CHEMICAL PROCESSES ACCOMPANYING
THE AUTOXIDATION OF PAINT FILMS

by

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TO

MY PARENTS,

IAN

K. and F.P.S.

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Abstract

Film forming systems were prepared from allyloxy compounds, in conjunction with polyacrylates, together with a redox promoter and solvent. The allyloxy compounds used were based upon two broad types namely (1) tris-(N-allyloxymethyl-N-methoxymethyl) melamine and (2) tri (2-(3'propenoxymethyl)ethylene) glycol 1-ethyl ether.

The structure of the crosslinked matrix appeared to consist mainly of polymerised allyloxy compound. If the polyacrylate, (derived from butyl acrylate, methyl methacrylate and methacrylic acid), used in the film forming system consisted of non-derivatised carboxyl groups along the chain, then no chemical interaction seemed to occur between the drying system and polymer. The polymer merely became entrapped in the crosslinking matrix of the allyloxy compound. However, if some of the free carboxyl groups were reacted with allyl glycidyl ether, so that some pendant allyloxy groups were present, then the rate of drying was marginally increased and more polymer was incorporated in the dried film than with the unmodified polyacrylate.

These conclusions were based upon a combination of results using G.P.C., FTIR and radiolabelling.

The 'yellowing' of alkyd films, particularly in the dark and at elevated temperatures was investigated by attempting the characterisation of the yellow products

derived from trans-2-hexenal. This compound has been identified as one of the autoxidative degradation products of both the methyl esters of linoleic and linolenic acids and alkyds derived therefrom.

Analysis by gc-ms, with EI and NH_3-CI and accurate mass measurement of the derivatised alkali soluble products derived from trans-2-hexenal, which had yellowed in the dark at 70°C, gave structures which showed epoxide formation with possible rearrangement to carbonyl compounds. 2-Propenal was identified as a by-product of the autoxidative degradation of the allyloxy drying systems. Similar analysis by gc-ms of 'yellowed' 2-propenal gave structures of the form $H(CH{=}CH{-}CHOH)_n{-}CH{=}CH{-}CHO$. It is postulated that with sufficiently large n and oxidation of the secondary alcohol function that compounds would have a chromophore in the yellow region of the spectrum.

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1. Introduction

1.1 Introduction to paint chemistry[1]

Many objects are susceptible to corrosion at their surfaces from attack by the elements, vermin, fungi, bacteria, and from the wear of daily use. In order to protect these articles examples of various surface coatings, that can be applied include, wallpaper, plastic sheet and chromium plating; coatings may also be used for decorative purposes.

Paint is an extremely versatile surface coating material which can be applied to any surface, however awkward its shape or size. The word 'paint' can refer to a whole range of materials: e.g. lacquers, varnishes, undercoats, primers, sealers, etc. These products are all formulated on the same basic principles and contain some or all of the four main ingredients, which are listed below:-

(i) pigment, which has both a decorative and protective use,

(ii) resin or 'film-former', which is a polymer and binds the pigment molecules together holding them onto the surface,

(iii) solvent, which enables the application of the paint onto the surfaces,

(iv) additives, which include drying promoters, anti-skinning agents to improve stability in the can, silica, silicates and resinous thickeners to increase the viscosity of the paint, silicone oils and surfactants, which lower the interfacial tensions within the paint film.

1.2 Alkyd resin technology

The composition of many of the decorative gloss paints are based upon alkyd resins, which are one of the most versatile and economical of resin types.

Alkyd resins are condensation polymers derived from the reaction of a polybasic acid with a polyfunctional alcohol in an esterification reaction; monofunctional acids are used to control the process and prevent gelation of the resin. The name alkyd is derived from the 'al' of alcohol and the 'cid' of acid.

Many combinations of acids and alcohols may be used to prepare alkyd resins. Some of the more common raw materials used in alkyd manufacture are given in table 1.

Table 1

Polybasic acids	Polyhydric alcohols	Monofunctional acids
Phthalic acid*	Ethylene glycol	"Drying oils" +
Isophthalic acid	Glycerol	Benzoic acid
Succinic acid	Pentaerythritol	Rosin
Adipic acid	Diethylene glycol	
Sebacic acid	1,2-Propylene glycol	
Terephthalic acid	Trimethylol propane	
Trimellitic acid*	Neo-pentyl glycol	

* used as the anhydride

+ used as the monobasic acids found in the glycerol triesters (see below)

Natural drying oils are the glycerol triesters of unsaturated and saturated C_{12} - C_{18} straight chain fatty acids; the properties of the oils are dependent upon the relative proportions of the different fatty acids. In alkyd manufacture it is the monobasic acids, that are found in the glycerol triesters, which are important for three main reasons:-

(i) to control gelation of the polyester,

(ii) to promote solubility in hydrocarbon based solvents,

(iii) to provide a method of cross-linking of films by autoxidation. (This important property is a function of the unsaturated fatty acids and will be discussed in section 1.8).

Some common fatty acids are shown in table 2 and the percentage composition of some typical 'drying' oils are given in table 3.

Table 2

Common fatty acids	
cis-9-octadecenoic acid (oleic acid)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
cis-9-cis-12-octadecadienoic acid (linoleic acid)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
cis-9-cis-12-cis-15- octadecatrienoic acid (linolenic acid)	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}$ $CH(CH_2)_7COOH$
cis-9-cis-11-cis-13- octadecatrienoic acid (eleostearic acid)	$CH_3(CH_2)_3(CH{=}CH)_3(CH_2)_7COOH$
octadecanoic acid (stearic acid)	$CH_3(CH_2)_{16}COOH$

Table 3

Oil	Oleic acid %	Linoleic acid %	Linolenic acid %	Saturated acids %	Special acids %
Linseed (raw)	9-16	32-37	37-42	6-9	-
Safflower	26-38	51-67	0.7-1	6-10	-
Soya	26-30	50-60	2-6	11-14	-
Sunflower	34-42	52-59	-	6-9	-
Tung	4-18	-	-	4-6	Eleostearic 72-86

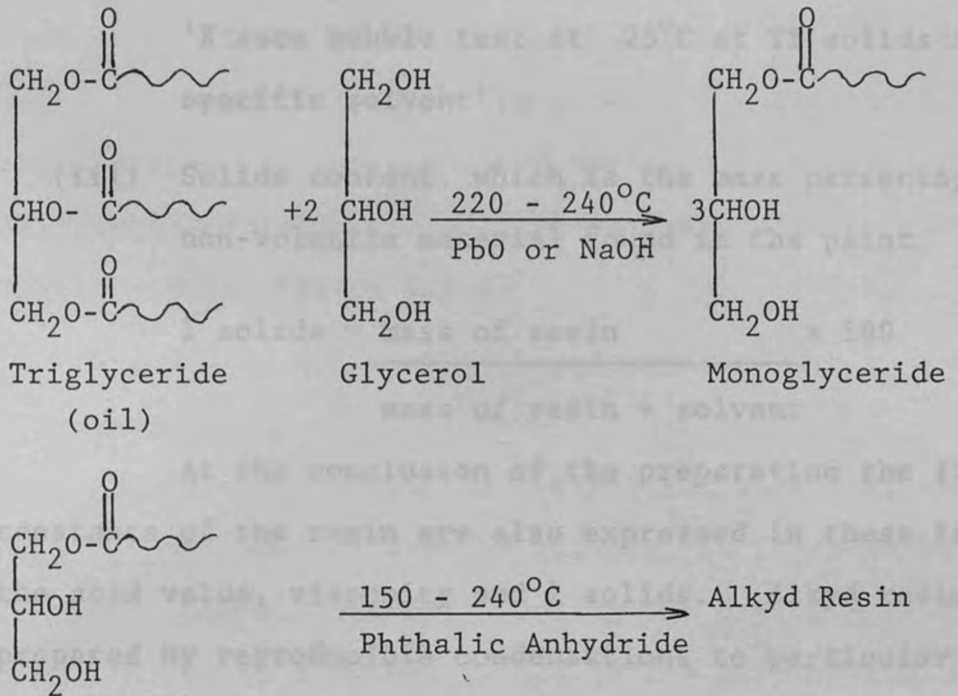
Two slightly different methods may be used for the manufacture of alkyds:-

(i) direct esterification where the polybasic acids, polyhydric alcohols and unsaturated fatty acids are heated at 240°C, under a blanket of nitrogen and where the water produced by the esterification process is azeotropically removed,

(ii) alcoholysis where the natural oil (triglycerides), (1 part), is heated at 240°C in the presence of the polyhydric alcohol, glycerol, (2 parts) and a catalyst (e.g. PbO or NaOH) to give a random mixture of glycerol, monoglycerides and diglycerides. The objective is to maximise the production of the monoglycerides and this to a certain extent can be controlled by the reaction conditions.

The resulting mixture is then reacted with the polybasic acid to produce the alkyd resin, scheme 1.2.1.

The alcoholysis route is used industrially as natural oils are cheaper than mixtures of the corresponding fatty acids.



Scheme 1.2.1.

The resin preparation is monitored to prevent total gelation. Three control tests are carried out which are particular to alkyd manufacturers:-

(i) 'Acid value' (AV) of the resin, which gives a measurement of the carboxyl end groups and thus the degree of reaction. This AV is expressed as 'mgKOH/g non-volatile resin'.

(ii) Viscosity, which gives a measure of molecular mass of the resin. This test is carried out using a stoppered glass tube almost filled with resin. The time taken for the bubble to rise through the resin when the tube is inverted is recorded.

The determination of viscosity is expressed as 'X secs bubble test at $25^{o}C$ at Y% solids in a specific solvent'.

(iii) Solids content, which is the mass percentage of non-volatile material found in the paint.

$$\% \text{ solids} = \frac{\text{mass of resin}}{\text{mass of resin + solvent}} \times 100$$

At the conclusion of the preparation the final constants of the resin are also expressed in these terms viz. the acid value, viscosity and % solids. Alkyd resins are prepared by reproducible condensations to particular acid values and viscosity specifications, depending upon the final use of the resin.

The conventional method of expressing alkyd resin composition is as follows:-

Polyhydric alcohol/Polybasic acid/fatty acid for example:

Pentaerythritol/Phthalic Anhydride/Tall oil fatty acids
2.1 2.25 3

where the numbers represent the molar ratios.

Alkyd resins are also defined by 'oil length', which is the % mass of oil (i.e. triglycerides) used to make the resin.

Below 45% oil is a 'short oil alkyd', 45 - 60% 'medium oil' and above 60%, 'long oil'. 'Long oil alkyds' are soluble in aliphatic hydrocarbons, such as white spirit, whereas 'short oil alkyds' require aromatic hydrocarbons.

Relative molecular masses of alkyds are believed to range from 1000 - 5000. For a 58% linseed oil glycerol phthalate alkyd, this might incorporate between two and ten fatty acid ester chains per average alkyd molecule. A simplified oleic fatty acid/pentaerythritol/phthalate alkyd resin[2] is illustrated in figure 1.2.1.

The drying of an alkyd based paint occurs by two processes:-

(i) By evaporation of the solvent such that when the polymer is free of solvent, it is relatively hard and not sticky. During the drying process there is no chemical change in the polymer i.e. no cross-linking. This type of drying is called 'lacquer drying'.

(ii) By air-drying, which involves autoxidation of the unsaturated fatty acid esters forming hydroperoxides. It is thought that the decomposition of these hydroperoxides to give alkoxy radicals provides the means for cross-linking the polymer to give a dry paint film.

The chemistry of hydroperoxide formation in the most commonly used unsaturated fatty acid derivatives will be outlined in sections 1.4, 1.5 and 1.6.

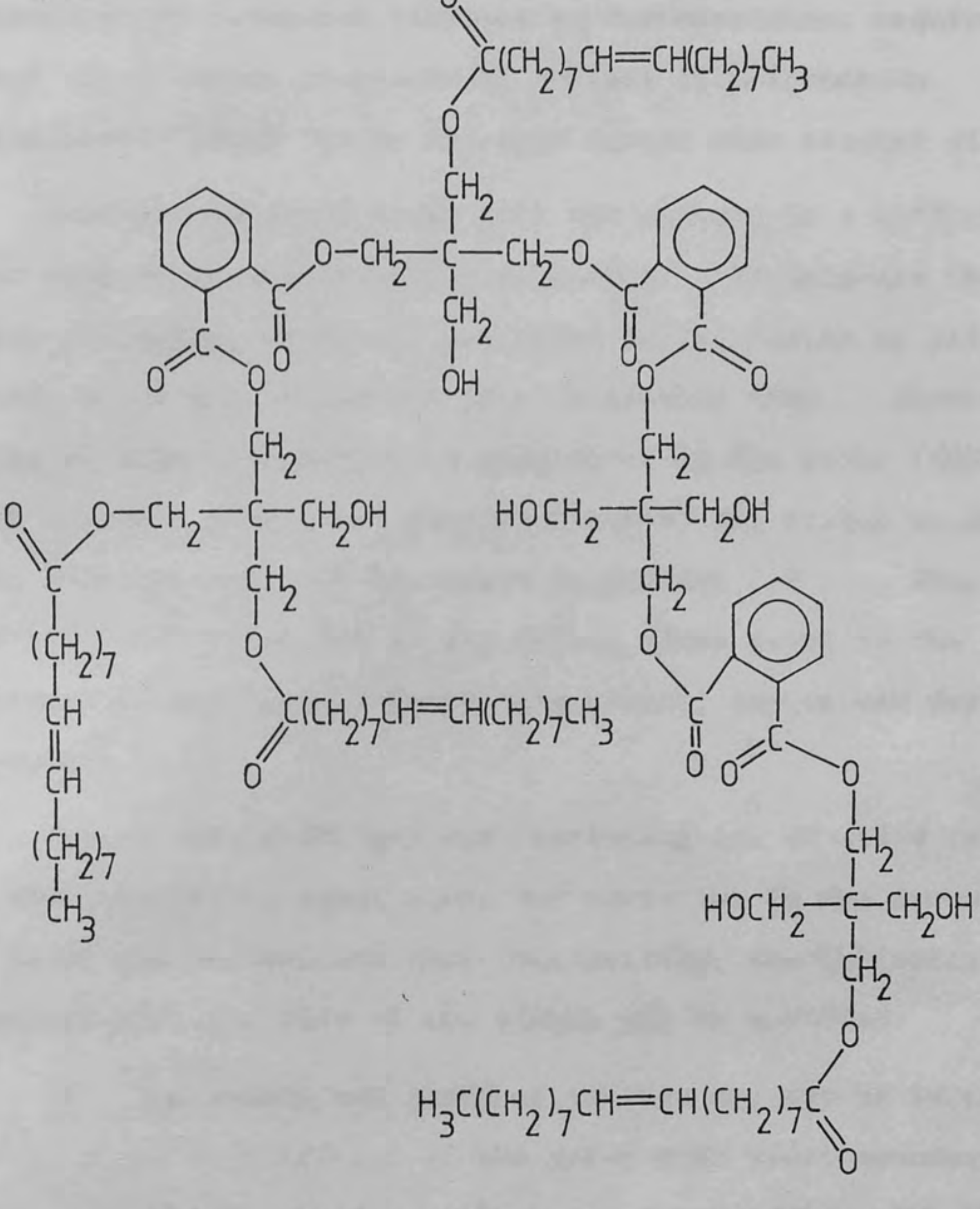


Figure 1.2.1.

Simplified Alkyd Resin

The natural oils will themselves dry and form a film but because of their relatively small size numerous cross-linking reactions are required for film formation. In contrast alkyd resins, owing to their initial greater molecular mass and greater number of potential sites for hydroperoxide formation followed by decomposition, require fewer crosslinking reactions to achieve film formation. Consequently alkyd resins dry much faster than natural oils.

Even so, an alkyd resin will not air-dry in a sufficiently fast time to provide a suitable product. To increase the rates of drying, promoters are added to the resins to give paints which will crosslink in a reasonable time. Several types of promoters have been considered by the paint industry such as redox catalysts, photoinitiators[3] and strong acids.[4] (The promoters will be discussed in section 1.9). Thus the required system for an air-drying alkyd paint is the presence of unsaturated fatty acid esters, oxygen and drying promoters.

One of the advantages and continuing use of alkyd resins is that they allow great scope for variation in the formulation of paint and to indicate their versatility, the following examples give outlines of how alkyds may be modified:

(i) The extent and speed of lacquer dry may be increased by modification of the alkyd with vinyl monomers. Typical monomers, which can copolymerise with the alkyds by grafting to the fatty acid chains, are styrene, vinyl toluene and methylmethacrylate. The reaction proceeds most readily if the double bonds of the fatty acid are conjugated.

(ii) Polyurethane alkyds are basically similar to ordinary alkyds but provide a good abrasion resistance and are used in varnishes for floors, boats and in industrial maintenance. A urethane alkyd is one in which a proportion of the dibasic acid typically used is replaced by diisocyanate. The ester links are formed first in the usual way, the diisocyanate is added and the remaining hydroxyls are reacted at 80 - 95°C to form urethane linkages. These are more resistant to alkalis than ordinary alkyds having only ester linkages.

(iii) Alkyd resins may also be used for stoving finishes, where the crosslinking occurs by an in situ chemical reaction; the finish is hardened by blending the alkyds with melamine or urea formaldehyde resins.

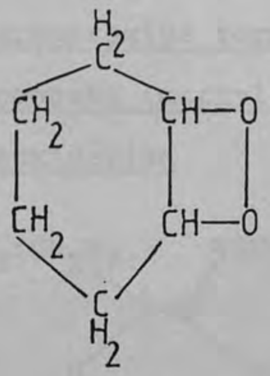
There are two undesirable properties which accompany the autoxidative drying of alkyd resin paints. These are the production of odourous volatile degradation products and the 'yellowing' of the films, particularly under the influence of heat, drying in the dark or the presence of foul atmospheres. These properties have led to the development of alternative types of drying systems. (This is discussed in section 1.10). The subject of this study has been concerned with investigations of these novel drying systems and with attempts to characterise the compounds which result in the yellowing of paint films.

1.3 Peroxide identification in autoxidation

The interaction of oxygen with organic compounds was first observed by Priestley, who showed that linseed oil removed the life giving element oxygen using rats and a bell jar. The term autoxidation was initially applied to slow oxidations which could be effected by free oxygen (e.g. air) at moderate temperatures. However, nowadays the term autoxidation is used to describe the reaction of a compound with molecular oxygen often at elevated temperatures; most autoxidations are conducted at temperatures between ambient and 200°C.[5]

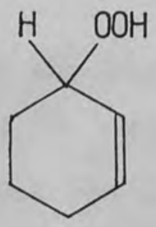
The formation of peroxides as products in autoxidation was first suggested almost simultaneously in 1897 by Bach[6] and by Engler and Wild.[7] Benzoyl hydroperoxide was identified in 1900 by Baeyer and Villiger.[8] Jorissen and Van der Beck[9] isolated this as the intermediate product in the autoxidation of benzaldehyde.

The autoxidation of simple unsaturated compounds, such as cyclohexene, was at first thought to consist of an initial attack on the double bonds of a particular system, thus giving peroxides which were cyclic in nature[10](I).



I

Later work showed that the products were non-cyclic α-methylenic hydroperoxides (II) and that the double bonds were still intact.[11,12,13]

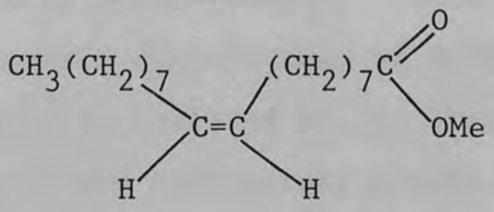


II

The isolation of hydroperoxides from autoxidation reactions has presented many problems. Early workers obtained hydroperoxides by distillation,[14] low temperature solvent crystallisation,[15] and adsorption chromatography.[14,16,17,18] These methods produced low yields of pure hydroperoxides probably owing to decomposition during the isolation processes. Purer hydroperoxides were obtained by either countercurrent solvent distribution,[19,20,21,22,23] or by fractionation of complexes with urea,[24] or by liquid partition chromatography.[25,26,2

Many hydroperoxides have now been isolated and identified from the autoxidation of olefins. Most of these have been described by Swern.[28]

1.4 Hydroperoxide formation in methyl cis-9-octadecenoate (methyl oleate) and mechanism of autoxidation



III

During the initial stages of the autoxidation of methyl cis-9-octadecenoate (III), early kinetic studies[29,30] estimated that hydroperoxides were formed in almost quantitative yields.

It was shown that the olefinic bond remained intact and no dimers were formed.[21] However, the olefinic bond was shown to isomerise from cis to trans, the more stable isomer.[19,31,32,33] The lower stability of the cis isomer led Swern et al[34] to propose that the cis form of the hydroperoxide would probably not be isolated during autoxidation. Positional isomerisation of the double bond was also observed from the original 9 position.[35]

Some confusion has occurred in the literature over the quantitative composition of the hydroperoxides obtained from methyl cis-9-octadecenoate (table 4).[36] This variation probably results from the long routes necessary for their characterisation and which result in low yields of the desired compounds.

Mercier[41] in her study of methyl oleate found that the resultant hydroperoxides separated into trans (85%) and cis (15%) fractions by $AgNO_3$-tlc, after solvent partition and purification. The presence of cis hydroperoxides contradicts Swern's earlier view, although the cis isomer is apparently less abundant. Work by Frankel et al[42] on the isomeric distribution of methyl oleate hydroperoxides showed that the isolated 8- and 11-hydroxy isomers, (after reduction of the hydroperoxy group), were slightly but consistently higher than the 9- and 10-hydroxy isomers.

Table 4

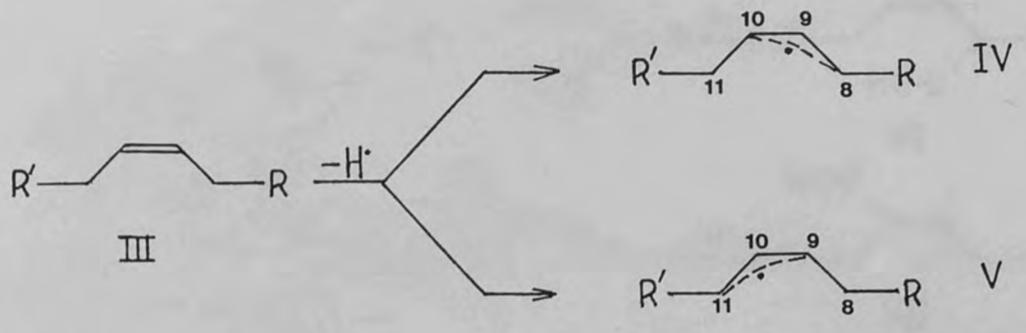
Analysis of the isomeric hydroperoxides of autoxidised methyl oleate

Autoxidation conditions	Basis of characterisation	Isomeric distribution	Reference
35°C-UV irradiation	Beckman rearrangement of oximes from keto derivatives	10-OH>11-OH>8-OH>9-OH	35
35°C	Infrared studies	9-OH=10-OH	36
Room temperature	Cleavage of acetyl derivatives	8-OH=9-OH=10-OH=11-OH	38
28°C	Cleavage of hydroxyl derivatives	9-OH=10-OH	39
Acidic MeOH	Cleavage of di Me acetal derivatives	8-OH>-11-OH>9-OH>10-OH	40
40-50°C	$AgNO_3$-TLC	8-OH=11-OH>9-OH=10-OH	41

This was the first study of its type which used authentic samples of 8-,9-,10- and 11-hydroxyoctadecanoates as references and a mass spectrometry-computer summation approach for quantitation. This study corrected an erroneous assumption made by Piretti[43,44,45] in a previous quantitative gc-ms analysis of purified oleate hydroperoxides.

At approximately the same time Garwood et al[46] analysed the stereochemistry of allylic hydroperoxides using ^{13}C n.m.r. The work of Frankel[42] and Garwood[46] has now been confirmed by Chan and Levett[47] using HPLC. The results of these studies showed that carbons 8,9,10 and 11 of methyl oleate are not equivalent in susceptibility to oxygen attack as was traditionally believed. More recently, Frankel et al[48] have developed methods, using ^{13}C n.m.r. and mass spectrometry, for the analysis of all eight cis and trans allylic 8-,9-,10- and 11-hydroperoxides formed on autoxidation of methyl oleate.

The classical mechanism for oleate autoxidation, which was first suggested by Farmer,[12] involves hydrogen abstraction at carbon 8 or carbon 11. The interactions between the unpaired electron on carbon 8 (or 11) and the π-electrons of the adjacent double bond[49] produce two allylic radicals (IV and V) with delocalised electrons distributed over three carbon atoms, scheme 1.4.1.



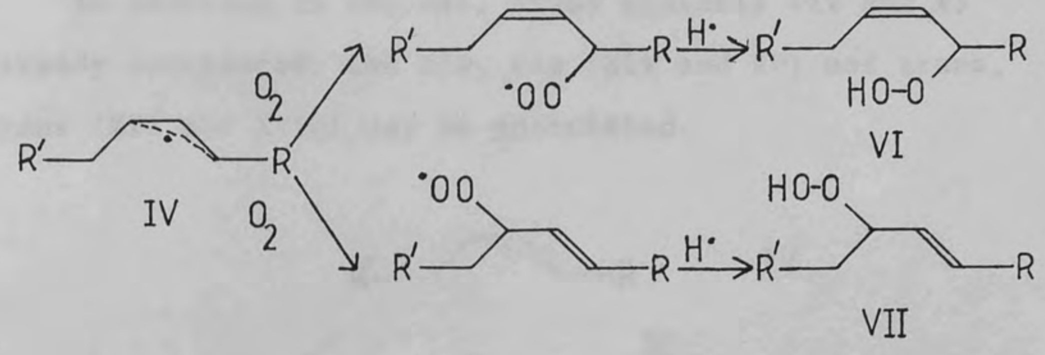
$R=(CH_2)_6COOCH_3$ $R'=(CH_2)_6CH_3$

Scheme 1.4.1.

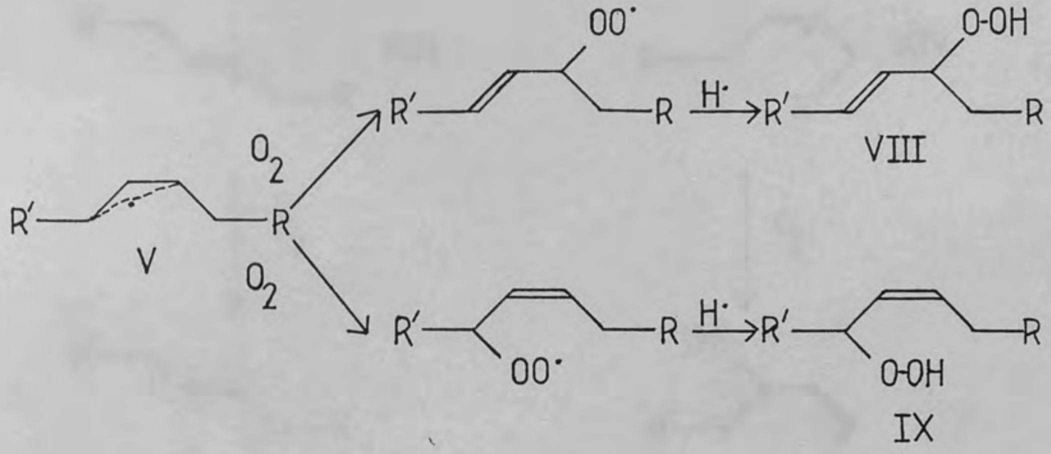
The allylic radical (IV) would be susceptible to oxygen attack at positions 8 and 10 (scheme 1.4.2) and the allylic radical (V) at positions 9 and 11 (scheme 1.4.3). This accounts for the formation of the following hydroperoxides.

Methyl 8-hydroperoxy-cis-9-octadecenoate	VI
Methyl 10-hydroperoxy-trans-8-octadecenoate	VII
Methyl 9-hydroperoxy-trans-10-octadecenoate	VIII
Methyl 11-hydroperoxy-cis-9-octadecenoate	IX

However, this classical mechanism does not account for the unequal proportions of both geometric and positional isomers, nor does it explain the following hydroperoxides, observed by Piretti,[43,44,45] Frankel,[42] Garwood[46] and Chan.[47]



Scheme 1.4.2.

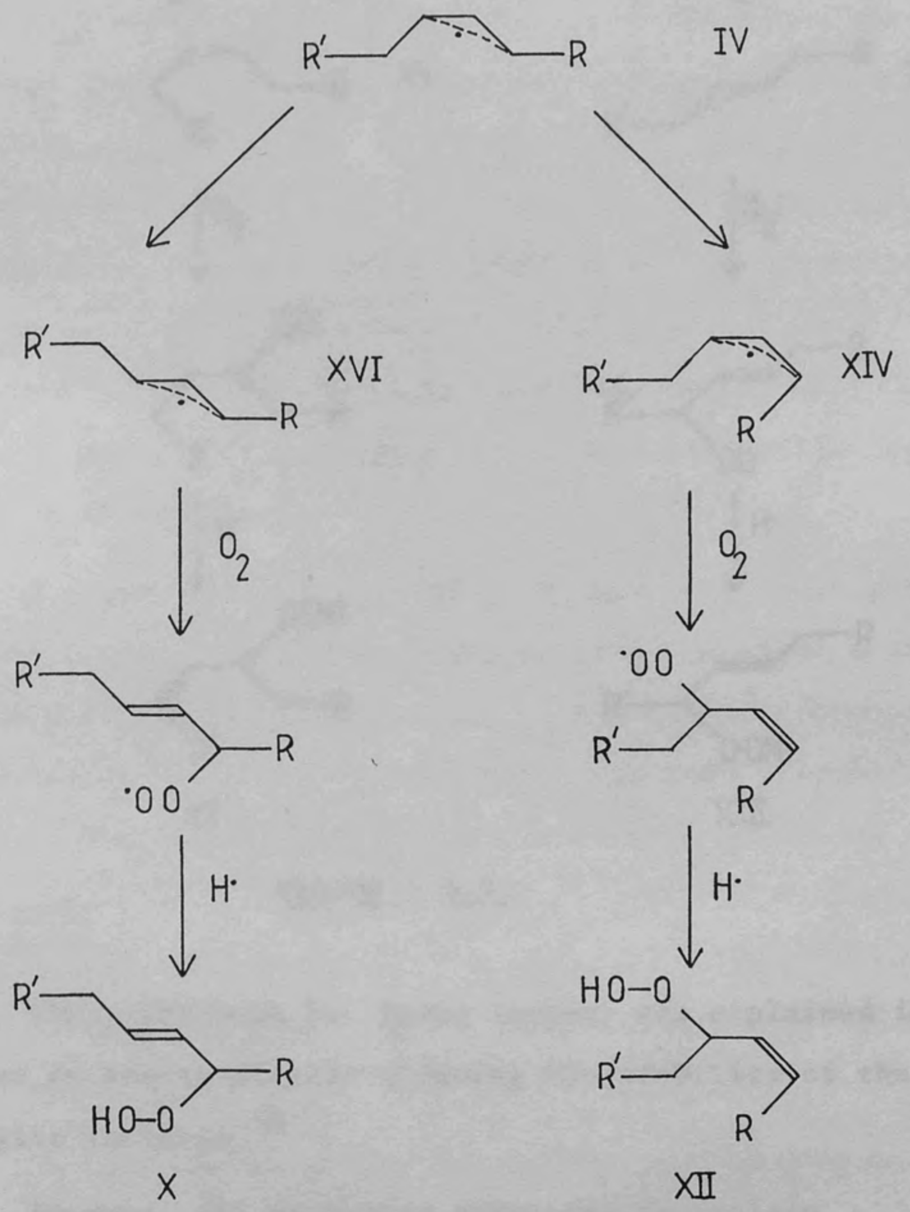


Scheme 1.4.3.

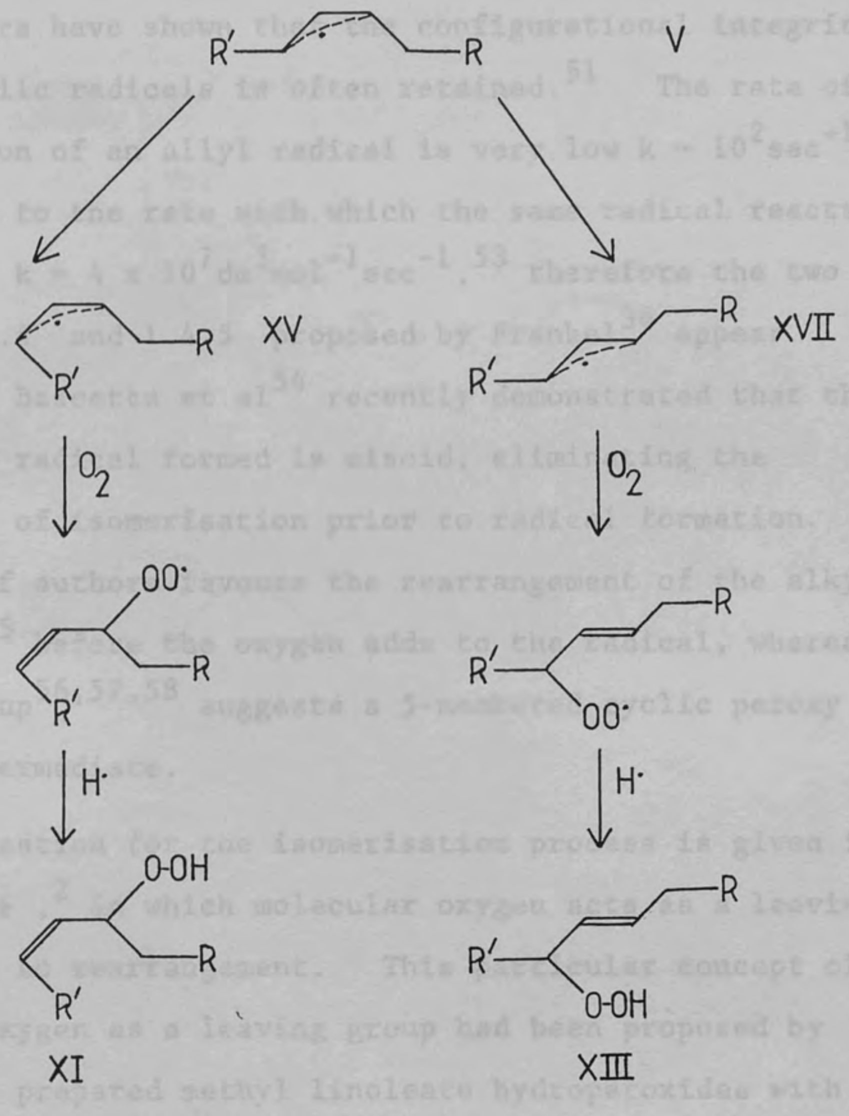
Methyl 8-hydroperoxy trans-9-octadecenoate	X
Methyl 9-hydroperoxy cis-10-octadecenoate	XI
Methyl 10-hydroperoxy cis-8-octadecenoate	XII
Methyl 11-hydroperoxy trans-9-octadecenoate	XIII

Frankel[36] proposed an alternative mechanism for the autoxidation of methyl oleate based on the configurational isomerisation of the allylic radicals, (see schemes 1.4.4 and 1.4.5).

In addition to the cis, trans radicals (IV and V) already considered, the cis, cis (XIV and XV) and trans, trans (XVI and XVII) may be postulated.



Scheme 1.4.4.



Scheme 1.4.5.

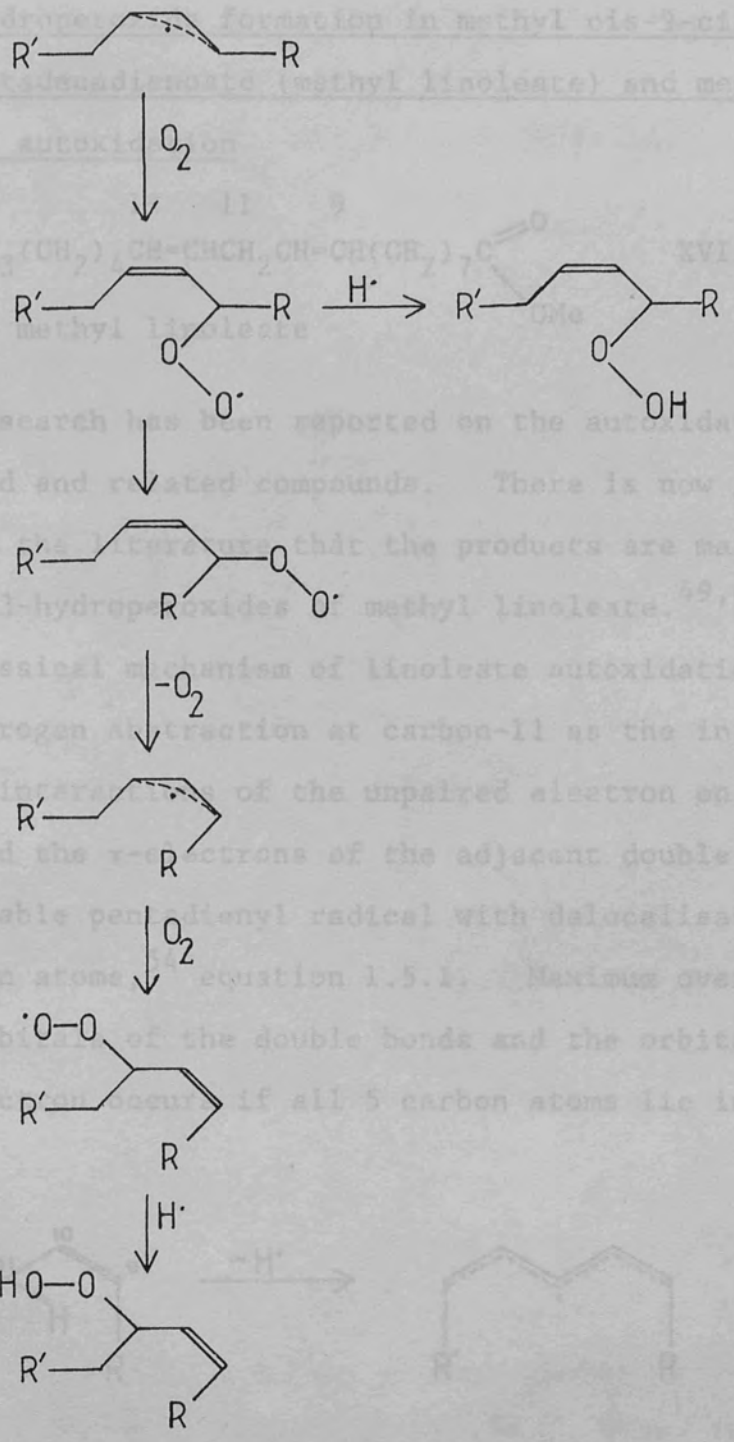
The preference for trans isomers was explained in terms of steric effects reducing the stability of the cis allylic radicals.[50]

However, the mechanism suggested to explain rearrangement of the hydroperoxide isomers is open to question as there are opposing views as to the type of radical (alkyl or peroxyl) which undergoes rearrangement.

Other workers have shown that the configurational integrity of the allylic radicals is often retained.[51] The rate of isomerisation of an allyl radical is very low $k = 10^2 \text{sec}^{-1}$ [52] in relation to the rate with which the same radical reacts with oxygen $k = 4 \times 10^7 \text{dm}^3\text{mol}^{-1}\text{sec}^{-1}$,[53] therefore the two schemes 1.4.4 and 1.4.5 proposed by Frankel[36] appear unlikely. Bascetta et al[54] recently demonstrated that the first alkyl radical formed is cisoid, eliminating the possibility of isomerisation prior to radical formation. One group of authors favours the rearrangement of the alkyl radical[37,55] before the oxygen adds to the radical, whereas another group[56,57,58] suggests a 5-membered cyclic peroxy radical intermediate.

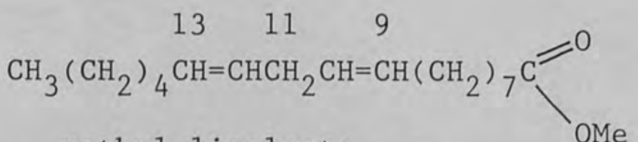
A suggestion for the isomerisation process is given in scheme 1.4.6 ,[2] in which molecular oxygen acts as a leaving group prior to rearrangement. This particular concept of molecular oxygen as a leaving group had been proposed by Chan,[59] who prepared methyl linoleate hydroperoxides with $^{18}O_2$ and allowed them to isomerise[60] under an atmosphere of $^{16}O_2$. The high amount of $^{18}O_2$ and lack of $^{18}O^{16}O$ found in the experimental atmosphere provided evidence for O_2 as a leaving group.

The mechanisms of lipid autoxidation, leading to the formation of primary oxidation products, i.e. mainly hydroperoxides, have been reviewed by Paquette et al[61] and also by Porter.[62]



Scheme 1.4.6.

1.5 Hydroperoxide formation in methyl cis-9-cis-12-octadecadienoate (methyl linoleate) and mechanism of autoxidation



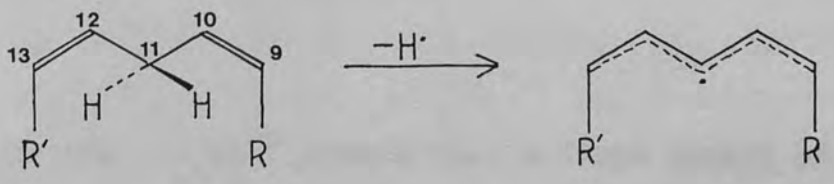
$$\overset{13}{C}H_3(CH_2)_4CH{=}CH\overset{11}{C}H_2CH{=}\overset{9}{C}H(CH_2)_7C(=O)OMe$$

XVIII

methyl linoleate

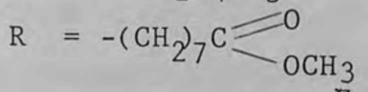
Much research has been reported on the autoxidation of linoleic acid and related compounds. There is now general agreement in the literature that the products are mainly the 9- and 13-hydroperoxides of methyl linoleate.[49,63-71]

The classical mechanism of linoleate autoxidation[49] involves hydrogen abstraction at carbon-11 as the initial step. The interactions of the unpaired electron on carbon-11 and the π-electrons of the adjacent double bonds produce a stable pentadienyl radical with delocalisation over 5 carbon atoms,[54] equation 1.5.1. Maximum overlap between π orbitals of the double bonds and the orbital of the unpaired electron occurs if all 5 carbon atoms lie in the same plane.



XVIII   XIX

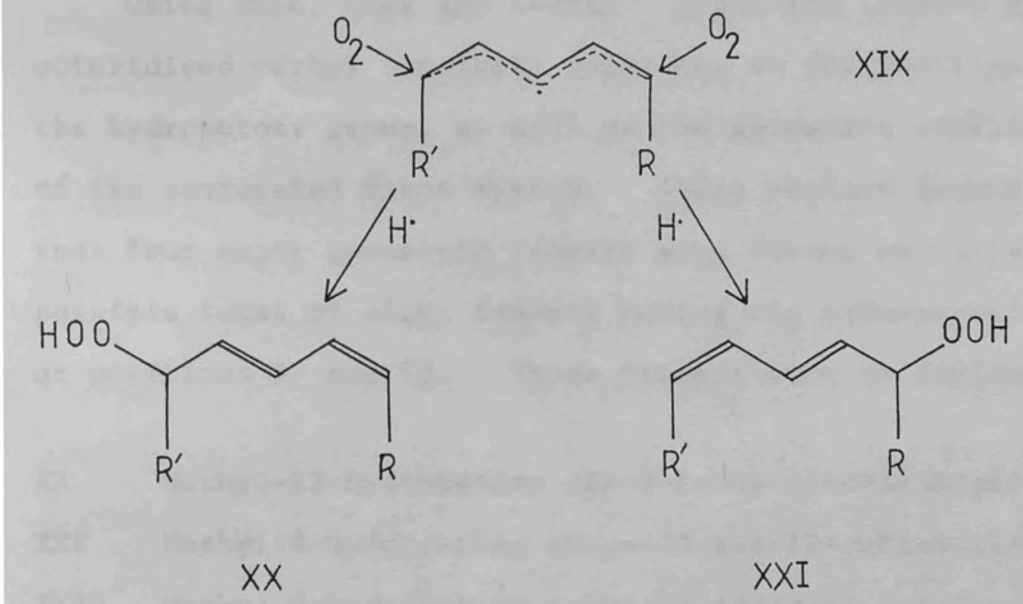
$R' = -(CH_2)_4CH_3$



$$R = -(CH_2)_7C(=O)OCH_3$$

Equation 1.5.1.

The terminal carbons of the pentadienyl radical, (XIX) are equivalent sites for oxygen attack such that equal amounts of 9- and 13-hydroperoxides are produced,[67] (scheme 1.5.2).



Scheme 1.5.2.

Frankel et al[72] showed that a large number of samples obtained at different peroxide values (93 to 3150) and autoxidation temperatures (40 - 80°C) all gave equal amounts of 9- and 13-hydroxy isomers. Early workers had reported conjugated diene hydroperoxide values ranging from

70 - 90%.[17,19,73] To explain these lower than expected values, it was suggested that unconjugated[17,73,74] and cis, cis conjugated diene hydroperoxides were formed.[75] These suggestions were discounted by Frankel[36] and also later by Chan and Levett,[64] who confirmed that the carefully purified hydroperoxides of linoleate are completely conjugated.

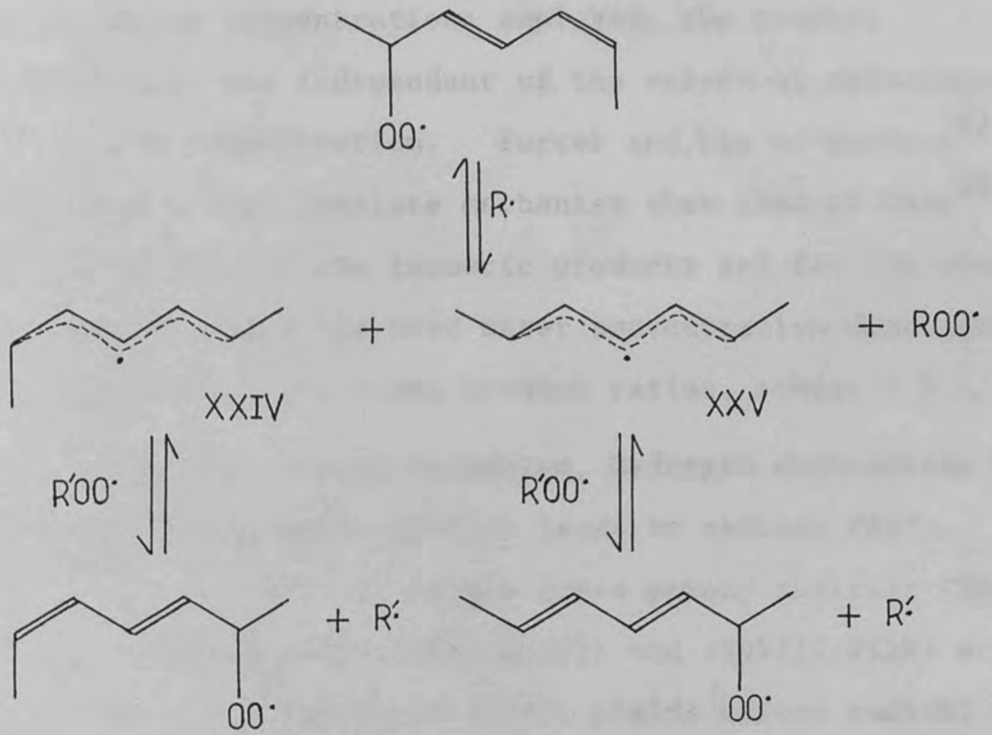
Using HPLC, Chan and Levett[66] separated isomers from autoxidised methyl linoleate according to the position of the hydroperoxy group, as well as the geometric configuration of the conjugated diene system. These workers demonstrated that four major geometric isomers were formed out of a possible total of eight isomers having the hydroperoxide group at positions 9- and 13. These isomers were as follows:-

XX	Methyl-13-hydroperoxy cis-9-trans-11-octadecadienoate
XXI	Methyl-9-hydroperoxy trans-10-cis-12-octadecadienoate
XXII	Methyl-9-hydroperoxy trans-10-trans-12-octadecadienoate
XXIII	Methyl-13-hydroperoxy trans-9-trans-11-octadecadienoate

The cis, cis isomers and the cis, trans isomers with the cis double bond adjacent to the hydroperoxide group were not formed to any appreciable extent. The possible route of isomerisation in affecting the distribution of product isomers has been the subject of many reports.

A variation in the proportion of cis,trans and trans, trans isomers with the temperature of autoxidation has been reported by several studies.[19,73,76] Chan et al[60] showed that it was possible to obtain an equilibrium mixture of all four isomeric linoleate hydroperoxides from each individual isomer (isolated in less than 73% purity) by heating at 40°C for 68 hours. Thus the rearrangement of linoleate hydroperoxides was non-stereoselective. The trans, trans isomers were also shown to undergo isomerisation, whereas previously only the isomerisation of cis, trans isomers was considered.[77] Observations of a decrease in reactivity towards rearrangement in polar solvents, the promotive effects of oxygen, metal ions and a free radical initiator, together with the inhibitory effect of BHT (butylated hydroxytoluene) led to the suggestion that the rearrangement involved a free radical chain reaction in which the C-O bond of the COO group is broken before its formation at the new location, (scheme 1.5.3).

Re-addition of oxygen at the opposite end of the radical forms the other isomer with either cis,trans or trans,trans configuration. In a study of thermal decomposition of individual linoleate hydroperoxides, Chan et al[78] reported similar volatile cleavage products from both the 9 and 13 isomers. This evidence was interpreted to indicate a degree of mobility of the peroxy group between carbons-9 and -13.

