. Org. Coat.* **2000**, *40*, 121.
[56] Z. O. Oyman, W. Ming, R. van der Linde, *Prog. Org. Coat.* **2003**, *48*, 80.
[57] J. C. Hubert, R. A. M. Venderbosch, W. J. Muizebelt, R. P. Klaasen, K. H. Zabel, *Prog. Org. Coat.* **1997**, *31*, 331.
[58] E. N. Frankel, R. F. Garwood, J. R. Vinson, B. C. L. Weedon, *J. Chem. Soc.-Perkin Trans. 1* **1982**, 2707.
[59] E. N. Frankel, R. F. Garwood, J. R. Vinson, B. C. L. Weedon, *J. Chem. Soc.-Perkin Trans. 1* **1982**, 2715.
[60] H. A. J. Carless, R. J. Batten, *J. Chem. Soc.-Perkin Trans. 1* **1987**, 1999.
[61] W. Meyer, G. Spiteller, *Lieb. Anal.* **1993**, 1253.
[62] J. C. Hubert, R. A. M. Venderbosch, W. J. Muizebelt, R. P. Klaasen, K. H. Zabel, *J. Coat. Tech.* **1997**, *69*, 59.
[63] J. H. Bieleman, in *Additives for Coatings* (Ed.: J. H. Bieleman), Wiley-VCH, Weinheim, **2000**, pp. 202.
[64] R. G. Middlemiss, D. J. Olszanski, *Am. Paint. Coat. J.* **1993**, *78*, 35.
[65] S. M. P. Meneghetti, R. F. de Souza, A. L. Monteiro, M. O. de Souza, *Prog. Org. Coat.* **1998**, *33*, 219.
[66] S. S. Lande, C. D. Falk, J. K. Kochi, *J. Inorg. Nucl. Chem.* **1971**, *33*, 4101.
[67] R. Lombard, L. Rommert, *Bull. Soc. Chim. France* **1956**, 36.
[68] M. L. Feldman, M. Landau, *patent US4331575*, **1982**
[69] S. J. Bellettiere, D. M. Mahoney, *J. Coat. Tech.* **1987**, *59*, 101.
[70] M. Ali, W. R. McWhinnie, *App. Organomet. Chem.* **1993**, *7*, 137.
[71] D. J. Love, *J. Oil. Col. Chem. Ass.* **1977**, *60*, 214.
[72] J. H. W. Turner, P. Womersley, *Chem. Ind.* **1975**, 203.
[73] W. J. Muizebelt, J. C. Hubert, R. A. M. Venderbosch, A. J. H. Lansbergen, R. P. Klaasen, K. H. Zabel, *J. Coat. Tech.* **1998**, *70*, 53.
[74] S. J. Bellettiere, R. Hurley, S. Hoch, *patent US4311465*, **1982**
[75] M. Landau, S. J. Bellettiere, S. Hoch, *patent US4175064*, **1979**
[76] M. Fefer, A. J. Lauer, *J. Am. Oil. Chem. Soc.* **1968**, *45*, 479.
[77] G. Ostberg, B. Bergenstahl, K. Sorenssen, *J. Coat. Tech.* **1992**, *64*, 33.
[78] S. J. Tuman, D. Chamberlain, K. M. Scholsky, M. D. Soucek, *Prog. Org. Coat.* **1996**, *28*, 251.
[79] V. D. Athawale, A. V. Chamanker, *Pigment & Resin Technology* **1997**, *26*, 378.
[80] J. Mallegol, J. Lemaire, J. L. Gardette, *Prog. Org. Coat.* **2000**, *39*, 107.
[81] J. Mallegol, A. M. Barry, E. Ciampi, P. M. Glover, P. J. McDonald, J. L. Keddie, M. Wallin, A. Motiejauskaite, P. K. Weissenborn, *J. Coat. Tech.* **2002**, *74*, 113.
[82] W. O. Lundberg, F. M. Greenawald, F. Scofield, E. B. Fitzgerald, *Ind. Eng. Chem.* **1954**, *46*, 570.
[83] D. G. Nicholson, *Ind. Eng. Chem.* **1949**, *34*, 1175.
[84] A. C. Zettlemoyer, D. M. Nace, *Ind. Eng. Chem.* **1950**, *42*, 491.
[85] D. G. Nicholson, *J. Am. Chem. Soc.* **1942**, *64*, 2820.
[86] E. S. Matsui, *J. Coat. Tech.* **1980**, *52*, 39.