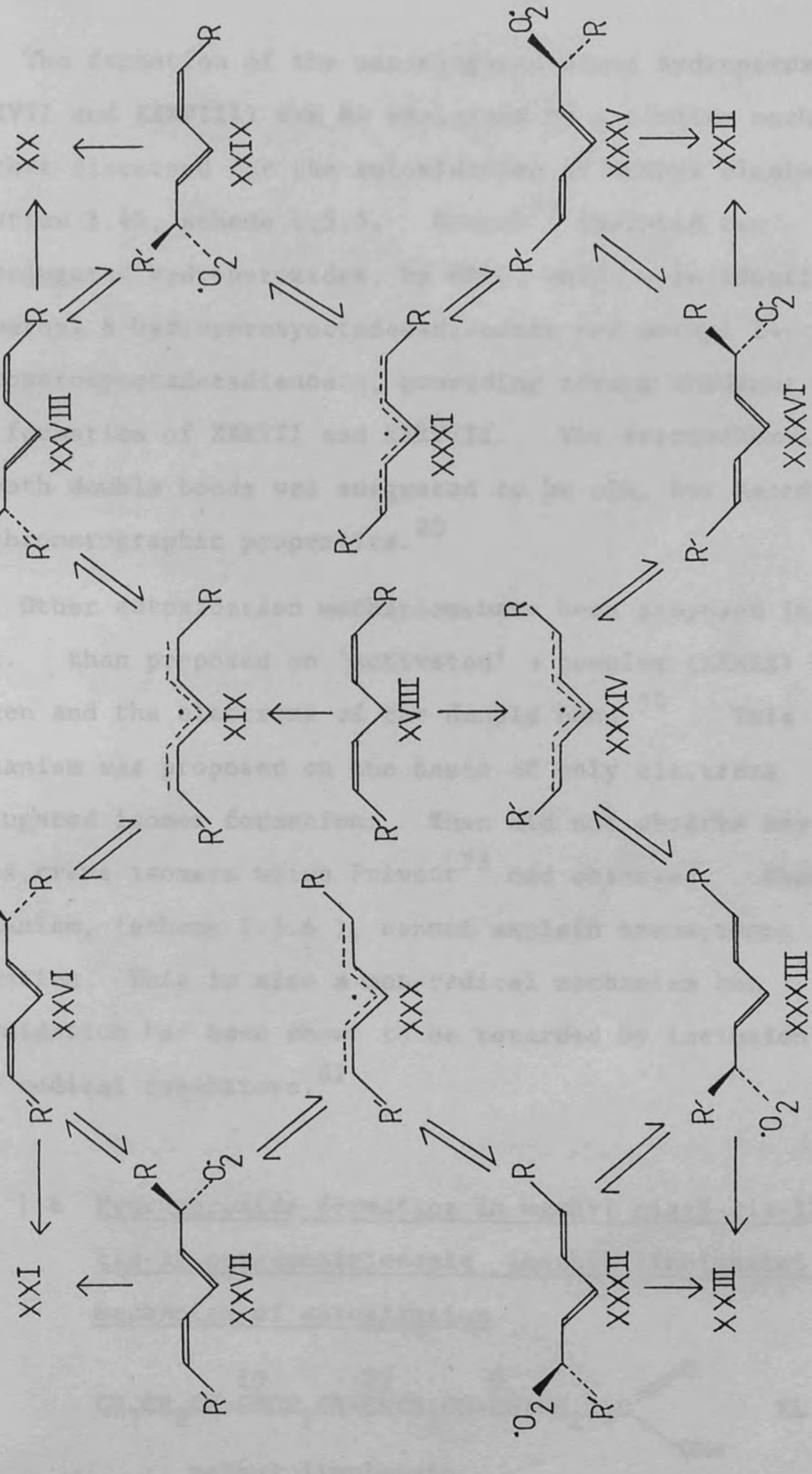


Scheme 1.5.3.

The formation of two conformations (XXIV and XXV) for the pentadienyl radical also provides a pathway for the isomerisation of linoleate hydroperoxides from cis,trans to the trans,trans that is observed at elevated temperatures and with high conversion.

Besides temperature, the concentration of fatty acid ester undergoing oxidation is also important in determining the distribution of product hydroperoxides. Porter et al[67] showed that by using shorter reaction times (2% total oxidation limit) and lower temperatures the isomerisation of the product hydroperoxides could be controlled. Under the autoxidation concentrations employed, the product distribution was independent of the extent of oxidation and the oxygen concentration. Porter and his co-workers[67,68,69] presented a more complete mechanism than that of Chan[60] which accounted for all the isomeric products and for the observed temperature and fatty acid ester concentration dependence of the trans,cis trans,trans product ratios, scheme 1.5.4.

According to this mechanism, hydrogen abstraction from that fatty acid ester (XVIII) leads to radical (XIX). Entrapment of (XIX) by oxygen gives peroxy radicals (XXVI - XXIX) of which pairs (XXVI/XXVII) and (XXVIII/XXIX) are conformers. Scission of (XXVI) yields carbon radical (XIX), while scission from (XXVII) gives the new carbon radical (XXX). Competing with the scission reactions of (XXVI/XXVII) is hydrogen abstraction leading to the 9-OOH, 10-trans, 12-cis product hydroperoxide. This crucial competition is what determines the trans,cis, trans,trans product ratio. This has been well demonstrated by correlating the ratio with the hydrogen atom donor capacity of the medium.[68,69] β-scission of peroxy radical (XXVI/XXVII) will lead to the trans, trans product, while hydrogen abstraction of (XXVI/XXVII) will give the trans,cis product. As in the case of oleic acid hydroperoxides, the specific details of this mechanism (alkyl vs peroxy radical rearrangement) are disputed by Frankel et al.[55]

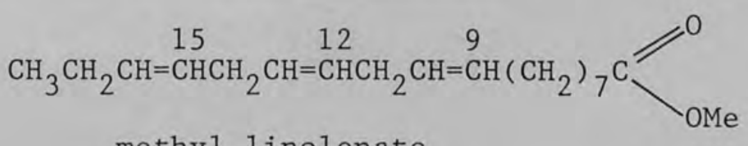

XXVIII
XXIX
XX
XXXI
XXXV
XXII
XXXVI
XIX
XVIII
XXXIV
XXVI
XXX
XXXIII
XXI
XXVII
XXXII
XXIII
R
R'
$\cdot O_2$
$O_2^{\cdot}$

Scheme 1.5.4.

The formation of the unconjugated diene hydroperoxides (XXXVII and XXXVIII) can be explained by a similar mechanism to that discussed for the autoxidation of methyl oleate (section 1.4), scheme 1.5.5. Grosch[79] isolated two unconjugated hydroperoxides, by HPLC, which were identified as methyl 8-hydroperoxyoctadecadienoate and methyl 14-hydroperoxyoctadecadienoate, providing strong evidence for the formation of XXXVII and XXXVIII. The stereochemsitry of both double bonds was suggested to be cis, but based only on chromatographic properties.[80]

Other autoxidation mechanismshave been proposed in the past. Khan proposed an 'activated' π complex (XXXIX) between oxygen and the electrons of the double bond.[50] This mechanism was proposed on the basis of only cis,trans conjugated isomer formation. Khan did not observe any trans,trans isomers which Privett[73] had observed. Khan's mechanism, (scheme 1.5.6), cannot explain trans,trans isomer formation. This is also a non-radical mechanism but autoxidation has been shown to be retarded by inclusion of free radical inhibitors.[81]

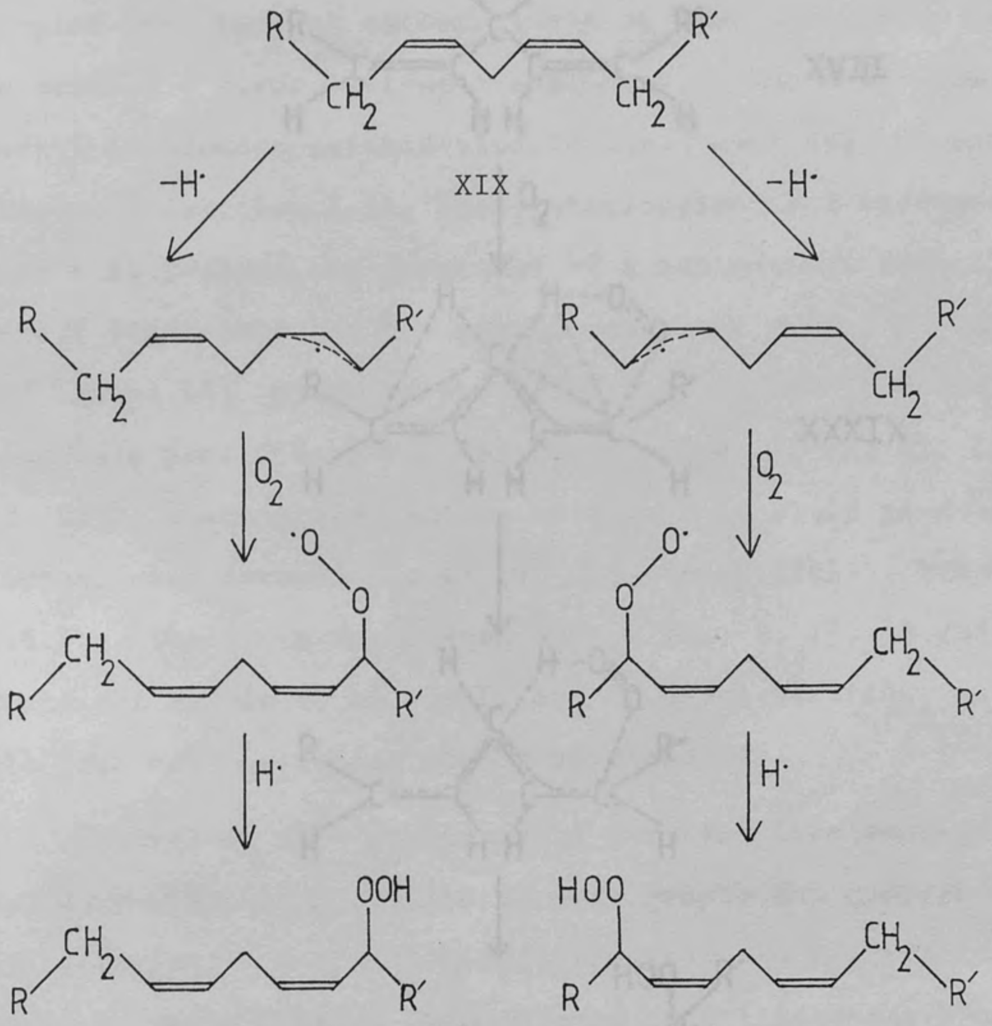
1.6 Hydroperoxide formation in methyl cis-9-cis-12-cis-15-octadecatrienoate (methyl linolenate) and mechanism of autoxidation



$$\mathrm{CH_3CH_2\overset{15}{C}H{=}CHCH_2\overset{12}{C}H{=}CHCH_2\overset{9}{C}H{=}CH(CH_2)_7C({=}O)OMe}$$

XL

methyl linolenate



XIX

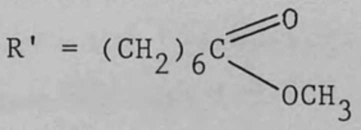
XXXVII

methyl 8-hydroperoxy-9-12-octadecadienoate

$R = (CH_2)_3CH_3$

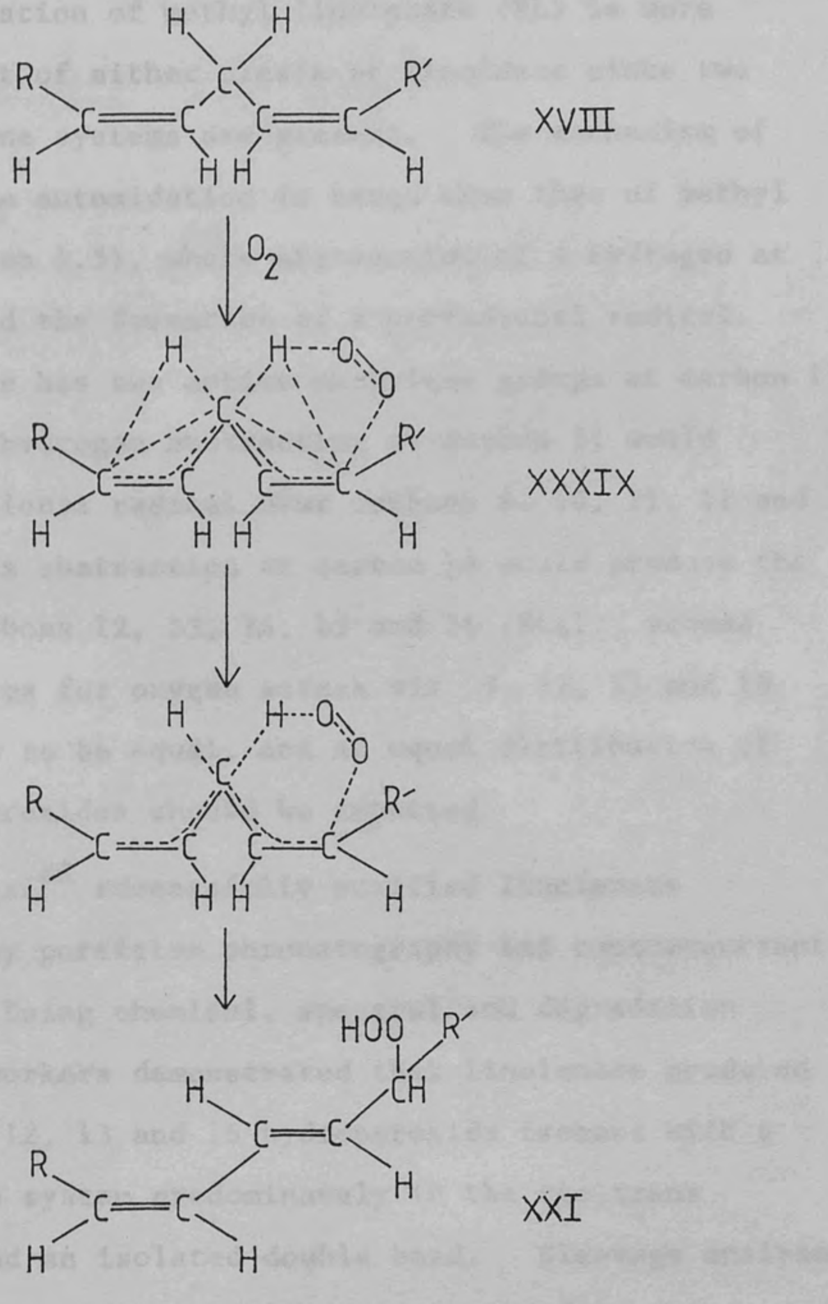
XXXVIII

methyl 14-hydroperoxy-9-12-octadecadienoate



$R' = (CH_2)_6C(=O)OCH_3$

Scheme 1.5.5.

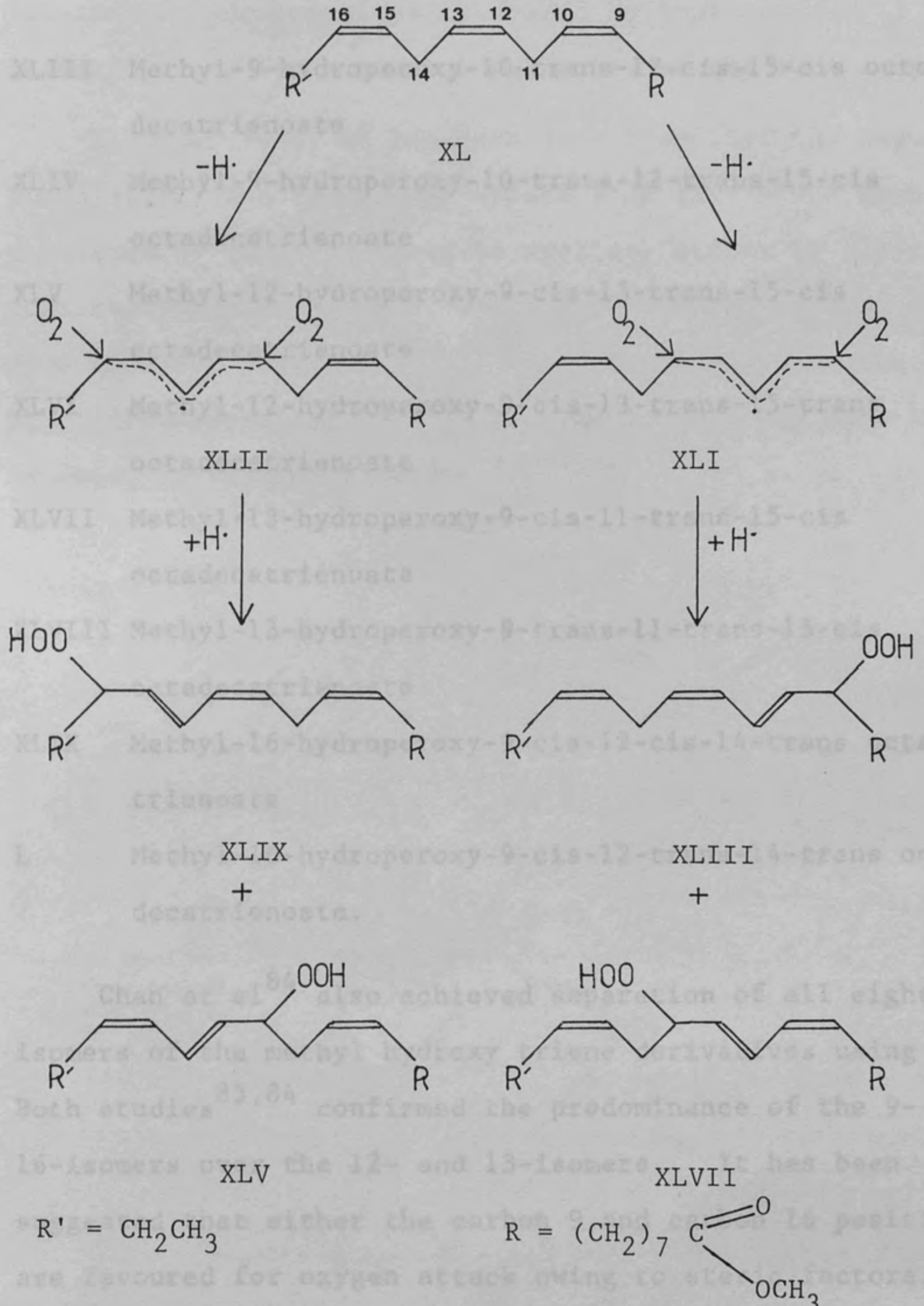


Scheme 1.5.6.

The autoxidation of methyl linolenate (XL) is more complex than that of either oleate or linoleate since two separate 1,4 diene systems are present. The mechanism of methyl linolenate autoxidation is based upon that of methyl linoleate (section 1.5), where abstraction of a hydrogen at carbon 11 yielded the formation of a pentadienyl radical. Methyl linolenate has two active methylene groups at carbon 11 and carbon 14; hydrogen abstraction at carbon 11 would produce a pentadienyl radical over carbons 9, 10, 11, 12 and 13 (XLI), whereas abstraction at carbon 14 would produce the radical over carbons 12, 13, 14, 15 and 16 (XLII), scheme 1.6.1. The sites for oxygen attack viz. 9, 12, 13 and 16 would all appear to be equal, and an equal distribution of all four hydroperoxides should be expected.

Frankel et al[82] successfully purified linolenate hydroperoxides by partition chromatography and countercurrent distribution. Using chemical, spectral and degradation studies, these workers demonstrated that linolenate produced a mixture of 9, 12, 13 and 16 hydroperoxide isomers with a conjugated diene system predominately in the cis,trans configuration and an isolated double bond. Cleavage analyses showed that the 9- and 16-hydroperoxides were formed in significantly higher proportion (35 and 48% respectively) than the 12- and 13-hydroperoxides (11 and 10%).

These results were confirmed by GC-MS[83] and HPLC[84] analyses. All eight geometric cis,trans and trans,trans conjugated diene isomers of the allylic hydroxy compounds


16
15
13
12
10
9
14
11
R'
R
XL
-H·
-H·
O2
O2
O2
O2
XLII
XLI
+H·
+H·
HOO
OOH
XLIX
+
XLIII
+
OOH
HOO
XLV
XLVII
R' = CH2CH3
R = (CH2)7 C=O OCH3

Scheme 1.6.1.

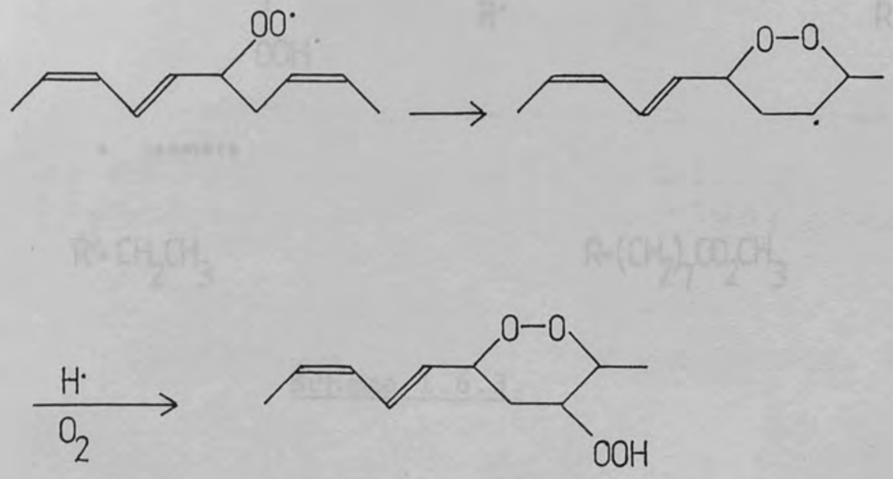
were separated and identified by glc as their TMS derivatives. The formation of the following hydroperoxides was indicated:-

XLIII	Methyl-9-hydroperoxy-10-trans-12-cis-15-cis octadecatrienoate
XLIV	Methyl-9-hydroperoxy-10-trans-12-trans-15-cis octadecatrienoate
XLV	Methyl-12-hydroperoxy-9-cis-13-trans-15-cis octadecatrienoate
XLVI	Methyl-12-hydroperoxy-9-cis-13-trans-15-trans octadecatrienoate
XLVII	Methyl-13-hydroperoxy-9-cis-11-trans-15-cis octadecatrienoate
XLVIII	Methyl-13-hydroperoxy-9-trans-11-trans-15-cis octadecatrienoate
XLIX	Methyl-16-hydroperoxy-9-cis-12-cis-14-trans octadecatrienoate
L	Methyl-16-hydroperoxy-9-cis-12-trans-14-trans octadecatrienoate.

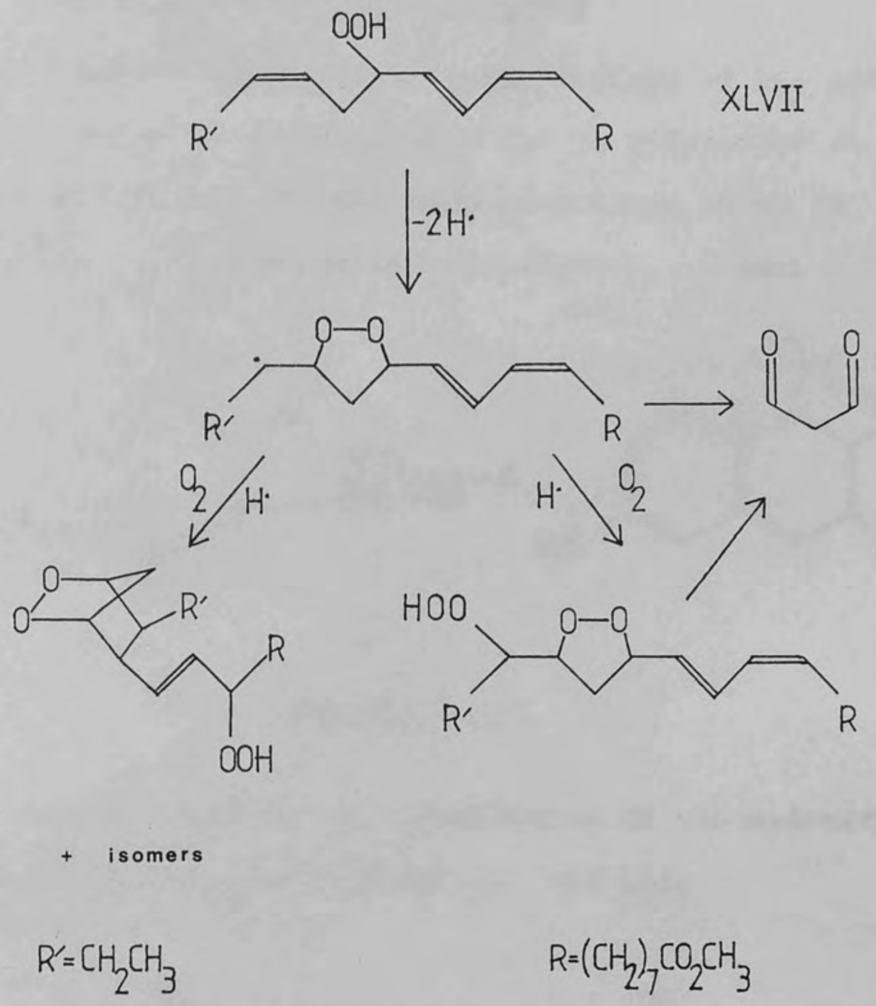
Chan et al[84] also achieved separation of all eight isomers of the methyl hydroxy triene derivatives using HPLC. Both studies[83,84] confirmed the predominance of the 9- and 16-isomers over the 12- and 13-isomers. It has been suggested that either the carbon 9 and carbon 16 positions are favoured for oxygen attack owing to steric factors, or else that the 12- and 13-isomers decompose more readily.[82]

However, Chan compared the decomposition of 9- and 13-linolenate hydroperoxides (prepared by lipoxygenase oxidation) and found them to decompose at the same rate.[84]

Alternatively, it has been suggested that the reduced yield of 12- and 13-hydroperoxides from linolenate might be explained by their tendency to cyclise, either to six-membered peroxides[85] (scheme 1.6.2) or more probably to five-membered peroxides,[83,86] or to prostaglandin-like bicycloendoperoxides[87,88,89] (scheme 1.6.3) and also their tendency to form diperoxides.[90,91,92]



Scheme 1.6.2.



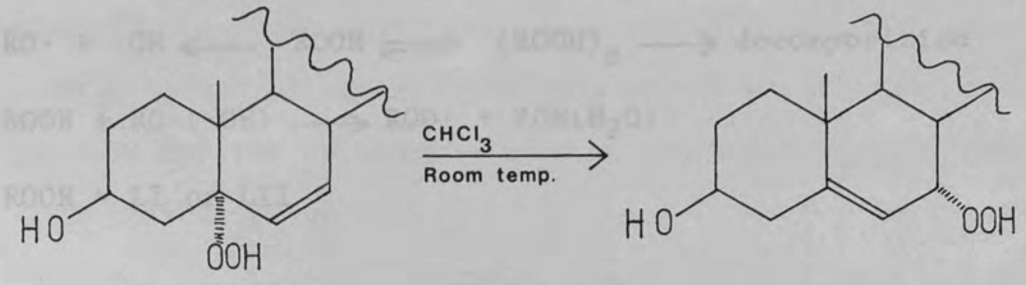
Scheme 1.6.3.

Recent work by Neff et al[86] has shown evidence for the 1,3-cyclisation scheme for the production of 5-membered cyclic peroxides.

The mechanisms suggested for the formation of these hydroperoxides from the autoxidation of methyl linolenate are similar to those proposed for linoleic acid, i.e. alkyl radical rearrangement[55] or reversible oxygen addition.[69]

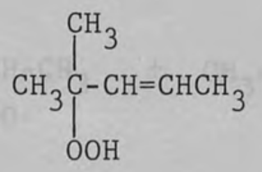
1.7 Isomerisation of hydroperoxides

Schenck[56] observed the isomerisation of the allylic hydroperoxide of cholesterol; the 5α hydroperoxide on standing in $CHCl_3$ at room temperature was shown to rearrange to 7α-hydroperoxy cholesterol, (scheme 1.7.1).

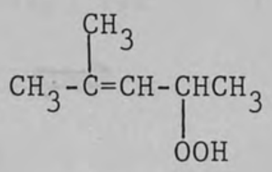


Scheme 1.7.1.

Brill[57] studied the autoxidation of trans-4-methyl-2-pentene and isolated peroxides LI and LII.


$CH_3C(CH_3)(OOH)-CH=CHCH_3$

LI


$CH_3-C(CH_3)=CH-CH(OOH)CH_3$

LII

trans-2-methyl-3-pentenyl-2 hydroperoxide	4-methyl-3-pentenyl-2-hydroperoxide

He demonstrated that either pure LI or LII isomerised to an equilibrium mixture containing approximately equal quantities of each hydroperoxide either in dilute solutions of hexane, carbon tetrachloride or trans-4-methyl-2-pentene at 40°C. The rate of isomerisation of LI or LII depends inversely on the total hydroperoxide concentration and the following mechanism was proposed, scheme 1.7.2.

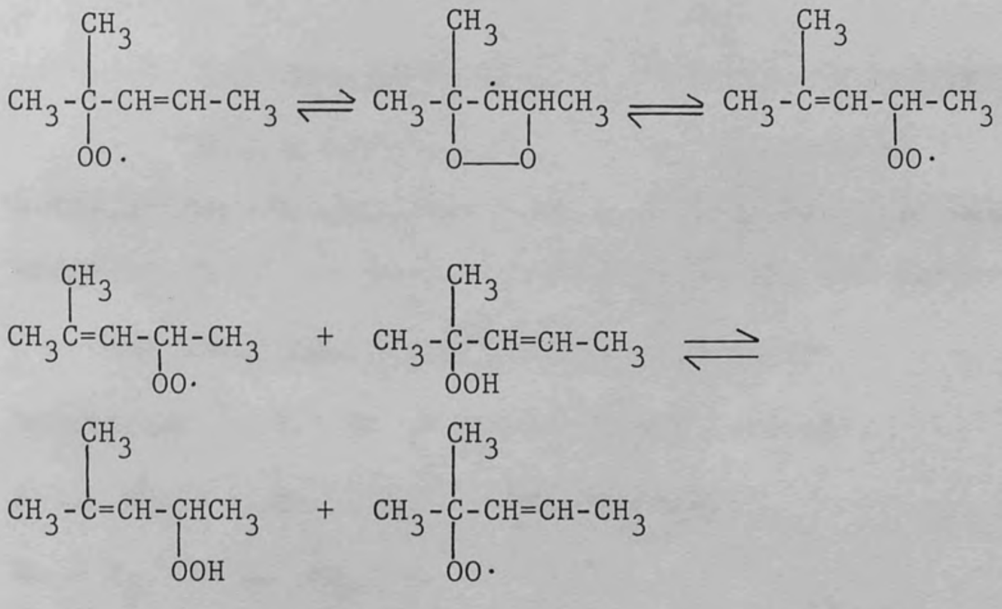
Initiation

$$RO\cdot + \cdot OH \longleftarrow ROOH \rightleftharpoons (ROOH)_n \longrightarrow \text{decomposition}$$

$$ROOH + RO\cdot(\cdot OH) \longrightarrow ROO\cdot + ROH(H_2O)$$

ROOH = LI or LII

Propagation



Scheme 1.7.2.

Chan[93] reported the first observations of hydroperoxide isomerisation process in methyl linoleate when hydroperoxides, which were predominantly 13 or 9, were stored in hexane. Interconversion of the positional isomers was observed by gc-ms of the corresponding hydroxystearates and of cis-trans isomerisation by infrared spectroscopy. Chan[60] also studied the interconversion process of individual isomers into products using HPLC and proposed[59] a mechanism to account for the interconversion in terms of oxygen behaving as a leaving group.

The concept of molecular oxygen as a leaving group has been discussed in section 1.4.

1.8 Peroxide decomposition and polymeric products

Having outlined the primary products of autoxidation of unsaturated fatty acid esters, the reactions which continue the autoxidation process are now discussed.

The basic equations[28] are as follows:-

Initiation $\longrightarrow$ 2X· (where X· is any radical) (1)

$X\cdot (\text{or } XO_2\cdot) + RH \longrightarrow R\cdot + XH\ (\text{or } XO_2H)$ (2)

$R\cdot + O_2 \longrightarrow RO_2\cdot$ (3)

$RO_2\cdot + RH \xrightarrow{kp} RO_2H + R\cdot$ (4)

$2RO_2\cdot \xrightarrow{k_t} RO_2R$ (or alcohol and carbonyl compounds) $+ O_2$ (5)

The rate equation for hydroperoxide formation and for oxygen consumption (if its reformation by reaction (5) is neglected) is:-

$$\frac{-\delta[O_2]}{\delta t} = \frac{\delta[RO_2H]}{\delta t} = \left(\frac{K_i}{k_t}\right)^{\frac{1}{2}} k_p \ [RH]$$

where K_i, the rate of initiation, takes in account reactions (1) and (2). Experiments show that the relative ease of autoxidation of RH roughly parallels the ease of breaking C-H bond[94] and for hydrocarbons this increases in the series n-alkanes<branched alkanes<aryl alkanes≅alkenes<alkynes.[95,96] Thus, both resonance and inductive effects on the stability of the resulting radical are important but the subsequent reaction of the alkyl radical with oxygen in reaction (3) is usually never rate limiting.[94]

Alternative termination reactions to (5) may also occur[94]:

$2R\cdot \longrightarrow R - R$ (6)

$ROO\cdot + R\cdot \longrightarrow ROOR$ (7)

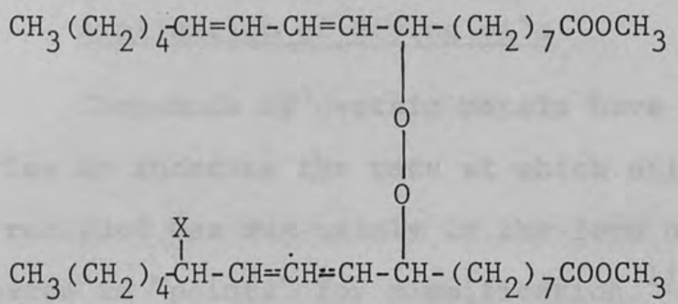
and it is by means of these termination reactions that the paint industry makes use of oxidative drying.

Oils containing unsaturated fatty acids, on drying, can absorb up to 12% of their mass in oxygen. In non-conjugated oils, oxygen uptake leads to formation of hydroperoxides and their decomposition accompanies cross-linking reactions.[1] By comparison with a film of linseed oil (non-conjugated) which requires 120 hrs to dry at 25°C in the presence of O_2, tung oil (conjugated) requires only 48 - 72 hours. The polymeric compounds which have been reported in the autoxidation of methyl linolenate[21] appear to be polyperoxides.[97-103]

O'Neill[104] has shown that when methyl oleate was heated with methyl oleate hydroperoxides, mainly oxygen bonded products were obtained. Other workers have reported that below 100°C the polymer linkages are mainly through oxygen,[105] i.e. -C-O-C- or -C-O-O-C- linkages.

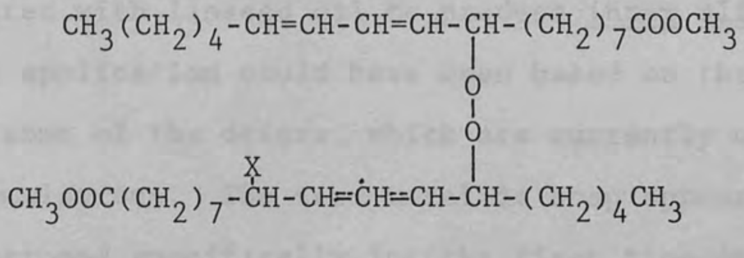
Chang and Kummerow[106,107] have isolated dimer and trimer fractions by solvent extraction of ethyl linoleate, which had been autoxidised by bubbling with dry air at 30°C for 350 hours. The analytical results obtained, on characterisation of the more polar polymer fractions, indicated that the oxidative polymers of ethyl linoleate were linked through carbon to oxygen bonds, rather than carbon to carbon bonds.

Miyashita[108] studied the formation of dimers in the autoxidation of methyl linoleate at 30°C for 192 hours. The oxidised ester, separated from the unreacted material by gel chromatography, was separated by HPLC into three fractions. One was assigned as methyl linoleate hydroperoxides and the others as dimers that were capable of being cleaved by reduction with sodium borohydride and therefore contain the -C-O-O-C- linkage. Further work[109] resolved by HPLC, one of the dimer fractions into four major components having mean molecular masses of between 643 - 655 amu. These components could contain two molecules of methyl linoleate together with three or four molecules of oxygen. Their reduction with stannous chloride, silylation and gc-ms gave three components:- the TMS derivatives of methyl-9 and/or 13-hydroxy octadecadienoate and methyl-9-, 13-dihydroxy octadecenoate. The following structures were proposed (LIII-LVI):



$$\begin{array}{l} \mathrm{CH_3(CH_2)_4\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH(O\text{-}O\text{-})\text{-}(CH_2)_7COOCH_3} \\ \mathrm{CH_3(CH_2)_4\text{-}CH(X)\text{-}CH\text{-}CH{=}\dot{C}H{=}CH\text{-}CH(\text{-}O\text{-}O)\text{-}(CH_2)_7COOCH_3} \end{array}$$

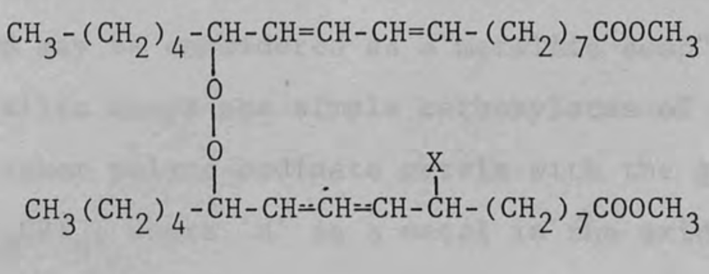
LIII



$$\begin{array}{l} \mathrm{CH_3(CH_2)_4\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH(O\text{-}O\text{-})\text{-}(CH_2)_7COOCH_3} \\ \mathrm{CH_3OOC(CH_2)_7\text{-}CH(X)\text{-}CH\text{-}CH{=}\dot{C}H{=}CH\text{-}CH(\text{-}O\text{-}O)\text{-}(CH_2)_4CH_3} \end{array}$$

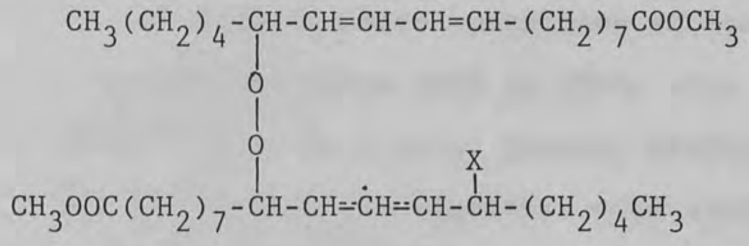
LIV

(X = OH or OOH)



$$\begin{array}{l} \mathrm{CH_3\text{-}(CH_2)_4\text{-}CH(O\text{-}O\text{-})\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_7COOCH_3} \\ \mathrm{CH_3(CH_2)_4\text{-}CH(\text{-}O\text{-}O)\text{-}CH{=}\dot{C}H{=}CH\text{-}CH(X)\text{-}(CH_2)_7COOCH_3} \end{array}$$

LV



$$\begin{array}{l} CH_3(CH_2)_4\text{-}CH\text{-}CH{=}CH\text{-}CH{=}CH\text{-}(CH_2)_7COOCH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad O \\ \qquad\qquad\quad | \\ \qquad\qquad\quad O \qquad\qquad\qquad X \\ \qquad\qquad\quad | \qquad\qquad\qquad\;\; | \\ CH_3OOC(CH_2)_7\text{-}CH\text{-}CH{=}\dot{C}H{=}CH\text{-}CH\text{-}(CH_2)_4CH_3 \end{array}$$

LVI

More recent studies by Miyashita et al[110,111,112] have confirmed this earlier work on the peroxy linkages in methyl linoleate dimers.

Two reviews on the drying oil occurrence are worth noting here.[113,114]

1.9 Redox promoters of autoxidation - Industrial application of drying oils

Compounds of certain metals have been known for centuries to increase the rate at which oils dry. Their first recorded use was mainly in the form of lead linoleates in "paints" for mummification.[115] It is suggested that litharge or some other oxide of lead was heated with linseed oil to produce inter alia lead linoleate. Its application could have been based on the same principle as some of the driers, which are currently used in varnish formulations. The term metallic soap appears to have been mentioned specifically for the first time in 1758 when Macquer stated that "combination of fat oil and calx of lead may be considered as a metallic soap". Thus, metallic soaps are simple carboxylates of alkaline earths or other polyco-ordinate metals with the general formula $M(O_2CR)_n$, where 'M' is a metal in the oxidation state 'n' and 'R' is an organic chain containing at least 6-7 carbon atoms. During the years 1835 to 1850, zinc oxide replaced white lead as a paint pigment thereby introducing the problem of drying the vegetable oils used as paint vehicles. However, with the synthesis of many metal soaps near the turn of the century, the basic needs of the paint industries could be satisfied.[116,117]

The materials normally classified as 'metallic driers' or promoters can be classified into two types. The first group, which includes such metals as cobalt, manganese, calcium, zirconium and iron, are known as 'primary' or surface driers. Certain useful criteria are that these active metals readily exist in two different oxidation states, the higher oxidation state being less stable. The lower oxidation state can be oxidised to the higher oxidation state by hydroperoxides, formed during the oxidation of the drying oils.[118] The second group are known as 'secondary' or through driers and include metals such as zinc and lead. These assist the drying of the lower layers of paint film and are essential as the 'surface driers' used alone produce 'shrivelled' films. The promoters typically used in modern paints are cobalt(II) bis-(2-ethyl hexanoate) and lead(II) bis-(2-ethyl hexanoate). However, due to environmental pressure, this lead compound is being replaced with zirconium(II) bis-(2-ethyl hexanoate). The eight carbon alkyl component of the carboxylate provides solubility for the promoter in the non-polar alkyd resin. These promotors are used at concentrations of 0.04% and 1.5% respectively (described as percentages of the mass of metal present relative to the mass of the drying oil present). In the presence of these promot-rs linseed oil will dry in 2 hours[1] (compared with 120 hours unpromoted), such a rate of drying is acceptable for a decorative gloss paint.

The study of hydroperoxides in the presence of metal ions really began when Fenton[119] described the reaction of hydrogen peroxide in the presence of Fe^{2+} ions. It was Haber and Weiss[120] who proposed the free radical process shown in equation 1.9.1.

$$H_2O_2 + Fe^{2+} \longrightarrow HO\cdot + OH^- + Fe^{3+}$$

Equation 1.9.1.

Many organic peroxides, such as alkyl, cycloalkyl and arylalkyl hydroperoxides are susceptible to metal ion decomposition. As with Fenton's reagent, the analogous reaction with these compounds appears to be the generation of alkoxy radicals, equation 1.9.2.

$$ROOH + M^{n+} \longrightarrow RO\cdot + OH^- + M^{(n+1)+}$$

Equation 1.9.2.

The decomposition of hydroperoxides by even millimolar amounts of transition metal ions, such as Co^{2+}, Mn^{2+} and Fe^{2+} is rapid even at room temperature.[121,122,123] In the absence of a reactive substrate, the reactions given in equation 1.9.3 thus provide a catalytic cycle.

$$RO_2H + M^{n+} \longrightarrow RO\cdot + M^{(n+1)^+} + OH^-$$
$$RO_2H + M^{(n+1)^+} \longrightarrow RO_2\cdot + M^{n+} + H^+$$

Equation 1.9.3.

Hiatt[123] studied the catalytic decomposition of t-butyl hydroperoxide using Co^{2+} (10 mM) which, at 25°C, gave t-butyl alcohol (~87%), t-butyl peroxide (~12%) and propanone (~0.5%). If the metal ions are present in larger quantities the alkoxy radical, (RO·), produced is converted to alkoxide and thence to the alcohol, as follows in equation 1.9.4.[124]

$$\begin{tikzcd}
RO\cdot + M^{n+} \arrow[r] & RO^- \arrow[d, "H^+"] + M^{(n+1)^+} \\
 & ROH
\end{tikzcd}$$

Equation 1.9.4.

The peroxy radicals, (ROO·), undergo a similar reduction,[125,126] equation 1.9.5.

$$RO_2\cdot + Mn^{2+} \longrightarrow RO_2^- + Mn^{3+}$$

Equation 1.9.5.

These ion-formation reactions constitute a termination route for the free radical processes discussed in section 1.8. This may provide an explanation as to why low concentrations of metal ions give optimum rates for catalysing autoxidations.[127,128] However, it has been reported that the drying time of an alkyd resin increases when the concentration of metal ion is increased.[128]

The choice of gegen ion as well as metal ion can effect the reactions given in equations 1.9.3 and 1.9.4 , e.g. cobalt(II) ethylenediaminetetraacetate complex ion is not oxidised by hydroperoxides,[129] although simple cobaltic carboxylates are reduced very rapidly.[123,130] Most Fe(II) salts do not reduce hydroperoxides readily, although iron(II) phthalocyanine complex does.[123]

The autoxidation of methyl linoleate and methyl linolenate in the presence of cobalt(II) and cobalt(III) cyclohexane carboxylate (naphthenate) in n-heptane was published by Hendricks.[131] This system was chosen as a model system for the drying of a paint film. He proposed a sequence of reactions to explain the autoxidation of the methyl ester; this reaction scheme has been simplified and is shown in scheme 1.9.6.

The cobalt(II) and cobalt(III) have two functions:

1. The cobalt(II) and cobalt(III) catalyse the uptake of oxygen, leading to the formation of peroxides and hydroperoxides, (mechanism uncertain).

2. These peroxides and hydroperoxides (ROOH) decompose generating free radicals, promoted by the cobalt(II) and cobalt(III) compounds, e.g.

$$Co^{II} + ROOH \longrightarrow \begin{cases} Co^{III} + RO\cdot + {}^{-}OH \\ Co^{III} + RO^{-} + {}^{\cdot}OH \end{cases}$$

$$Co^{III} + ROOH \longrightarrow Co^{II} + ROO\cdot + H^{+}$$

$$Co^{III} + {}^{-}OH \longrightarrow Co^{II} + {}^{\cdot}OH$$

$$Co^{III} + RO^{-} \longrightarrow Co^{II} + RO\cdot$$

$$2ROOH \xrightarrow{[Co^{II/III}]} RO\cdot + ROO\cdot + H_2O$$

Co^{II} oxidation

$$2Co^{II} + ROOH \xrightarrow{2H^{+}} 2Co^{III} + ROH + H_2O$$

(ROOH represents hydroperoxides of methyl linoleate or methyl linolenate).

Scheme 1.9.6.

Metal ions in their higher oxidation state may genrate free radicals directly from an organic substrate, both in polar and non-polar solvents, by a one electron transfer reaction,[132] as shown in equation 1.9.7.

$$RH + M^{(n+1)^{+}} \longrightarrow R\cdot + H^{+} + M^{n+}$$

Equation 1.9.7.

However, this type of initiation is masked by the reaction of accumulated hydroperoxides with the metal ion. Bawn,[133,134] however, showed that cobalt(III) acetate catalysed autoxidation of benzaldehyde in acetic acid proceeded by equation 1.9.7. Further evidence that this route is important in metal catalysed autoxidations was reported by Heiba,[135] who studied the cobalt acetate catalysed oxidation of alkyl aromatic hydrocarbons in acetic acid in the absence of oxygen. ESR studies by Dessau[136] has also added support for one electron transfer reactions occurring in this type of autoxidation.

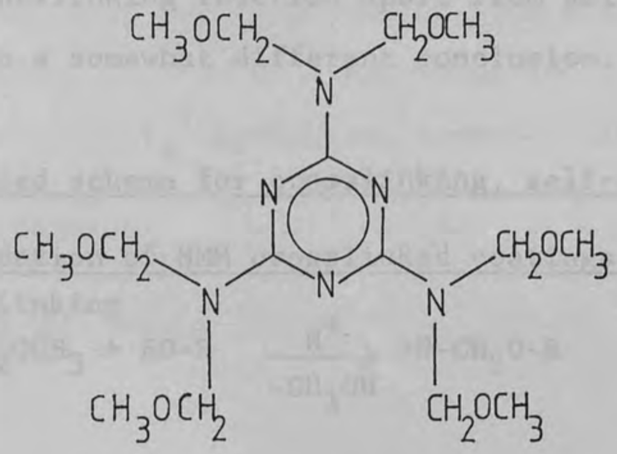
1.10 Novel drying systems

The coatings industry has needed to reformulate its products over recent years because of two main reasons,[137] viz. (i) reduced energy requirements and (ii) tighter anti-pollution regulations.

As a result of these two requirements, research in the paint industry has led to two emerging technologies, (a) water-borne coatings and (b) "high solid" finishes. Both of these new technologies rely on new products and methods, which for the most part, represent a departure from conventional practice. For example, the use of high solids, low molecular mass binders, which can be cross-linked with monomeric crosslinking agents such as N,N,N',N',N'',N'', hexakis(methoxymethyl)1,3,5 triazine-2,4,6 triamine,[hexa (methoxymethyl)melamine] (LVII), which will be referred to as HMM, in the presence of catalysts to produce tough, solvent resistant films. This offers a possible solution to both the requirements of lower energy costs and reduced solvent emissions.

HMM was first noted[138] during investigations concerned with melamine condensation products. Over the years HMM and related products have been the subject of much research in the coatings industry.[139,140,141]

The curing of highly etherified triazine resins such as HMM has been shown to follow a different pathway than that attributed to conventional butylated resins.[142]



LVII

The latter types because of high levels of N-hydroxy methyl (>N-CH_2OH) and >NH groups present, exhibit a much greater tendency to self-condense. Self-condensation reactions of melamine and urea resins generally contribute to surface hardness of the film and such properties as tack, print resistance and stain resistance. However, too much self-condensation may result in drawbacks, such as film embrittlement, lower solvent resistance and poorer durability, package stability, flexibility and adhesion. The N-methoxymethyl groups of HMM reportedly do not self-condense.[142] Based upon the analysis of the volatile by-products, it was found that the rate of crosslinking of carboxyl groups was approximately 20 times faster than the self-condensation reaction.[143] Primary hydroxyl groups would react at an even faster rate.

However, studies by Biethan and co-workers[144,145,146] on the crosslinking reaction apart from self-condensation have led to a somewhat different conclusion, (scheme 1.10.1).

Proposed scheme for crosslinking, self-condensation and degradation of HMM crosslinked coatings.[144]

Crosslinking

$$>N\text{-}CH_2OCH_3 + HO\text{-}R \xrightarrow[-CH_3OH]{H^+} >N\text{-}CH_2O\text{-}R$$

Self-condensation

$$>N\text{-}CH_2OCH_3 + H_2O \xrightarrow[-CH_3OH]{H^+} >N\text{-}CH_2OH$$

$$>N\text{-}CH_2OH \xrightarrow[-CH_2O]{} >NH$$

$$>N\text{-}CH_2OH + >NH \xrightarrow[-H_2O]{} >N\text{-}CH_2\text{-}N<$$

Degradation

$$>N\text{-}CH_2O\text{-}R + H_2O \xrightarrow{H^+} >N\text{-}CH_2OH + HO\text{-}R$$

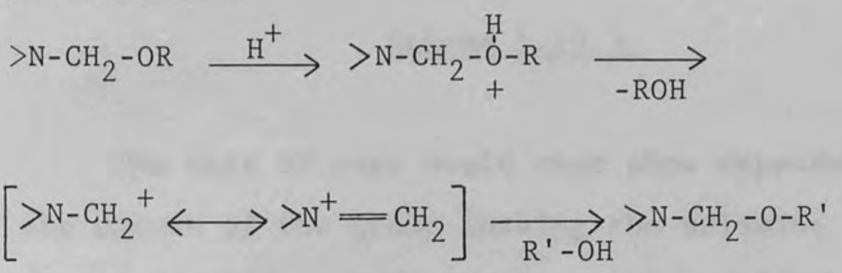
R may represent an alkyl group

Scheme 1.10.1.

The critical difference between this mechanism and the one proposed by Saxon and Lestienne[143] is the role of water in the self-condensation process. It was also demonstrated that under normal curing conditions, self-condensation can become very competitive with crosslinking, even for fully etherified melamines.

Previous studies[147,148] have indicated that the rate limiting step for crosslinking with N-alkoxymethyl groups was the generation of a carbonium ion, $>N-\overset{+}{C}H_2$ via a conventional $S_N{}^1$ mechanism, (scheme 1.10.2).

$S_N{}^1$ mechanism



$$>N-CH_2-OR \xrightarrow{H^+} >N-CH_2-\overset{H}{\underset{+}{O}}-R \xrightarrow[-ROH]{}$$

$$\left[>N-CH_2{}^+ \longleftrightarrow >N^+{=}CH_2\right] \xrightarrow[R'-OH]{} >N-CH_2-O-R'$$

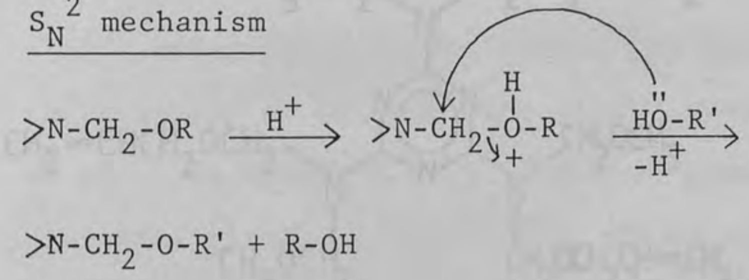
$R = CH_3$

R' = Alkyl or polymer chain

Scheme 1.10.2.

However, this view does not adequately explain the observed differences in curing rates between mercapto, -SH, hydroxyl, -OH and carboxyl,-COOH, functional groups with amino resins.[149] If the nucleophilic attack on the carbonium ion occurred after the rate limiting step, then it would have little or no effect on cure rate. Recent studies by Holmberg[150] have found that both crosslinking and self-condensation reactions of melamine resins proceed via a bimolecular displacement $S_N{}^2$ reaction, (scheme 1.10.3).

S_N2 mechanism



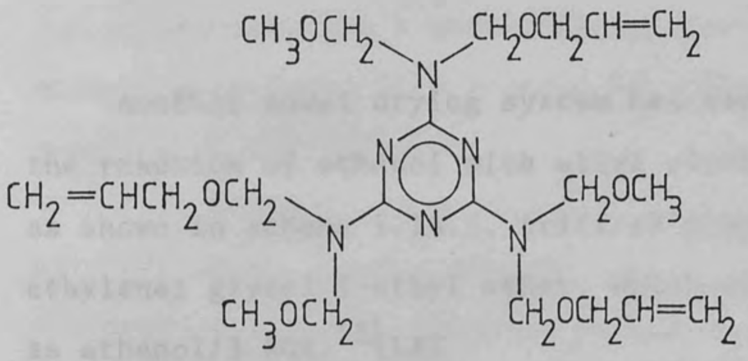
$$>N-CH_2-OR \xrightarrow{H^+} >N-CH_2-\overset{H}{\overset{|}{O}}{}^{+}-R \xrightarrow[-H^+]{H\ddot{O}-R'}$$

$$>N-CH_2-O-R' + R-OH$$

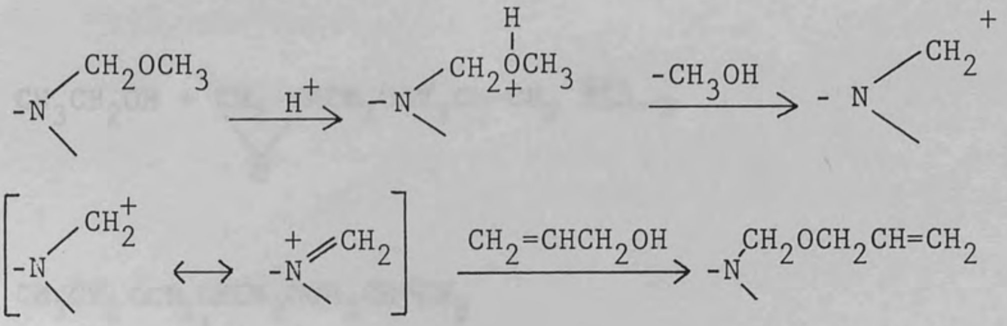
Scheme 1.10.3.

The rate of cure would then show dependence upon both the nature of the group leaving the melamine derivative and the nucleophiles of the binder resin. If these reactions are truly bimolecular, then steric effects exerted by the reacting species and the catalyst may further influence the reaction pathways, i.e., crosslinking or self-condensation, would be kinetically favoured. Additional mechanistic studies and a greater knowledge of the structure of the transition state going from reactants to products would be helpful in clarifying this question.

HMM is also known as cymel 300 in its most pure form and cymel 303 is approximately 97% pure. Recent research at ICI Paints Division has involved reacting HMM (cymel 303) with allyl alcohol[151] in the presence of p-toluene sulphonic acid to give a compound cymel 303/3 allyl alcohol, an idealised structure is shown below LVIII, containing approximately three allyl groups, (scheme 1.10.4).

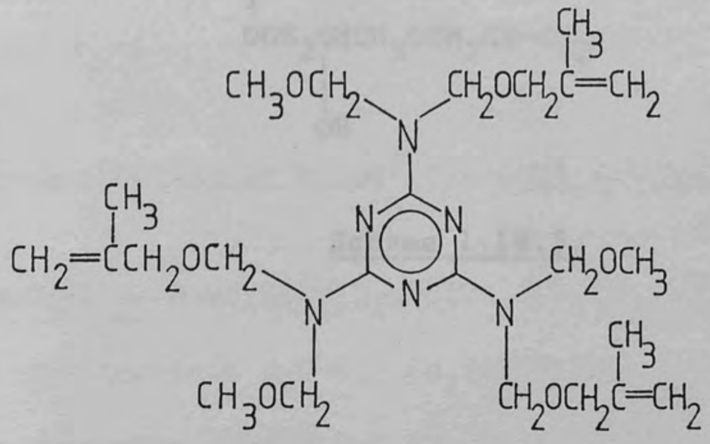


LVIII



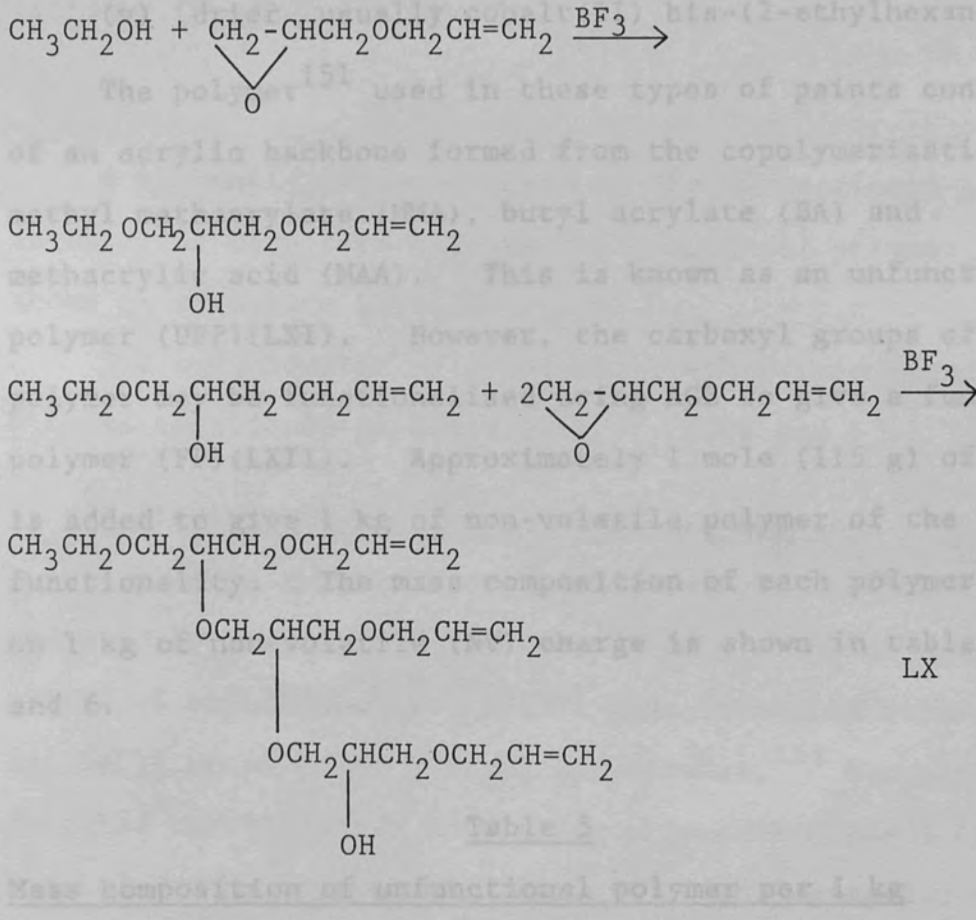
Scheme 1.10.4.

This type of reaction has been used with other alcohols to give other novel drying systems such as cymel 303/3 methallyl alcohol[151], an idealised structure is shown below (LIX).



LIX

Another novel drying system has been produced from the reaction of ethanol with allyl glycidyl ether (AGE), as shown in scheme 1.10.5, tri(2-(3'propenoxymethyl) ethylene) glycol 1-ethyl ether, which will be referred to as ethanol/3 AGE,[151] (LX).



Scheme 1.10.5.

A paint, using a novel drying system, as the means to produce a hardened film surface by crosslinking, typically consists of the following:-

(i) pigment
(ii) novel drying system
(iii) polymer (soluble in solvent used)
(iv) solvent
(v) drier, usually cobalt(II) bis-(2-ethylhexanoate).

The polymer[151] used in these types of paints consists of an acrylic backbone formed from the copolymerisation of methyl methacrylate (MMA), butyl acrylate (BA) and methacrylic acid (MAA). This is known as an unfunctional polymer (UFP)(LXI). However, the carboxyl groups of the polymer may be functionalised using AGE to give a functional polymer (FP)(LXII). Approximately 1 mole (115 g) of AGE is added to give 1 kg of non-volatile polymer of the required functionality. The mass composition of each polymer based on 1 kg of non-volatile (NV) charge is shown in tables 5 and 6.

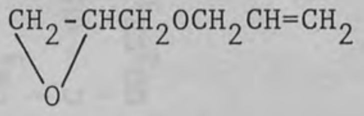
Table 5

Mass composition of unfunctional polymer per 1 kg

	Mass/g	Mol.
methyl methacrylate $H_2C{=}C(CH_3)CO_2CH_3$	733	7.32
butyl acrylate $H_2C{=}C(H)CO_2(CH_2)_3CH_3$	167	1.30
methacrylic acid $H_2C{=}C(CH_3)CO_2H$	100	1.16

Table 6

Mass composition of functional polymer per 1 kg

	Mass/g	Mol.
methyl methacrylate $H_2C=C(CH_3)CO_2CH_3$	540	5.39
butyl acrylate $H_2C=C(H)CO_2(CH_2)_3CH_3$	170	1.33
methacrylic acid $H_2C=C(CH_3)CO_2H$	175	2.03
allyl glycidyl ether	115	1.01
(AGE)  $CH_2-CHCH_2OCH_2CH=CH_2$		

A schematic representation of the unfunctional polymer is shown in structure LXI and the functional polymer is shown in structure LXII.

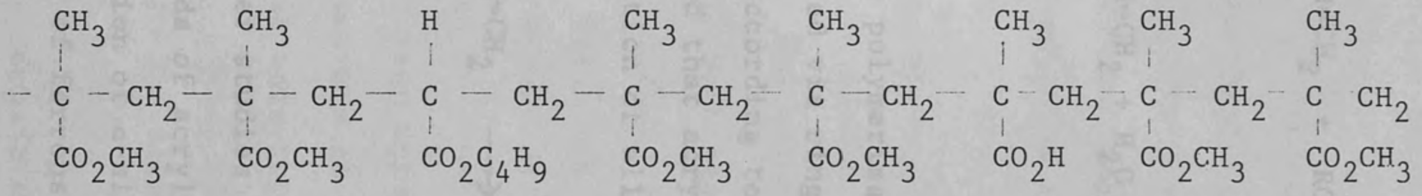
The autoxidation of these allyl ether type compounds will be considered in sections 1.11, 1.12 and 1.13.

1.11 Autoxidation of allyl ether compounds

The autoxidation of allyl ethers was first observed by Nichols and Yanovsky[152] in a study of allyl ethers of carbohydrates. Allyl glucosides had been initially prepared by Fischer and Strauss,[153] but a more detailed investigation into their preparation was later carried out by Tomecko and Adams.[154] The oxidation of these allyl ether compounds was explained by the following scheme;[155] (scheme 1.11.1).

Schematic representations of UFP and FP

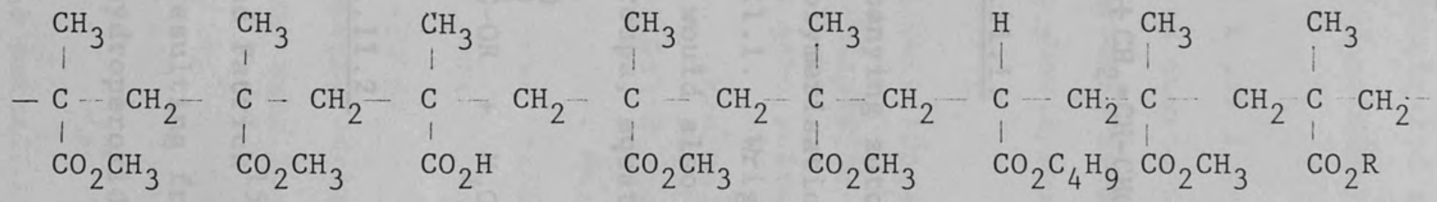
UFP



$-C(CH_3)(CO_2CH_3)-CH_2-C(CH_3)(CO_2CH_3)-CH_2-CH(CO_2C_4H_9)-CH_2-C(CH_3)(CO_2CH_3)-CH_2-C(CH_3)(CO_2CH_3)-CH_2-C(CH_3)(CO_2H)-CH_2-C(CH_3)(CO_2CH_3)-CH_2-C(CH_3)(CO_2CH_3)-CH_2$

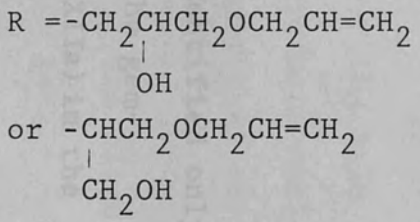
LXI

FSP



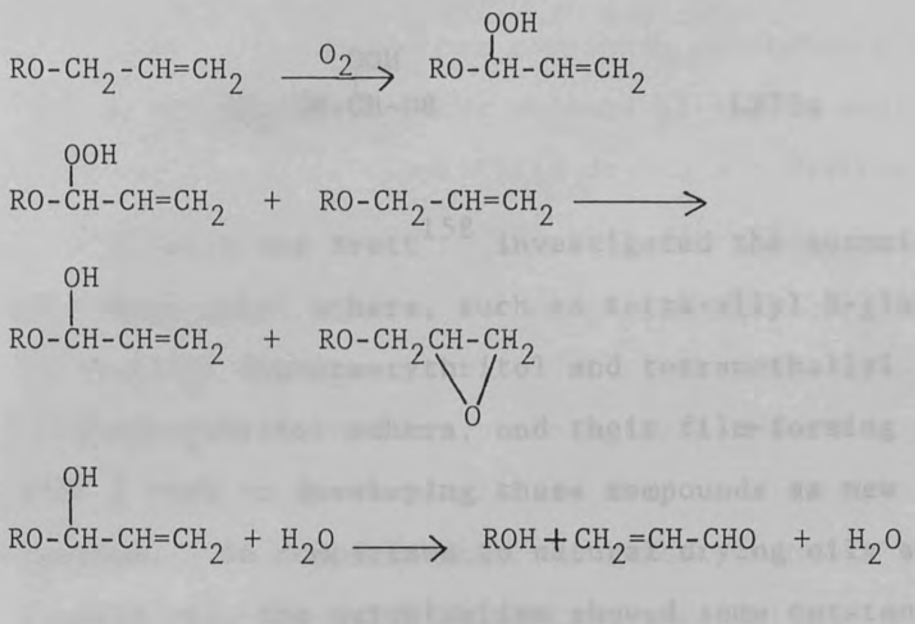
$-C(CH_3)(CO_2CH_3)-CH_2-C(CH_3)(CO_2CH_3)-CH_2-C(CH_3)(CO_2H)-CH_2-C(CH_3)(CO_2CH_3)-CH_2-C(CH_3)(CO_2CH_3)-CH_2-CH(CO_2C_4H_9)-CH_2-C(CH_3)(CO_2CH_3)-CH_2-C(CH_3)(CO_2R)-CH_2-$

LXII



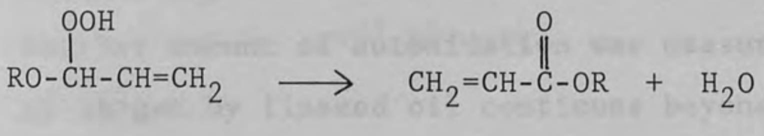
$R = -CH_2CH(OH)CH_2OCH_2CH=CH_2$

or $-CH(CH_2OH)CH_2OCH_2CH=CH_2$



Scheme 1.11.1.

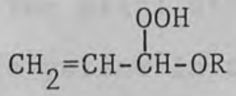
The polymerisation accompanying autoxidation was thought to proceed via ring-opening polymerisation of epoxy groups formed according to scheme 1.11.1. Wrigley and Yanovsky[156] suspected that acrylic esters would also be formed in the autoxidation of allyl ether groups, equation 1.11.2.



$$RO\text{-}\overset{OOH}{CH}\text{-}CH{=}CH_2 \longrightarrow CH_2{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR + H_2O$$

Equation 1.11.2.

Later studies by Sharp and Patrick[157] identified only low yields of acrylate ester resulting from the gem-dehydration of α-alkoxyallyl hydroperoxide (LXIIa) in the presence of ferrous sulphate.



$CH_2=CH-CH(OOH)-OR$ LXIIa

O'Neill and Brett[158] investigated the autoxidation of simple allyl ethers, such as tetra-allyl D-glucitol, tetra-allyl dipentaerythritol and tetramethallyl dipentaerythritol ethers, and their film-forming properties, with a view to developing these compounds as new drying systems. In comparison to natural drying oils such as linseed oil, the autoxidation showed some outstanding differences, namely:

(i) The 'touch dry time' was longer but the allyl ethers eventually dried more sharply to hard, rather brittle films. The methallyl ethers gave softer films.

(ii) Much less oxygen was taken up in the drying process; the amount taken up by tetra-allyl D-glucitol in the drying process was found to be about 12% by mass after which no further amount of autoxidation was measurable. The uptake of oxygen by linseed oil continues beyond 30%. Comparison of the oxygen uptake and the change in mass of the film gave a measure of the volatile degradation products evolved and these were found to be very much less for the allyl ether.

(iii) The solvent inextractable content of the films was much higher.

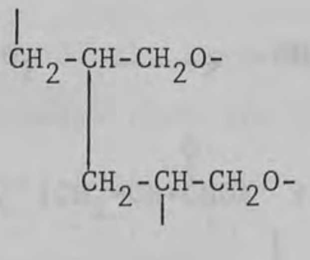
(iv) Cobalt catalysed the autoxidation, but lead and manganese were inhibitors.

(v) The allyl ether compounds exhibited a reduced tendency to yellow in the absence of light, when compared with yellowing in autoxidised drying oil systems; the methallyl ethers were almost non-yellowing.

Although the film properties of the allyl ethers showed some attractive features, there were also disadvantages, such as, poor pigment dispersing properties and wetting of substrates, which would render them unsuitable as sole media. It was concluded that the properties of the allyl groups would be best utilised either in combination with, or else built into, more developed media.

O'Neill and Brett also observed the chemical changes in allyl ethers during oxidative film formation, using IR spectroscopy and this provided further verification of the course of the reaction. They noted the formation of both carbonyl and carboxyl groups together with hydroxyl or hydroperoxide groups. This occurred with simultaneous loss of unsaturation and the ether groups appeared to be retained in the oxidised film.

They proposed that the mechanism of autoxidation included polymerisation reactions involving the initially formed alkoxyallyl hydroperoxides, but the exact mechanism, as with drying oils was difficult to establish. Radicals formed from breakdown of the hydroperoxide, (stimulated by the presence of cobalt drier), could initiate polymerisation of the allyl double bond giving polymers with the grouping (LXIII).

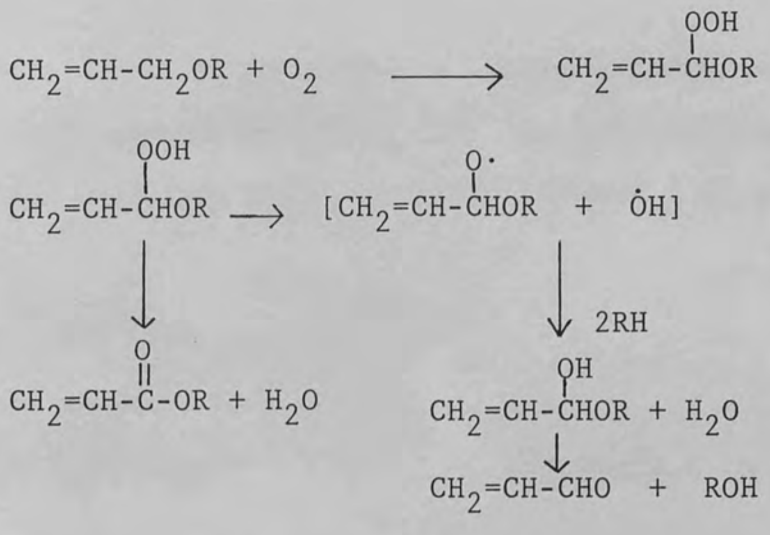


LXIII

However, it was thought that the polymer chains would be very short as termination processes compete very effectively with propagation. (It was known that polymers having a high degree of polymerisation could not be produced by radical polymerisation of allyl ethers). Since the compounds examined contained several allyl groups, it was felt that even dimerisation of an allyl group could lead to an overall cross-linked polymer.

Further studies on the structural effects of some allyl ether compounds during autoxidation, by Mleziva et al,[159] measured the autoxidation rates for a number of allyl ethers and found the rate of oxygen uptake to depend upon the electron density on the methylene carbon adjacent to the ethereal oxygen in the allyl group; the lower the electron density the higher the rate of autoxidation.

The initial step in the autoxidation of allyl ethers, (shown in scheme 1.11.3),[160] as with the unsaturated fatty acid esters used in alkyd based paints, is the uptake of oxygen leading to the formation of hydroperoxides. These hydroperoxides decompose to give either ester or alcohol and propenal products, or may undergo termination reactions to give cross-linked polymers. (For the equations of autoxidation, see section 1.8).



Scheme 1.11.3.

The polymerisation of allylic compounds[161] depends upon the competition between hydrogen abstraction and addition reactions. Hydrogen abstraction from allyl compounds may proceed as follows, equation 1.11.4:-

$$R\cdot + R'CH_2CH{=}CH_2 \longrightarrow RH + R'\dot{C}HCH{=}CH_2 \longleftrightarrow R'CH{=}CH\text{-}\dot{C}H_2$$

resonance stabilised

Equation 1.11.4.

$R'CH{=}CH\text{-}\dot{C}H_2$ is more stable than the radical formed by addition to a double bond, equation 1.11.5, vide infra.

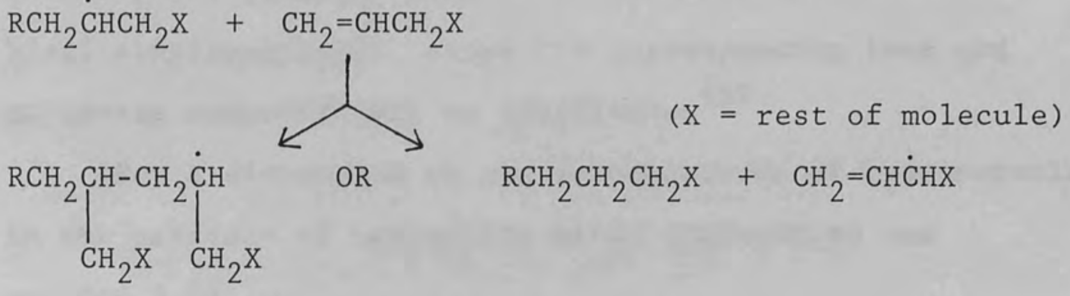
$$R\cdot + R'CH_2CH{=}CH_2 \rightleftharpoons R'CH_2\dot{C}HCH_2R$$

Equation 1.11.5.

Comparison between hydrogen abstraction and addition shows:-

(i) The activation energy is greater for abstraction than addition; rate of abstraction increases with temperature.

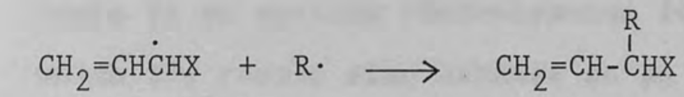
(ii) Alkyl radicals formed in addition reactions are very reactive because they are not stabilised by resonance and they may react further, (scheme 1.11.6).



(X = rest of molecule)

Scheme 1.11.6.

(iii) Resonance stabilised radicals tend to undergo combination with other radicals, (scheme 1.11.7).



$$CH_2=CH\dot{C}HX + R\cdot \longrightarrow CH_2=CH-\overset{R}{C}HX$$

(where R· could be another allylic radical)

Scheme 1.11.7.

A range of products is then to be expected from different types of reaction. As to whether abstraction or addition occurs, depends upon the nature of X. Allyl ethyl ether radicals favour abstraction followed by radical termination, which leads to low molecular mass polymers.

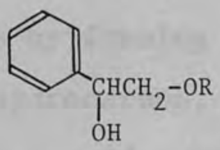
The rate of decomposition of hydroperoxides formed from the autoxidation of allyl ethers may also be increased by the presence of metal ions, as in the case of the hydroperoxides formed in the traditional alkyd based paints. However, the promoter used is usually cobalt(II) bis(2-ethylhexanoate), since the corresponding lead and manganese compounds act as inhibitors.[158]

(For a discussion on the decomposition of hydroperoxides in the presence of transition metal derivatives see section 1.9).

1.12 Autoxidation of allyl ether alcohols

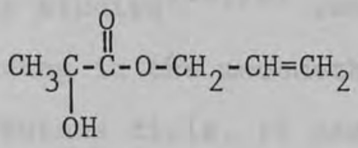
Recent studies by Toivonen[162] on the cobalt catalysed liquid phase autoxidation of primary and secondary allyl ether alcohols, at 30 - 40°C, have revealed that there is an optimum concentration for this catalyst above which the cobalt also behaves as an inhibitor. Examples of some of the structures of allyl ether alcohols used are shown in table 7.

Table 7

Primary allyl ether alcohols*	Secondary allyl ether alcohols*
$CH_2(OH)CH_2{-}OR$ 2-(2-propenyloxy)-ethanol	$CH_3CH(OH)CH_2{-}OR$ 1-(2-propenyloxy)-2-propanol
$CH_2(OH)CH_2CH_2{-}OR$ 3-(2-propenyloxy)-1-propanol	
$CH_2(OH)CH_2CH_2CH_2{-}OR$ 4-(2-propenyloxy)-1-butanol	 1-phenyl-2-(2-propenyloxy)-1-ethanol

* $R{=}{-}CH_2CH{=}CH_2$

In addition he observed that the autoxidation of secondary allyl alcohols commenced immediately upon adding the catalyst, (with the exception of allyl lactate LXIV), but the reactions of the allyl ethers of the primary alcohols were preceded by induction periods, which were dependent on the number of carbon atoms in the chain. The longer the chain, the longer the induction period. On methylating the primary hydroxyl groups induction periods were not observed. This led to the conclusion that hydrogen bonding by the hydroxyl group has an important role in the control of the autoxidation of allyl ether alcohols.



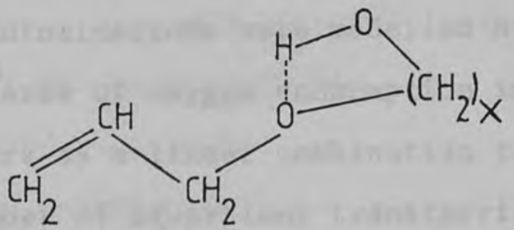
$$CH_3\underset{\underset{OH}{|}}{C}-\overset{\overset{O}{\parallel}}{C}-O-CH_2-CH=CH_2$$

LXIV

Alcohols and compounds containing hydroxyl groups in general have often been found to either retard or inhibit autoxidation processes.[163] However, cases where the addition of an alcohol has accelerated the oxidation process have been reported. Frye et al[164] reported that alcohols, e.g. methanol, ethanol and 2-propanol, may either accelerate or inhibit autoxidation of hydrocarbons depending on the structure of the hydrocarbon. The structure of the alcohol was found to make little difference. It was thought that the alcohols controlled oxidations by forming alkoxy radicals which, depending on the hydrocarbon, either accelerated the formation of hydroperoxides or acted as chain-breaking agents. Other workers[165] have described the inhibition effect in terms of hydrogen bonding leading to the deactivation of hydroperoxy and alkylperoxy radicals.

Toivonen thought that inhibition in the autoxidations of allyl ether alcohols could be better explained by hydrogen bonding of the hydroxyl groups to the ethereal oxygen, leading to a decrease in the electron density at the ethereal oxygen and consequent lower stability of the adjacent allylic radical. The inhibition of the autoxidation of allyl lactate (LXIV) can similarly be explained as the result of a decrease in the electron density on the ethereal oxygen owing to the resonance of its electron pair with the adjacent carbonyl.

From the studies[166,167] concerning the intramolecular hydrogen bonding in the monomethyl ethers of ethane, propane and butane diols, it can be concluded that the monoallyl ethers of these diols are able to exist in the cyclic conformation (LXV).

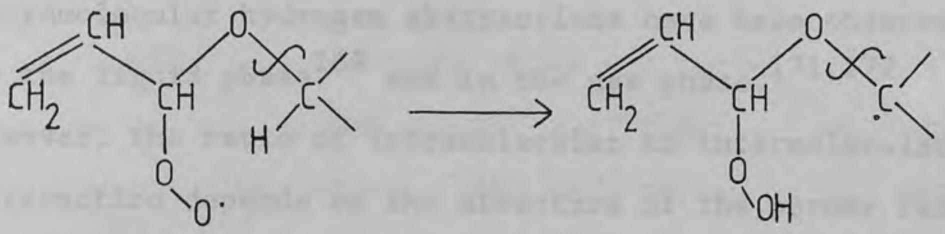


LXV

Thus, the phenomena of the autoxidations are alternatively explained as a result of inter- and intramolecular hydrogen bonding, decreasing the electron density on the ethereal oxygen.

1.13 Autoxidation of alkyl allyl ethers

Investigations by Toivonen[168] into the effect of the structure of alkyl allyl ethers on their cobalt catalysed liquid phase autoxidation behaviour, at 30°C, have shown that the oxidation rates vary considerably depending on the structure of the alkyl group. The structural effects on the oxidation rates were interpreted as being due to differences in the rate limiting isomerisation of peroxy radicals via intramolecular hydrogen transfers, (scheme 1.13.1).



Scheme 1.13.1.

The autoxidations were modelled by presenting the measured rates of oxygen consumption in oxidations of alkyl allyl ethers as a linear combination term, each consisting of the number of equivalent transferring hydrogens and a weighting factor describing the reactivity of these hydrogens. Intramolecular peroxy radical attack was observed to be most favourable for hydrogens attached to β carbons, relative to the ethereal oxygen, in the alkyl group. This requires a 7-membered ring in the transition state in the rate limiting step. Further, the ease of hydrogen atom transfers decreases in the order tert>sec>prim.

These conclusions are supported from studies carried out on autoxidations of a number of hydrocarbons. Generally, the rate limiting step is the formation of hydroperoxides through the reactions of peroxy radicals with the substrate,[132] equation 1.13.2.

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot$$

Equation 1.13.2.

The attack of peroxy radicals upon carbon hydrogen bonds can occur both inter- and intramolecularly.[169,170,171] Intramolecular hydrogen abstractions have been observed both in the liquid phase[169] and in the gas phase.[171,172] However, the ratio of intramolecular to intermolecular abstraction depends on the structure of the peroxy radical. Isomerisation has in some cases been found more favourable than external hydrogen transfers in liquid-phase autoxidation[169,173] and in more concentrated systems.[169,174] In contrast to the results for allyl ethers, (vide supra), Rust[169] found that isomerisation of peroxy radicals in hydrocarbon autoxidations was most efficient when the transition state involved a 6-membered ring and somewhat less efficient in the case of a 7-membered ring. Intramolecular peroxy radical[175] attack was most favoured when the reactive hydrogen was attached to a carbon in the β position.

2. Results and Discussion

2.1 Preliminary investigations concerned with novel drying systems, based upon allyl ethers and either functional or unfunctional polymer (non-quantitative)

(For experimental details see section 3.4).

The following compounds were used in preliminary investigations:- (1) cymel 303/3 allyl alcohol (LVIII), (2) cymel 303/3 methallyl alcohol (LIX), (3) ethanol/3 AGE (EtOH/3 AGE) (LX), (4) functional polymer (FP) (LXII), (5) unfunctional polymer (UFP) (LXI).

Prepared blends of the above compounds were spread onto microscope slides and allowed to dry for 24 hours. After which time, it was found that each film was soluble in cold ethanol.

The investigation was repeated but cobalt (II) bis-(2-ethylhexanoate) was added as a promoter to each blend. The solubility of the films, having an allyloxy component, which had been allowed to dry for 24 hours, was tested in a variety of solvents; the results of which are shown in table 8. The films formed from FP and UFP were still readily soluble in cold ethanol indicating that crosslinking had not occurred after 24 hours. However, the films of the cobalt promoted allyl ether drying systems had undergone some crosslinking reactions, as was shown from the solubility tests. It was observed that the film from the cymel 303/3 methallyl alcohol blend seemed to become opaque in nature, while showing signs of some solubility.

Table 8

Solubility of films from novel drying systems, 24 hours dry (cobalt promoted)

Solvent	Cymel 303/3 allyl alcohol	Cymel 303/3 methallyl alcohol	Ethanol/3 AGE
ethanol-cold	s	s	s
-hot	s	s	s
hexane-cold	n	n	n
-hot	n	n	n
ethyl acetate -cold	s	s	n
-hot	s	s	s
carbon tetrachloride -cold	n	n	n
-hot	n	s	n
toluene-cold	s	s	n
-hot	s	s	n
dichloromethane cold	s	s	s

Key: s = Film peeled away from surface of slide but remained partly intact. Some may have been soluble.

n = Film remained on slide, no evidence of any solubility.

Observations from other preliminary investigations included:-

(1) Since the uncrosslinked allyl ether compounds could be extracted from microscope slides, which had been spread with a film of this material and allowed to dry, using soxhlet extraction apparatus, weighings were taken of the amount of extractable material (a) and compared with the amount of material (excluding solvent) applied to the slides before extraction (a + b). The microscope slides appeared very clean after extraction and it seemed that the value of (a) was almost equal to (a + b), (% error ~ 0.02%).

From this result, it also appeared that the uncrosslinked material was not absorbed on the soxhlet thimble.

(2) Comparison between 1 hour and 18 hour soxhlet extractions carried out on films, of cymel 303/3 allyl alcohol and cobalt promoter in ethanol, spread on microscope slides and allowed to dry for 24 hours, seemed to suggest that the extraction could be completed within 1 hour. The ratio $\frac{b}{a + b}$, where (b) is the amount of non-extractable material determined by subtraction, appeared to be similar, (% error ~0.02%).

(3) Films, for FP with cobalt promoter, allowed to dry at room temperature for 24 hours, 48 hours and 1 week and for 24 hours and 48 hours, similarly with UFP, gave slides that appeared clean after soxhlet extraction. The weighing results gave no evidence of crosslinking occurring in these polymer blend films, (table 9).

Table 9 (Mass/g)

Blend	Fraction	Drying time before extraction 24 hours	 48 hours	 1 week
FP + Co(II)bis-(2-ethylhexanoate) + solvent	a + b	0.0208	0.0296	0.0287
	a	0.0330	0.0307	0.0373
UFP + Co(II)bis-(2-ethylhexanoate) + solvent	a + b	0.0436	0.0381	-
	a	0.0477	0.0444	-

(4) The allyl ether compoundswere found to be soluble in toluene, ethanol and chloroform. The FP and UFP were soluble in chloroform, ethanol and in ethanol/toluene (4:1) but only partially soluble in toluene alone.

2.2 Investigations concerned with the crosslinking ability of drying systems based upon allyl ethers

The following drying systems were examined in three series of blends (1 - 3):- (i) cymel 303/3 allyl alcohol (LVIII), (ii) cymel 303/3 methallyl alcohol (LIX), (iii) cymel 303/3 (4.2 ethylene oxide (EO) + allyl alcohol) (LXVI), (iv) cymel 303/3 (4.2 ethylene oxide (EO) + methallyl alcohol)(LXVII), (v) ethanol/3 AGE (EtOH/3 AGE) (LX).

The blends prepared were:-

(1) novel drying system cobalt promoter and solvent,

(2) novel drying system, FP, cobalt promoter and solvent,

(3) novel drying system, UFP, cobalt promoter and solvent.

(For experimental details, see sections 3.5.1, 3.5.2 and 3.5.3).

The non-extractable film formed from the above blends was examined in two ways viz. by using Fourier transfer infrared (FTIR) spectroscopy (section 2.2.1) and by determinations of the mass of non-extractable film formed (section 2.2.2).

2.2.1 FTIR studies of the non-extractable film formed from drying systems based upon allyl ethers

FTIR spectroscopy was used to study the components of each blend (prepared as above in section 2.2), i.e. allyloxy compound, FP, UFP and also the non-extractable films formed from these blends, after soxhlet extraction of the dried films, which had been spread onto microscope slides and allowed to dry at room temperature for given time periods. Figures 2.2.1.1, 2.2.1.2 and 2.2.1.3 show the FTIR spectra obtained for FP, UFP and the cymel 303/3 allyl alcohol compound. Strong absorptions at 1729 cm^{-1} and 1733 cm^{-1} were observed in the FP and UFP respectively, due to $>$C=O stretching but no absorptions were noted in this region in the cymel 303/3 allyl alcohol compound.

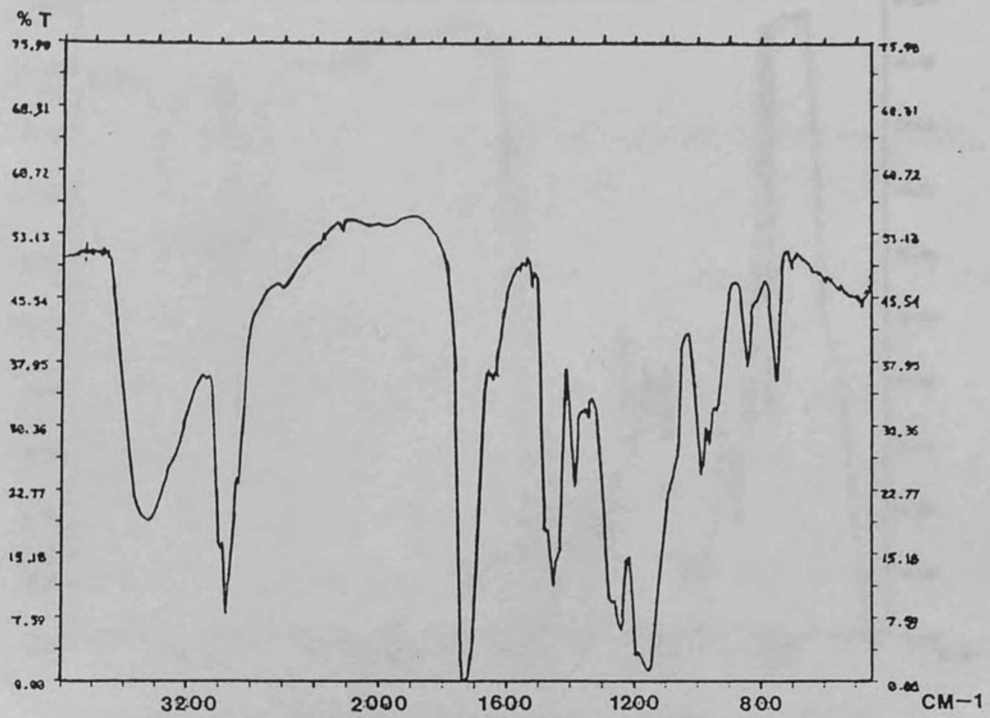


Fig. 2.2.1.1. FTIR spectrum of functional polymer (FP)

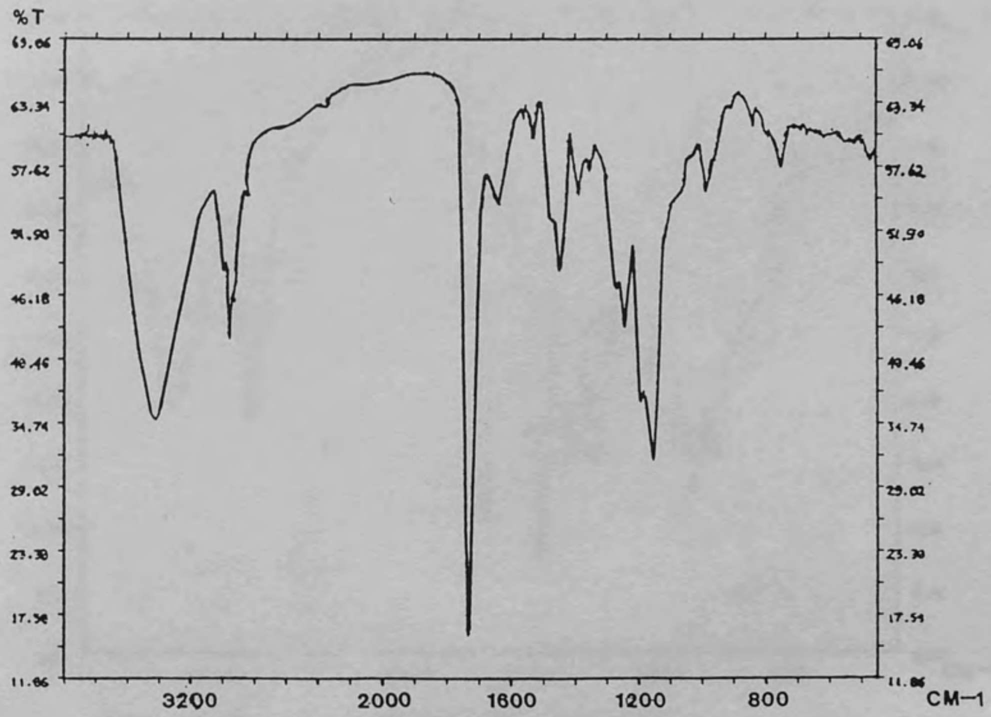


Fig. 2.2.1.2. FTIR spectrum of unfunctional polymer (UFP)

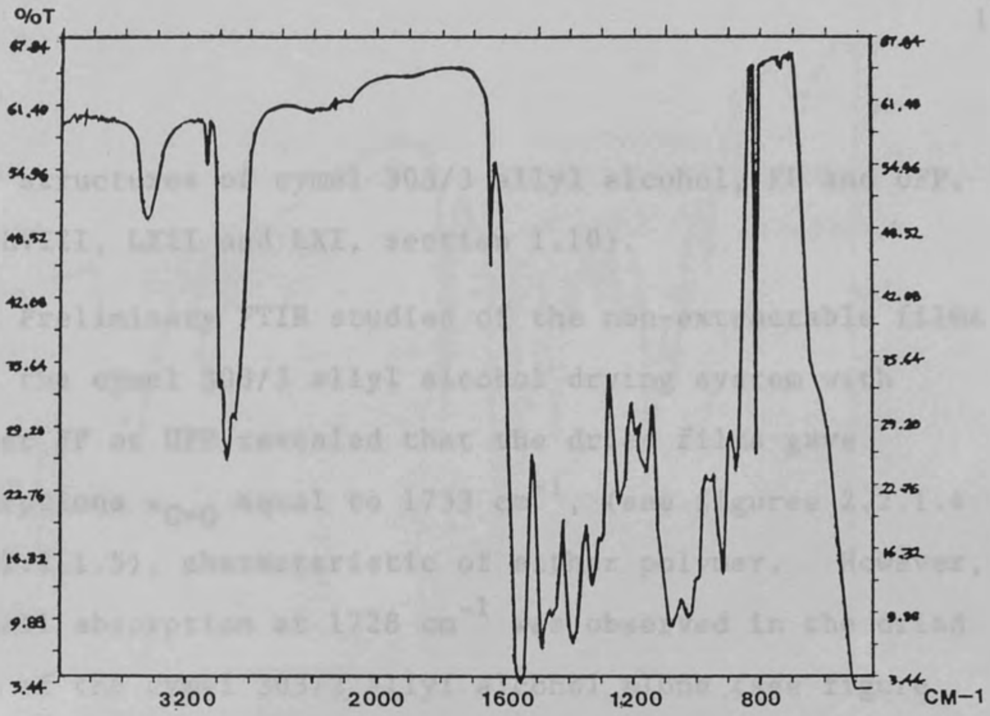


Fig. 2.2.1.3. FTIR spectrum of cymel 303/3 allyl alcohol

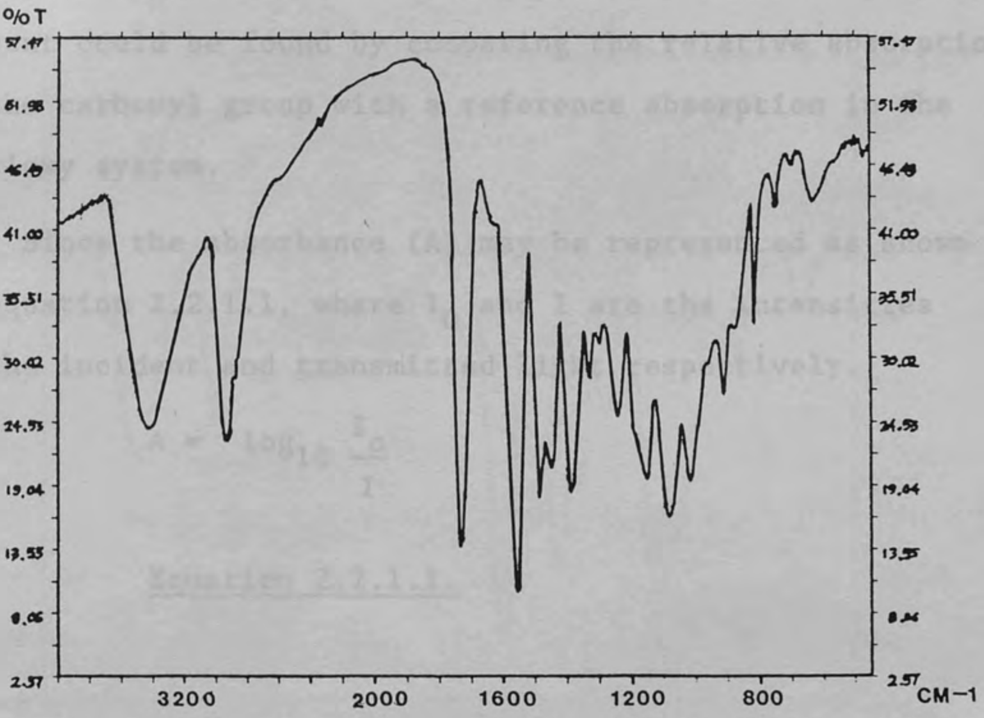


Fig. 2.2.1.4. FTIR spectrum of non-extractable film from cymel 303/3 allyl alcohol and FP blend, (i), (2)

(For structures of cymel 303/3 allyl alcohol, FP and UFP, see LVIII, LXII and LXI, section 1.10).

Preliminary FTIR studies of the non-extractable films from the cymel 303/3 allyl alcohol drying system with either FP or UFP revealed that the dried films gave absorptions $\nu_{C=O}$ equal to 1733 cm^{-1}, (see figures 2.2.1.4 and 2.2.1.5), characteristic of either polymer. However, a small absorption at 1728 cm^{-1} was observed in the dried film of the cymel 303/3 allyl alcohol alone (see figure 2.2.1.6). This carbonyl bond absorption probably arose from the products of decomposition of hydroperoxides formed during the oxidation of the allyl ether. It was thought that possibly some idea of the proportion of ester polymer present could be found by comparing the relative absorptions of the carbonyl group with a reference absorption in the allyloxy system.

Since the absorbance (A) may be represented as shown in equation 2.2.1.1, where I_0 and I are the intensities of the incident and transmitted light respectively.

$$A = \log_{10} \frac{I_o}{I}$$

<u>Equation 2.2.1.1.</u>

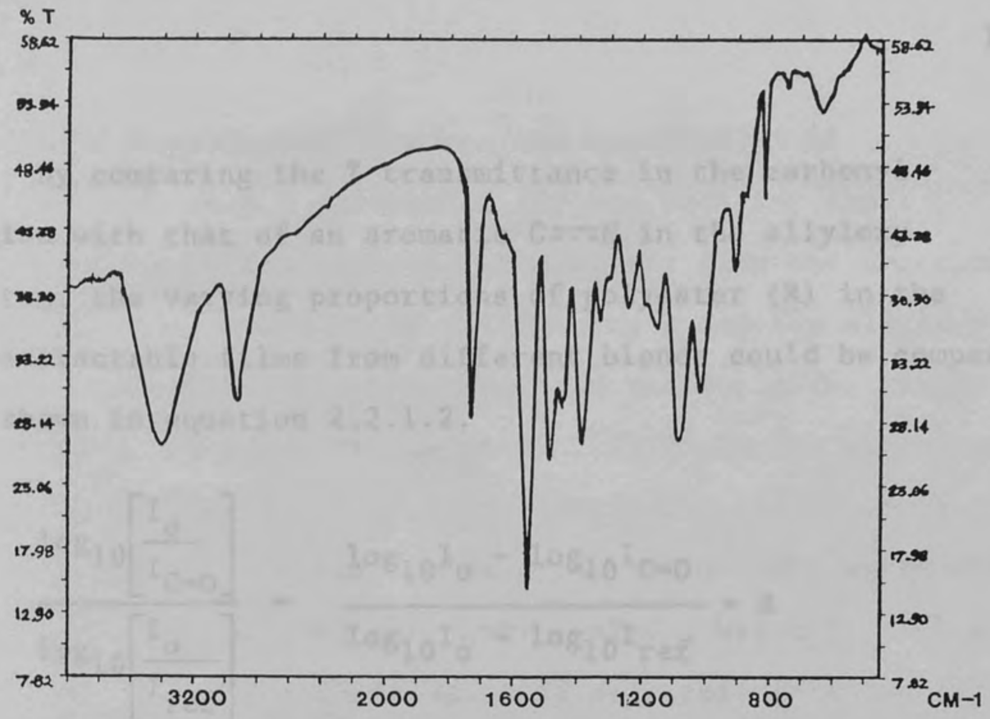


Fig. 2.2.1.5. FTIR spectrum of non-extractable film from cymel 303/3 allyl alcohol and UFP blend, (i), (3)

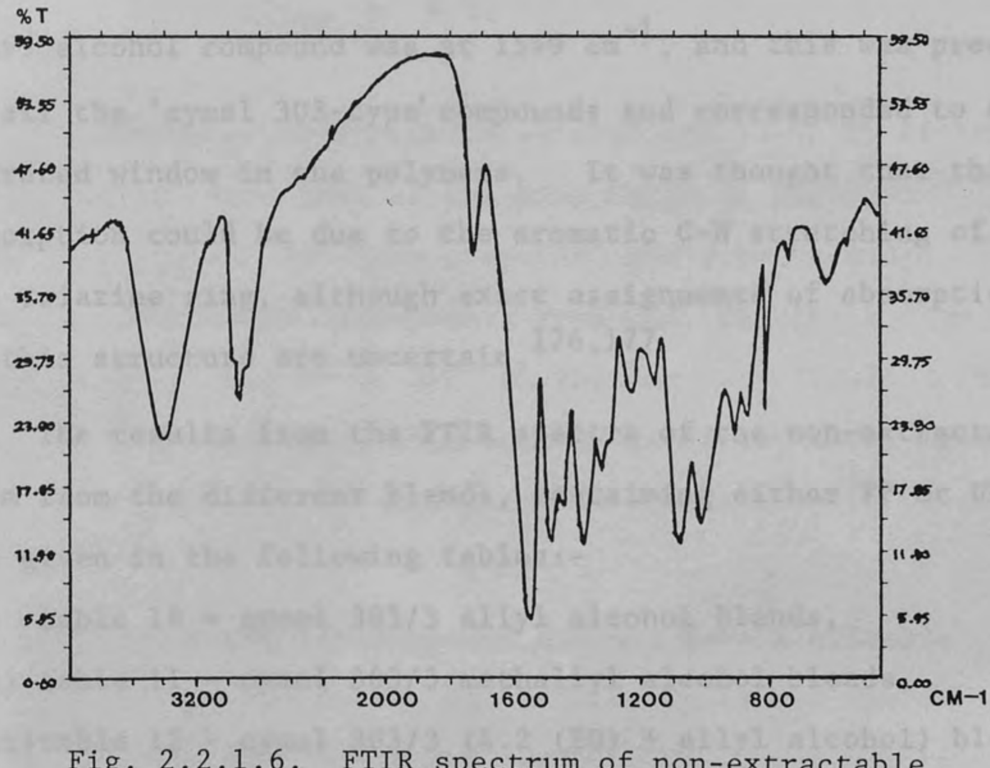


Fig. 2.2.1.6. FTIR spectrum of non-extractable film from cymel 303/3 allyl alcohol blend (i), (1)

By comparing the % transmittance in the carbonyl region with that of an aromatic C$\equiv$N in the allyloxy system, the varying proportions of polyester (R) in the non-extractable films from different blends could be compared as shown in equation 2.2.1.2.

$$\therefore \quad \frac{\log_{10}\left[\frac{I_o}{I_{C=O}}\right]}{\log_{10}\left[\frac{I_o}{I_{ref}}\right]} = \frac{\log_{10}I_o - \log_{10}I_{C=O}}{\log_{10}I_o - \log_{10}I_{ref}} = R$$

Equation 2.2.1.2.

The reference absorption used from the cymel 303/3 allyl alcohol compound was at 1549 cm^{-1}, and this was present in all the 'cymel 303-type' compounds and corresponded to an infrared window in the polymers. It was thought that this absorption could be due to the aromatic C-N stretching of the triazine ring, although exact assignments of absorptions of this structure are uncertain.[176,177]

The results from the FTIR spectra of the non-extractable film from the different blends, containing either FP or UFP, are given in the following tables:-

(i) table 10 - cymel 303/3 allyl alcohol blends,
(ii) table 11 - cymel 303/3 methallyl alcohol blends,
(iii) table 12 - cymel 303/3 (4.2 (EO) + allyl alcohol) blends,
(iv) table 13 - cymel 303/3 (4.2 (EO) + methallyl alcohol) blends.

(For experimental details see section 3.5.4).

In each case a correction (C) was made for the contribution to the carbonyl absorptions from the autoxidised allyloxy ether products by determining R for the allyloxy ether alone with cobalt promoter and solvent after either 24 hours or 48 hours drying time. FTIR spectra were also obtained of the 'cold' (i.e. no cobalt catalyst) blends of cymel 303/3 allyl alcohol with either FP or UFP, where the mass ratio of allyloxy compound: polymer was 1:1. (The cymel 303/3 allyl alcohol was used as a reference for all the 'cymel 303-type compounds'). R was determined for each blend and the results were as follows:-

$$R\ (1{:}1)_{FP} = 0.60$$

$$R\ (1{:}1)_{UFP} = 0.52$$

By dividing the corrected absorptions (R-C) by either 0.60 or 0.52, some idea of the mass ratio of carbonyl compound: 'cymel 303-type compound' could be obtained. Thus the proportion of carbonyl compound, resulting from the presence of either FP or UFP, in the non-extractable dried film could be expressed as a percentage of the total amount of this non-extractable film. (See tables 10, 11, 12 and 13).

The ethanol/3 AGE compound did not have a suitable absorption band, which was not present in either the FP or UFP, that would enable the ratio of ester polymer to

Table 10

Blend	Time*	I_o	$I_{C=O}$	I_{ref}	R	R-C	$\frac{R-C}{R(1:1)}$ FP or UFP	% of polymer (FP or UFP) present in non-extractable film
(i) 1) Cymel 303/3 allyl alcohol + Co(II) bis (2-ethylhexanoate) + solvent (Correction 'C')	24 hrs	54.50	39.50	14.72	0.25	-	-	-
(i) 2) Cymel 303/3 allyl alcohol + FP + Co(II) bis (2-ethylhexanoate) + solvent	24 hrs	55.82	13.71	9.86	0.81	0.56	0.93	48.19
	48 hrs	54.65	26.99	22.50	0.80	0.55	0.92	47.92
	1 wk	76.40	42.62	41.87	0.97	0.72	1.20	54.55
	5 wks	34.50	6.37	5.78	0.95	0.70	1.17	53.92
(i) 3) Cymel 303/3 allyl alcohol + UFP + Co(II) bis (2-ethylhexanoate) + solvent	24 hrs	49.98	28.35	14.87	0.47	0.22	0.42	29.58
	48 hrs	48.90	30.46	17.95	0.47	0.22	0.42	29.58
	1 wk	77.46	49.27	36.19	0.59	0.34	0.65	39.39
	5 wks	83.58	57.14	49.28	0.72	0.47	0.90	47.37

* refers to drying time before extraction

Table 11

Blend	Time*	I_o	$I_{C=O}$	I_{ref}	R	R-C	$\frac{R-C}{R(1:1)}$ FP or UFP	% of polymer (FP or UFP) present in non-extractable film
(ii) 1) Cymel 303/3 methallyl alcohol + Co(II) bis (2-ethylhexanoate) + solvent (Correction 'C')	24 hrs	Slides clean - no film				-	-	-
	48 hrs	75.54	57.31	12.64	0.15	-	-	-
(ii) 2) Cymel 303/3 methallyl alcohol + FP + Co(II) bis (2-ethylhexanoate) + solvent	24 hrs	72.71	48.48	50.04	1.08	0.93	1.55	60.78
	48 hrs	62.05	17.97	16.48	0.93	0.78	1.30	56.52
	1 wk	73.57	24.41	22.73	0.94	0.79	1.32	56.90
	5 wks$^+$	58.64	28.94	29.82	1.04	0.89	1.48	59.68
(ii) 3) Cymel 303/3 methallyl alcohol + UFP + Co(II) bis (2-ethylhexanoate) + solvent	24 hrs	Negligible crosslinking					-	-
	48 hrs	"			"		-	-
	1 wk	"			"		-	-
	5 wks	"			"		-	-

* refers to drying time before extraction

\+ FTIR spectrum not very satisfactory consequent upon difficulties in grinding film for KBr disc.

Table 12

Blend	Time*	I_o	$I_{C=O}$	I_{ref}	R	R-C	$\frac{R-C}{R(1:1)}$ FP or UFP	% polymer (FP or UFP) present in non-extractable film
(iii) 1) Cymel 303/3 (4.2 (EO) + allyl alcohol) + Co(II) bis(2-ethylhexanoate) + solvent (Correction 'C')	24 hrs+	24.10	9.18	2.74	0.44	-	-	-
(iii) 2) Cymel 303/3 (4.2 (EO) + allyl alcohol) + FP + Co(II) bis (2-ethylhexanoate) + solvent	24 hrs	57.65	32.70	31.89	0.96	0.52	0.87	46.52
	48 hrs	53.81	43.70	43.14	0.94	0.50	0.83	45.36
	1 wk	65.72	32.40	30.65	0.93	0.49	0.82	45.05
	5 wks	62.35	45.27	46.45	1.09	0.65	1.08	51.92
(iii) 3) Cymel 303/3 (4.2 (EO) + allyl alcohol) + UFP + Co(II) bis(2-ethyl hexanoate) + solvent	24 hrs+	56.47	46.54	46.36	0.98	0.54	1.04	50.98
	48 hrs	40.64	27.84	27.44	0.96	0.52	1.00	50.00
	1 wk	60.26	38.96	37.90	0.94	0.50	0.96	48.98
	5 wks	70.14	47.51	43.96	0.83	0.39	0.75	42.86

* refers to drying time before extraction

+ FTIR spectrum not very satisfactory consequent upon difficulties in grinding film for KBr disc.

Table 13

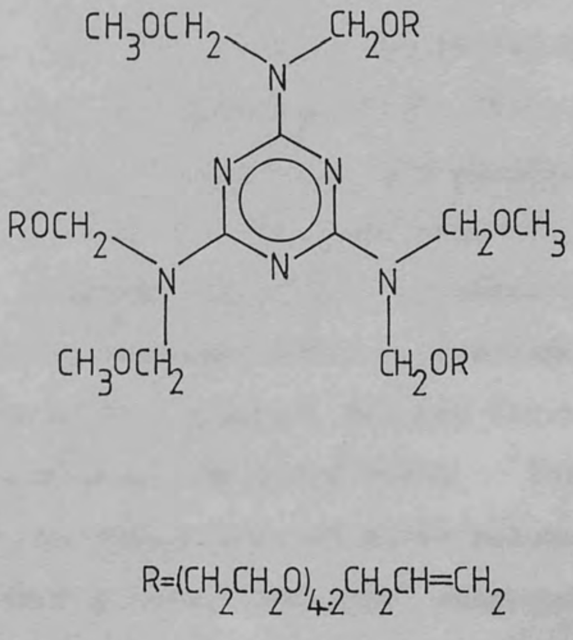
Blend	Time*	I_o	$I_{C=0}$	I_{ref}	R	R-C	$\frac{R-C}{R(1:1)}$ FP or UFP	% polymer (FP or UFP) present in non-extractable film
(iv) 1) Cymel 303/3 (4.2 (EO) + methallyl alcohol) + Co(II) bis (2-ethylhexanoate) + solvent (Correction 'C')	24 hrs	67.34	58.56	42.65	0.30	-	-	-
(iv) 2) Cymel 303/3 (4.2 (EO) + methallyl alcohol) + FP + Co(II) bis(2-ethylhexanoate) + solvent	24 hrs+	61.04	41.91	42.43	1.03	0.73	1.22	54.95
	48 hrs+	73.10	49.86	50.24	1.02	0.72	1.20	54.55
	1 wk	75.00	43.19	44.20	1.04	0.74	1.23	55.16
	5 wks	80.00	37.86	44.95	1.30	1.00	1.67	62.55
(iv) 3) Cymel 303/3 (4.2 (EO) + methallyl alcohol)+ UFP + Co(II) bis(2-ethylhexanoate) + solvent	24 hrs	74.22	43.85	46.07	1.10	0.80	1.54	60.63
	48 hrs	72.00	27.09	30.05	1.12	0.82	1.58	61.24
	1 wk	82.16	54.14	55.64	1.07	0.77	1.48	59.68
	5 wks	78.67	50.84	52.18	1.06	0.76	1.46	59.35

* refers to drying time before extraction

\+ FTIR spectrum not very satisfactory consequent upon difficulties in grinding film for KBr disc.

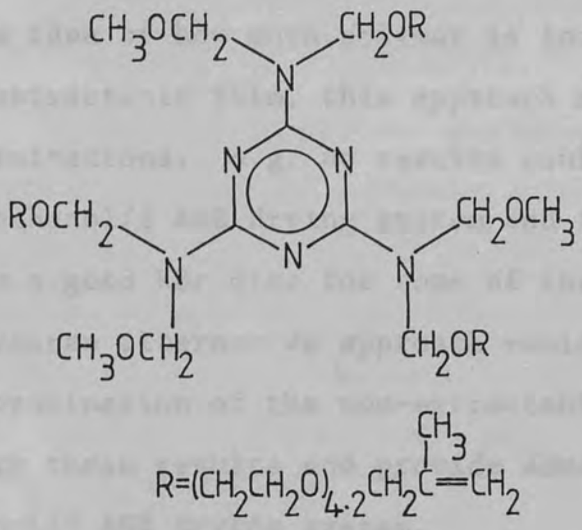
polymerised drying system in the non-extractable film of different blends to be determined. Thus comparable results to the 'cymel 303-type' compounds could not be obtained.

In case (i), using the cymel 303/3 allyl alcohol,[‡] (see structure LVIII), as the drying system, it appeared that the blend containing the FP showed a higher ratio of carbonyl groups relative to the blend containing UFP, after correction. This observation suggested that more FP was incorporated into the non-extractable film than with the UFP blend. With cymel 303/3 methallyl alcohol,[‡] (case ii), (see structure LIX), the correction term was obtained after 48 hours), since after 24 hours no film formation had occurred. In fact this correction term was smaller than that obtained for case (i). It also seemed that the film from the blend containing FP showed it to constitute a higher proportion of FP here than case (i). Thus it appeared that the crosslinking of the methallyloxy system alone was slower, so that the role of the methallyloxy modified with FP becomes enhanced in the drying process. However, on attempting to obtain drying for the UFP blend, only negligible crosslinking occurred, which meant that it was not possible to acquire reasonable FTIR spectra for this blend. In cases (iii) and (iv) where the blends contained the ethylene oxide modified compounds of cases (i) and (ii), as the drying systems, larger correction terms were obtained than in the unmodified cases. The value of R-C for the FP and UFP blends seemed to be comparable, possibly indicating that the FP and UFP blends were now incorporated equally into the non-extractable film. The idealised structures of cymel 303/3 (4.2 (EO) + allyl alcohol)‡ and cymel 303/3 (4.2 (EO) + methallyl alcohol)‡ are shown below in structures LXVI and LXVII respectively; the average number of ethylene oxide groups present in each of the allyloxy groups is given as 4.2.[151]



$R{=}(CH_2CH_2O)_{4.2}CH_2CH{=}CH_2$

LXVI



LXVII

Thus, it seems from these FTIR spectra that there is some difference in the way that the FP and UFP can be incorporated into the non-extractable film. The FP (LXII) does have an allyl functionality and probably this can undergo crosslinking reactions with the allyloxy compound and itself. However, the UFP (LXI) would not be expected to participate in the free radical crosslinking of the allyloxy compound but probably becomes entrapped in the crosslinked matrix of the dried blend. The trends observed for the proportions of ester polymers in films using the modified 'cymel 303-type' compounds, being less sensitive to the nature of the polymer, could imply that film formation from the unmodified compounds of this type merely entrapped the ester polymers (FP and UFP).

Although the observations from the FTIR spectra did give some idea of how much polymer is incorporated in the non-extractable film, this approach also showed severe limitations; e.g. no results could be determined for the ethanol/3 AGE drying system and it was difficult to obtain a good KBr disc for some of the films. Thus, it was felt that an alternative approach would be necessary for the examination of the non-extractable film in order to confirm these results and provide some information about the ethanol/3 AGE drying system.

‡ These idealised structures (LVIII, LIX, LXVI and LXVII) will be referred to as the names given in the text but they may also be referred to as follows:-

(i) (LVIII), tris-(N-allyloxymethyl-N-methoxymethyl) melamine,

(ii) (LIX), tris-(N-methallyloxymethyl-N-methoxymethyl) melamine,

(iii) (LXVI), tris-(N-(allyloxy, ethoxy, ethoxy, ethoxy, ethoxymethyl)-N-methoxymethyl)melamine,

(iv) (LXVII), tris-(N-(methallyloxy, ethoxy, ethoxy, ethoxy, ethoxymethyl)-N-methoxymethyl)melamine.

2.2.2 Investigations concerned with the extent of film formation from drying systems based upon allyl ethers

The drying systems and blends listed in section 2.2 were used in the following studies.

Determinations of the amounts of soxhlet extractable material (a) as compared with the amounts applied to microscope slides (a+b) and the amounts of non-extractable material (b) deduced by subtraction, after room temperature drying for 24 hrs, 48 hrs, 1 wk and 5 weeks, are represented in the following tables:-

(i) table 14 - cymel 303/3 allyl alcohol blends,

(ii) table 15 - cymel 303/3 methallyl alcohol blends,

(iii) table 16 - cymel 303/3 (4.2(EO) + allyl alcohol) blends,

(iv) table 17 - cymel 303/3 (4.2(EO) + methallyl alcohol) blends,

(v) table 18 - ethanol/3 AGE blends.

Graphs of $\frac{b}{a+b}$ plotted against time are illustrated in figures 2.2.2.1, 2.2.2.2, 2.2.2.3, 2.2.2.4 and 2.2.2.5 corresponding to data in tables 14-18. (For experimental details, see section 3.5.5).

These weighing experiments were repeated with the cymel 303/3 allyl alcohol drying system using fresh samples and similar results were obtained. The exact values of (a), (b) and (a+b) were not reproducible from the different batches, but the same trends in the crosslinking ability of the separate blends were observed.

Table 14 (Mass/g)$^+$

BLEND	FRACTION	DRYING TIME BEFORE EXTRACTION			
		24 hours	48 hours	1 week	5 weeks
(i) 1					
cymel 303/3 allyl alcohol	a + b	0.4111	0.4257	0.4368	0.5011
+ Co(II) bis-(2-ethyl-	a	0.4064	0.3005	0.1917	0.1273
hexanoate) + solvent	b	0.0047	0.1252	0.2451	0.3738
	$\frac{b}{a+b}$	0.0114	0.2941	0.5611	0.7460
(i) 2					
cymel 303/3 allyl alcohol	a + b	0.3450	0.3500	0.3480	0.3290
+ FP + Co(II) bis-(2-ethyl-	a	0.2748	0.2314	0.1639	0.1250
hexanoate) + solvent	b	0.0702	0.1186	0.1841	0.2040
	$\frac{b}{a+b}$	0.2035	0.3389	0.5290	0.6201
(i) 3					
cymel 303/3 allyl alcohol	a + b	0.3548	0.3196	0.3358	0.3424
+ UFP + Co(II) bis-(2-ethyl-	a	0.3694	0.3048	0.2444	0.2194
hexanoate) + solvent	b	-	0.0148	0.0914	0.1230
	$\frac{b}{a+b}$	*	0.0463	0.2722	0.3592

* conclude that crosslinking is negligible

$^+$ errors ~ ±0.0161

Table 15 (mass/g)$^{+}$

BLEND	FRACTION	DRYING TIME BEFORE EXTRACTION 24 hours	48 hours	1 week	5 weeks
(ii) 1	a + b	0.4356	0.4267	0.4241	0.3560
cymel 303/3 methallyl	a	0.4398	0.4244	0.3830	0.3220
alcohol + Co(II)	b	-	0.0023	0.0411	0.0340
bis-(2-ethylhexanoate) + solvent	$\frac{b}{a+b}$	*	0.0054	0.0969	0.0955
(ii) 2	a + b	0.3254	0.3306	0.3250	0.3052
cymel 303/3 methallyl	a	0.3044	0.2813	0.2697	0.1920
alcohol + FP + Co(II)	b	0.0210	0.0493	0.0553	0.1132
bis-(2-ethylhexanoate) + solvent	$\frac{b}{a+b}$	0.0645	0.1491	0.1702	0.3709
(ii) 3	a + b	0.3056	0.2985	0.3101	0.2891
cymel 303/3 methallyl	a	0.3199	0.2936	0.3044	0.3020
alcohol + UFP + Co(II)	b	-	0.0049	0.0057	-
bis-(2-ethylhexanoate) + solvent	$\frac{b}{a+b}$	*	0.0164	0.0184	*

*conclude that crosslinking is negligible

$^{+}$errors ~ ±0.0161

Table 16 (Mass/g)$^{+}$

BLEND	FRACTION	DRYING TIME BEFORE EXTRACTION			
		24 hours	48 hours	1 week	5 weeks
(iii) 1					
cymel 303/3 (4.2(EO) +	a + b	0.4060	0.3646	0.3394	0.2961
allyl alcohol) + Co(II)	a	0.1032	0.1271	0.1675	0.1383
bis-(2-ethylhexanoate)	b	0.3028	0.2375	0.1719	0.1578
+ solvent	$\frac{b}{a+b}$	0.7458	0.6514	0.5065	0.5329
(iii) 2					
cymel 303/3 (4.2(EO) +	a + b	0.3308	0.3273	0.3013	0.2684
allyl alcohol) + FP	a	0.1178	0.1089	0.1066	0.1362
+ Co(II) bis-(2-ethyl-	b	0.2130	0.2184	0.1947	0.1322
hexanoate) + solvent	$\frac{b}{a+b}$	0.6439	0.6673	0.6462	0.4925
(iii) 3					
cymel 303/3 (4.2(EO) +	a + b	0.3352	0.3689	0.3286	0.3038
allyl alcohol) + UFP +	a	0.2377	0.2510	0.1947	0.2759
Co(II) bis-(2-ethyl-	b	0.0975	0.1179	0.1339	0.0279
hexanoate) + solvent	$\frac{b}{a+b}$	0.2909	0.3196	0.4075	0.0918

$^{+}$ errors ~ ±0.0161

Table 17 (Mass/g)$^{+}$

BLEND	FRACTION	DRYING TIME BEFORE EXTRACTION			
		24 hours	48 hours	1 week	5 weeks
(iv) 1					
cymel 303/3 (4.2(EO) +	a + b	0.3731	0.3745	0.2863	0.1868
methallyl alcohol) + Co(II)	a	0.2752	0.3260	0.2796	0.1368
bis-(2-ethylhexanoate) +	b	0.0979	0.0485	0.0067	0.0500
solvent	$\frac{b}{a+b}$	0.2624	0.1295	0.0234	0.2677
(iv) 2					
cymel 303/3 (4.2(EO) +	a + b	0.3296	0.3244	0.3012	0.2394
methallyl alcohol) + FP +	a	0.1502	0.1470	0.1404	0.1655
Co(II) bis-(2-ethyl-	b	0.1794	0.1774	0.1608	0.0739
hexanoate) + solvent	$\frac{b}{a+b}$	0.5443	0.5469	0.5339	0.3087
(iv) 3					
cymel 303/3 (4.2(EO) +	a + b	0.3427	0.3227	0.3073	0.2622
methallyl alcohol) + UFP +	a	0.2980	0.2694	0.2571	0.2454
Co(II)bis-(2-ethyl-	b	0.0447	0.0533	0.0502	0.0168
hexanoate) + solvent	$\frac{b}{a+b}$	0.1304	0.1652	0.1634	0.0641

$^{+}$ errors ~ ±0.0161

Table 18 (Mass/g)$^{+}$

BLEND	FRACTION	DRYING TIME BEFORE EXTRACTION 24 hours	48 hours	1 week	5 weeks*
(v) 1 EtOH/3AGE + Co(II) bis-	a + b	0.4617	0.4845	0.4748	-
(2-ethylhexanoate) +	a	0.1112	0.0933	0.0918	-
solvent	b	0.3505	0.3912	0.3830	-
	$\frac{b}{a+b}$	0.7592	0.8074	0.8067	-
(v) 2 EtOH/3AGE + FP + Co(II)	a + b	0.3074	0.3025	0.3129	-
bis-(2-ethylhexanoate) +	a	0.1036	0.0802	0.0644	-
solvent	b	0.2038	0.2223	0.2485	-
	$\frac{b}{a+b}$	0.6630	0.7349	0.7942	-
(v) 3 EtOH/3AGE + UFP + Co(II)	a + b	0.3366	0.3344	0.3480	-
bis-(2-ethylhexanoate) +	a	0.1850	0.1351	0.1341	-
solvent	b	0.1516	0.1993	0.2139	-
	$\frac{b}{a+b}$	0.4504	0.5960	0.6147	-

*reaction seems almost complete after 1 week

$^{+}$errors ~± 0.0161

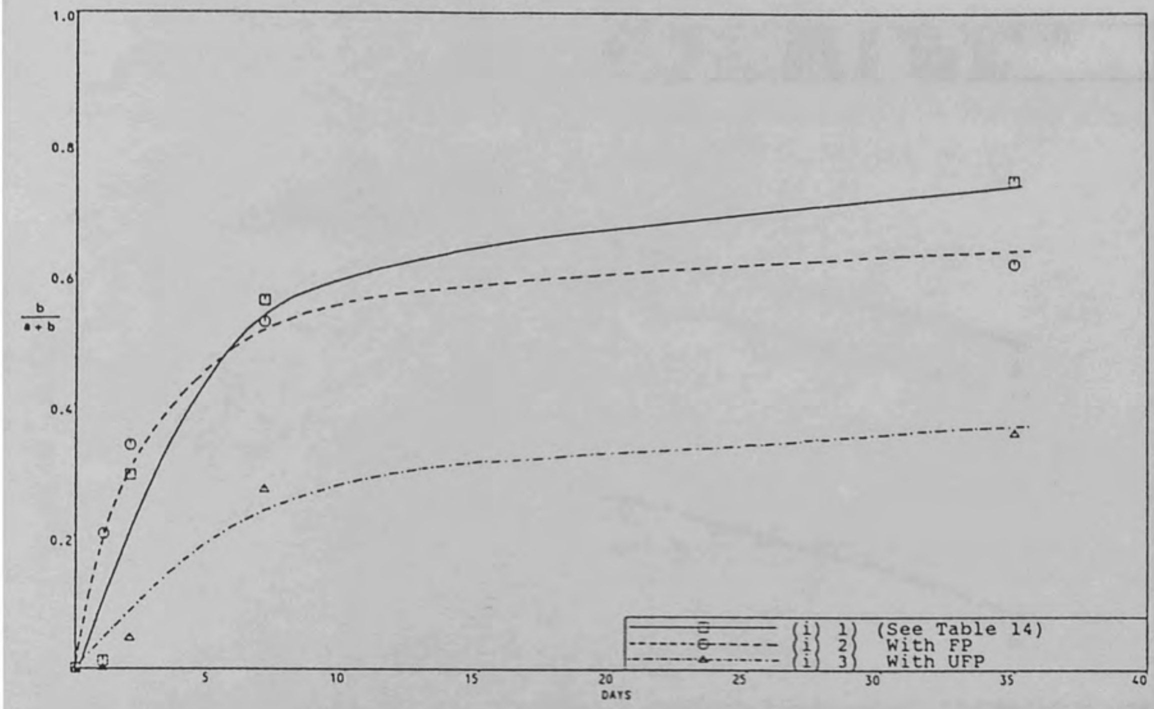


Fig 2.2.2.1 Graph to show b/(a+b) against Time
for blends prepared using Cymel 303/3 Allyl Alcohol(i)

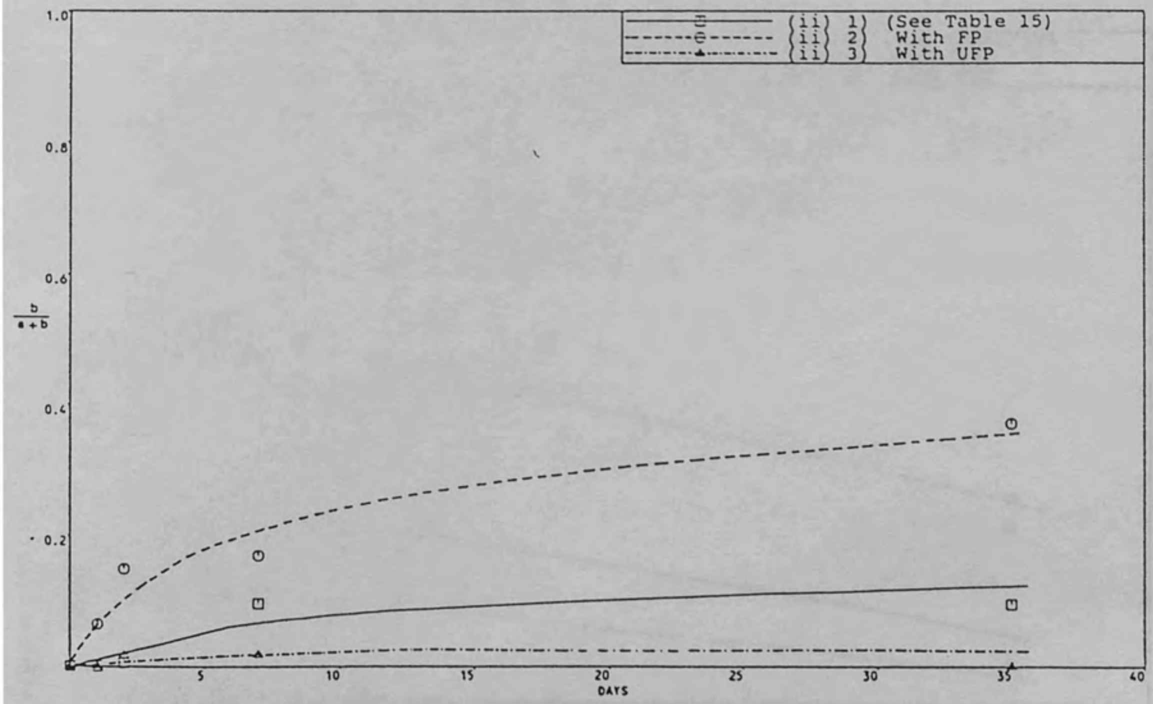


Fig 2.2.2.2 Graph to show b/(a+b) against Time
for blends prepared using Cymel 303/3 Methallyl Alcohol(ii)

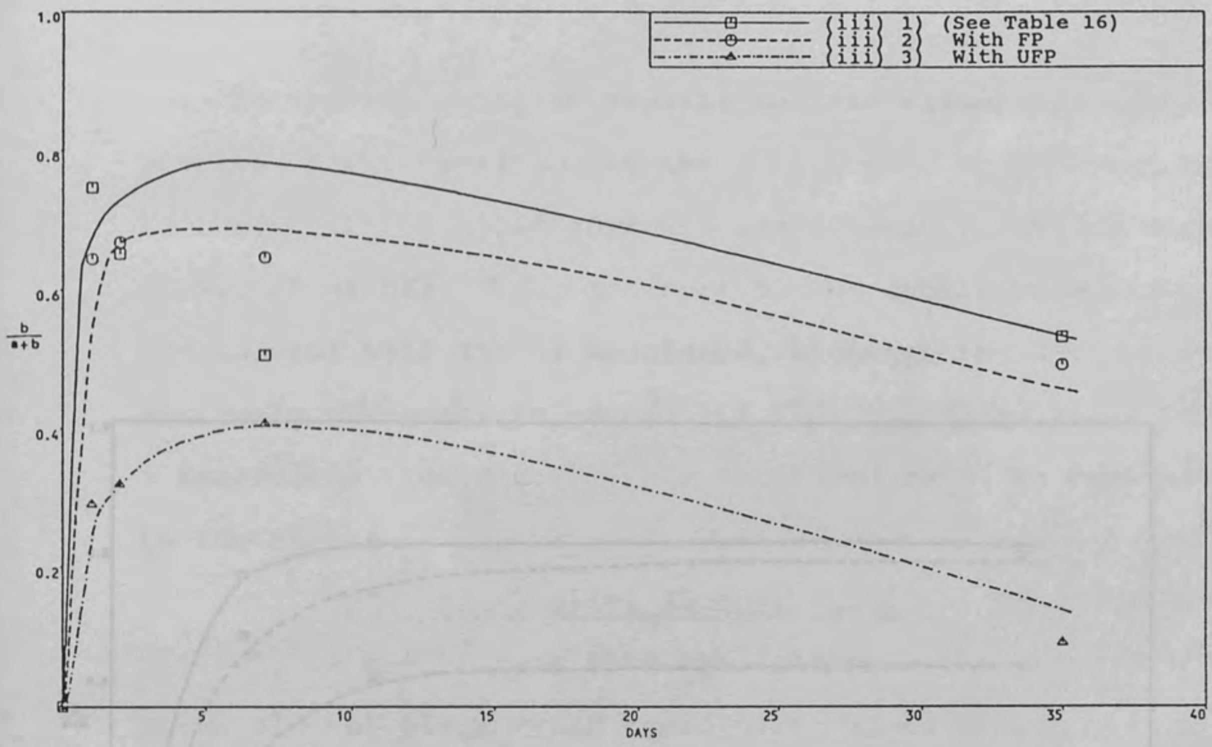


Fig 2.2.2.3 Graph to show b/(a+b) against Time
for blends prepared using Cymel 303/3 (4.2(EO) + Allyl Alcohol) (iii)

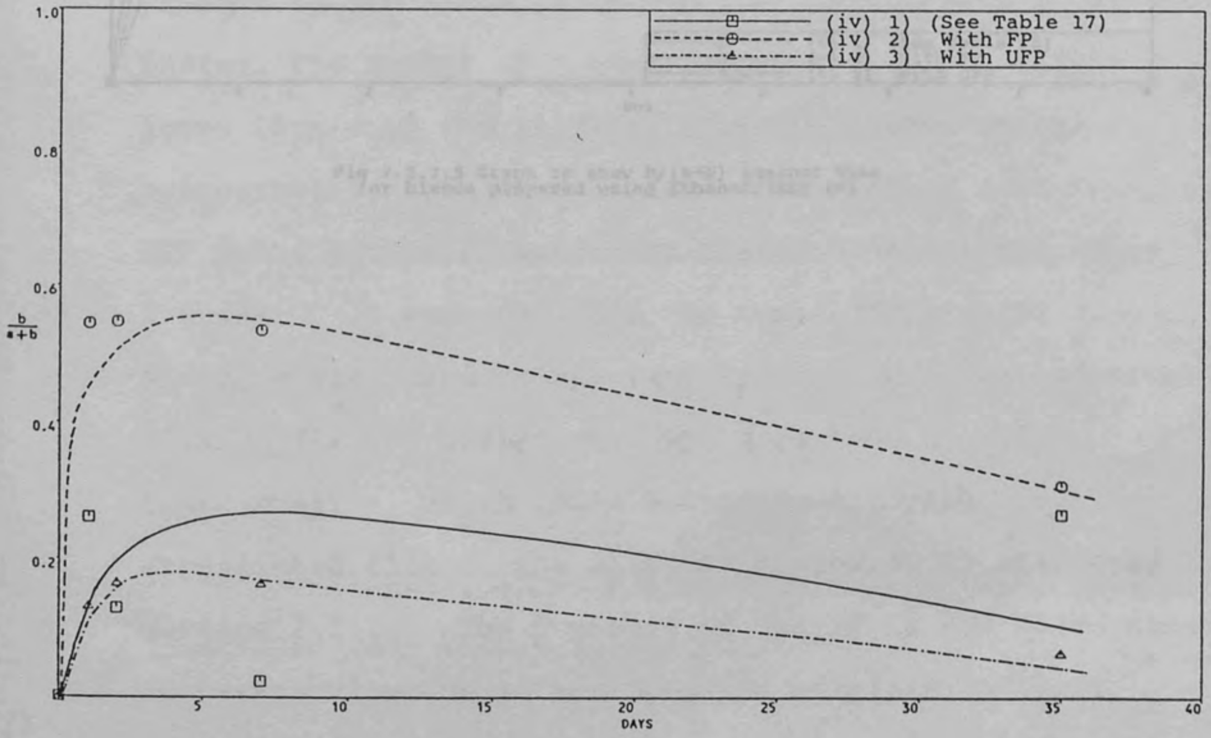


Fig 2.2.2.4 Graph to show b/(a+b) against Time
for blends prepared using Cymel 303/3 (4.2(EO) + Methallyl Alcohol) (iv)

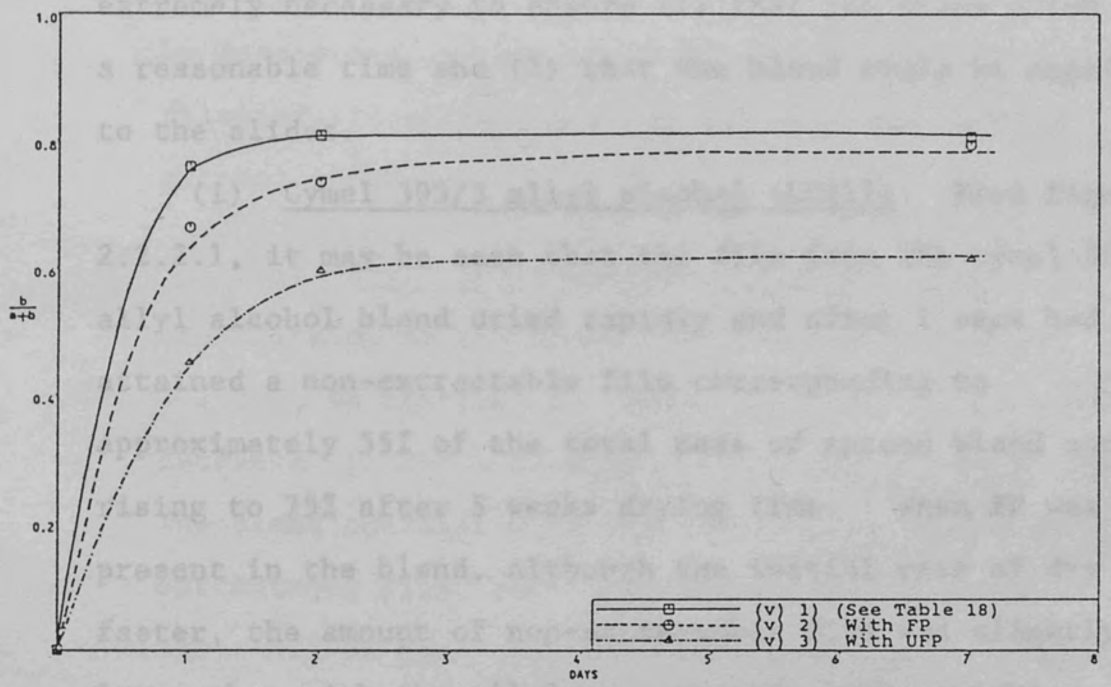


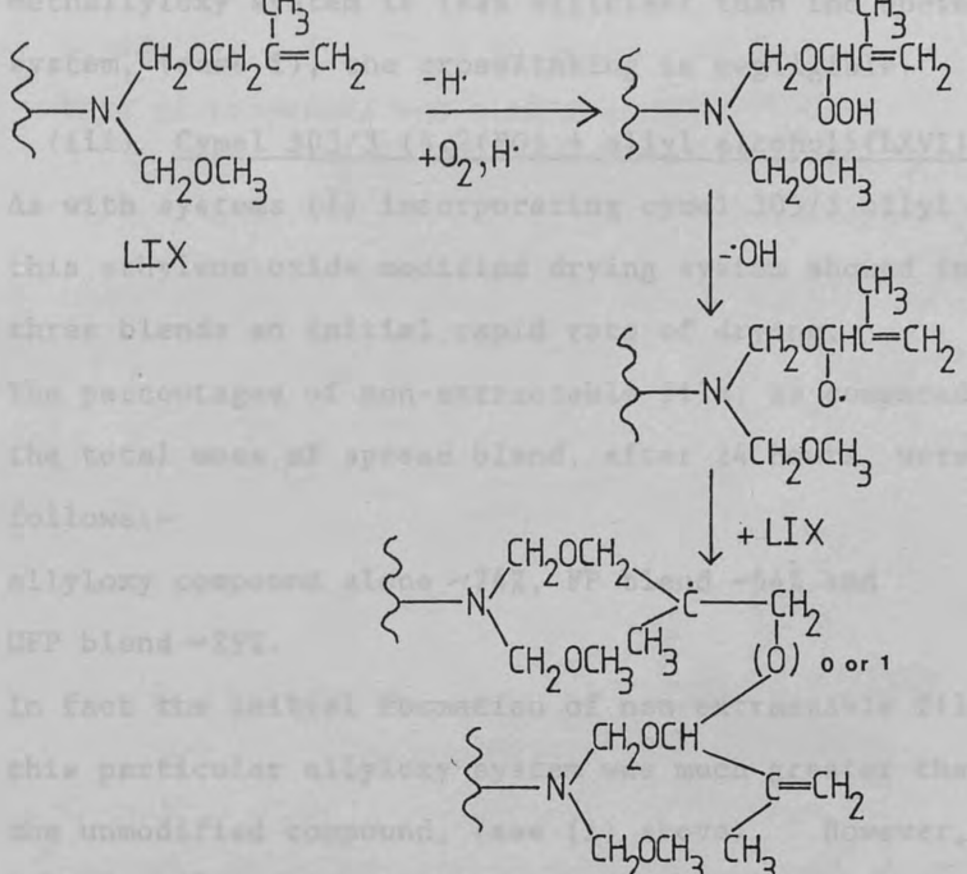
Fig 2.2.2.5 Graph to show b/(a+b) against Time for blends prepared using Ethanol/3AGE (v)

In the following interpretation and discussion of the results, the composition of the blends will be referred to as though the allyloxy compound was present alone, or with either FP or UFP. The presence of the cobalt promoter and solvent will not be mentioned, although these were extremely necessary to ensure (1) that the films dried in a reasonable time and (2) that the blend could be applied to the slides.

(i) Cymel 303/3 allyl alcohol (LVIII): From figure 2.2.2.1, it may be seen that the film from the cymel 303/3 allyl alcohol blend dried rapidly and after 1 week had attained a non-extractable film corresponding to approximately 55% of the total mass of spread blend and rising to 75% after 5 weeks drying time. When FP was present in the blend, although the initial rate of dry was faster, the amount of non-extractable film was slightly lower than with the allyloxy compound alone, reaching approximately 65% after 5 weeks. The blend containing the UFP dried at the slowest rate rising to about 35% after 5 weeks. It appeared that the cymel 303/3 allyl alcohol alone, crosslinked fairly rapidly to give a non-extractable film. The FP, unlike the UFP, does have an allyl functionality, which could become incorporated in the crosslinked film of the allyloxy compound, as discussed in section 2.2.1. The presence of the FP in the blend seems to have a dilution effect upon the allyloxy radicals undergoing crosslinking, reducing the amount of non-extractable film formed; some of the FP may become incorporated and some may just be entangled in the crosslinking chains. The presence of the UFP in the blend causes even less non-extractable film formation, as in this case the UFP may only be present in the film by entrapment and the ester polymer causes an even greater diluting effect on the crosslinking cymel 303/3 allyl alcohol compound.

(ii) Cymel 303/3 methallyl alcohol (LIX): The crosslinking of the cymel 303/3 methallyl alcohol, figure 2.2.2.2, in contrast to figure 2.2.2.1, showed a marked decrease in the amount of non-extractable film present. The blend containing FP had the largest amount of non-extractable film, after 5 weeks drying time, which was about 37% of the total mass of spread blend, whereas the allyloxy system on its own was only at about 10%. The blend containing the UFP showed only a slight tendency to crosslink.

The polymerisation of allyl ether compounds normally proceeds by the initial formation of α-alkoxyallyl hydroperoxides, which then decompose leading to cross-linking, (see section 1.11). However, with the cymel 303/3 methallyl alcohol compound, the presence of a methyl group attached to a carbon of the double bond may lead to steric hindrance. Reaction will be impeded whenever a methallyl radical or the corresponding alkoxy radical approaches another double bond bearing a methyl substituent, during the crosslinking of the film[178], (see scheme 2.2.2.1).

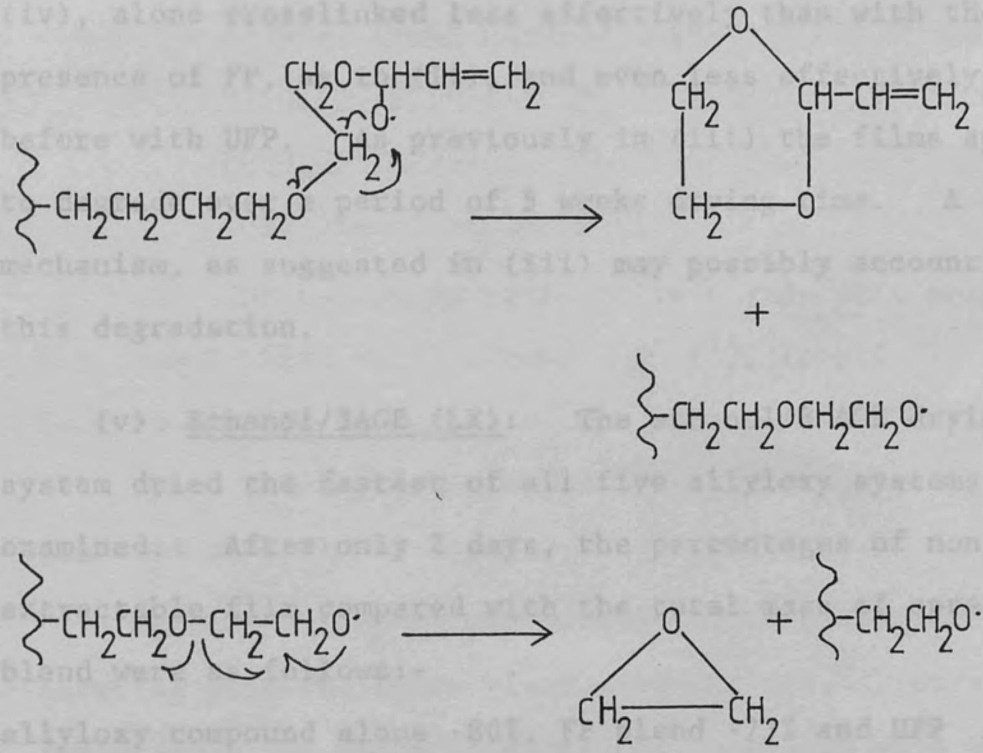


Scheme 2.2.2.1

This "lack of dry" of methallyl ether compounds has been previously observed.[158] If now the relative rate of crosslinking consequent upon the decomposition of hydroperoxides formed on the allyl function of the polymer exceeds that for the cymel 303/3 methallyl alcohol, then more of the crosslinking would be expected to incorporate the FP and to occur more readily than with the methallyloxy compound alone. The amount of non-extractable film from the blend containing FP does indeed exceed that for the cymel 303/3 methallyl alcohol alone. The UFP can only become entrapped in the crosslinking film and since this methallyloxy system is less efficient than the above drying system, (case i), the crosslinking is negligible.

(iii) Cymel 303/3 (4.2(EO) + allyl alcohol)(LXVI):
As with systems (i) incorporating cymel 303/3 allyl alcohol, this ethylene oxide modified drying system showed in all three blends an initial rapid rate of drying.
The percentages of non-extractable film, as compared with the total mass of spread blend, after 24 hours, were as follows:-
allyloxy compound alone ~74%, FP blend ~64% and
UFP blend ~29%.
In fact the initial formation of non-extractable film with this particular allyloxy system was much greater than with the unmodified compound, (see (i) above). However, after 5 weeks drying time, it was evident that rather than increasing in the amount of non-extractable material formed, the films were degrading in some way, since the percentage of non-extractable film decreased for all three blends, (see figure 2.2.2.3). It was thought that the effect of either FP or UFP on this allyloxy system, (iii) could be accounted for in a similar manner to case (i) above.

The method of degradation may occur by a type of 'de-polymerisation' mechanism, whereby the alkoxy radical attacks an ethylene oxide within the same chain causing fission of the cymel 303/3 (4.2 (EO) + allyl alcohol) compound. A suggestion for this mechanism is shown in scheme 2.2.2.2. This phenomenon of degradation of these type of compounds has been observed.[151]



Scheme 2.2.2.2.

(iv) <u>Cymel 303/3 (4.2(EO) + methallyl alcohol)(LXVII)</u>: The cymel 303/3 methallyl alcohol modified with EO also showed a similar trend as in case (iii). Again all three blends dried more rapidly than the corresponding blends, (ii), using cymel 303/3 methallyl alcohol. The percentages of non-extractable film, after 24 hours, were about 26% for the allyloxy system alone, approximately 54% for the blend with FP and about 13% for the blend containing UFP, (see figure 2.2.2.4). Again the allyloxy system, (iv), alone crosslinked less effectively than with the presence of FP, as in (ii), and even less effectively as before with UFP. As previously in (iii) the films appeared to degrade over a period of 5 weeks drying time. A similar mechanism, as suggested in (iii) may possibly account for this degradation.

(v) <u>Ethanol/3AGE (LX)</u>: The ethanol/3 AGE drying system dried the fastest of all five allyloxy systems examined. After only 2 days, the percentages of non-extractable film compared with the total mass of spread blend were as follows:-
allyloxy compound alone ~80%, FP blend ~73% and UFP blend ~59%.
In fact after 1 week of drying the crosslinking reactions seemed almost complete. As previously described the effect of the presence of either FP or UFP in the blend can be accounted for as in case (i).

Overall, it appears that the crosslinking ability of ethanol/3 AGE is the best of all the five allyloxy systems, followed by cymel 303/3 allyl alcohol. Cymel 303/3 methallyl alcohol shows a much less efficient film formation and the long term stability of allyloxy compounds modified with EO is poor. The presence of UFP seems to slow the rate of film formation, as does FP, but the effect is not quite so apparent as with UFP.

2.3 Radioactivity studies - investigations concerned with the crosslinking ability of blends based upon cymel 303/3 allyl alcohol and either ^{14}C labelled FP or ^{14}C labelled UFP

The following radioactive blends were prepared:-

(1) cymel 303/3 allyl alcohol, FP (^{14}C labelled), Co promoter and solvent,

(2) cymel 303/3 allyl alcohol, UFP (^{14}C labelled), Co promoter and solvent.

Determinations of the activities of the extractable material from the above blends (1) and (2), dried at room temperature for given time periods, together with the amounts of material applied to the microscope slides, after solvent evaporation, (a + b) are shown in tables 21 and 22 respectively. The radioactivity of known masses of ^{14}C labelled FP and UFP was also measured, as well as the non-radioactive polymers and cymel 303/3 allyl alcohol. These results are shown in tables 19 and 20.

For experimental details see sections 3.6, 3.7, 3.8 and 3.9.

Table 19

CPM* of known masses of FP and UFP (^{14}C labelled)

Polymer	Mass/g	CPM	CPM g^{-1}
FP	0.1000	2,851	28,510
	0.1751	5,394	30,805
	0.2000	5,377	26,885
UFP	0.1000	4,629	46,290
	0.1751	7,418	42,364
	0.2000	8,931	44,655

* CPM (counts per minute)

Mean CPM g^{-1} for FP = 28,733

Mean CPM g^{-1} for UFP = 44,436

(% error 6.86%)

Table 20

Background CPM for non-radioactive FP, UFP and allyl ether compound

Compound	Mass/g	CPM	CPM g^{-1}
FP	0.1751	43	246
UFP	0.1751	41	234
Cymel 303/3 allyl alcohol	0.1751	42	240

As the CPM g^{-1} for the non-radioactive materials was less than 1% of the CPM g^{-1} for the radioactive polymers, no allowance was made for this background radiation in the following calculations.

Extraction of the films at time = 0 hr was used to determine the amount of radioactive polymers applied to the microscope slides. Since the blends consisted of 1:1 mixture of allyloxy compound and polymer, the total mass of spread film, at t = 0 hr, was given by:

mass of spread film = 2 x mass of polymer .

The CPM for different extraction times were normalised to permit comparisons between these figures, the data at time = 0 hr being used as a reference as follows:-

$$\text{Normalised CPM at X hr} = \text{CPM at X hr} \times \frac{(a+b) \text{ at 0 hr}}{(a'+b') \text{ at X hr}} .$$

The normalised CPM was used to determine the amount of extractable polymer present by comparison with the CPM of a known mass of radioactive polymer as follows:-

$$\text{Mass of extractable polymer at X hr} = \text{Normalised CPM at X hr} \div \text{Mean CPM g}^{-1} \text{ of radioactive polymer.}$$

Hence, the amount of non-extractable polymer present in the crosslinked film at X hr was found by subtracting the mass of extractable polymer at X hr from the reference mass of polymer at 0 hr.

The CPM data for these extraction studies using ^{14}C labelled FP is shown in table 21 and for the ^{14}C labelled UFP in table 22. Graphs showing the amount of polymer incorporated in the non-extractable film against time are illustrated in figures 2.3.1 and 2.3.2 corresponding to FP and UFP.

With blend 1,(FP), only the 12 hr extraction gave a negative value (table 21), whereas with blend 2, (UFP), several of the earlier extractions gave rise to a negative figure (table 22). In the initial stages of drying, when the amount of crosslinked film is minimal, particularly with the blend containing UFP, the experimental conditions used may show some limitation. However, any systematic experimental errors incurred will be similar with either blend. Thus, these negative values were treated as though negligible crosslinking had occurred.

Table 21

Radiolabelling data for drying of cymel 303/3 allyl alcohol and FP, (blend 1)

Time	Material on slides after solvent evaporation/g (a + b)	CPM	Normalised CPM	Mass of FP determined from normalised count/g	Mass of FP incorporated in non-extractable film/g
0 hr	(0.3404)	4891	4891	0.1702	0.0000
12 hr	0.3036	5099	5334	0.1856	-(0.0154)
24 hr	0.3174	4800	4803	0.1672	0.0030
48 hr	0.3034	3714	3888	0.1353	0.0349
72 hr	0.3073	3404	3518	0.1224	0.0478
5 days	0.3372	3411	3213	0.1118	0.0584
1 wk	0.3530	2516	2264	0.0788	0.0914
18 days	0.3174	2329	2330	0.0811	0.0891
4 wks	0.3081	2177	2244	0.0781	0.0921

Table 22

Radiolabelling data for drying of cymel 303/3 allyl alcohol and UFP, (blend 2)

Time	Material on slides after solvent evaporation/g (a + b)	CPM	Normalised CPM	Mass of UFP determined from normalised count/g	Mass of UFP incorporated in non-extractable film/g
0 hr	(0.3608)	8015	8015	0.1804	0.0000
12 hr	0.3575	8083	8556	0.1925	-(0.0121)
24 hr	0.3653	7777	8056	0.1813	-(0.0009)
48 hr	0.3556	7434	7911	0.1780	0.0024
72 hr	0.3532	7590	8132	0.1830	-(0.0026)
5 days	0.3518	7592	8166	0.1838	-(0.0034)
1 wk	0.3733	7825	7932	0.1785	0.0019
18 days	0.3659	5936	6139	0.1382	0.0422
4 wks	0.3546	7181	7663	0.1725	0.0079

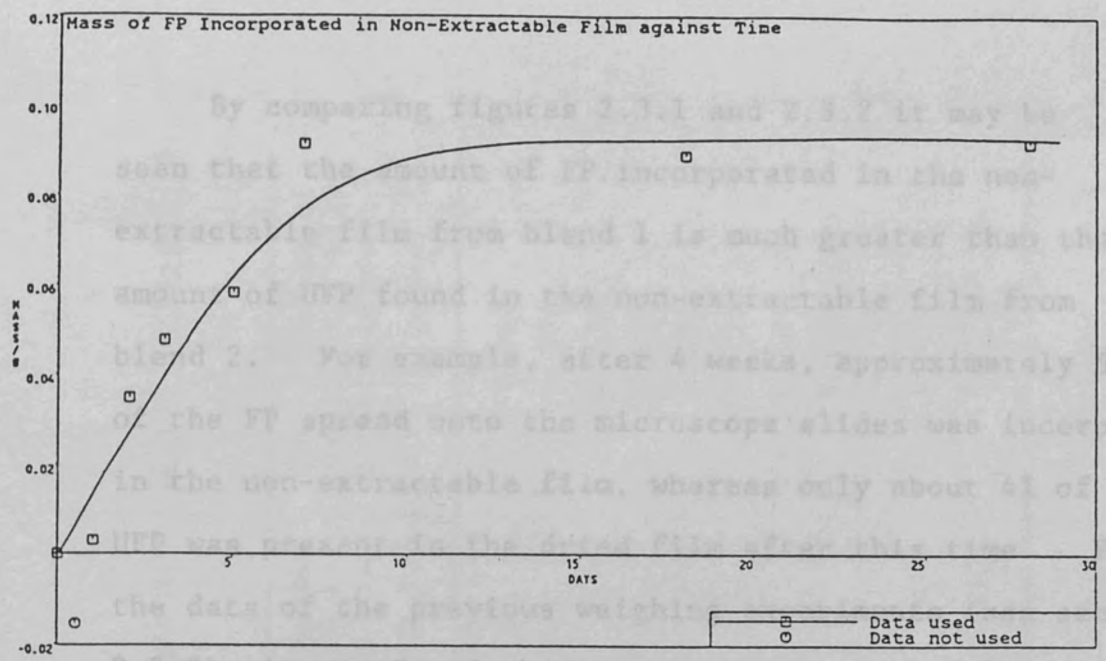


Fig 2.3.1 Graph to show amount of Functional Polymer(FP) which remains on Slides after Extraction (i.e. amount of FP incorporated in Film)

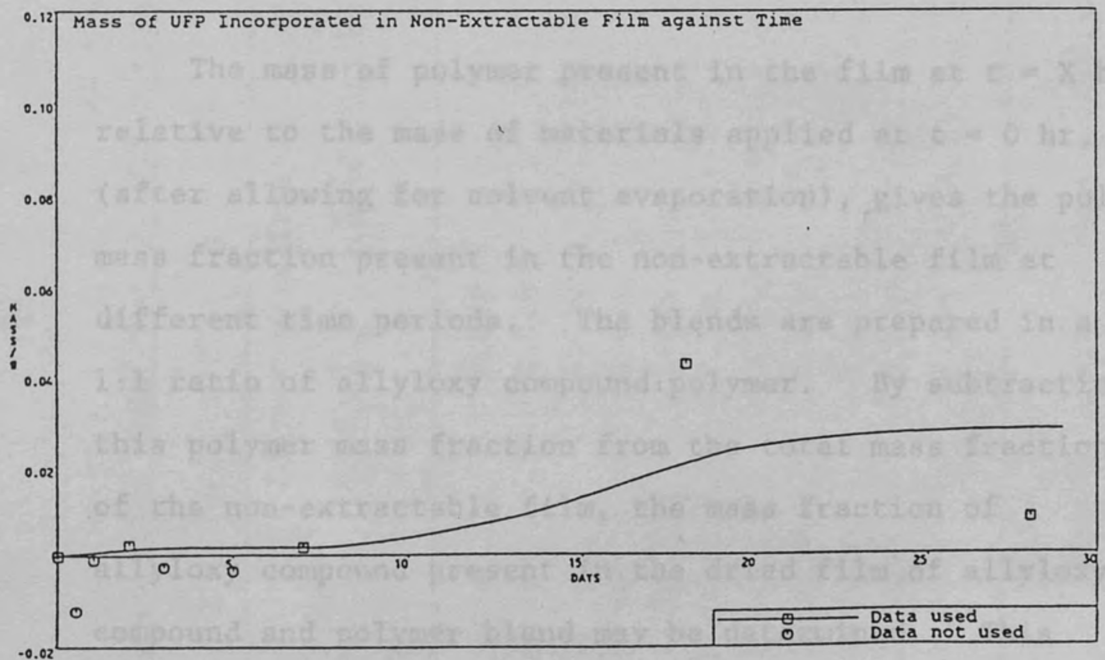


Fig 2.3.2 Graph to show amount of Unfunctional Polymer(UFP) which remains on Slides after Extraction (i.e. amount of UFP incorporated in Film)

By comparing figures 2.3.1 and 2.3.2 it may be seen that the amount of FP incorporated in the non-extractable film from blend 1 is much greater than the amount of UFP found in the non-extractable film from blend 2. For example, after 4 weeks, approximately 50% of the FP spread onto the microscope slides was incorporated in the non-extractable film, whereas only about 4% of the UFP was present in the dried film after this time. From the data of the previous weighing experiments (see section 2.2.2), it was found that more non-extractable film was produced from the cymel 303/3 allyl alcohol blend containing FP than with the corresponding blend containing UFP. By using this data and the above results from the radio-labelling investigations, some idea of the composition of the dried film may be obtained, vide infra.

The mass of polymer present in the film at t = X hr relative to the mass of materials applied at t = 0 hr, (after allowing for solvent evaporation), gives the polymer mass fraction present in the non-extractable film at different time periods. The blends are prepared in a 1:1 ratio of allyloxy compound:polymer. By subtracting this polymer mass fraction from the total mass fraction of the non-extractable film, the mass fraction of allyloxy compound present in the dried film of allyloxy compound and polymer blend may be determined. This composition data of the dried film using FP (blend 1) is shown in table 23 and for UFP (blend 2) in table 24.

Table 23

Composition data[*] for the dried film of cymel 303/3 allyl alcohol and FP (blend 1)

Time	Polymer mass fraction $\frac{\text{mass of FP in film at X hr}}{2 \times 0.1702}$	Total mass fraction for cymel 303/3 allyl alcohol and FP film ($\frac{b}{a+b}$ from fig.2.2.2.1)	Mass fraction of cymel 303/3 allyl alcohol present in film
0 hr	0.000	0.000	0.000
12 hr	0.024	0.100	0.076
24 hr	0.050	0.165	0.115
48 hr	0.094	0.300	0.206
72 hr	0.129	0.375	0.246
5 days	0.191	0.470	0.279
1 wk	0.229	0.515	0.286
11 days	0.259	0.555	0.296
18 days	0.261	0.595	0.334
23 days	0.261	0.625	0.364
4 wks	0.264	0.645	0.381

[*] Some data points were determined using information from figures 2.2.2.1 and 2.3.1.

Table 24

Composition data* for the dried film of cymel 303/3 allyl alcohol and UFP (blend 2)

Time	Polymer mass fraction $\frac{\text{mass of UFP in film at X hr}}{2 \times 0.1804}$	Total mass fraction for cymel 303/3 allyl alcohol and UFP film ($\frac{b}{a+b}$ from fig.2.2.2.1)	Mass fraction of cymel 303/3 allyl alcohol present in film
0 hr	0.000	0.000	0.000
12 hr	0.000	0.015	0.015
24 hr	0.000	0.035	0.035
48 hr	0.006	0.070	0.064
72 hr	0.006	0.105	0.099
5 days	0.006	0.180	0.174
1 wk	0.011	0.250	0.239
11 days	0.030	0.285	0.255
18 days	0.055	0.305	0.250
23 days	0.064	0.315	0.251
4 wks	0.067	0.320	0.253

*Some data points were determined using information from figures 2.2.2.1 and 2.3.2.

Graphs showing the composition of the dried films formed from these blends are illustrated in figures 2.3.3 and 2.3.4.

It appears that after 4 weeks drying time the ratio of allyloxy compound:FP in the non-extractable film from the cymel 303/3 allyl alcohol and FP blend is almost 1:1, (figure 2.3.3), although there is slightly more of the allyloxy compound present in the dried film. However, during the initial stages of drying the composition of the film shows a larger proportion of allyloxy compound present than FP. With the cymel 303/3 allyl alcohol and UFP blend, the composition of the dried film after 4 weeks drying time appears to contain a much larger proportion of allyloxy material than UFP, (figure 2.3.4). In the initial stages of drying the film seems to consist virtually of polymerised allyloxy compound alone. These observations seem to suggest that after 4 weeks drying time, whereas the FP can make up quite a large proportion of the non-extractable film, the UFP cannot. The allyl functionality of the FP probably enables this polymer to become actively involved in the crosslinking reactions of the cymel 303/3 allyl alcohol. However, it would appear that the UFP can probably only become entrapped in the crosslinking matrix of the allyloxy compound. In the initial stages of drying, it seems relatively easy to extract the UFP and, as shown, the composition of the dried film is mainly crosslinked allyloxy compound.

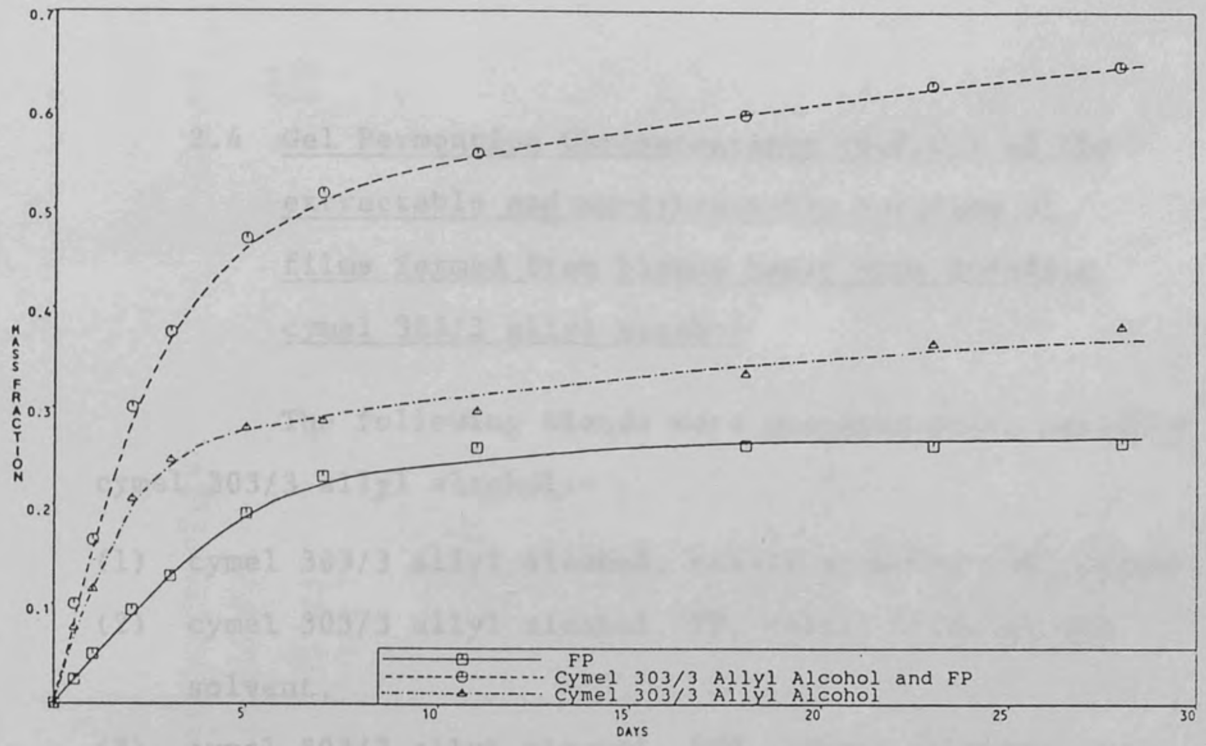


Fig 2.3.3 Graph to show Composition data of Dried Film from Cymel 303/3 Allyl Alcohol and FP (blend 1) against Time

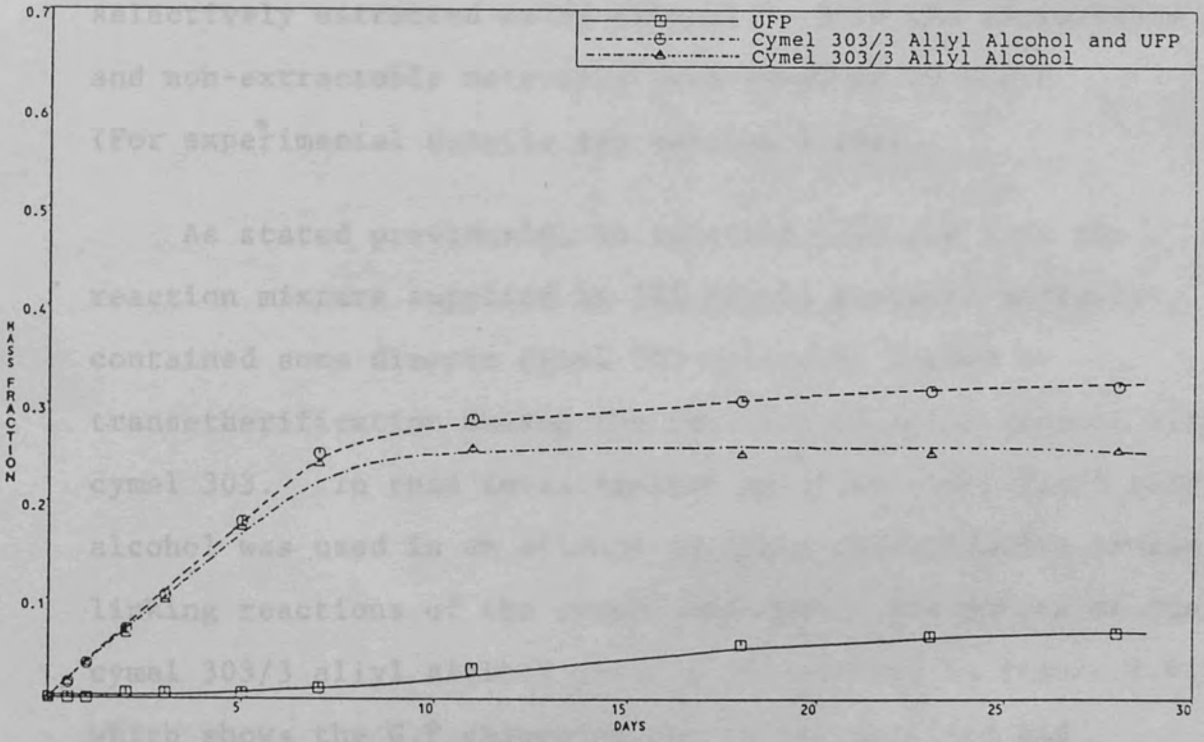


Fig 2.3.4 Graph to show Composition data of Dried Film from Cymel 303/3 Allyl Alcohol and UFP (blend 2) against Time

2.4 Gel Permeation Chromatography (G.P.C.) of the extractable and non-extractable portions of films formed from blends based upon purified cymel 303/3 allyl alcohol

The following blends were prepared using purified cymel 303/3 allyl alcohol:-

(1) cymel 303/3 allyl alcohol, cobalt promoter and solvent,
(2) cymel 303/3 allyl alcohol, FP, cobalt promoter and solvent,
(3) cymel 303/3 allyl alcohol, UFP, cobalt promoter and solvent.

These blends, allowed to dry for given times, were selectively extracted using ethanol. Both the extractable and non-extractable materials were examined by G.P.C. (For experimental details see section 3.10).

As stated previously, in sections 1.10 and 3.3, the reaction mixture supplied by ICI Paints Division probably contained some dimeric cymel 303 molecules formed by transetherification during the reaction of allyl alcohol with cymel 303. In this investigation purified cymel 303/3 allyl alcohol was used in an attempt to limit the oxidative cross-linking reactions of the cymel compound. The purity of the cymel 303/3 allyl alcohol used is illustrated in figure 2.4.1, which shows the G.P.chromatograms of the purified and unpurified cymel 303/3 allyl alcohol. A G.P.C. examination was also made of the FP and UFP, see figure 2.4.2.

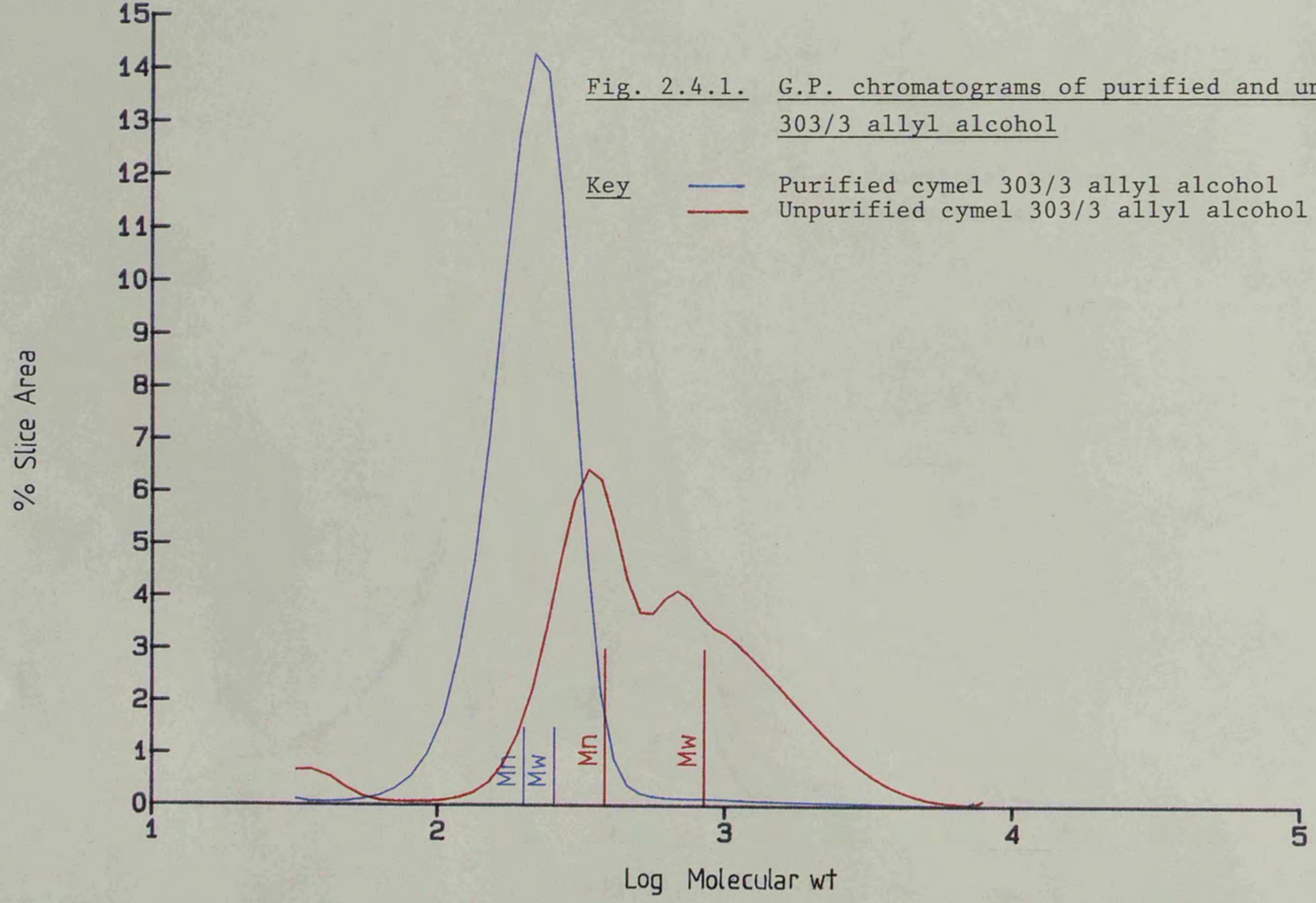


Fig. 2.4.1. G.P. chromatograms of purified and unpurified cymel 303/3 allyl alcohol

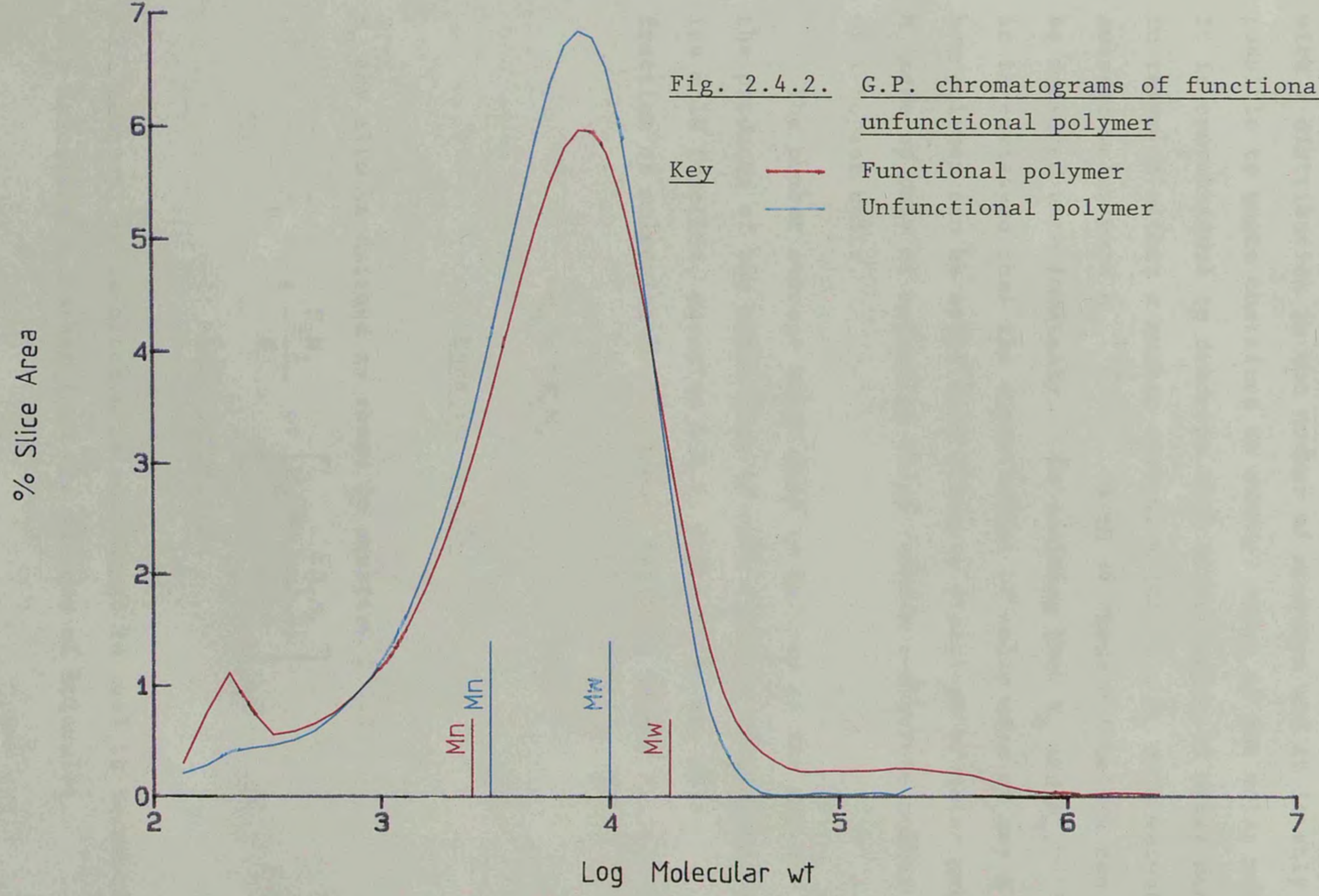


Fig. 2.4.2. G.P. chromatograms of functional polymer and unfunctional polymer

Typical synthetic polymers contain mixtures of molecules with a distribution in the number of monomers and it is only possible to quote therefore an average value of the molar mass. It is conventional to describe this distribution of molar mass in terms of either a number average molar mass $\bar{M}_n$ or a weight average molar mass $\bar{M}_w$.[179,180] Both of these parameters can be measured experimentally. In defining both $\bar{M}_n$ and $\bar{M}_w$, it is envisaged that the distribution of molar mass of say a homopolymer can be split into discrete fractions of molar mass M_i made up only of molecules which contain a discrete number of i repeat units.

The number average molar mass is defined as the sum of the products of the molar mass of each fraction multiplied by its mole fraction, equation 2.4.1, where X_i is the mole fraction of molecules formed from i monomers namely $\frac{N_i}{N}$.

$$\bar{M}_n = \Sigma X_i M_i$$

Equation 2.4.1.

$\bar{M}_n$ may also be defined as shown in equation 2.4.2.

$$\bar{M}_n = \Sigma \frac{N_i M_i}{N} \quad \text{or} \quad \left[\bar{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \right]$$

Equation 2.4.2.

However, it is often more convenient to deal in terms of mass fractions w_i rather than the numbers of molecules.

The mass fraction w_i is defined as the mass of molecules formed from i monomers divided by the total mass of all the molecules, (equation 2.4.3).

$$w_i = \frac{N_i M_i}{\Sigma N_i M_i}$$

Equation 2.4.3.

Thus, the weight average molar mass $\bar{M}_w$ is defined as the sum of the products of each fraction multiplied by its mass fraction w_i, equation 2.4.4.

$$\bar{M}_w = \Sigma w_i M_i$$

Equation 2.4.4.

M_w may also be defined as shown in equation 2.4.5, by combining equations 2.4.3 and 2.4.4.

$$\bar{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

Equation 2.4.5.

The G.P.C. traces for the extractable portion of the film from the blend containing cymel 303/3 allyl alcohol alone showed the presence of the unreacted allyl ether compound and possibly oligomers of low molecular mass. These could be extracted even after 1 week of drying time. After the initial 12 hours drying no non-extractable film was present. As the drying time increased, small distributions of higher molecular mass material appeared to be formed, see figure 2.4.3. Figure 2.4.3 shows the chromatograms of the extractable and non-extractable portions of the film after 72 hours drying, together with the trace corresponding to the complete film, (i.e. the addition of chromatograms of the extractable and non-extractable materials).

The G.P. chromatograms of the extractable material obtained from the blends containing either FP or UFP after 12 hours drying showed the presence of both cymel 303/3 allyl alcohol and FP or UFP respectively. However, from the G.P.C. traces it appeared that the contribution from both the allyl ether compound and FP seemed to decrease with time, whereas the contribution of the UFP seemed to remain fairly constant. (Figures 2.4.4 and 2.4.5 correspond to the extractable materials from all three blends after 12 hours and 1 week drying respectively).

The presence of the UFP in the extractable material is illustrated more clearly in figure 2.4.6, using G.P.C. data after 24 hours drying. Here, the chromatographic data corresponding to the extractable part of the film from the allyl ether compound alone,(red line), was subtracted from the data obtained for the extraction of the film of the blend containing UFP, (blue line), leaving the UFP (green line).

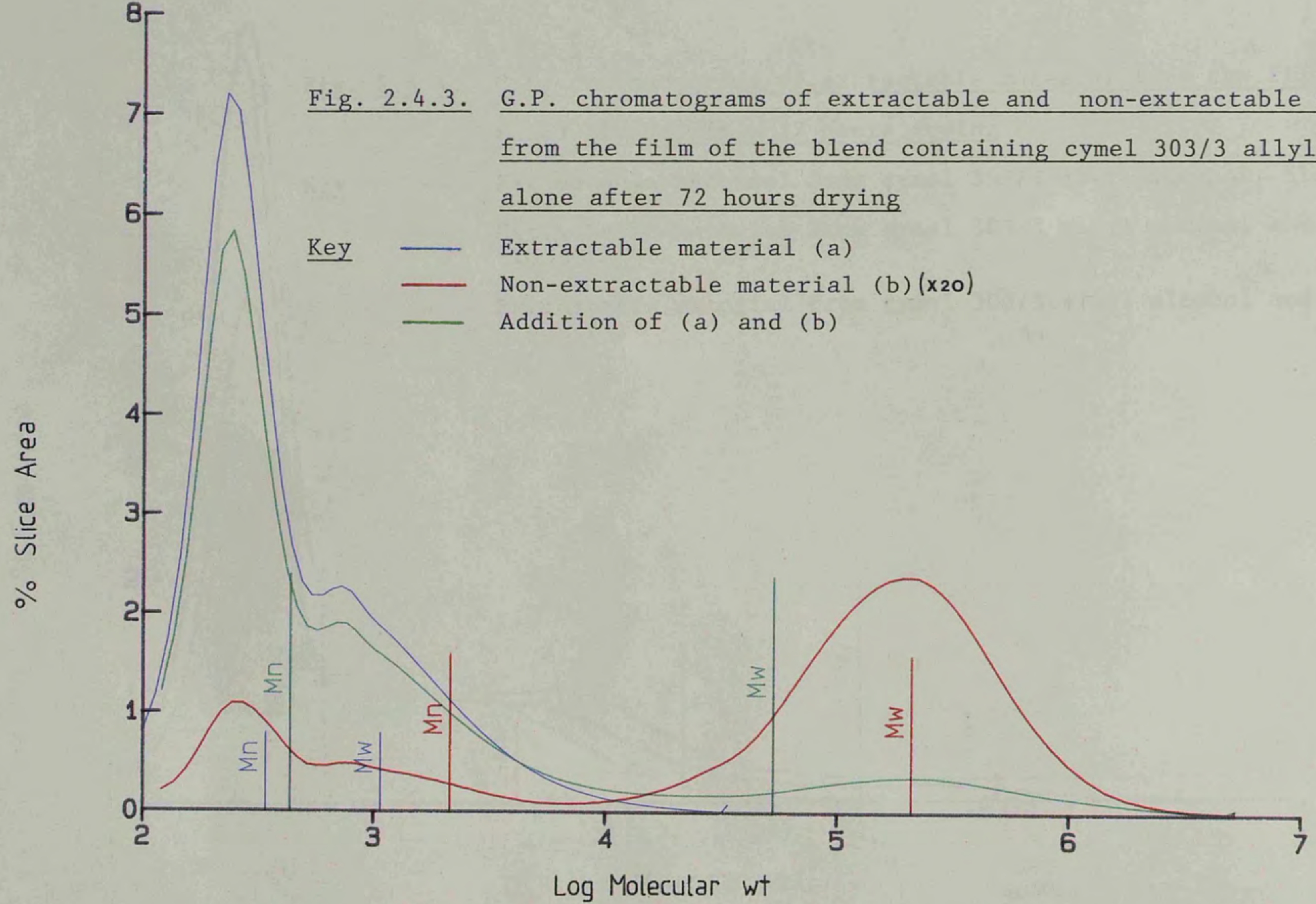


Fig. 2.4.3. G.P. chromatograms of extractable and non-extractable material from the film of the blend containing cymel 303/3 allyl alcohol alone after 72 hours drying

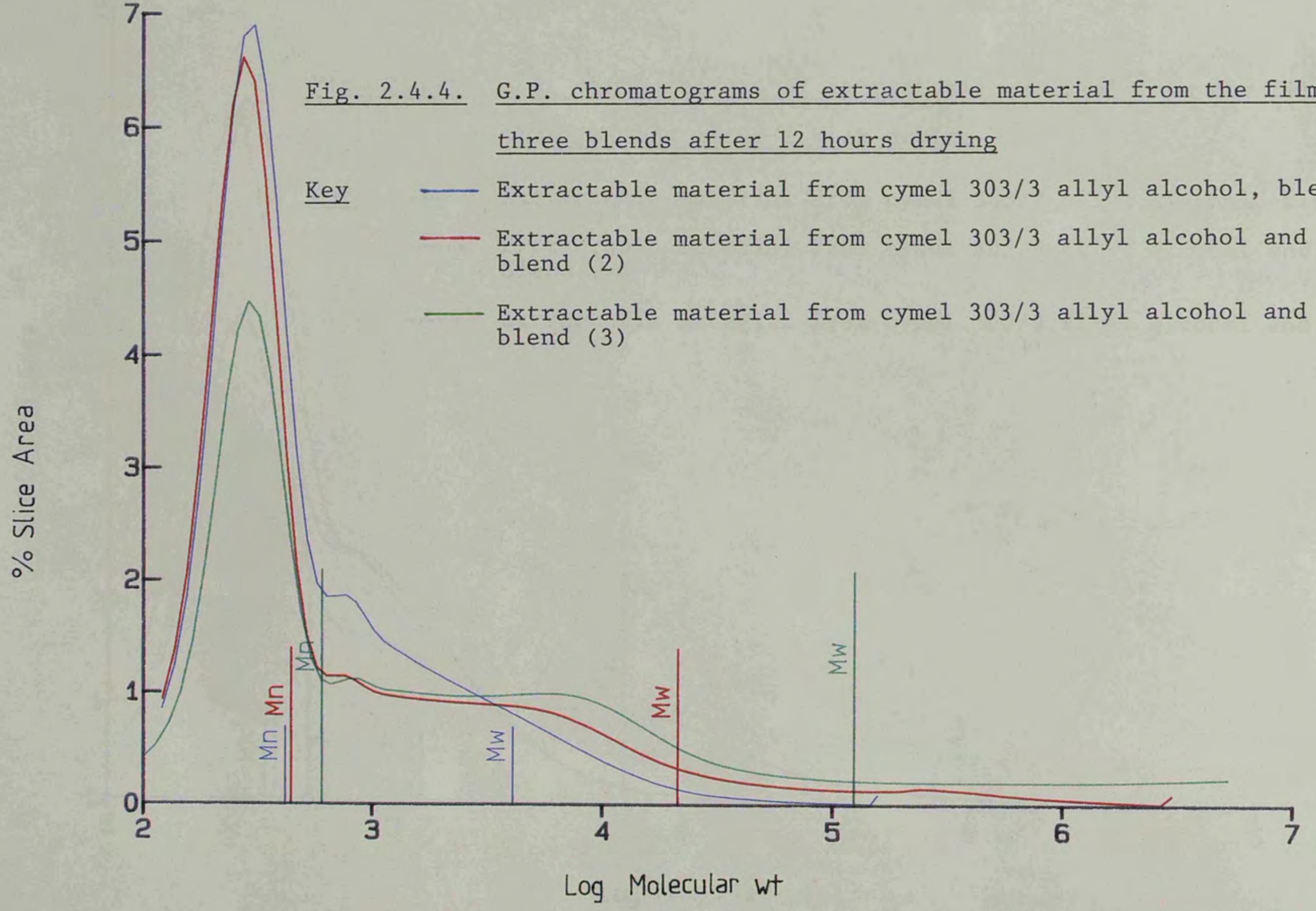


Fig. 2.4.4. G.P. chromatograms of extractable material from the films of all three blends after 12 hours drying

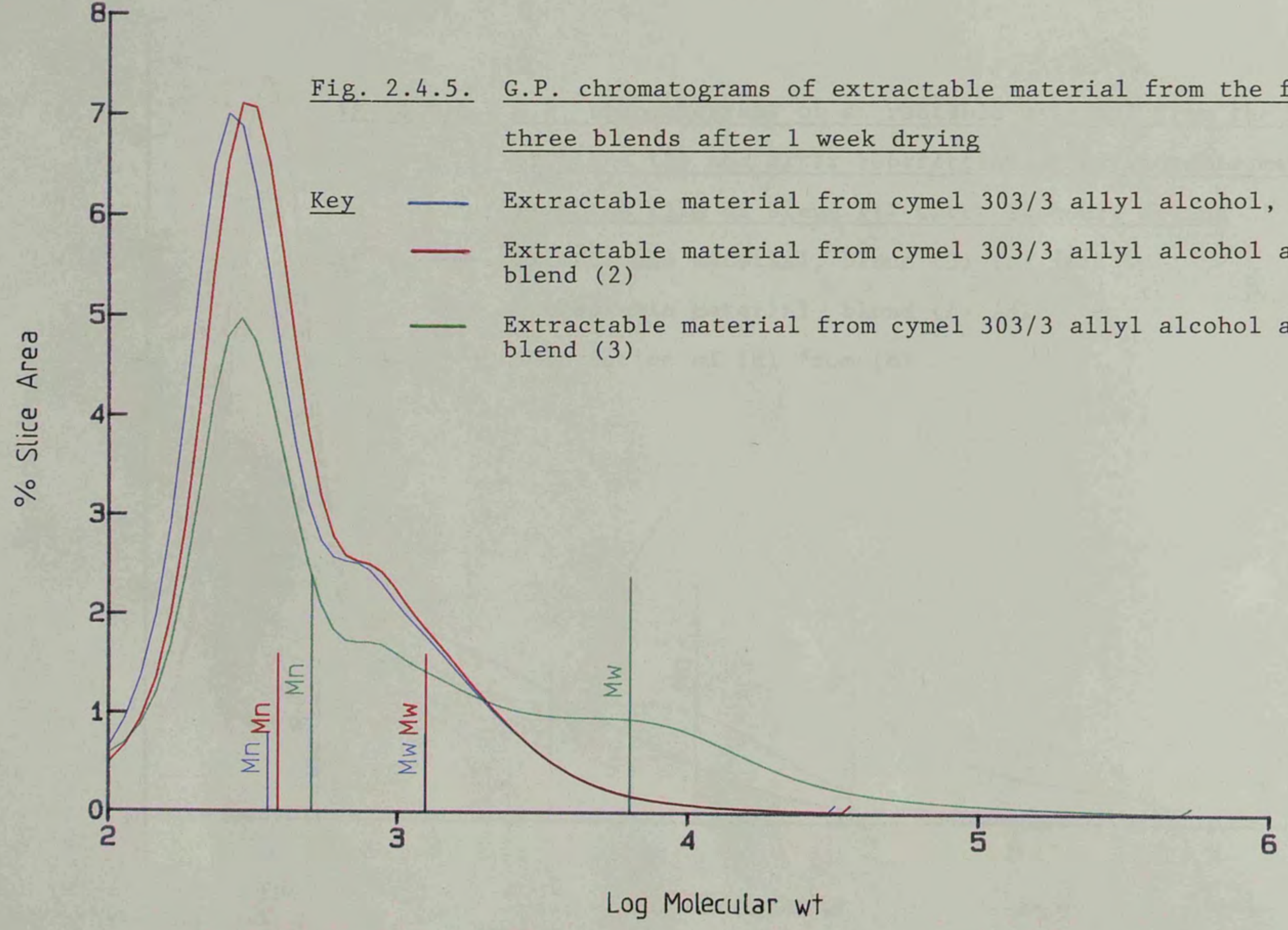


Fig. 2.4.5. G.P. chromatograms of extractable material from the films of all three blends after 1 week drying

Key

— Extractable material from cymel 303/3 allyl alcohol, blend (1)

— Extractable material from cymel 303/3 allyl alcohol and FP, blend (2)

— Extractable material from cymel 303/3 allyl alcohol and UFP, blend (3)

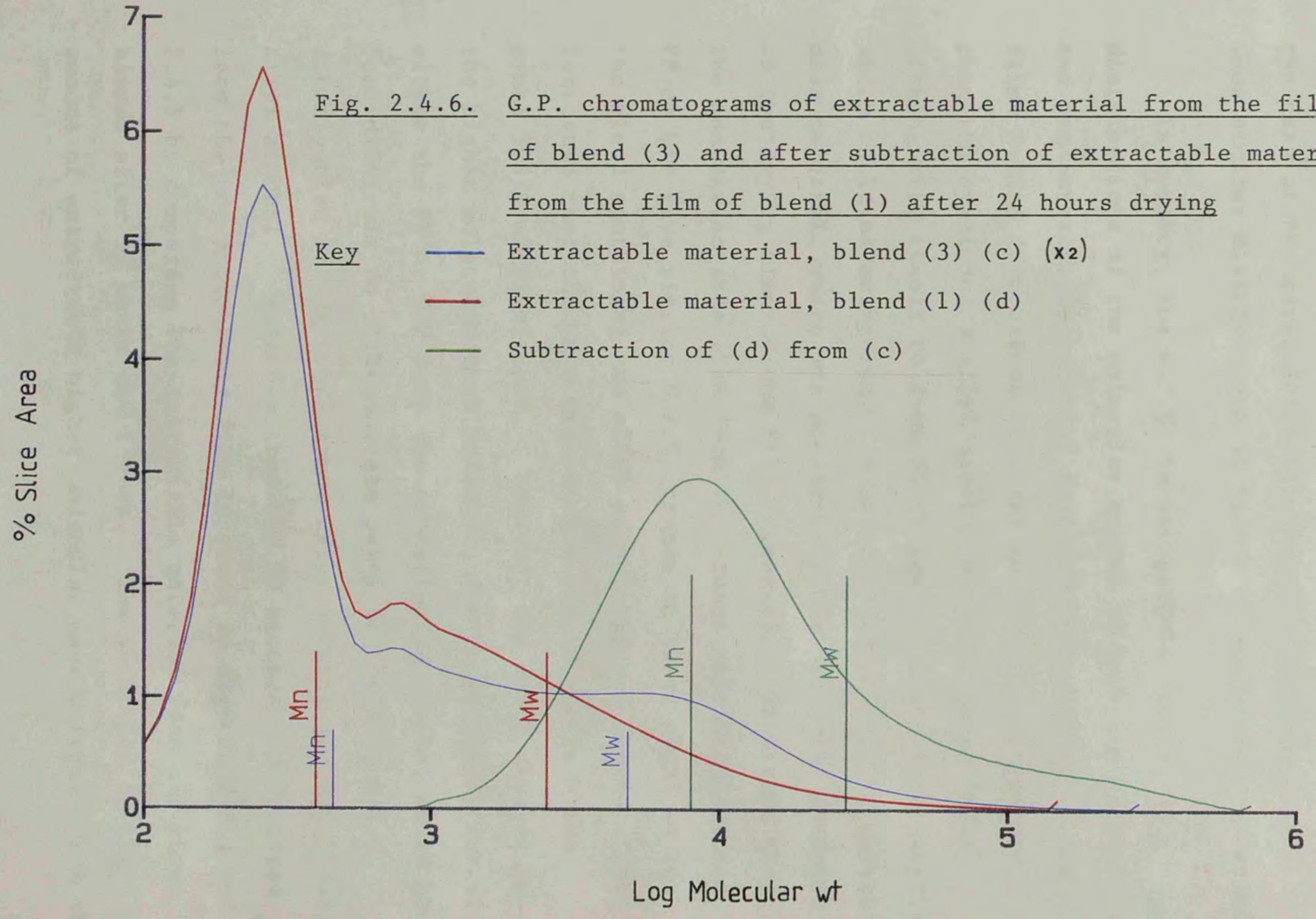


Fig. 2.4.6. G.P. chromatograms of extractable material from the film of blend (3) and after subtraction of extractable material from the film of blend (1) after 24 hours drying

The G.P. chromatograms of the non-extractable material obtained from the blends containing either FP or UFP, as in the case of the cymel 303/3 allyl alcohol all appeared to show similar distributions of higher molecular mass material.

In summary, the G.P.C. investigations showed the distributions of the molecular masses of both the extractable and non-extractable material found upon extraction of the films formed from blends (1), (2) and (3). It appeared that the cymel 303/3 allyl alcohol was capable of crosslinking with itself to form first low molecular mass material, which could be extracted. A distribution of higher molecular mass material, which was non-extractable, was also detected as the drying time of the film increased. It seemed that the non-extractable film from the blends containing either FP or UFP gave similar G.P.C. traces to those obtained for the blend containing the allyl ether compound alone. This indicated that the main crosslinked matrix was from the cymel 303/3 allyl alcohol. However, any small changes in the higher molecular mass material, due to incorporation of either the FP or UFP into the crosslinking matrix, would have been difficult to differentiate owing to the wide G.P.C. distribution of the crosslinked material from the cymel 303/3 allyl alcohol. Evidence that the FP becomes incorporated into the non-extractable film is shown in figures 2.4.4 and 2.4.5 by comparing the extractable material from all three blends after 12 hours and 1 week. The reduction in the amount of extractable higher molecular mass material from the

FP blend after 1 week would possibly indicate the incorporation of the FP in the crosslinked film, whereas the UFP appeared to be still extractable after 1 week. As previously discussed, the UFP is probably only entrapped in the crosslinked matrix, whereas the FP having an allyl functionality is able to participate in the crosslinking reaction (see section 2.2.1).

As some problems were encountered in preparing the samples for G.P.C. analysis, e.g., it was difficult to ascertain exactly how much of the non-extractable film dissolved in THF in preparing the G.P.C. sample, all samples were treated in exactly the same manner, in order to minimise experimental error.

The G.P.C. analysis provided another method of examining the crosslinking ability of a drying system based upon one of the novel allyl ether compounds. The information obtained, although not as quantitative as the IR, weighing and radioactivity data, (see sections 2.2.1, 2.2.2 and 2.3), nevertheless, still showed the same pattern of crosslinking of the cymel 303/3 allyl alcohol as found in these previous studies. In addition it is observed that the structure of the film is dominated by the polymerised cymel 303/3 allyl alcohol. The molecular mass of the idealised structure of cymel 303/3 allyl alcohol (LVIII) is 468 g, which means that there are 3 moles of allyl alcohol per 468 g. The mass composition of the functional polymer is based upon having reacted 1 mole of AGE per 1 kg of polymer (table 6,section

1.10). As all the blend preparations containing the polymers were made in a 1:1 mass ratio of allyl ether compound:polymer, then the ratio of the number of moles of allyl group in the allyl ether compound: functional polymer is 6.4:1. This means there is a greater probability of an allyl group, attached to a cymel 303 molecule, finding a similarly positioned allyl group to undergo crosslinking reactions, than finding a pendant allyl group incorporated in the functional polymer chain.

2.5 Yellowing of paint films

It has long been recognised that not only does autoxidation lead to the successful drying of traditional alkyd paints, but also to the production of odourous volatile degradation products and 'yellowing of films'. As mentioned in section 1.2,it was in an effort to avoid these undesirable properties that led to the development of newer types of drying system based on allyl ethers. These were thought to be less susceptible to form yellow products.

It is know that the traditional alkyd paints yellow with age, particularly in the dark, and that the tendency to yellow may be accelerated by heat[181] and ammoniacal atmospheres. In addition discoloration has been shown in the presence of either organic base or hydrochloric acid vapours.[181] Other atmospheric conditions such as the presence of tobacco smoke and an increased relative humidity may also promote yellowing.[181] Under all these conditions, although the outcome is the same, i.e. the paint film yellows, it may well be that the mechanism in each case is different; for example, it could be that when the paint film is placed in the ammonia atmosphere, the ammonia reacts with products in the film rather than acts as a base. In other environments precursors could be formed, perhaps by degradation of the film, which react further to give yellow compounds. These precursors and/or these yellow compounds themselves could be strongly susceptible to reaction with ammonia.

The scope of this present work has been limited mainly to the effects of yellowing in the dark, accelerated only by the presence of heat.

2.5.1 'Yellowing' of traditional alkyd based paints and paints based on allyl ethers (novel drying systems)

A series of paint blends were prepared using either an alkyd resin, or an allyl ether system as the film former, (for experimental details see section 3.11). The paint blends prepared were as follows:-

(i) soya bean oil alkyd (long oil length),
(ii) oleic acid alkyd,
(iii) linoleic acid alkyd,
(iv) cymel 303/3 allyl alcohol, (LVIII),
(v) cymel 303/3 (3-methyl-3-buten-2-ol), (CLXXIX),
(vi) a commercially available white alkyd gloss paint (used as a standard).

Each paint was separately spread on tin plate panels and subjected to different environments for 1 week. Any yellowing of the paint was detected by measuring its reflectance in order to determine the colour index (CI).[182] Increasing positive values of CI indicate an increase in the yellow tone of the paint. The results of the yellowing tests are shown in table 25.

In all three test conditions - the ammonia atmosphere, 40°C in the dark and 70°C in the dark, the four traditional alkyd based paints all showed appreciable yellowing. The ΔCI values from the panels placed in an ammonia atmosphere were higher because of the severity of the test. However, at different oven temperatures the oleic acid alkyd paint gave smaller ΔCI values than the linoleic acid alkyd paint, thus showing that less unsaturation in the alkyd could lead to less yellowing. The panels at room temperature in the light showed some slight change both positively and negatively.

The paints based on the novel drying system of allyloxy compounds gave the smallest ΔCI values for all test conditions. A problem encountered with the cymel 303/3 (3-methyl-3-buten-2-ol) paint was that, although it gave the best non-yellowing results, the degree of cross-linking was very small, as measured by the number of 'xylene rubs' required to break down the dried film.

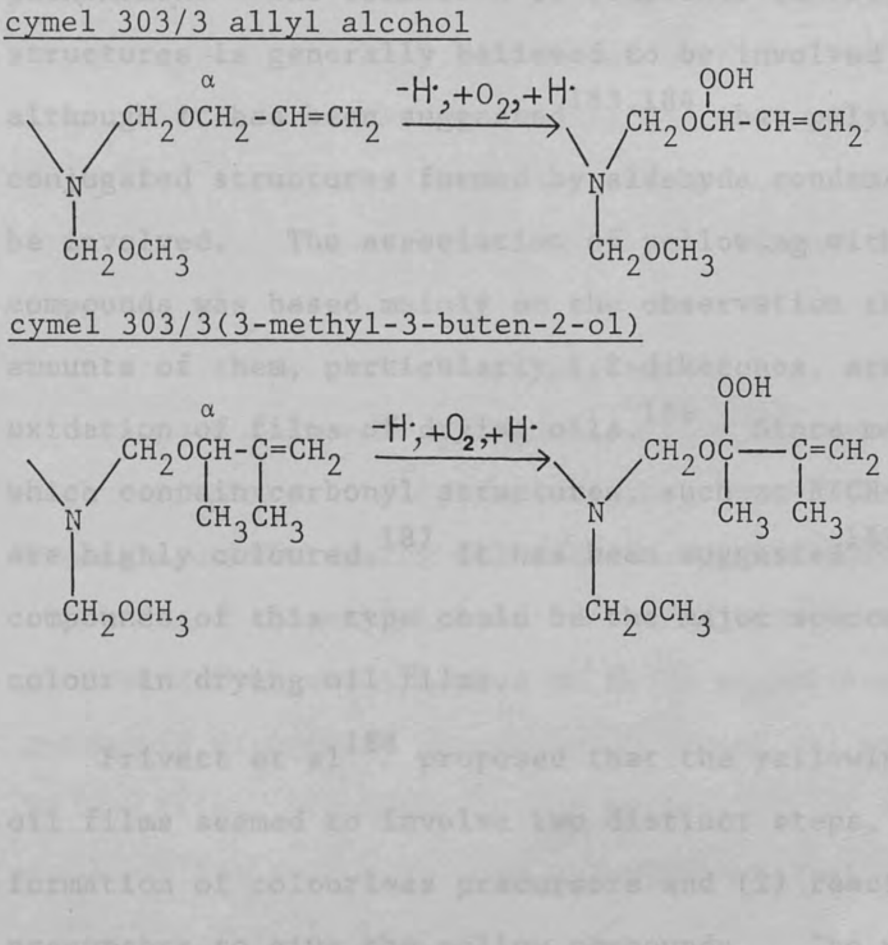
Table 25

Paint Blend	CI Values	Ammonia Atmosphere	$40^{o}C$ in dark	$70^{o}C$ in dark	Room temperature ($22^{o}C$) in light
(i) Soya bean	Final CI	15.39	5.12	10.45	2.35
oil alkyd	Initial CI	2.60	2.38	2.60	2.38
	ΔCI	12.79	2.74	7.85	-0.03
(ii) Oleic acid	Final CI	16.44	4.23	8.13	2.67
alkyd	Initial CI	2.78	2.64	2.78	2.64
	ΔCI	13.66	1.59	5.35	0.03
(iii) Linoleic	Final CI	15.64	4.76	11.92	2.25
acid alkyd	Initial CI	2.06	2.18	2.06	2.18
	ΔCI	13.58	2.58	9.86	0.07
(iv) Cymel 303/	Final CI	5.20	2.74	5.54	0.95
3 allyl	Initial CI	1.29	1.22	1.29	1.22
alcohol	ΔCI	3.91	1.52	4.25	-0.27

Table 25 (continued)

Paint blend	CI Values	Ammonia Atmosphere	$40^{o}C$ in dark	$70^{o}C$ in dark	Room temperature ($22^{o}C$) in light
(v) Cymel 303/3	Final CI	-0.14	0.46	-1.04	0.94
(3-methyl-3	Initial CI	0.79	0.86	0.79	0.86
buten-2-ol)	ΔCI	-0.93	-0.40	-1.83	0.08
(vi) White alkyd	Final CI	11.95	4.13	9.97	1.82
gloss paint	Initial CI	1.65	1.74	1.65	1.74
(used as standard)	Δ CI	10.30	2.39	8.32	0.08

As a measure of the degree of crosslinking, the amount of lower molecular mass material soluble in xylene was empirically determined; this measure is often referred to as 'xylene rubs'. The polymerisation of allyl ether compounds normally proceeds by the initial formation of α alkoxyallyl hydroperoxides which then decompose, (see section 1.11). The "lack of dry" and crosslinking of the film could have been caused by the reduction in the number of primary sites α to the double bond, as illustrated in scheme 2.5.1.1.



Scheme 2.5.1.1.

As shown from this investigation, the paints prepared using the 'cymel 303-type' compounds were more resistant to yellowing than the alkyd based paints, when placed under the test conditions. However, although the problem of yellowing in dried films has long been recognised, relatively little is known about the chemical nature of the problem. Studies by Johnston and Fitzgerald,[183,184] as well as Hess and O'Hare[185] showed that the higher unsaturated fatty acid components of resins are the main starting materials for the phenomenon. The formation of compounds containing carbonyl structures is generally believed to be involved in yellowing, although it has been suggested[183,184] that polyunsaturated conjugated structures formed by aldehyde condensation may also be involved. The association of yellowing with carbonyl compounds was based mainly on the observation that appreciable amounts of them, particularly 1,2-diketones, are formed in the oxidation of films of drying oils.[186] Since many compounds which contain carbonyl structures, such as $R(CH=CH)_4COCOOH$ are highly coloured,[187] it has been suggested[183] that compounds of this type could be the major source of yellow colour in drying oil films.

Privett et al[188] proposed that the yellowing of drying oil films seemed to involve two distinct steps, (1) the formation of colourless precursors and (2) reaction of the precursors to give the yellow compounds. The workers attempted to isolate these yellow compounds by extraction with dilute base and by adsorption on calcium chloride. However, no specific physical or chemical property could be related quantitatively to the yellow compounds. It was thought that difficulties were encountered from (i) the inhomogenity of the coloured compounds and (ii) the difficulty of concentrating them from non-coloured substances. Of course if the yellow compounds are highly coloured only a few tenths, or hundreths of a percent, may be all that is necessary to produce the colour normally observed in aged films. Robey and Rybicka[181] also tried to isolate the yellow chromophores present in the dried films of methyl esters of drying oil fatty acids using silica column chromatography. They also noted that the yellowing of these films was accelerated by ammonia vapours. McAdie and Nicholls[189] suggested that the yellow colour might result from the presence of benzoquinone structures formed during the oxidation of films of pure esters of linoleic and linolenic acids through cyclisation of some such structure as a conjugated ethenoid diketone. They observed a strong absorption band at 250 mμ during U.V. absorption spectral analysis on the ageing films of methyl linoleate and linolenate. Benzoquinone structures have an absorption band at 245 mμ and this led to their suggestion that quinonoid structures are responsible for the yellow colour in the films. However, other workers[181,188] found no evidence for such quinonoid structures indicating that yellowing must largely be explained in another way. Privett[188] observed that low molecular mass aldehydes, such as propanal and hexanal retarded yellowing promoted by stoving at 50°C in a nitrogen atmosphere.

More recently Rakoff[190] has investigated the reversibility of the yellowing phenomenon in linseed-based paints by observing that such paints can be taken through several cycles of yellowing and bleaching. Other studies on yellowing have been concerned with the drier composition of linseed oil films[191] and the influence of the grade of titanium dioxide[182] used in paint formulation.

2.5.2 Volatile products produced by the autoxidation of unsaturated fatty acid esters

As it seems feasible that the yellowing of alkyd paint films may be related to autoxidative degradation processes, the volatile products so produced from unsaturated fatty acid esters will now be briefly considered. The possible mechanisms whereby some of these compounds are formed will be outlined.

2.5.2.1 Volatile products produced from the autoxidation of methyl oleate

Several workers[192,193,194,195,196] have attempted to characterise the volatile products produced from the thermal autoxidation of methyl oleate; however, the most complete study of this type was reported by Frankel.[197] The hydroperoxides were decomposed in the injector port of a gas chromatograph and identified by gc-ms; the results obtained are summarised in table 26.

Table 26

Comparison of volatile products formed from (1) thermally decomposed methyl oleate hydroperoxides and (2) during the autoxidation of methyl oleate in the presence of promoters

Compound	(1) Autoxidation (rel. %)	(2) Autoxidation (rel. %)
Heptane	4.4	-
Octane	2.7	-
Heptanal	0.5	20.0
1-Heptanol	0.4	-
Octanal	11.0	14.1
Methyl heptanoate	1.5	-
1-Octanol	0.4	-
Nonanal	15.0	4.2
Methyl octanoate	5.0	3.1
2-Nonenal	0.5	-
Decanal	3.9	-
Methyl nonanoate	1.5	-
2-Decenal	5.4	-
2-Undecenal	1.7	-
Methyl 8-oxooctanoate	3.5	-
Methyl 9-oxononanoate	15.0	-
Methyl 10-oxodecanoate	12.0	-
Methyl 10-oxo-8-decenoate	3.4	-
Methyl 11-oxo-9-undecenoate	5.8	-
3-Heptanone	-	18.7
3-Octanone	-	trace

Table 26 (continued)

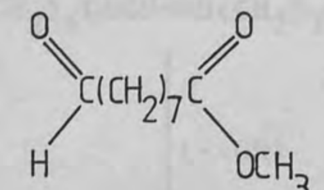
Compound	(1) Autoxidation (rel. %)	(2) Autoxidation (rel. %)
2(3H) Dihydrofuranone	-	2.7
Pentanal	-	trace
Hexanal	-	1.8
1-Pentanol	-	trace
1-Hexanol	-	trace
3-Heptanol	-	1.3
Methyl-2-ethylhexanoate	-	20.4
Heptyl formate	-	trace
Formic acid	-	trace
Acetic acid	-	trace
2-Ethyl hexanoic acid	-	trace

The major volatile products are carbonyl compounds, viz. octanal, nonanal and methyl 9-oxononanoate. These compounds are believed to result from decomposition of the hydroperoxides into alkoxy radicals followed by β scission of carbon-carbon bonds to form these volatile aldehydes. Hydroperoxides are a ready source of alkoxy radicals from pyrolysis or photolysis of the peroxide bond (dissociation energy 125 - 167 kJ mol^{-1} [198]). The position of hydroperoxide formation in the autoxidation of methyl oleate corresponds to the position of cleavage, thus providing some evidence for the above mechanistic approach. The work of Walling[199] on some aspects of the chemistry of alkoxy radicals is worth noting here.

Leeves[2] investigated the volatile products produced at room temperature from promoted autoxidations of methyl oleate, using cobalt and lead promoters. The degradation products were collected in a cold trap and analysed using gc-ms; the compounds identified are also shown in table 26.

The similarities between the volatile compounds from the promoted autoxidations and the products from the thermal decomposition (table 26) suggest a common mechanism of formation.

However, there are some major discrepancies between the compounds identified from the promoted autoxidations at ambient temperatures and those detected from the thermal decomposition, for example the absence of the higher molecular mass materials such as methyl 9-oxononanoate (LXVIII).



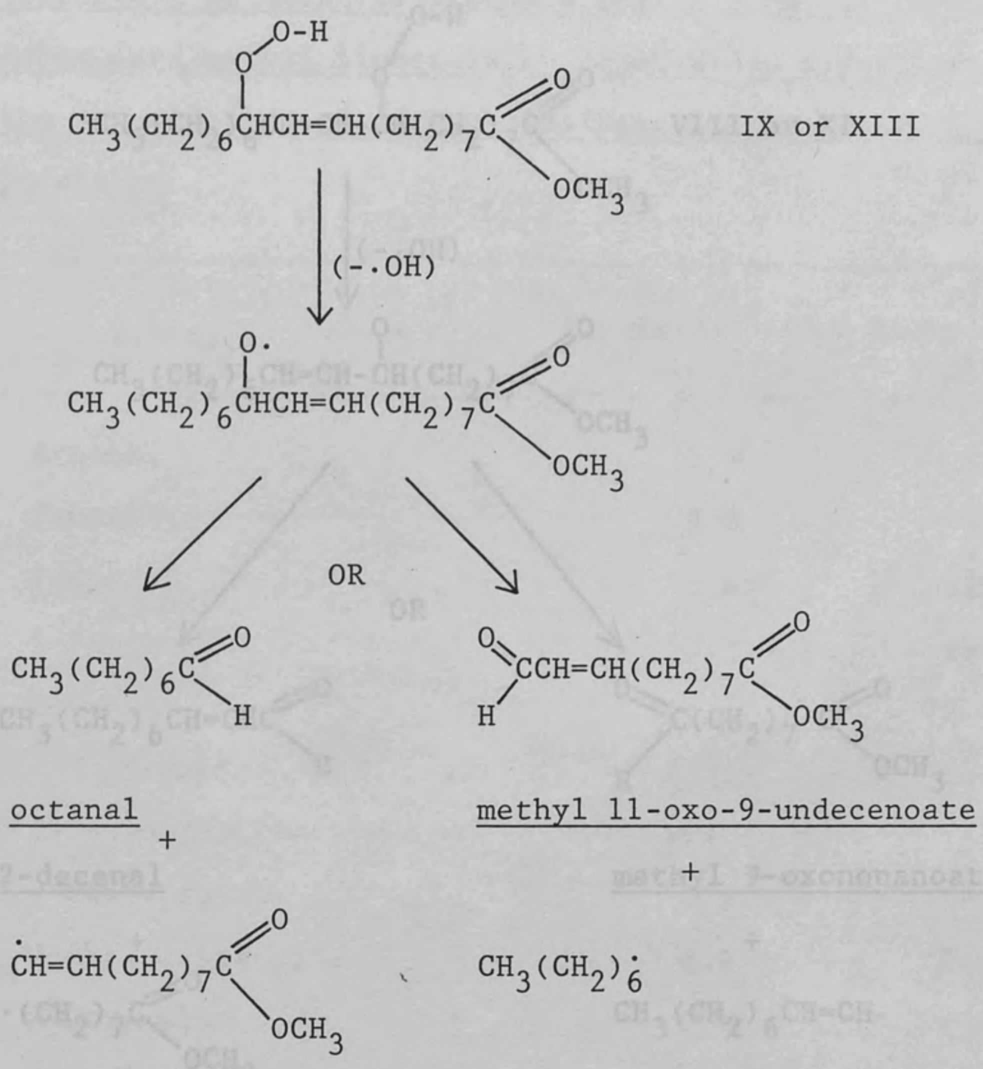
LXVIII

These types of compounds are probably formed in the promoted autoxidation of methyl oleate but owing to their lower volatility are not transported to the cold trap. In contrast the thermal degradation of the methyl oleate hydroperoxides is carried out in the injection part of the gc chromatograph, and hence all the products are analysed.

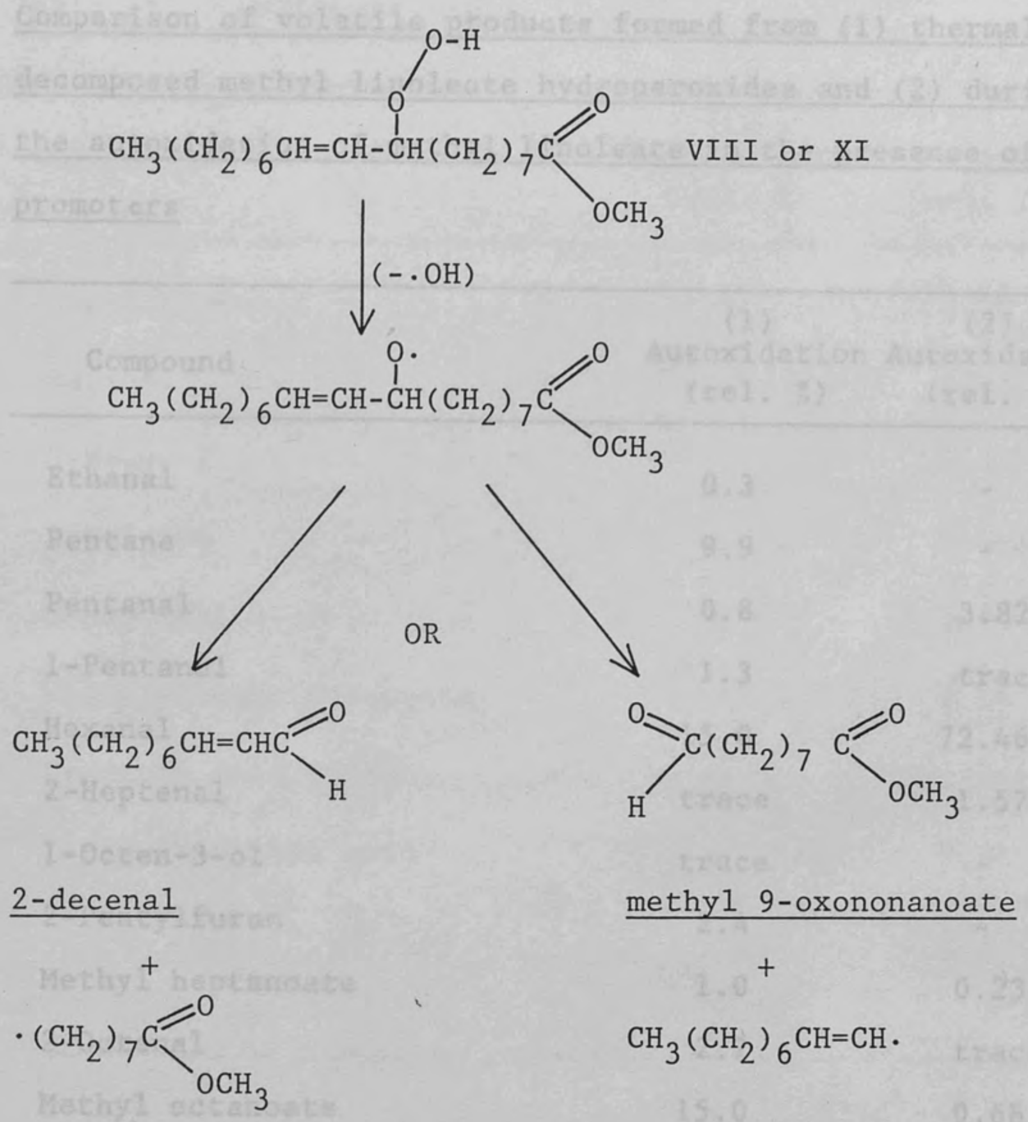
The proposed mechanism of formation of some of the products resulting from the β-scission of carbon-carbon bonds of alkoxy radicals are shown in schemes 2.5.2.1.1 and 2.5.2.1.2.

2.5.2.2 Volatile products produced from the autoxidation of methyl linoleate

As with methyl oleate, several research groups[106,200,201,202,203,204,205,206] have attempted to characterise the volatile products produced from the thermal autoxidation of linoleic acid and its derivatives but again Frankel[197] has provided the most complete study of these thermal degradation products; the results he obtained are shown in table 27.



Scheme 2.5.2.1.1 Formation of octanal and methyl 11-oxo-9-undecenoate



Scheme 2.5.2.1.2 Formation of 2-decenal and methyl 9-oxononanoate

Table 27

Comparison of volatile products formed from (1) thermally decomposed methyl linoleate hydroperoxides and (2) during the autoxidation of methyl linoleate in the presence of promoters

Compound	(1) Autoxidation (rel. %)	(2) Autoxidation (rel. %)
Ethanal	0.3	-
Pentane	9.9	-
Pentanal	0.8	3.82
1-Pentanol	1.3	trace
Hexanal	15.0	72.46
2-Heptenal	trace	1.57
1-Octen-3-ol	trace	-
2-Pentylfuran	2.4	-
Methyl heptanoate	1.0	0.23
2-Octenal	2.7	trace
Methyl octanoate	15.0	0.68
2-Nonenal	1.4	-
2,4-Nonadienal	0.3	-
2,4-Decadienal	14.0	-
Methyl 8-oxooctanoate	1.3	-
Methyl 9-oxononanoate	19.0	-
Methyl 10-oxodecanoate	0.7	
Methyl 10-oxo-8-decenoate	4.9	-

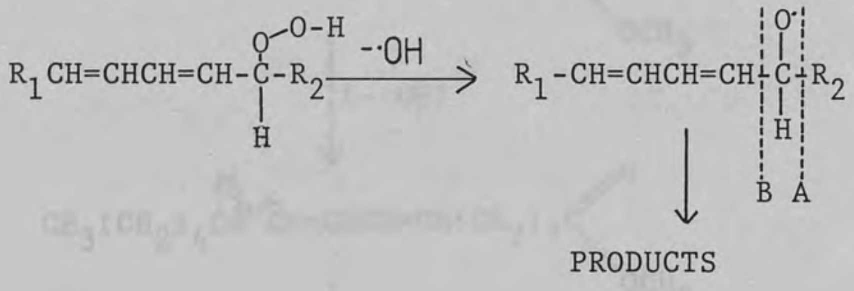
Table 27 (continued)

Compound	(1) Autoxidation (rel. %)	(2) Autoxidation (rel. %)
3-Heptanone	-	0.90
Butanal	-	4.71
2-Hexenal	-	0.24
2-Butanol	-	trace
3-Heptanol	-	0.68
Methyl-2-ethylhexanoate	-	0.46
Hexanoic acid	-	trace
2-Ethylhexanoic acid	-	0.77

As previously, Leeves[2] investigated the volatile products produced from promoted autoxidations of methyl linoleate (using cobalt and lead promoters); the compounds so identified are also shown in table 27.

Both reaction conditions produced similar compounds indicating a common degradation pathway. However, there are some similar differences in the volatile products identified, as with methyl oleate (see section 2.5.2.1), which probably arises again from the lower volatility of the higher molecular mass compounds.

Bell,[207] Frankel,[208] and Komoto and Gaddis[209] have proposed that monohydroperoxides decompose to alkoxy radicals, and carbonyl compound formation results from the β-fragmentation of these radicals, (see scheme 2.5.2.2.1).



$$R_1CH{=}CHCH{=}CH{-}\overset{O-O-H}{\underset{H}{C}}{-}R_2 \xrightarrow{-\cdot OH} R_1{-}CH{=}CHCH{=}CH{-}\overset{O\cdot}{\underset{H}{C}}{-}R_2 \longrightarrow \text{PRODUCTS}$$

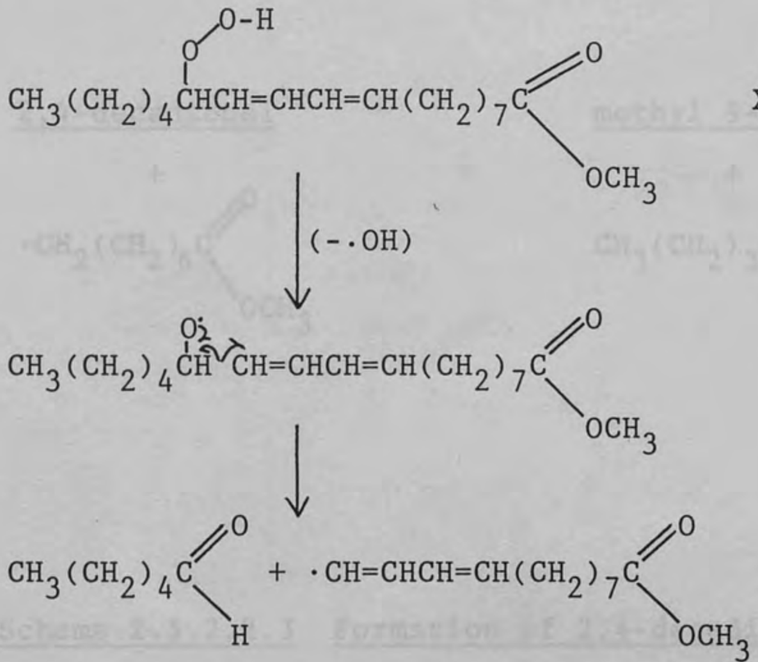
<u>Scission A gives</u> R_1-CH=CHCH=CHCHO + $\cdot R_2$

<u>Scission B gives</u> R_1-CH=CHCH=CH· + R_2CHO

Scheme 2.5.2.2.1

(The fragmentation of alkoxy radicals has been mentioned in section 2.5.2.1). Scission of the C-C bond on the side of the oxygen-bearing carbon away from the olefinic linkages (Scission A), will result in an aldehyde and an alkyl radical, while scission of the C-C bond between the vinyl function and the carbon atom bearing the oxygen atom (Scission B), gives rise to a vinyl radical and an aldehyde.

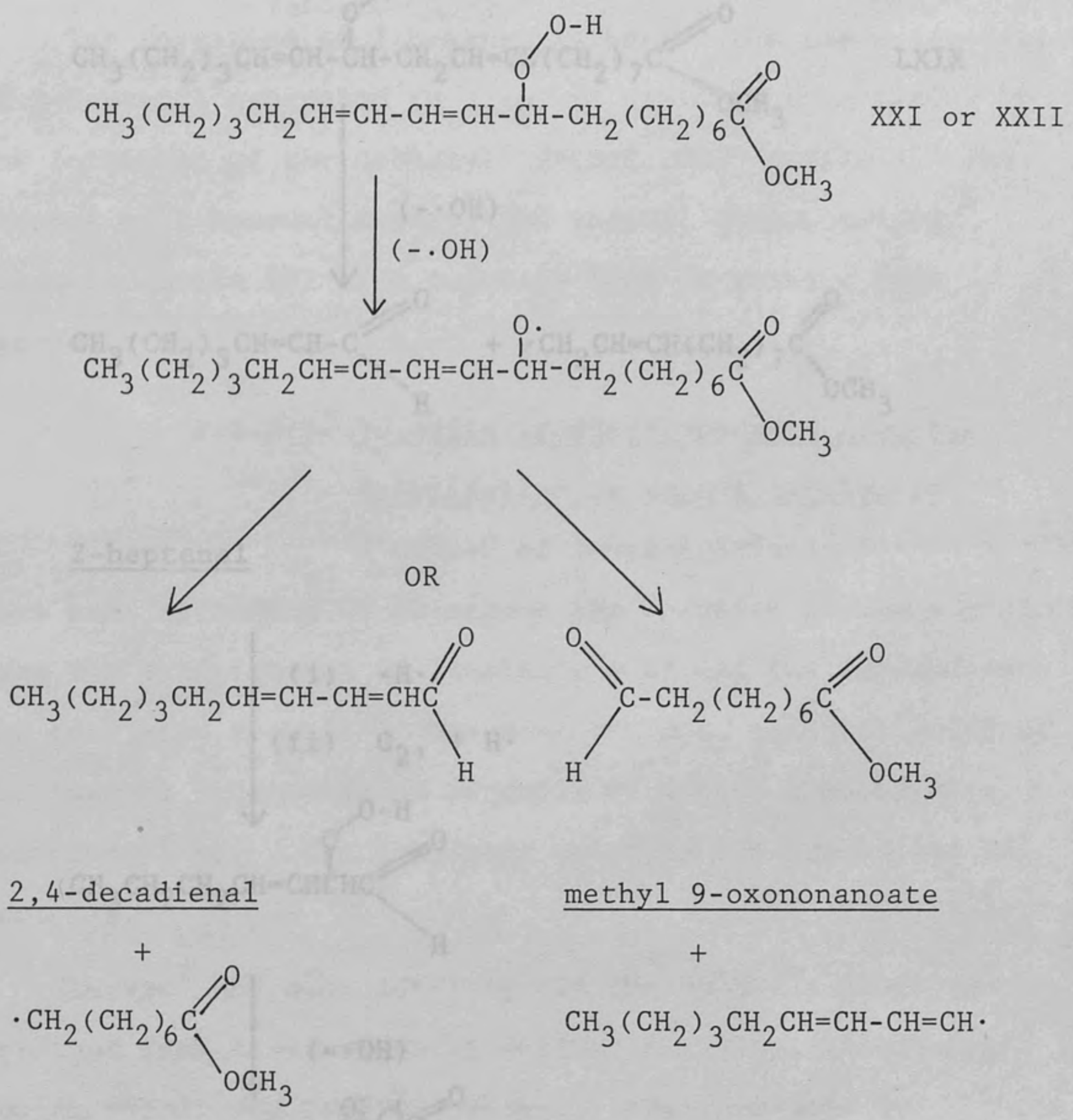
The proposed mechanism of formation of some of the volatile products from these autoxidation studies viz. hexanal, 2-4 decadienal, methyl 9-oxononanoate and 2-hexenal are shown in schemes 2.5.2.2.2, 2.5.2.2.3 and 2.5.2.2.4.



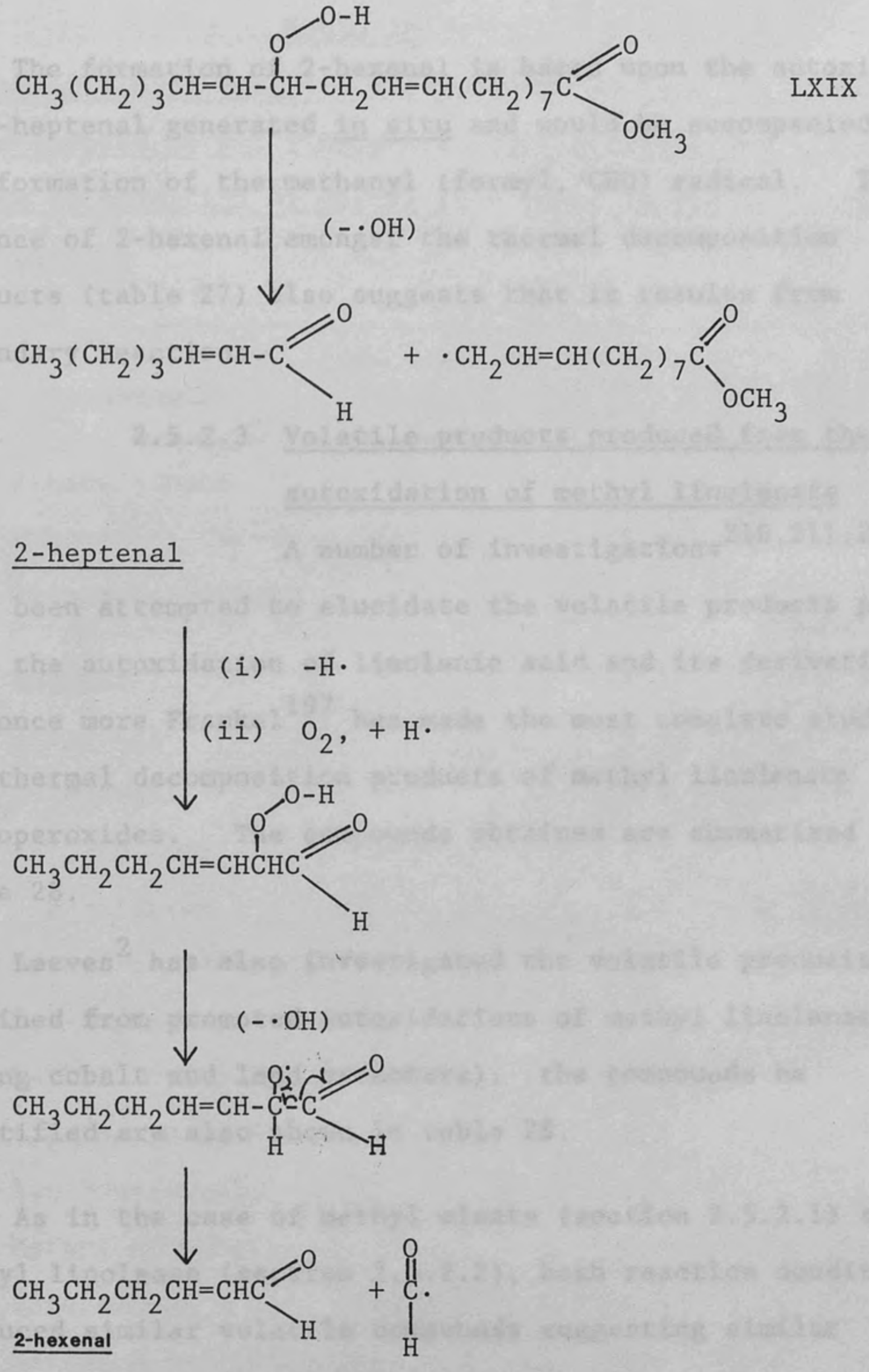
XX or XXIII

HEXANAL

Scheme 2.5.2.2.2 Formation of hexanal



Scheme 2.5.2.2.3 Formation of 2,4-decadienal and methyl 9-oxononanoate



Scheme 2.5.2.2.4 Formation of 2-hexenal

The formation of 2-hexenal is based upon the autoxidation of 2-heptenal generated in situ and would be accompanied by the formation of the methanyl (formyl, ·CHO) radical. The absence of 2-hexenal amongst the thermal decomposition products (table 27) also suggests that it results from secondary reactions.

2.5.2.3 Volatile products produced from the autoxidation of methyl linolenate

A number of investigations[210,211,212,213] have been attempted to elucidate the volatile products produced from the autoxidation of linolenic acid and its derivatives, but once more Frankel[197] has made the most complete study of the thermal decomposition products of methyl linolenate hydroperoxides. The compounds obtained are summarised in table 28.

Leeves[2] has also investigated the volatile products obtained from promoted autoxidations of methyl linolenate (using cobalt and lead promoters); the compounds he identified are also shown in table 28.

As in the case of methyl oleate (section 2.5.2.1) and methyl linoleate (section 2.5.2.2), both reaction conditions produced similar volatile compounds suggesting similar degradation pathways from the hydroperoxide. The proposed mechanism of formation of some of the volatile products resulting from the β-scission of carbon-carbon bonds of alkoxy radicals are shown in schemes 2.5.2.3.1 and 2.5.2.3.2.

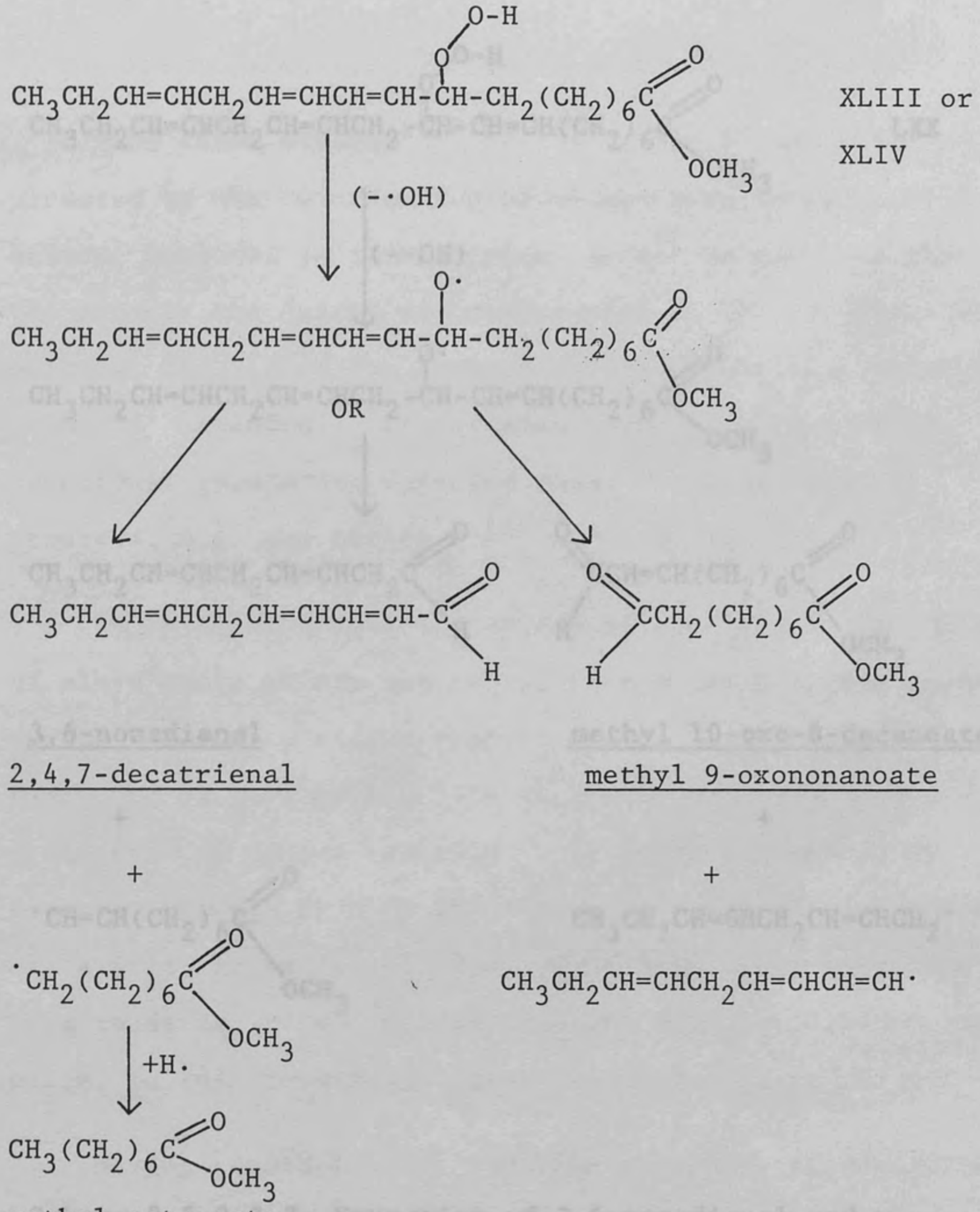
Table 28

Comparison of volatile products formed from (1) thermally decomposed methyl linolenate hydroperoxides and (2) during the autoxidation of methyl linolenate in the presence of promoters

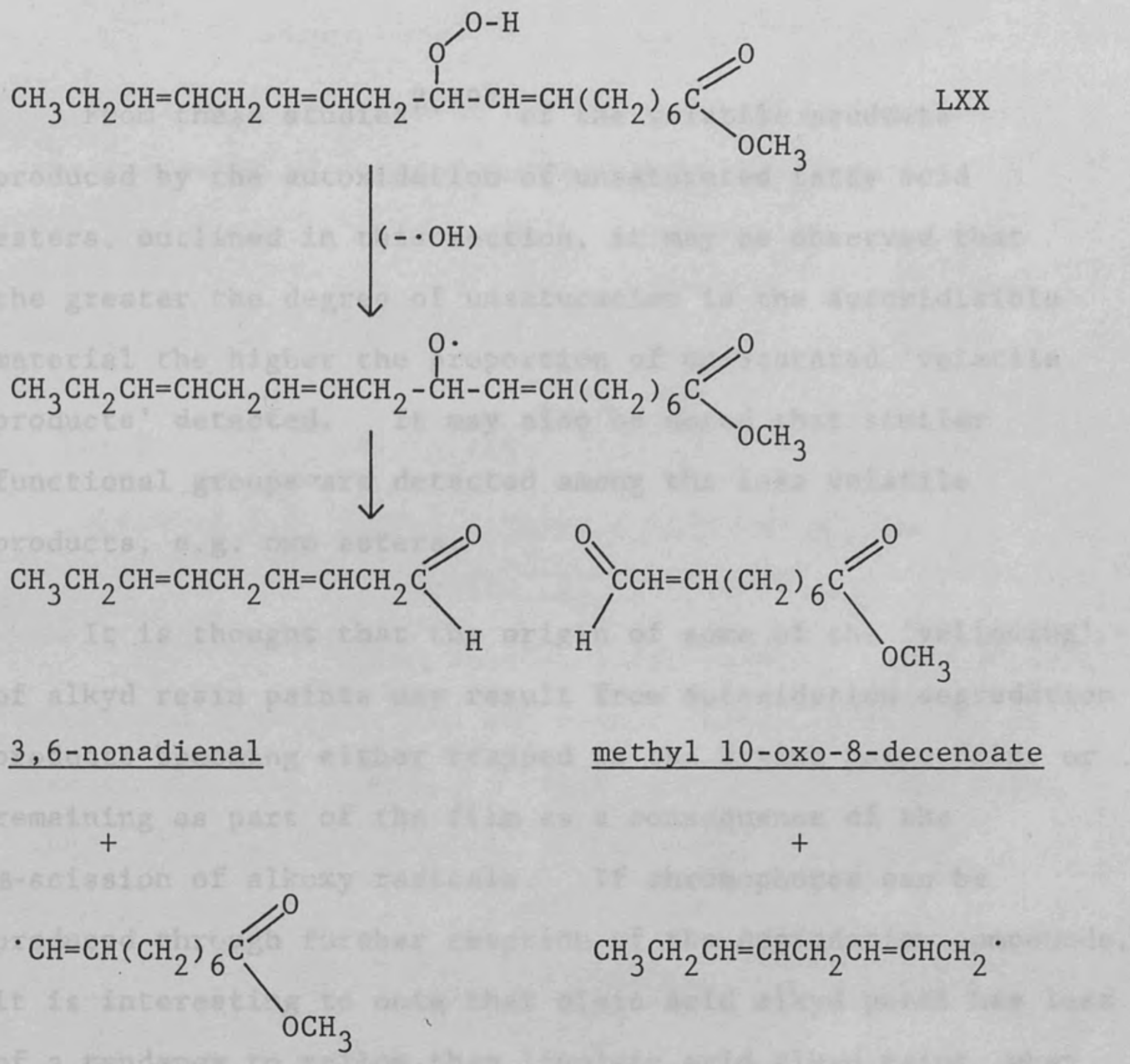
Compound	(1) Autoxidation (rel. %)	(2) Autoxidation (rel.%)
Ethane/ethene	10.0	-
Ethanal	0.8	-
Propanal/propenal	7.7	27.80 (propanal)
Butanal	0.1	-
2-Butenal	0.5	-
2-Pentenal	1.6	9.42
2-/3-Hexenal	1.4	-
2-Butylfuran	0.5	-
Methyl heptanoate	1.8	-
2,4-Heptadienal	9.3	2.02
Methyl octanoate	22.0	7.42
4,5-Epoxyhepta-2-enal	0.2	-
3,6-Nonadienal	0.5	-
Methyl nonanoate	0.7	-
Decatrienal	14.0	-
Methyl 8-oxo-octanoate	0.6	-
Methyl 9-oxo-nonanoate	13.0	-
Methyl 10-oxo-decanoate	1.0	-
Methyl 10-oxo-8-decenoate	4.2	-
1-Pentene-3-one	-	0.95

Table 28 (continued)

Compound	(1) Autoxidation (rel. %)	(2) Autoxidation (rel. %)
2,3-Pentadione	-	0.22
Methanol	-	trace
Ethanol	-	26.00
1-Pentene-3-ol	-	14.70
3-Heptanol	-	trace
Methyl-2-ethylhexanoate	-	1.23
2-Ethylhexanoic acid	-	0.07



Scheme 2.5.2.3.1 Formation of 2,4,7-decatrienal, methyl 9-oxononanoate and methyl octanoate



Scheme 2.5.2.3.2 Formation of 3,6-nonadienal and methyl 10-oxo-8-decenoate

From these studies[2,197] of the volatile products produced by the autoxidation of unsaturated fatty acid esters, outlined in this section, it may be observed that the greater the degree of unsaturation in the autoxidisible material the higher the proportion of unsaturated 'volatile products' detected. It may also be noted that similar functional groups are detected among the less volatile products, e.g. oxo esters.

It is thought that the origin of some of the 'yellowing' of alkyd resin paints may result from autoxidation degradation products becoming either trapped in the drying paint film, or remaining as part of the film as a consequence of the β-scission of alkoxy radicals. If chromophores can be produced through further reaction of the degradation compounds, it is interesting to note that oleic acid alkyd paint has less of a tendency to yellow than linoleic acid alkyd paint, when placed in test conditions, see section 2.5.1.

Having regard for the volatile compounds produced from autoxidation studies on these unsaturated fatty acid esters, it was felt that it could be helpful to observe the yellowing of a representative of a class of volatiles, such as an α/β unsaturated aldehyde. Such compounds are known to have a tendency to yellow if left standing in air. Trans-2-hexenal (LXXI) was chosen as the aldehyde to be investigated, since it fitted the above criteria and was readily available from suppliers.

Attempts to identify some of the products formed during the yellowing of trans-2-hexenal forms part of the work for this study.

$CH_3CH_2CH_2CH{=}CHCHO$ (LXXI)

2.5.3 Investigations concerned with the 'yellowing' of trans-2-hexenal

These initial investigations were primarily concerned with observing any colour change in samples of trans-2-hexenal (LXXI) and other aldehydes for comparison when subjected to different environments.

2.5.3.1 Yellowing of aldehydes in oxygen at 70°C

Dry oxygen gas was bubbled through samples of hexanal, trans-2-hexenal, 2-4 hexadienal and 2-butenal at 70°C in the dark. The colour of each sample was examined after 15 hours and 39 hours. (For experimental details see section 3.12.1). The observations are shown in table 29.

Table 29

Sample	0 hrs (freshly distilled)	15 hrs	39 hrs
hexanal	colourless	very pale yellow	very pale yellow
2-hexenal	colourless	pale yellow	yellow
2-4-hexadienal	pale yellow	yellow/orange	orange/brown
2-butenal	colourless	pale yellow	yellow

It appeared that all the aldehydes would yellow to an extent in the dark at 70°C but this tendency was heightened if the aldehyde was unsaturated. The 2-4 hexadienal sample showed the most change in colour.

Trans-2-hexenoic acid, a white crystalline solid, when placed under the same conditions, appeared to show no change in colour at 70°C in the dark.

2.5.3.2 Effect of free radical initiator and inhibitor on trans-2-hexenal

Small amounts of either an inhibitor or an initiator were added to freshly distilled samples of trans-2-hexenal. The samples were either left in the light at room temperature (r.t.),(21°C), or else sealed in an ampoule and left at 70°C in the dark.

The initiator was Perkadox 16N (bis(4-t-butylcyclohexyl)peroxy dicarbonate) and the inhibitor used was POM (primary octylmercaptan). The samples at room temperature were examined for any colour change after 1 wk and 2½ mths, whereas the samples at 70°C were examined after 16 days. These observations are shown in table 30. (For experimental details see section 3.12.2).

It seemed that the presence of the free radical initiator Perkadox 16N increased the intensity of yellow colour produced by the trans-2-hexenal in the light at room temperature over a period of 2½ months. This effect was accelerated at 70°C in the dark. However, the addition of POM used as the inhibitor appeared to slow down the rate of formation of these coloured products.

Table 30

Sample	0 hrs	1 week in light (r.t.)	2½ months in light (r.t.)	16 days in dark (70°C)
2-hexenal	colourless	pale yellow	pale yellow	pale yellow
2-hexenal + POM	colourless	colourless	colourless	pale yellow
2-hexenal + Perkadox 16N	colourless	pale yellow	yellow	deep yellow

2.5.3.3 Effect of aqueous base on 'yellowed' samples of trans-2-hexenal

Extractions using aqueous base were carried out on samples of 2-hexenal, which had been 'yellowed' at 70°C in the dark. (For experimental details see sections 3.12.3 and 3.12.4). It was noted that the yellow colour was effected by the presence of acid or base. On extraction with aqueous potassium hydroxide the deep yellow colour was carried into the aqueous alkali layer, but when this aqueous layer was acidified, the yellow colour decreased in intensity.

2.5.3.4 T.L.C. analysis of 'yellowed' trans-2-hexenal

Attempts to analyse the yellow liquid produced from heating trans-2-hexenal in the dark by T.L.C. proved to be negative. Although various solvent systems were tried, the solutions from the yellowed trans-2-hexenal were always streaked and unresolved on the silica T.L.C. plates. Further attempts at respotting the streaked material also failed to resolve the yellow liquid.

Column chromatography and flash chromatography were also attempted several times to separate the yellow residue but these methods proved ineffectual. (See section 3.12.5 for experimental details).

These preliminary investigations concerned with separating the yellow components of trans-2-hexenal illustrated the similar problems encountered by other workers,[188] investigating the yellowing of drying oil films viz., the difficulty of concentrating the yellow components from non-coloured substances. Another fact that was also substantiated was that only minute quantities of yellow materials were necessary for the aldehyde to adopt a yellow colour.

2.5.4 Volatile products produced by the autoxidation of allyl ether compounds

Having discussed the volatile products produced from some unsaturated fatty acids, the corresponding volatile products from the autoxidation of one of the novel allyl ether drying systems is now briefly considered.

2.5.4.1 Autoxidation of ethanol/3 AGE and identification of volatile product

It has been shown that autoxidation of allyl ether compounds leads to the formation of esters, alcohols and aldehydes,[157] (see section 1.11). The autoxidation of ethanol/3 AGE was carried out and the volatile products trapped using silica gel coated with 2,4-dinitrophenylhydrazine (DNP). The extracted silica gel was examined by T.L.C. and compared with standard 2,4-dinitrophenylhydrazones (DNPH) of several aldehydes. Both silica gel and reverse phase plates were used; the R_f values obtained are shown in table 31. (For experimental details see section 3.13).

These T.L.C. R_f values for both the silica gel (0.89) and reverse phase (0.62) plates seem to indicate that the 2,4-DNPH derivative found on the 2,4-DNP coated silica gel, after exposure to the volatile products of the EtOH/3 AGE autoxidation, was that of 2-propenal. (The second spot seemed to possibly correspond to unreacted 2,4-DNP).

Thus, it appears that 2-propenal is a predominant volatile product formed during the autoxidation of this drying system.

In conjunction with the 'yellowing' of trans-2-hexenal, it was decided to investigate the yellowing of a corresponding volatile observed from the autoxidation of the novel allyl ether drying systems, viz. 2-propenal, (LXXII). (See section 3.14 for expeirmental details).

$$CH_2 = CHCHO$$

LXXII

Table 31

Sample	R_f values Reverse phase KC_{18} plates: $MeCN/H_2O$ (80/20)	R_f values Silica gel plates: $MeOH/CHCl_3$ (5/95)
Methanal	0.71	0.86
Ethanal	0.64	0.88
Propanal	0.59	0.91
2-Propenal	0.61	0.89
Butanal	0.48	0.91
2-Butenal	0.53	0.91
Pentanal	0.42	0.91
2,4-DNP	0.82	0.48
2,4-DNP coated silica gel	0.89	0.20
EtOH/3 AGE	(0.92)	0.89
sample	0.62	(0.13)

2.5.5 Doping of lacquer paints with α/β unsaturated carbonyl compounds[151]

Research at ICI Paints Division has involved doping a standard lacquer paint with either 2-propenal, 2-methyl-2-propenal or methyl vinyl ketone in the presence of a variety of bases ranging from ammonia, dimethylaminoethanol (DMAE) to lithium hydroxide. Any yellowing of the spread lacquer paint was detected by measuring the change in the colour index (CI) after 1 week at 70°C in the dark, as before in section 2.5.1. The results of these yellowing tests are shown in table 32.

It appeared that the paint doped with 2-propenal gave the highest ΔCI values, when subjected to the different base conditions, whereas the smallest ΔCI values were obtained when the paint had been doped with 2-methyl-2-propenal. 2-Propenal as discussed in section 2.5.4.1 is a predominant volatile product from the autoxidation of the allyl ether compounds. It seems that probably the degree of yellowing of the 2-propenal doped paint is dependent upon the base used, ammonia showing the largest ΔCI value and lithium hydroxide the smallest. Possibly the methyl group attached to the double bond in 2-methyl-2-propenal prevents the formation of precursors, which are able to react further with the bases to give yellow compounds.

Table 32

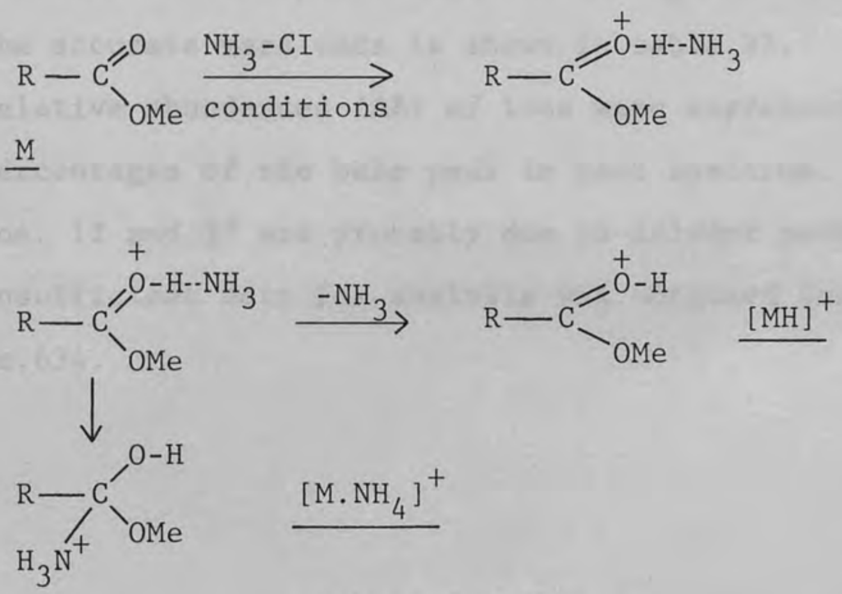
Table to show the CI values of a doped standard lacquer paint after 1 week at 70°C in the dark

Added Base	DOPING MATERIAL		
	2-Propenal $CH_2=CHCHO$	2-Methyl-2-propenal $CH_2=\underset{CH_3}{\underset{\mid}{C}}CHO$	Methyl vinyl ketone $CH_2=CHCOCH_3$
Nil	0.17	0.29	0.41
NH_3	8.84	2.24	5.10
NH_3/H_2O	7.33	1.86	4.20
Dimethyl-amino ethanol (DMAE)	4.32	0.16	0.53
$DMAE/H_2O$	7.00	0.27	0.36
LiOH	0.88	0.56	0.46
$LiOH/H_2O$	1.15	0.18	0.27

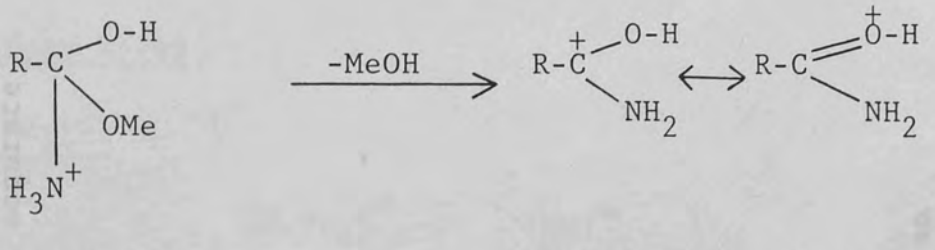
2.6 GC-MS analysis of autoxidised samples of (1)trans-2-hexenal and (2) 2-propenal

Samples of trans-2-hexenal and 2-propenal, which had been 'yellowed' separately in the dark at 70 ± 1°C and 47 ± 1°C respectively, were derivatised using boron trifluoride/methanol complex (BF_3/CH_3OH). The derivatised samples were analysed by both packed column and capillary column g.l.c., as well as by gc-ms using EI and NH_3-CI. (For experimental details see sections 3.15, 3.15.1, 3.16 and 3.17). Accurate mass measurements were made of ions produced by NH_3-CI by the SERC Mass Spectrometry Centre at the University College of Swansea.

The use of NH_3-CI to determine the molecular mass of a compound, M_r, results in the formation of two quasi molecular ions, corresponding to $[M.NH_4]^+$ and $[MH]^+$, as illustrated in scheme 2.6.1. However, sometimes the $[M.NH_4]^+$ ions from methyl esters lose methanol in preference to ammonia giving ions, $[M.NH_4-CH_3OH]^+$, (scheme 2.6.2).



Scheme 2.6.1.



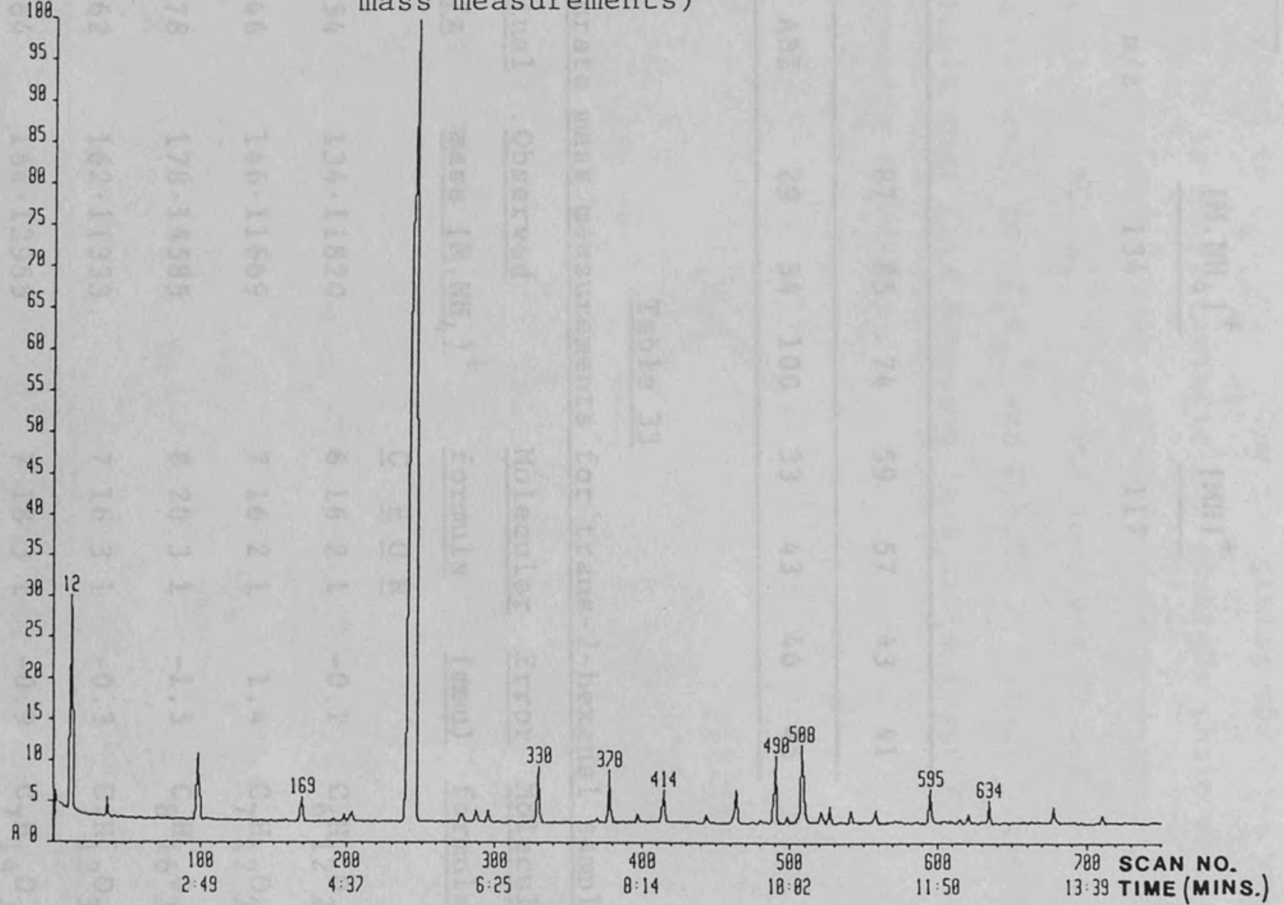
$[M.NH_4]^+$ $[M.NH_4-CH_3OH]^+$

Scheme 2.6.2.

2.6.1 GC-MS analysis of derivatised samples of autoxidised trans-2-hexenal (with accurate mass measurements)

Derivatised samples of autoxidised trans-2-hexenal were analysed by the manner discussed in section 2.6. The total ion current chromatogram obtained from the capillary gc-ms analysis is shown in figure 2.6.1.1 with the EI and NH_3-CI spectra being obtained at the apex of each chromatographic peak. The accurate mass data is shown in table 33. The relative abundances (AB) of ions were expressed as percentages of the base peak in each spectrum. Scan Nos. 12 and 37 are probably due to solvent peaks; insufficient data for analysis was obtained for scan No.634.

Fig. 2.6.1.1. Capillary total ion current chromatogram of derivatised samples of autoxidised trans-2-hexenal (with accurate mass measurements)



Scan No.99

NH_3-CI

	$[M.NH_4]^+$	$[MH]^+$
m/z	134	117

EI

m/z	87	85	74	59	57	43	41
Rel AB%	29	34	100	33	43	46	45

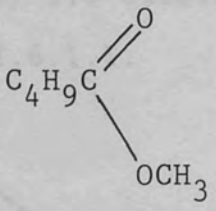
Table 33

Accurate mass measurements for trans-2-hexenal sample

Nominal m/z	Observed mass $[M.NH_4]^+$	Molecular formula C	H	O	N	Error (mmu)	Molecular formula M (m/z)
134	134·11820	6	16	2	1	-0.1	$C_6H_{12}O_2$(116)
146	146·11669	7	16	2	1	1.4	$C_7H_{12}O_2$(128)
178	178·14585	8	20	3	1	-1.5	$C_8H_{16}O_3$(160)
162	162·11333	7	16	3	1	-0.3	$C_7H_{12}O_3$(144)
164	164·12955	7	18	3	1	-0.9	$C_7H_{14}O_3$(146)
208	208·15490	9	22	4	1	-0.0	$C_9H_{18}O_4$(190)
194	194·13898	8	20	4	1	0.3	$C_8H_{16}O_4$(176)

$M_r = 116$

The accurate mass data gives a molecular formula M equivalent to $C_6H_{12}O_2$. The ion giving the base peak at m/z 74 is characteristic for straight chain methyl esters, resulting from a McLafferty rearrangement to give $CH_2{=}C(OH)OCH_3]^{+\cdot}$.[214] The ions m/z 57 and m/z 85 give evidence for $C_4H_9^+$ and $C_4H_9CO^+$. Thus it seems probable that this compound is a trace impurity of methyl pentanoate (LXXIII).



LXXIII

Scan No.169

NH_3-CI

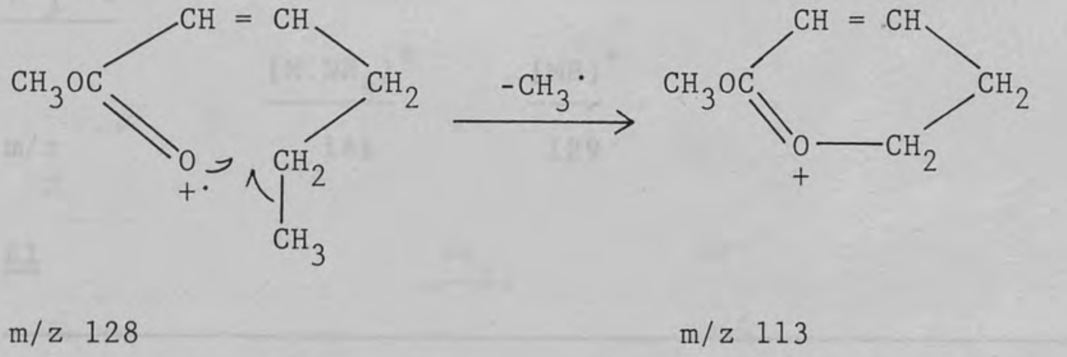
	$[M.NH_4]^+$	$[MH]^+$
m/z	146	129

EI

m/z	128	113	97	87	81	74	68	55	53	41	39
Rel AB%	9	37	25	18	42	34	53	100	35	84	75

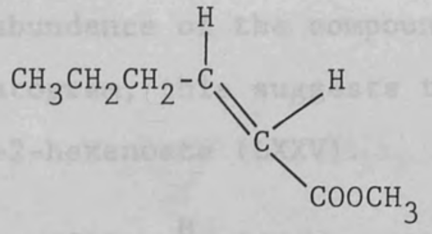
M_r = 128

The accurate mass data gives a molecular formula M equivalent to $C_7H_{12}O_2$. The mass spectra provide evidence that this compound is likely to be the methyl ester of the α/β unsaturated acid, 2-hexenoic acid, (M_r equals 128). The loss of $CH_3\cdot$(M-15) and $CH_3O\cdot$ (M-31) leads to the formation of m/z 113, $C_3H_7CH{=}CH\overset{+}{C}OO$ and m/z 97, $C_3H_7CH{=}CH\overset{+}{C}O$, respectively. The loss of the terminal CH_3 group may occur by 5,6 cleavage to give a cyclic ion,[214] m/z 113, scheme 2.6.1.1.



Scheme 2.6.1.1

The base peak corresponding to m/z 55 could arise from the formation of $CH_2{=}CHCO^+$. One point to note is the fairly abundant ion m/z 74, which is normally associated with β cleavage and associated γ-hydrogen rearrangement, indicating that possibly a double bond shift occurs before cleavage. From the low abundance of this compound indicated in the total ion current chromatogram, it seems probable that this compound is methyl cis-2-hexenoate (LXXIV).



LXXIV

Comparison with the standard spectrum of methyl 2-hexenoate[215] confirmed the presence of this compound.

Scan No. 246

NH_3-CI

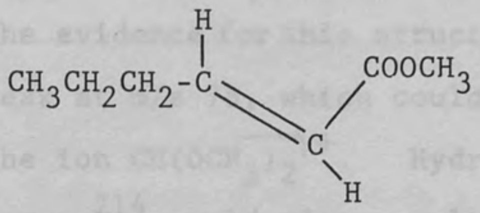
	$[M.NH_4]^+$	$[MH]^+$
m/z	146	129

EI

m/z	128	113	97	87	81	74	69	68	55	42	41	39
Rel AB%	12	29	44	53	20	33	31	54	98	46	100	95

M_r = 128

The accurate mass data gives a molecular formula M equivalent to $C_7H_{12}O_2$. The mass spectra data from this scan is similar to the previous scan No.169. From the high abundance of the compound indicated in the total ion chromatogram, this suggests that the compound is methyl trans-2-hexenoate (LXXV).



LXXV

Comparison with the standard spectrum of methyl 2-hexenoate[215] confirmed the presence of this compound.

Scan No.330

NH_3-CI

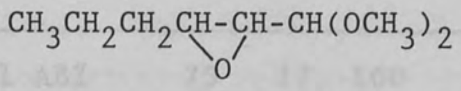
	$[M.NH_4]^+$	$[MH]^+$
	178	161

EI

m/z	101	87	75	54	45
Rel AB%	6	20	100	8	25

$M_r = 160$

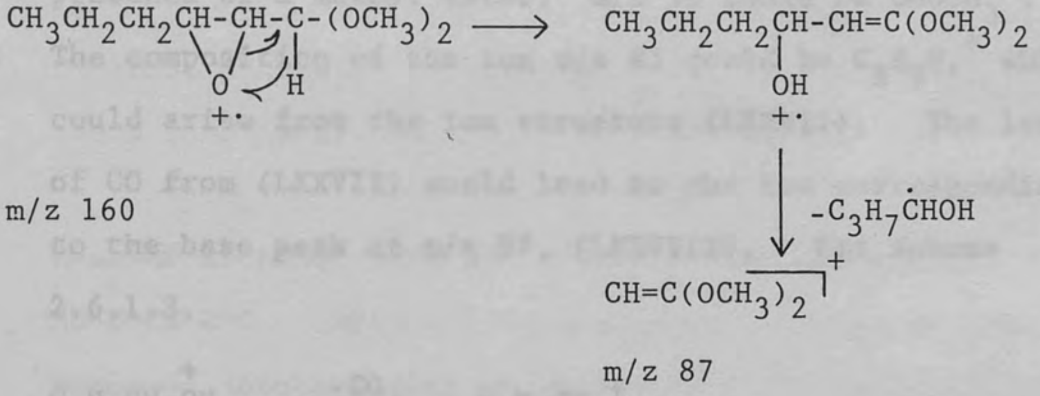
The accurate mass data gives a molecular formula M equivalent to $C_8H_{16}O_3$. The base peak at m/z 75 shows the presence of an ion composed of $C_3H_7O_2^+$. The mass spectra seem to suggest that this compound is the epoxide 1,1-dimethoxy-2,3-epoxyhexane (LXXVI).



$CH_3CH_2CH_2CH-CH-CH(OCH_3)_2$ (O bridging)

LXXVI

The evidence for this structure is given by the strong base peak at m/z 75, which could arise from α-cleavage to give the ion $\overline{CH(OCH_3)_2}^{+}$. Hydrogen rearrangement followed by cleavage[214] could also result in the formation of the ion at m/z 87, $\overline{CH=C(OCH_3)_2}^{+}$, as shown in scheme 2.6.1.2.



Scheme 2.6.1.2.

Scan No. 378

NH_3-CI

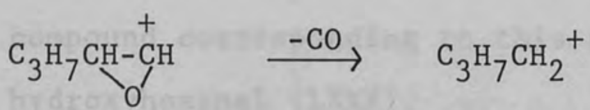
	$[M.NH_4]^+$	$[MH]^+$
m/z	162	not observed

EI

m/z	85	59	57	54	41	39
Rel AB%	75	17	100	15	63	20

$M_r = 144$

The accurate mass data gives a molecular formula M equivalent to $C_7H_{12}O_3$. The ion m/z 85 formed by a loss of 59 daltons from the molecular ion, suggests the presence of a methyl ester; m/z 59 could be $COOCH_3^+$. The composition of the ion m/z 85 could be $C_5H_9O,^+$ which could arise from the ion structure (LXXVII). The loss of CO from (LXXVII) would lead to the ion corresponding to the base peak at m/z 57, (LXXVIII). See scheme 2.6.1.3.



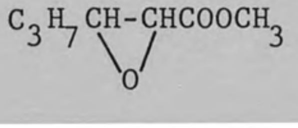
$C_3H_7CH\text{-}\overset{+}{C}H \xrightarrow{-CO} C_3H_7CH_2^+$

m/z 85 m/z 57

LXXVII LXXVIII

Scheme 2.6.1.3.

Thus, the structure of this compound would seem to be that of methyl 2,3-epoxyhexanoate (LXXIX).



$C_3H_7CH\text{-}CHCOOCH_3$

LXXIX

Scan No. 414

NH_3-CI

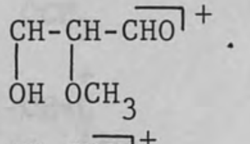
$[M.NH_4]^+$	$[MH]^+$
164	147

EI

m/z	103	97	73	71	61	55	45	43	41
Rel AB%	46	6	60	85	37	32	24	100	26

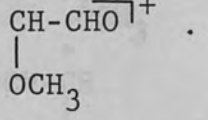
$M_r = 146$

The accurate mass data gives a molecular formula M equivalent to $C_7H_{14}O_3$. The loss of $C_3H_7^{\cdot}$ (M-43) leaves a fragment ion of m/z 103 of composition $C_4H_7O_3^+$. A possible suggestion for the structure of the ion m/z 103 is



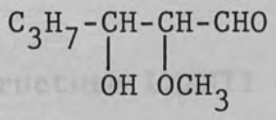
$\underset{OH}{CH}-\underset{OCH_3}{CH}-CHO]^+$.

Cleavage of the radical ion $M^{+\cdot}$ could lead to m/z 73,



$\underset{OCH_3}{CH}-CHO]^+$.

Loss of methanol from m/z 103 would lead to m/z 71, $HO-\overset{+}{C}=CH-CHO$. This information seems to suggest that the compound corresponding to this scan could be 2-methoxy-3-hydroxyhexanal (LXXX).



$C_3H_7-\underset{OH}{CH}-\underset{OCH_3}{CH}-CHO$

LXXX

Scan No. 464

NH_3-CI

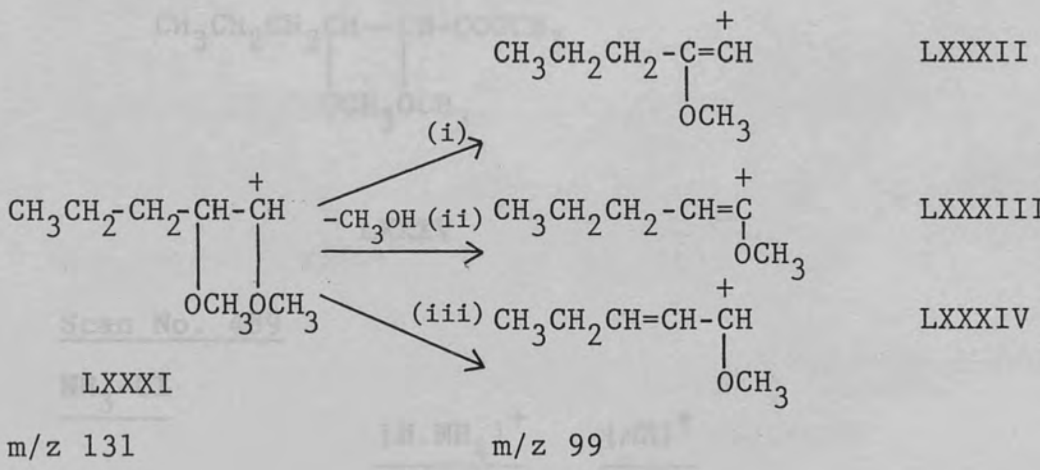
	$[M.NH_4]^+$	$[MH]^+$	$[M.NH_4-CH_3OH]^+$
m/z	208	not observed	176

EI

m/z	159	131	113	99	84	72	59	57	55	44	41	40
Rel AB%	6	97	18	8	20	39	52	100	37	39	46	51

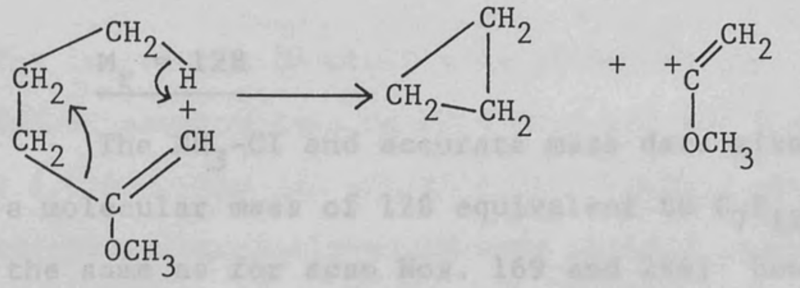
M_r = 190

The accurate mass data gives a molecular formula M equivalent to $C_9H_{18}O_4$. Ions of (M-31) and (M-59) suggest a methyl ester. Thus, the ion at m/z 131 could be $C_7H_{15}O_2^+$, which could have the structure (LXXXI). Loss of methanol could occur in three ways to give m/z 99 (LXXXII, LXXXIII and LXXXIV). See scheme 2.6.1.4.



Scheme 2.6.1.4.

Structure LXXXII could possibly undergo further rearrangement leading to the formation of cyclopropane and the ion corresponding to the base peak at m/z 57. See scheme 2.6.1.5.

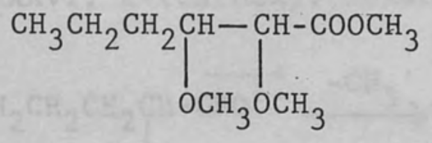


m/z 99 m/z 57

LXXXII

Scheme 2.6.1.5.

The mass spectra data seems to indicate that the compound for this scan is possibly methyl 2,3-dimethoxyhexanoate (LXXXV).



$CH_3CH_2CH_2\underset{OCH_3}{CH}-\underset{OCH_3}{CH}-COOCH_3$

LXXXV

Scan No. 489

NH_3-CI

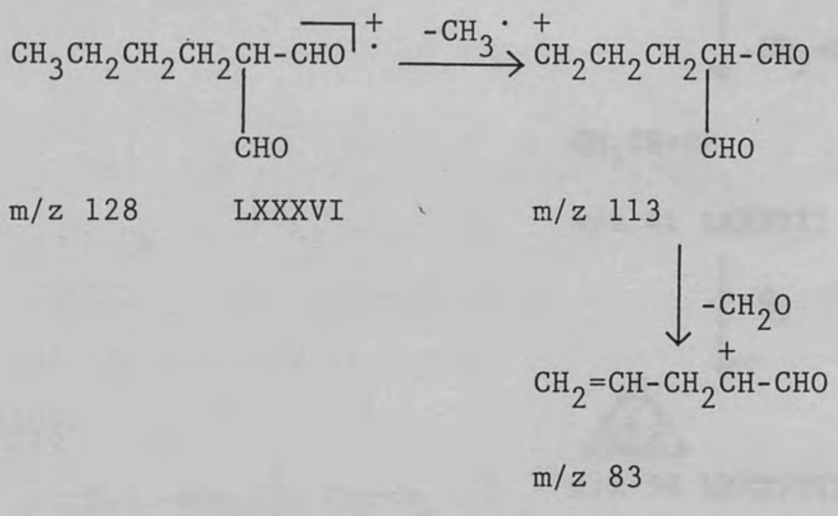
	$[M.NH_4]^+$	$[MH]^+$
m/z	146	129

EI

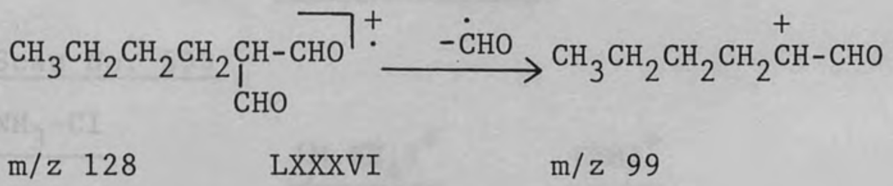
m/z	128	113	99	97	83	71	69	56	41	40	39
Rel AB%	6	32	95	40	11	48	23	30	94	63	100

$M_r = 128$

The NH_3-CI and accurate mass data give this compound a molecular mass of 128 equivalent to $C_7H_{12}O_2$, which is the same as for scan Nos. 169 and 246; however, the EI spectra are different. Ions of (M-15) and (M-29) indicate the presence of CH_3 and CHO groups; (see schemes 2.6.1.6 and 2.6.1.7 respectively). The ion at m/z 71 could be composed of $C_3H_3O_2^{+}$, which could have the structure $\overline{CH(CHO)_2}]^{+}$. As the structure, $C_7H_{12}O_2$, is isomeric with methyl 2-hexenoate, (LXXIV and LXXV), it seems that the structure of this compound could be that of LXXXVI, 2-(carboxy) hexanal.

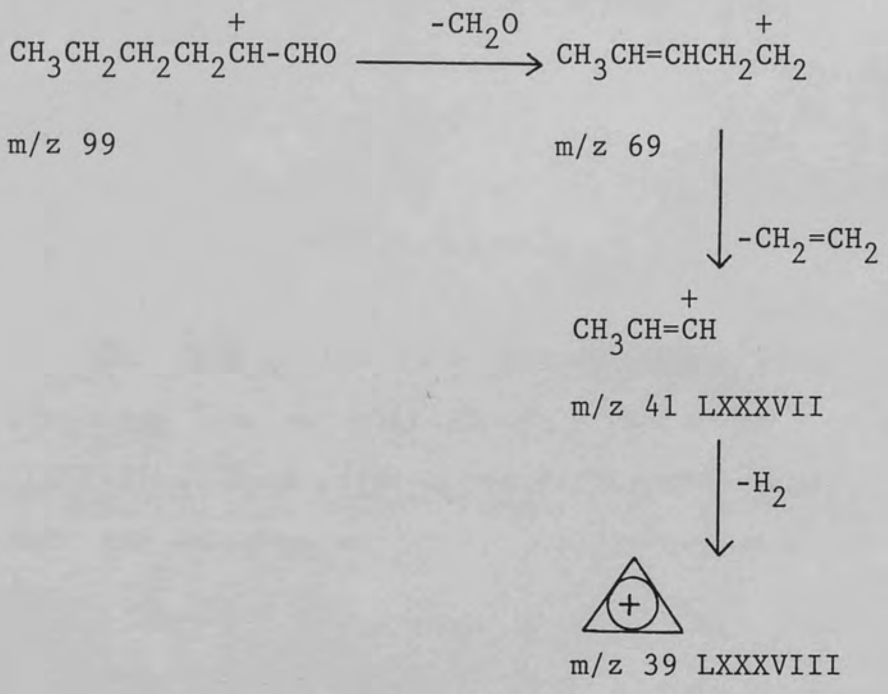


Scheme 2.6.1.6.



Scheme 2.6.1.7.

The ion at m/z 83 could arise from hydrogen rearrangement and subsequent loss of CH_2O from the ion m/z 113, scheme 2.6.1.6. The ion m/z 99 could possibly undergo hydrogen rearrangement followed by loss of CH_2O leading to the formation of m/z 69, which could further lose $CH_2=CH_2$ to give the ion m/z 41 (LXXXVII). This propyl cation could further fragment leading to the ion m/z 39 (LXXXVIII), which corresponds to the base peak. A tentative route is shown in scheme 2.6.1.8.



Scheme 2.6.1.8.

Scan No. 508

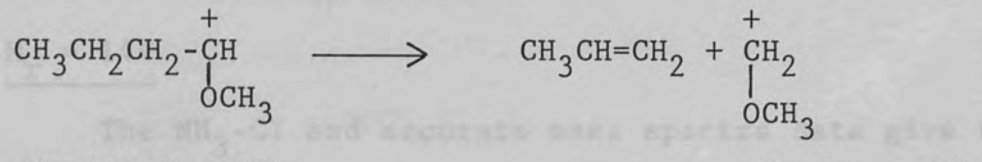
NH_3-CI	$[M.NH_4]^+$	$[MH]^+$
m/z	194	177

EI

m/z	117	87	55	45	41	39
Rel AB%	3	61	22	100	11	7

$\underline{M_r = 176}$

The accurate mass data gives a molecular formula M equivalent to $C_8H_{16}O_4$. The ion at (M-59) suggests the presence of a methyl ester. The fairly abundant ion at m/z 87 could correspond to the ion of $C_5H_{11}O^+$;a possible structure for this ion is shown below at LXXXIX. Rearrangement of this ion followed by fragmentation could lead to the ion corresponding to the base peak at m/z 45 (XC). See Scheme 2.6.1.9.

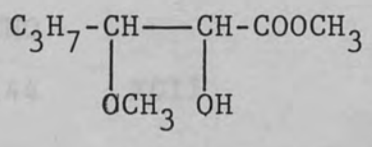


$$CH_3CH_2CH_2\text{-}\underset{\substack{|\\ OCH_3}}{\overset{+}{C}H} \longrightarrow CH_3CH=CH_2 + \underset{\substack{|\\ OCH_3}}{\overset{+}{C}H_2}$$

m/z 87 LXXXIX m/z 45 XC

Scheme 2.6.1.9.

The peak at m/z 55 is probably $C_4H_7^+$, $(CH_3CH_2CH=\overset{+}{C}H)$, resulting from the elimination of methanol from m/z 87 (LXXXIX). Thus piecing these fragments together suggests that the compound is methyl 2-hydroxy-3-methoxyhexanoate (XCI).



$$C_3H_7\text{-}\underset{\substack{|\\ OCH_3}}{CH}\text{—}\underset{\substack{|\\ OH}}{CH}\text{-}COOCH_3$$

XCI

Scan No. 595

NH_3-CI

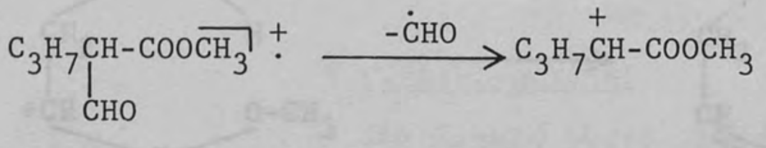
	$[M.NH_4]^+$	$[MH]^+$	$[M.NH_4-CH_3OH]^+$
m/z	162	not observed	130

EI

m/z	115	87	83	58	55	41	40	39
Rel AB%	62	100	56	44	76	21	20	22

$M_r = 144$

The NH_3-CI and accurate mass spectra data give this compound a molecular mass of 144 and a composition of $C_7H_{12}O_3$, which is the same as for Scan No. 378; however, the EI spectra are different. The loss of 29 daltons suggests the presence of the CHO group, leaving the ion m/z 115 of $C_6H_{11}O_2^+$ (XCIII). A tentative structure for this compound of $C_7H_{12}O_3$ is shown below, (XCII) in scheme 2.6.1.10.

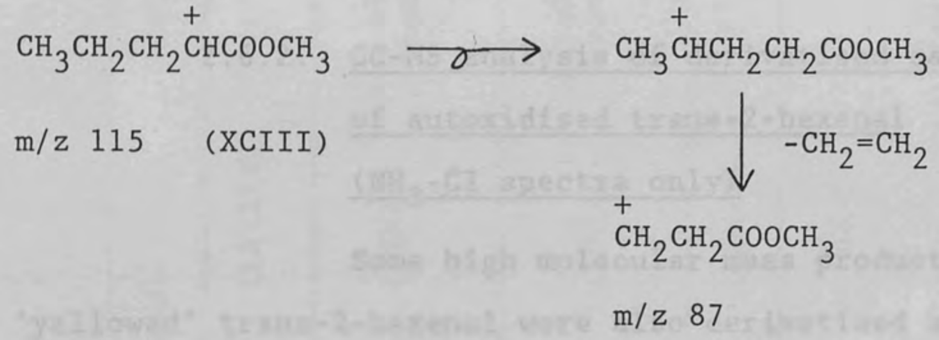


$$C_3H_7\underset{\text{CHO}}{\underset{|}{C}}H\text{-COO}\overline{CH_3}]^{+\cdot} \xrightarrow{-\dot{C}HO} C_3H_7\overset{+}{C}H\text{-COOCH}_3$$

m/z 144 XCII m/z 115 XCIII

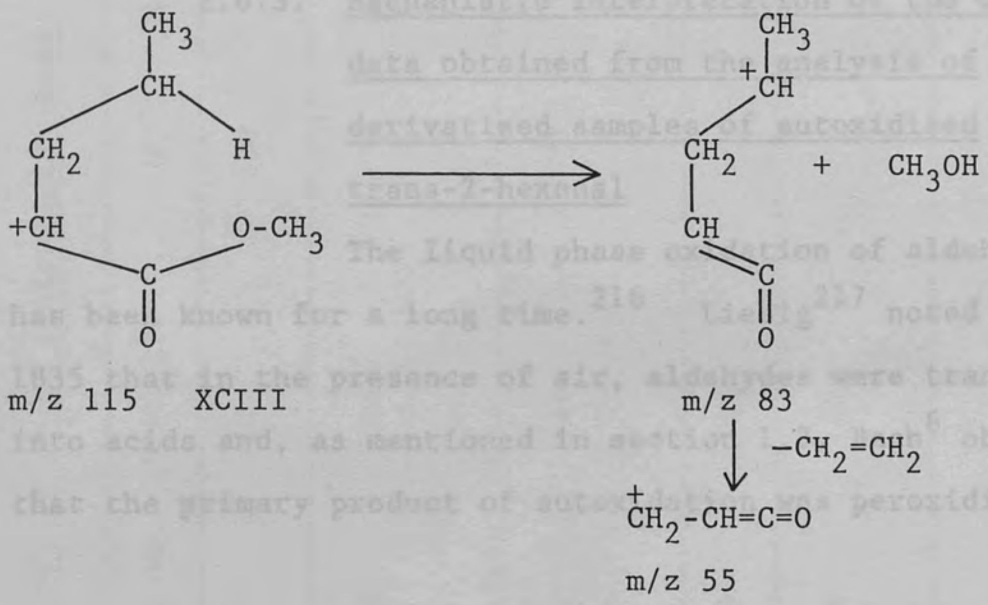
Scheme 2.6.1.10.

The ion at m/z 115 (XCIII) could undergo a 1,3-hydrogen shift followed by subsequent loss of $CH_2{=}CH_2$ to give the ion at m/z 87, corresponding to the base peak. See scheme 2.6.1.11.



Scheme 2.6.1.11.

However, the ion at m/z 115 (XCIII) could probably also lose methanol to give the ion at m/z 83. Further loss of $CH_2{=}CH_2$ from this ion would lead to the ion at m/z 55. A tentative route for this suggestion is shown in scheme 2.6.1.12.



Scheme 2.6.1.12.

Using this mass spectra data, it seems that the compound could be 2-(carbomethoxy)pentanal (XCII).

A summary of all these assignments is made in table 34.

2.6.2. GC-MS analysis of derivatised samples of autoxidised trans-2-hexenal (NH_3-CI spectra only)

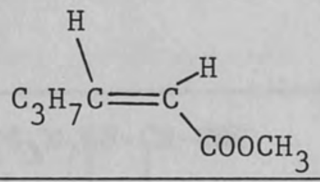
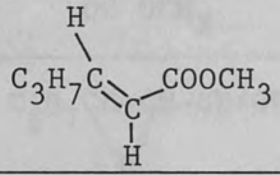
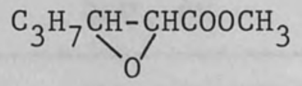
Some high molecular mass products of 'yellowed' trans-2-hexenal were also derivatised and examined at PCMU Harwell but using only NH_3-CI. The total ion current chromatogram (Scan Nos. 25.P - 263.P) obtained from this particular gc-ms analysis is shown in figure 2.6.2.1. The NH_3-CI data is shown in table 35, together with tentative suggestions as to the possible structures. Scan Nos. 25.P and 34.P are probably due to solvent peaks.

2.6.3. Mechanistic interpretation of the GC-MS data obtained from the analysis of derivatised samples of autoxidised trans-2-hexenal

The liquid phase oxidation of aldehydes has been known for a long time.[216] Liebig[217] noted in 1835 that in the presence of air, aldehydes were transformed into acids and, as mentioned in section 1.3, Bach[6] observed that the primary product of autoxidation was peroxidic.

Table 34

Summary of gc-ms assignments made in Section 2.6.1.

Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Suggested Structure		Notes
99	134	117	116	$C_4H_9COOCH_3$	(LXXIII)	
169	146	129	128		(LXXIV)	See also LXXV trans isomer scan No.246
246	146	129	128		(LXXV)	See also LXXIV cis isomer scan No.169
489	146	129	128	$C_4H_9CH(CHO)_2$	(LXXXVI)	
378	162	not observed	144		(LXXIX)	

<u>Table 34</u> (continued)

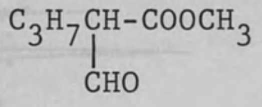
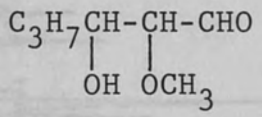
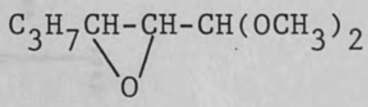
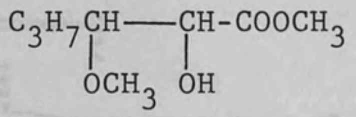
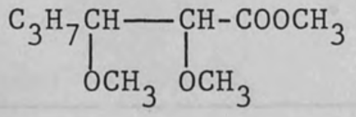
Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Suggested Structure	Notes
595	162	not observed $[M.NH_4-CH_3OH]^+$ present	144	 $\mathrm{C_3H_7\underset{\overset{\vert}{CHO}}{CH}{-}COOCH_3}$ (XCII)	
414	164	147	146	 $\mathrm{C_3H_7\underset{\overset{\vert}{OH}}{CH}{-}\underset{\overset{\vert}{OCH_3}}{CH}{-}CHO}$ (LXXX)	
330	178	161	160	 $\mathrm{C_3H_7\underbrace{CH{-}CH}_{O}{-}CH(OCH_3)_2}$ (LXXVI)	
508	194	177	176	 $\mathrm{C_3H_7\underset{\overset{\vert}{OCH_3}}{CH}{-}\underset{\overset{\vert}{OH}}{CH}{-}COOCH_3}$ (XCI)	
464	208	not observed $[M.NH_4-CH_3OH]^+$ present	190	 $\mathrm{C_3H_7\underset{\overset{\vert}{OCH_3}}{CH}{-}\underset{\overset{\vert}{OCH_3}}{CH}{-}COOCH_3}$ (LXXXV)	

Fig. 2.6.2.1. Capillary total ion current chromatogram of derivatised samples of autoxidised trans-2-hexenal (NH_3-CI spectra only)

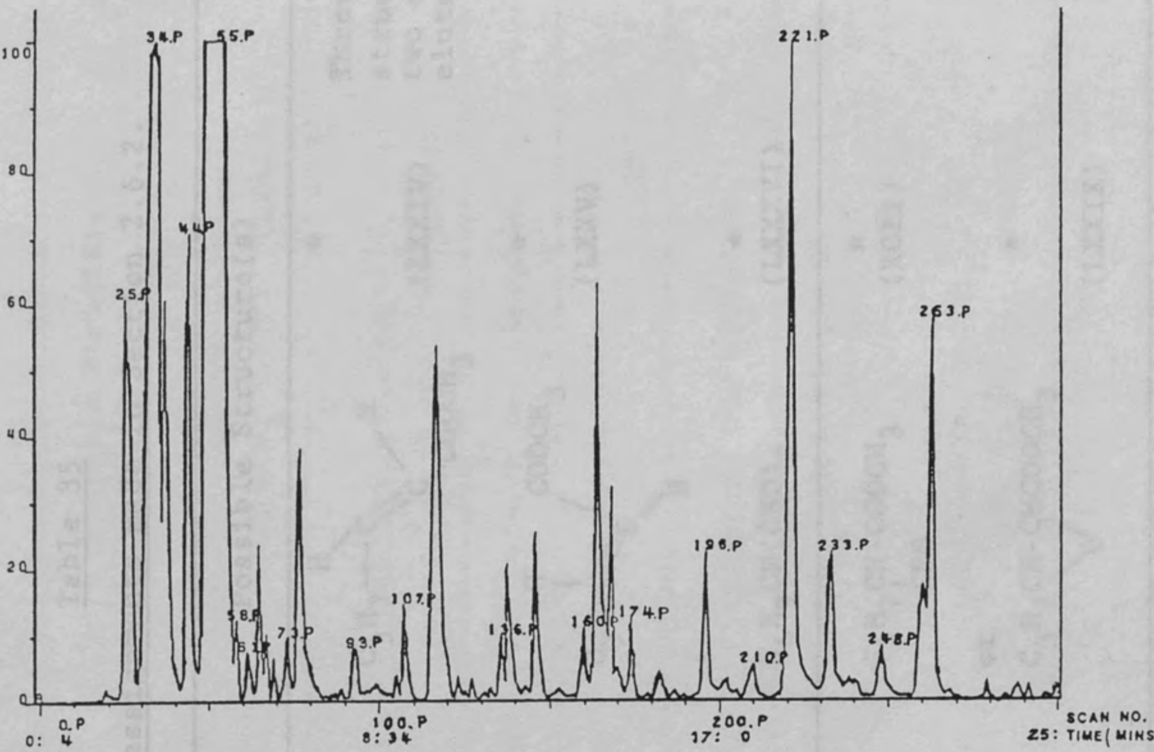
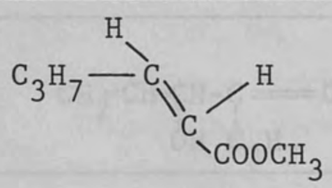
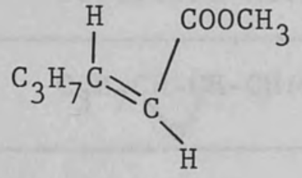
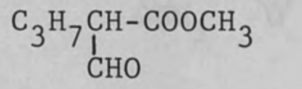
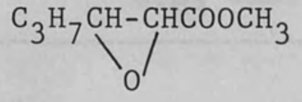


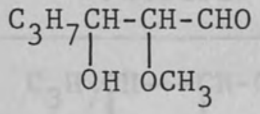
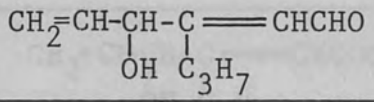
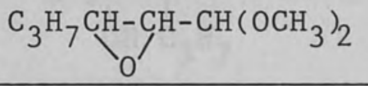
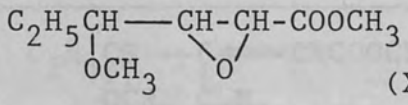
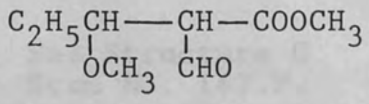
Table 35

Summary of possible gc-ms assignments made in Section 2.6.2.

Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Possible Structure(s)		Notes
44.P	146	129	128		* (LXXIV)	Three alternative structures for two compounds eluted
56.P	146	129	128		* (LXXV)	
				$C_4H_9CH(CHO)_2$	* (LXXXVI)	
221.P	162	145	144	 $C_3H_7CH(CHO)\text{-}COOCH_3$ or 	* (XCII) * (LXXIX)	

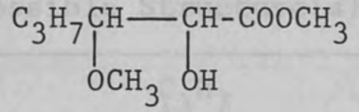
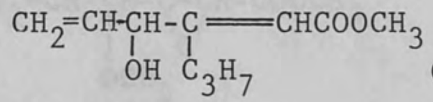
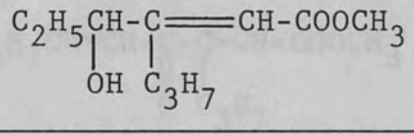
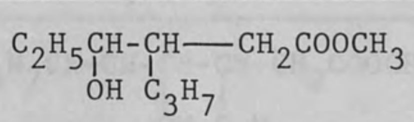
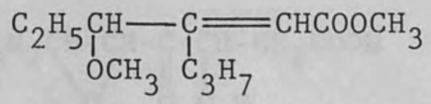
* structure assigned in section 2.6.1.

Table 35 (continued)

Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Possible Structure(s)	Notes
117.P	164	147	146	 $C_3H_7\underset{OH}{CH}-\underset{OCH_3}{CH}-CHO$ * (LXXX)	
93.P	172	155	154	 $CH_2{=}CH-\underset{OH}{CH}-\underset{C_3H_7}{C}{=}CHCHO$ (XCIV)	
136.P	176	159	158	Structure not assigned.	
65.P	178	161	160	 $C_3H_7CH-CH-CH(OCH_3)_2$ (epoxide, O bridging) * (LXXVI)	
210.P	186	169	168	Structure not assigned.	
107.P	192	175	174	 $C_2H_5\underset{OCH_3}{CH}-CH-CH-COOCH_3$ (XCV)	Two alternative structures for two compounds eluted
160.P	192	175	174	 $C_2H_5\underset{OCH_3}{CH}-\underset{CHO}{CH}-COOCH_3$ (XCVI)	

* structure assigned in section 2.6.1.

Table 35 (continued)

Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Possible Structure(s)	Notes
164.P	194	177	176	 $C_3H_7\underset{OCH_3}{CH}-\underset{OH}{CH}-COOCH_3$ * (XCI)	
76.P	202	185	184	 $CH_2=CH-\underset{OH}{CH}-\underset{C_3H_7}{C}=CHCOOCH_3$ (XCVII)	
146.P	204	187	186	 $C_2H_5\underset{OH}{CH}-\underset{C_3H_7}{C}=CH-COOCH_3$ (XCVIII)	
138.P	206	189	188	 $C_2H_5\underset{OH}{CH}-\underset{C_3H_7}{CH}-CH_2COOCH_3$ (XCIX)	
167.P	218	201	200	 $C_2H_5\underset{OCH_3}{CH}-\underset{C_3H_7}{C}=CHCOOCH_3$ (C)	Cis or trans isomer
174.P	218	201	200	See Structure C Scan No. 167.P.	

* structure assigned in section 2.6.1.

Table 35 (continued)

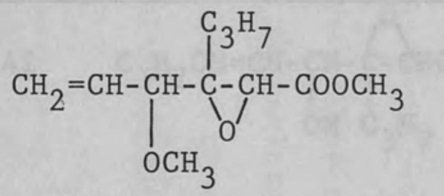
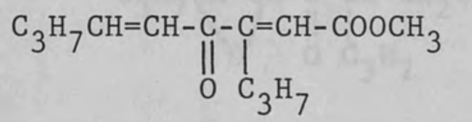
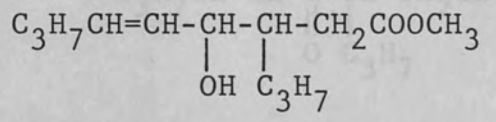
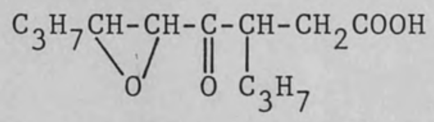
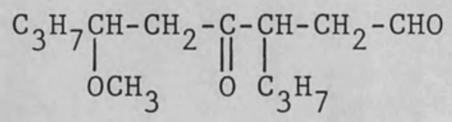
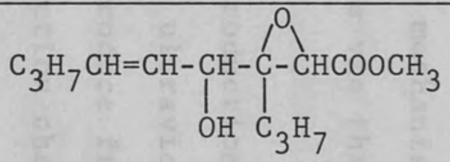
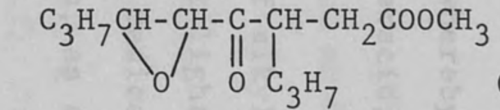
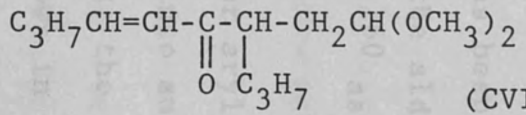
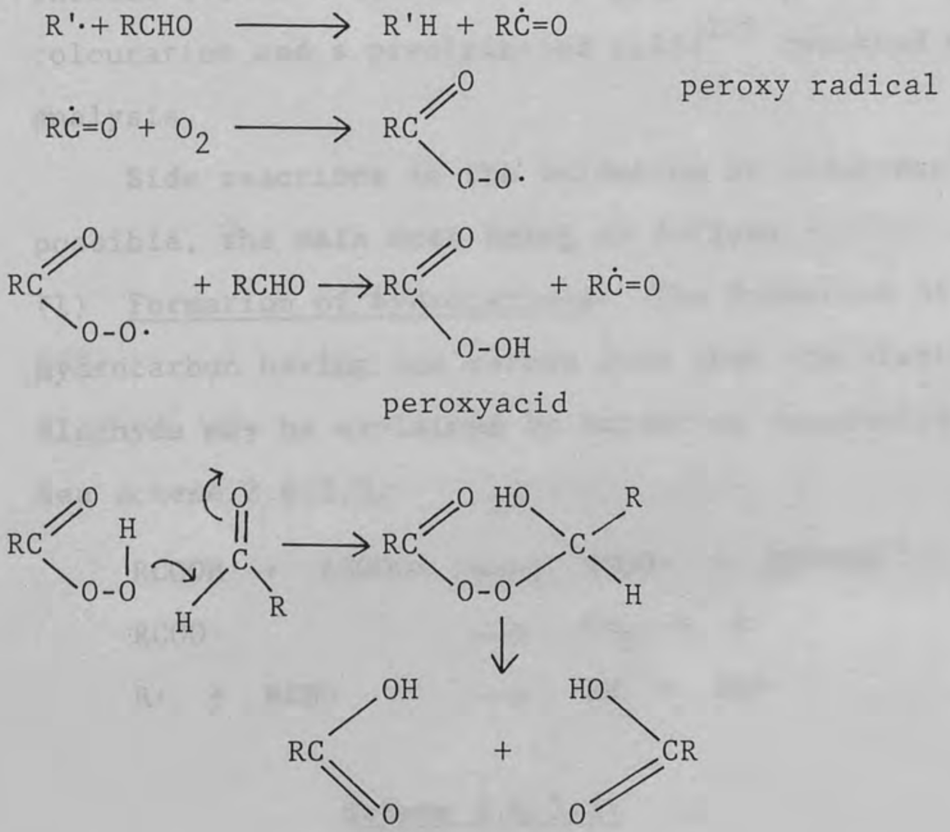
Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Possible Structure(s)	Notes
196.P	232	215	214	 (CI)	
248.P	242	225	224	 $C_3H_7CH=CH-C(=O)-C(C_3H_7)=CH-COOCH_3$ (CII)	
233.P	246	229	228	 $C_3H_7CH=CH-CH(OH)-CH(C_3H_7)-CH_2COOCH_3$ (CIII)	Three alternative structures for one compound eluted
				 (CIV)	
				 $C_3H_7CH(OCH_3)-CH_2-C(=O)-CH(C_3H_7)-CH_2-CHO$ (CV)	

Table 35 (continued)

Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Possible Structure(s)	Notes
263.P	260	243	242	 $C_3H_7CH{=}CH{-}CH(OH){-}C(C_3H_7)(O){-}CHCOOCH_3$ (CVI)  $C_3H_7CH{-}CH(O){-}C(=O){-}CH(C_3H_7){-}CH_2COOCH_3$ (CVII)  $C_3H_7CH{=}CH{-}C(=O){-}CH(C_3H_7){-}CH_2CH(OCH_3)_2$ (CVIII)	Three alternative structures for one compound eluted

Over the years the oxidation of aldehydes has been the subject of much reseach using either thermal, photochemical or catalytic autoxidation. Two references written in 1955 are worth noting here,[218,219] which review the early work on the autoxidation of aldehydes. Later reviews include work by Maslov and Blyumberg,[220] as well as Denisov.[160] From these investigations, it has been concluded that the free radical mechanism whereby the aldehyde is oxidised to the acid goes via the peracid,[5,160] as shown in scheme 2.6.3.1.

The introduction of alkyl or aryl peroxides, metal-ion catalysts or ultraviolet light into an aldehyde-oxygen system can produce free radicals, the effect of which is to initiate reaction chains, as shown in scheme 2.6.3.1.



<u>Scheme 2.6.3.1.</u>

One mechanism suggested for the primary process in the thermal oxidation of aldehydes[221,222] is shown in scheme 2.6.3.2.

$$\mathrm{RCHO} + \mathrm{O_2} \longrightarrow \mathrm{HO_2}\cdot + \mathrm{R\dot{C}O}$$

Scheme 2.6.3.2.

This implies that the subsequent reactions of the $\mathrm{R\dot{C}O}$ radical are the same as in photochemical or catalytic oxidation.

From early investigations, other products reported, besides the peracid, peracid-aldehyde complex and the expected acid corresponding to the particular aldehyde, include carbon dioxide,[223,224] products giving a yellow colouration and a precipitated solid[225] reported without analysis.

Side reactions in the oxidation of aldehydes[226] are possible, the main ones being as follows:-

(1) Formation of hydrocarbons: The formation of a hydrocarbon having one carbon less than the starting aldehyde may be explained by oxidative decarboxylation.[220,227] See scheme 2.6.3.3.

$$\begin{aligned}
&\mathrm{RCOOH} + \mathrm{RCOOO}\cdot &&\longrightarrow \mathrm{RCOO}\cdot + \mathrm{RCOOOH}\\
&\mathrm{RCOO}\cdot &&\longrightarrow \mathrm{CO_2} + \mathrm{R}\cdot\\
&\mathrm{R}\cdot + \mathrm{RCHO} &&\longrightarrow \mathrm{RH} + \mathrm{RCO}\cdot
\end{aligned}$$

Scheme 2.6.3.3.

(2) Formation of alcohols and ketones: Secondary alcohols having one carbon less than the starting aldehyde are found only in the oxidation of α branched aldehydes. The formation of alcohols proceeds initially analogously to the formation of hydrocarbons i.e., decarbonylation of the acyl radical. See scheme 2.6.3.4.

$$R\dot{C}O \longrightarrow R\cdot + CO$$

Scheme 2.6.3.4.

The secondary or tertiary alkyl radical formed is more stable than the primary radical formed from unbranched aldehydes and is thus more susceptible to oxidation to the alkylperoxy radical. See scheme 2.6.3.5.

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

$$ROO\cdot + RCHO \longrightarrow ROOH + RCO\cdot$$

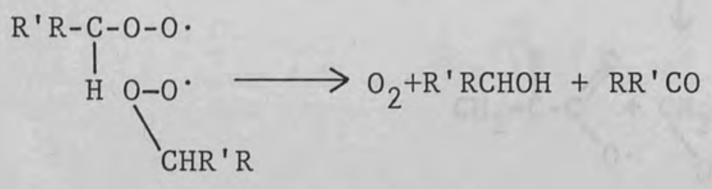
Scheme 2.6.3.5.

The hydroperoxide ROOH can undergo thermal, (see scheme 2.6.3.6), or catalytic (see scheme 1.9.6, section 1.9) decomposition to form alkoxy radicals leading to alcohols.

$$2ROOH \longrightarrow 2RO\cdot + H_2O \xrightarrow{RCHO} ROH + RCO\cdot$$

Scheme 2.6.3.6.

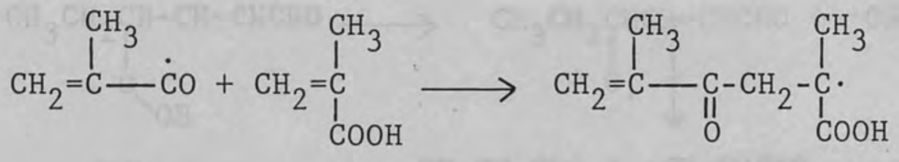
According to Russell[228] an alternative route is the bimolecular recombination of secondary alkylperoxy radicals to give alcohols, ketones and oxygen. See scheme 2.6.3.7.



$$\mathrm{R'R{-}\underset{H}{C}{-}O{-}O\cdot \quad \cdot O{-}O{-}CHR'R \longrightarrow O_2{+}R'RCHOH + RR'CO}$$

Scheme 2.6.3.7.

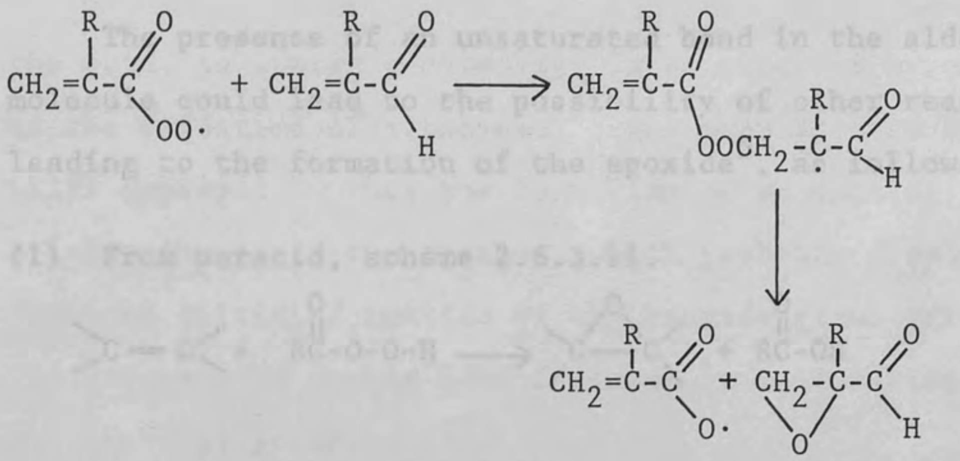
The autoxidation of unsaturated aldehydes yields the corresponding acid, as shown for saturated aldehydes. See scheme 2.6.3.1. However, the reaction is complicated by the fact that the acyl radical from the aldehyde can initiate polymerisation of the acid product,[160] as shown in scheme 2.6.3.8.



$$\mathrm{CH_2{=}\overset{CH_3}{C}{-}\dot{C}O + CH_2{=}\underset{COOH}{\overset{CH_3}{C}} \longrightarrow CH_2{=}\overset{CH_3}{C}{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}\underset{COOH}{\overset{CH_3}{C}}\cdot}$$

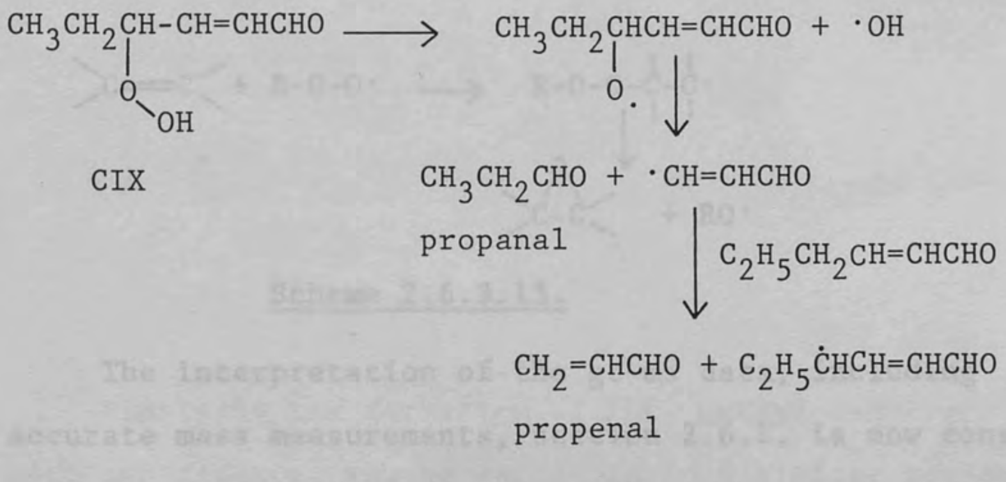
Scheme 2.6.3.8.

Besides the mechanisms of side product formation discussed earlier, it is thought that epoxidation of the unsaturated aldehydes reaction may occur by an addition of the acylperoxy-radical to the double bond of the aldehyde.[220,226] See scheme 2.6.3.9.



Scheme 2.6.3.9.

Autoxidation of an unsaturated aldehyde such as trans-2-hexenal may lead to the formation of the hydroperoxide on carbon C(4), i.e. α position to the double bond (CIX). Decomposition of this hydroperoxide would probably give propanal and propenal, as the main products. See scheme 2.6.3.10.

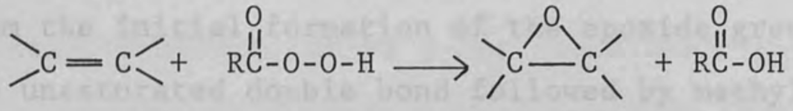


CIX

Scheme 2.6.3.10.

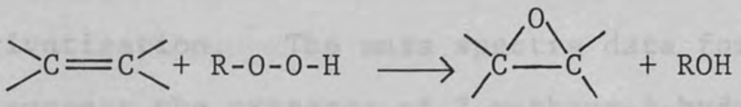
The presence of an unsaturated bond in the aldehyde molecule could lead to the possibility of other reactions leading to the formation of the epoxide[5], as follows:-

(1) From peracid, scheme 2.6.3.11.



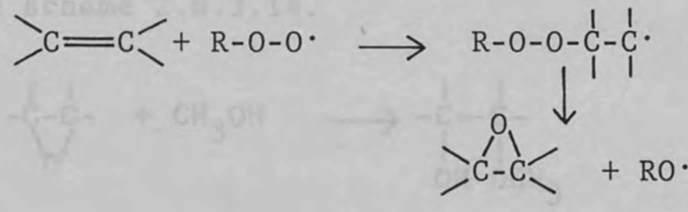
Scheme 2.6.3.11.

(2) From alkyl hydroperoxide, scheme 2.6.3.12.



Scheme 2.6.3.12.

(3) From peroxy radical, scheme 2.6.3.13.

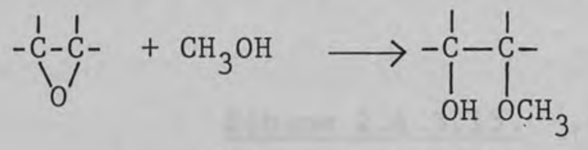


Scheme 2.6.3.13.

The interpretation of the gc-ms data, including accurate mass measurements, section 2.6.1, is now considered.

Compounds LXXIV and LXXV in table 34 (see section 2.6.1) seemed to suggest the presence of cis and trans methyl-2-hexenoate respectively, which could arise from the methylation of 2-hexenoic acid. The formation of the acid, as stated previously, is an expected product of the oxidation of aldehydes. The mass spectra for LXXVI appeared to show the formation of an epoxide, 1,1-dimethoxy-2,3-epoxyhexane, which probably resulted from the initial formation of the epoxide group across the unsaturated double bond followed by methylation of the carbonyl group.

Similarly, LXXIX also suggested the formation of an epoxide, but in this case, it appeared that the aldehyde had simultaneously been oxidised to the acid prior to derivatisation. The mass spectra data for LXXX seemed to suggest the presence of 2-methoxy-3-hydroxy-hexanal. This compound could have arisen via the formation of an epoxide during the autoxidation of 2-hexenal followed by subsequent alcoholysis of the epoxide by the methanol.[229] See scheme 2.6.3.14.

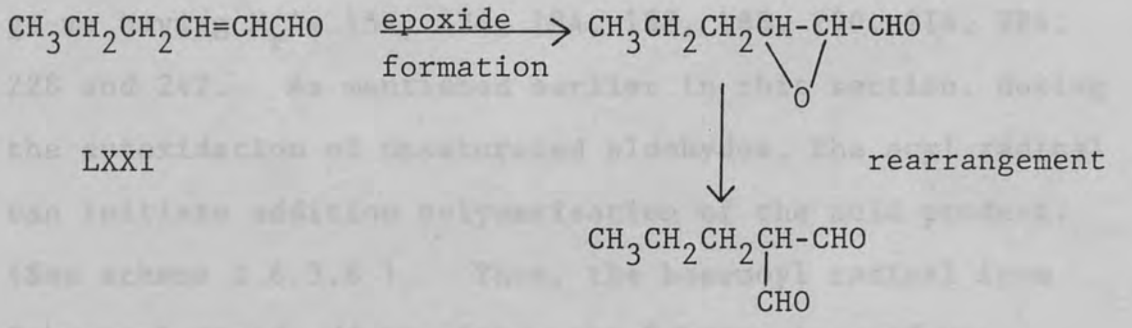


Scheme 2.6.3.14.

Similarly the formation of XCI, methyl-2-hydroxy-3-methoxyhexanoate, can be explained in a similar manner to LXXX. However, here the aldehyde has undergone oxidation to the carboxylic acid and subsequently to the methyl ester. LXXXV suggested the formation of methyl 2,3-dimethoxyhexanoate. A tentative route for the formation of this compound may have been epoxidation and

and oxidation of the aldehydic group. Complete derivatisation by the BF_3/CH_3OH may then have occurred at the epoxide and at the acid groups.

The mass spectra data for XCII seemed possibly to indicate the formation of 2-(carbomethoxy)pentanal. This compound could well have arisen from the initial formation of the epoxide group across the double bond of 2-hexenal (LXXI) followed by rearrangement.[230,231] See scheme 2.6.3.15. Subsequent oxidation of one of the carbonyl groups to the acid followed by methylation would lead to the compound (XCII).



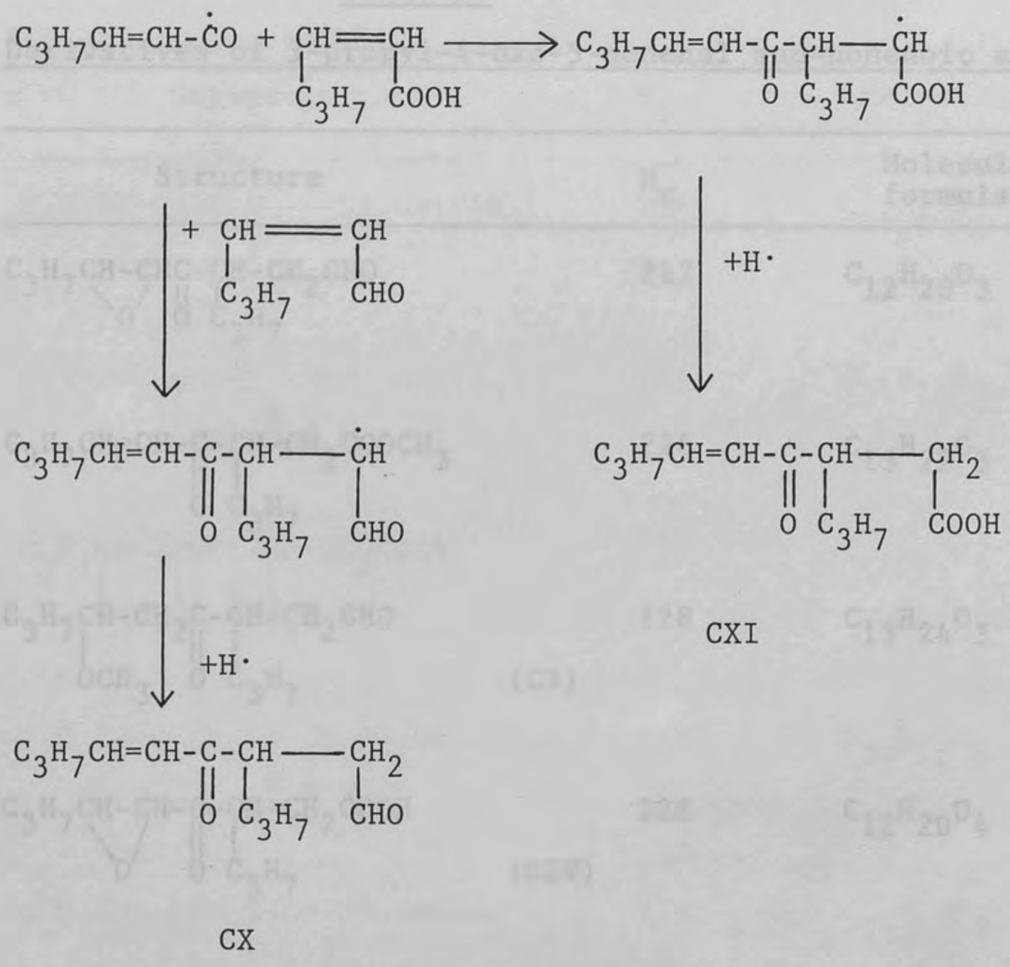
Scheme 2.6.3.15.

The mass spectra data for LXXXVI suggested the presence of 2-(carboxy)hexanal, formed through a similar epoxide formation as with XCII, followed by rearrangement from 2-heptenal. Thus, it appeared that both LXXXVI and LXXIII (methyl pentanoate) corresponded to compounds that were formed through autoxidation of impurities in trans-2-hexenal.

The compounds identified from the accurate mass measurements showed the major component to be the methyl ester of trans-2-hexenoic acid, which would be the expected product. The analysis of the other compounds showed a predominance of epoxide type compounds prior to derivatisation.

The possible structures proposed for the gc-ms data obtained from some of the higher molecular mass material, using NH_3-CI spectra only (see Table 35, section 2.6.2), will now be considered.

Structural formulae have to be assigned to compounds, whose relative molecular mass was assigned from NH_3-CI gc-ms having M_r's 154, 174, 184, 186, 188, 200, 214, 224, 228 and 242. As mentioned earlier in this section, during the autoxidation of unsaturated aldehydes, the acyl radical can initiate addition polymerisation of the acid product. (See scheme 2.6.3.8). Thus, the hexenoyl radical from 2-hexenal could add to either the 2-hexenoic acid or 2-hexenal itself, as shown in scheme 2.6.3.16. Under the conditions of methylation, a variety of compounds could be formed from these products. Table 36 shows the different structures which might be formed from varying degrees of methylation of CX and CXI; structures formed from epoxidation of the double bond are also included.



CXI

CX

Scheme 2.6.3.16.

Only the structures CV and CIV as well as CVIII and CVII, have relative molecular masses 228 and 242 respectively, that have been shown to correspond to compounds in the gc-ms experiments. All the other compounds (in table 36) were not observed. Thus, it seems likely that the majority of suggested products in table 35 must arise by an alternative route. A possible suggestion is that a type of Prins addition[232,233] occurs

Table 36

Derivatives of 3-propyl-4-oxo-5-nonenal and-nonenoic acid

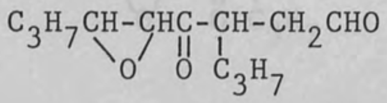
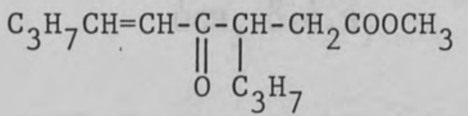
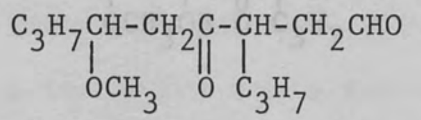
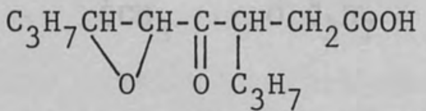
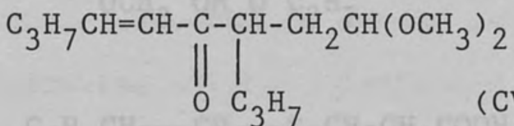
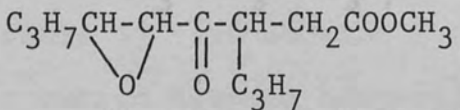
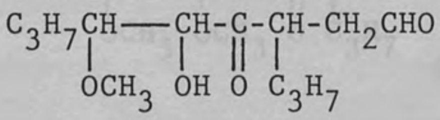
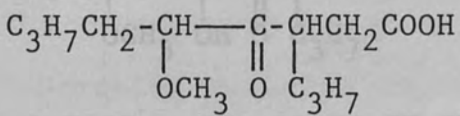
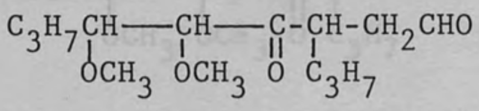
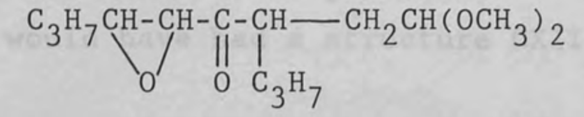
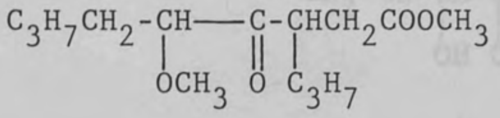
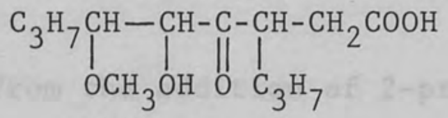
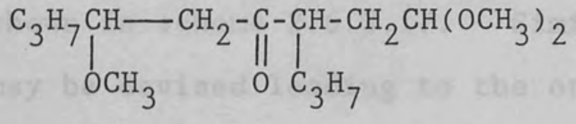
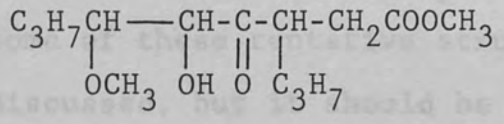
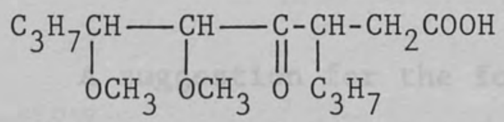
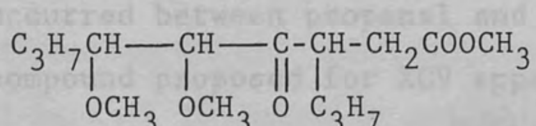
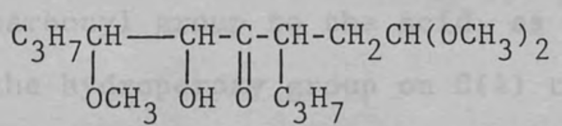
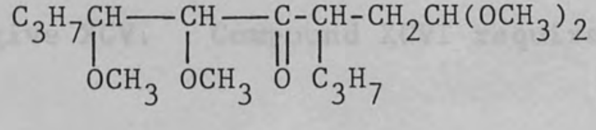
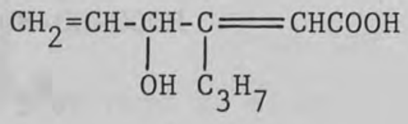
Structure	M_r	Molecular formula
	212	$C_{12}H_{20}O_3$
 $C_3H_7CH{=}CH\text{-}\underset{O}{\underset{\Vert}{C}}\text{-}\underset{C_3H_7}{\underset{\vert}{CH}}\text{-}CH_2COOCH_3$	226	$C_{13}H_{22}O_3$
 $C_3H_7\underset{OCH_3}{\underset{\vert}{CH}}\text{-}CH_2\underset{O}{\underset{\Vert}{C}}\text{-}\underset{C_3H_7}{\underset{\vert}{CH}}\text{-}CH_2CHO$ (CV)	228	$C_{13}H_{24}O_3$
 (CIV)	228	$C_{12}H_{20}O_4$
 $C_3H_7CH{=}CH\text{-}\underset{O}{\underset{\Vert}{C}}\text{-}\underset{C_3H_7}{\underset{\vert}{CH}}\text{-}CH_2CH(OCH_3)_2$ (CVIII)	242	$C_{14}H_{26}O_3$
 (CVII)	242	$C_{13}H_{22}O_4$
 $C_3H_7\underset{OCH_3}{\underset{\vert}{CH}}\text{—}\underset{OH}{\underset{\vert}{CH}}\text{-}\underset{O}{\underset{\Vert}{C}}\text{-}\underset{C_3H_7}{\underset{\vert}{CH}}\text{-}CH_2CHO$	244	$C_{13}H_{24}O_4$
 $C_3H_7CH_2\text{-}\underset{OCH_3}{\underset{\vert}{CH}}\text{—}\underset{O}{\underset{\Vert}{C}}\text{-}\underset{C_3H_7}{\underset{\vert}{CH}}CH_2COOH$	244	$C_{13}H_{24}O_4$
 $C_3H_7\underset{OCH_3}{\underset{\vert}{CH}}\text{—}\underset{OCH_3}{\underset{\vert}{CH}}\text{—}\underset{O}{\underset{\Vert}{C}}\text{-}\underset{C_3H_7}{\underset{\vert}{CH}}\text{-}CH_2CHO$	258	$C_{14}H_{26}O_4$

Table 36 (continued)

Structure	M_r	Molecular formula
 $C_3H_7\underset{\diagdown O\diagup}{CH-CH}-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{C_3H_7}}{CH}-CH_2CH(OCH_3)_2$	258	$C_{14}H_{26}O_4$
 $C_3H_7CH_2-\underset{\overset{|}{OCH_3}}{CH}-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{C_3H_7}}{CH}CH_2COOCH_3$	258	$C_{14}H_{26}O_4$
 $C_3H_7\underset{\overset{|}{OCH_3}}{CH}-\underset{\overset{|}{OH}}{CH}-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{C_3H_7}}{CH}-CH_2COOH$	260	$C_{13}H_{24}O_5$
 $C_3H_7\underset{\overset{|}{OCH_3}}{CH}-CH_2-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{C_3H_7}}{CH}-CH_2CH(OCH_3)_2$	274	$C_{15}H_{30}O_4$
 $C_3H_7\underset{\overset{|}{OCH_3}}{CH}-\underset{\overset{|}{OH}}{CH}-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{C_3H_7}}{CH}-CH_2COOCH_3$	274	$C_{14}H_{26}O_5$
 $C_3H_7\underset{\overset{|}{OCH_3}}{CH}-\underset{\overset{|}{OCH_3}}{CH}-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{C_3H_7}}{CH}-CH_2COOH$	274	$C_{14}H_{26}O_5$
 $C_3H_7\underset{\overset{|}{OCH_3}}{CH}-\underset{\overset{|}{OCH_3}}{CH}-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{C_3H_7}}{CH}-CH_2COOCH_3$	288	$C_{15}H_{28}O_5$
 $C_3H_7\underset{\overset{|}{OCH_3}}{CH}-\underset{\overset{|}{OH}}{CH}-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{C_3H_7}}{CH}-CH_2CH(OCH_3)_2$	290	$C_{15}H_{30}O_5$
 $C_3H_7\underset{\overset{|}{OCH_3}}{CH}-\underset{\overset{|}{OCH_3}}{CH}-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{C_3H_7}}{CH}-CH_2CH(OCH_3)_2$	304	$C_{16}H_{32}O_5$

between the decomposition products of 4-hydroperoxy-2-hexenal, (i.e. propanal and propenal, see scheme 2.6.3.10), with 2-hexenal, as well as with itself. For example, compound XCVII (M_r 184) from table 35 prior to derivatisation would have had a structure CXII. This could have arisen

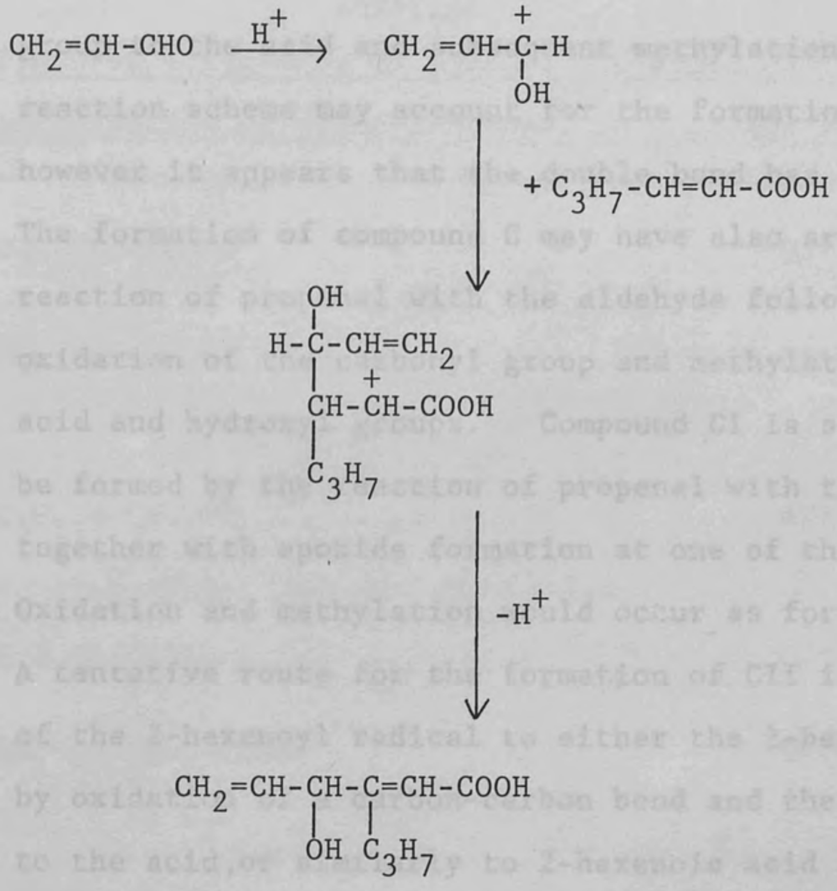


$$CH_2{=}CH{-}\underset{OH}{CH}{-}\underset{C_3H_7}{C}{=}CHCOOH$$

CXII

from the addition of 2-propenal to 2-hexenoic acid. A tentative route for the formation of CXII in this way is shown in scheme 2.6.3.17. Similar types of reaction schemes may be devised leading to the other suggested structures for the measured values of M_r. The possible manner in which some of these tentative structures may have arisen is now discussed, but it should be noted that none of the molecular formulae has been confirmed by accurate mass measurements.

A suggestion for the formation of compound XCIV, table 35 (see section 2.6.2) is that a reaction had occurred between propenal and trans-2-hexenal. The compound proposed for XCV appeared to show epoxidation across the carbon-carbon double bond and oxidation of the carbonyl group to the acid, as well as decomposition of the hydroperoxy group on C(4) to the hydroxyl group. Subsequent methylation at the acid and hydroxyl sites would give XCV. Compound XCVI requires there to have been



CXII

Scheme 2.6.3.17.

decomposition of the hydroperoxy group on C(4) of 2-hexenal followed by methylation. This is accompanied by an initial formation of the epoxide group across the double bond of 2-hexenal followed by rearrangement (see scheme 2.6.3.15) and methylation of one of the carbonyl groups. Compound XCVIII suggested that reaction had occurred between propanal and 2-hexenal followed by oxidation of the carbonyl

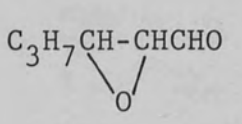
group to the acid and subsequent methylation. A similar reaction scheme may account for the formation of XCIX, however it appears that the double bond has been reduced. The formation of compound C may have also arisen from the reaction of propanal with the aldehyde followed by oxidation of the carbonyl group and methylation of both acid and hydroxyl groups. Compound CI is suggested to be formed by the reaction of propenal with the hexenal together with epoxide formation at one of the double bonds. Oxidation and methylation would occur as for C.
A tentative route for the formation of CII is the addition of the 2-hexenoyl radical to either the 2-hexenal followed by oxidation of a carbon-carbon bond and the carbonyl group to the acid,or similarly to 2-hexenoic acid and subsequent methylation. Compounds CIII and CVI (Mr's 228 and 242 respectively) might be formed by the addition of trans-2-hexenal to itself with subsequent oxidation and methylation to varying degrees. However, for these two relative molecular masses, it is possible that the alternative structures (CIV, CV, CVII and CVIII) may be appropriate. See table 36 and earlier discussion in this section.

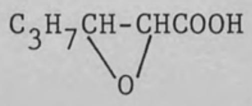
Table 37 shows the proposed structures of some of the compounds formed from the autoxidation of trans-2-hexenal in the dark at 70°C, prior to their derivatisation by BF_3/CH_3OH complex. They are derived from both the accurate mass data (section 2.6.1) and the NH_3-CI gc-ms (section 2.6.2). However, it must be noted that none of the

Table 37

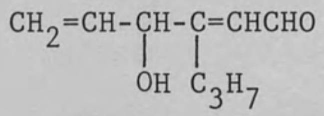
Proposed structures of some of the compounds formed from autoxidation of trans-2-hexenal in the dark at 70°C

$C_3H_7CH=CHCOOH$ CXIII

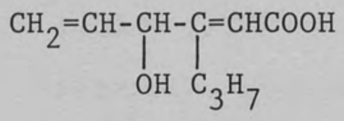

CXIV


CXV

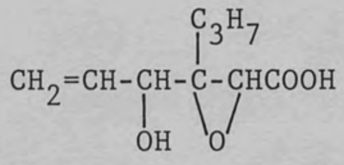
$C_3H_7CH(CHO)_2$ CXVI

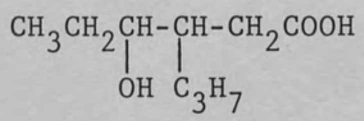

$CH_2=CH-\underset{OH}{CH}-\underset{C_3H_7}{C}=CHCHO$

CXVII

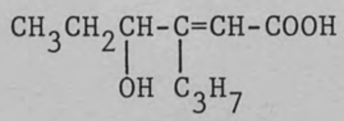

$CH_2=CH-\underset{OH}{CH}-\underset{C_3H_7}{C}=CHCOOH$

CXII

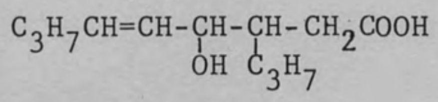

CXVIII


$CH_3CH_2\underset{OH}{CH}-\underset{C_3H_7}{CH}-CH_2COOH$

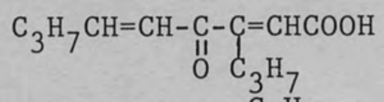
CXIX


$CH_3CH_2\underset{OH}{CH}-\underset{C_3H_7}{C}=CH-COOH$

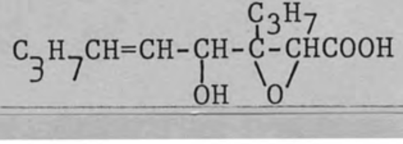
CXX


$C_3H_7CH=CH-\underset{OH}{CH}-\underset{C_3H_7}{CH}-CH_2COOH$

CXXI


$C_3H_7CH=CH-\underset{O}{\overset{\|}{C}}-\underset{C_3H_7}{C}=CHCOOH$

CXXII


CXXIII

molecular formulae of the derivatised compounds of structures (CXVII-CXXIII) and CXII were confirmed by accurate mass measurements.

None of the structures in table 37 has sufficient conjugation to give them a chromophore characteristic of a yellow colour. Although the major product of the autoxidation of trans-2-hexenal in the dark at 70°C is the acid, it would appear that side reactions do occur to give small quantities of other products.

It could be envisaged that some of the compounds having structures shown in table 37 could undergo further addition and oxidation reactions and as the amount of conjugation builds up some products may absorb to give a yellow colouration. This type of higher molecular mass material, undoubtedly present in the autoxidation mixture, was probably not analysed under the experimental conditions used. However, it seems probable that the precursors of some of these types of yellow compounds were analysed.

2.6.4 GC-MS analysis of derivatised samples produced under autoxidation conditions of 2-propenal (with accurate mass measurements

Derivatised samples of autoxidised 2-propenal were analysed by the manner discussed in section 2.6. The total ion current chromatogram obtained from the capillary gc-ms analysis is shown in figure 2.6.4.1. With the EI and NH_3-CI spectra being obtained at the apex of each chromatographic peak. The accurate mass data is shown in table 38. The relative abundances (AB) of ions were expressed as percentages of the base peak in each spectrum. Scan No.12 is probably due to a solvent peak.

Scan No.99

NH_3-CI	$[M.NH_4]^+$	$[MH]^+$
m/z	106	not observed

EI

m/z	87	60	57	45	43
Rel AB%	8	59	18	100	19

The accurate mass data was not obtained but CI/MS suggested M_r = 88.

Fig. 2.6.4.1. Capillary total ion current chromatogram of derivatised samples produced under autoxidation conditions of 2-propenal (with accurate mass measurements)

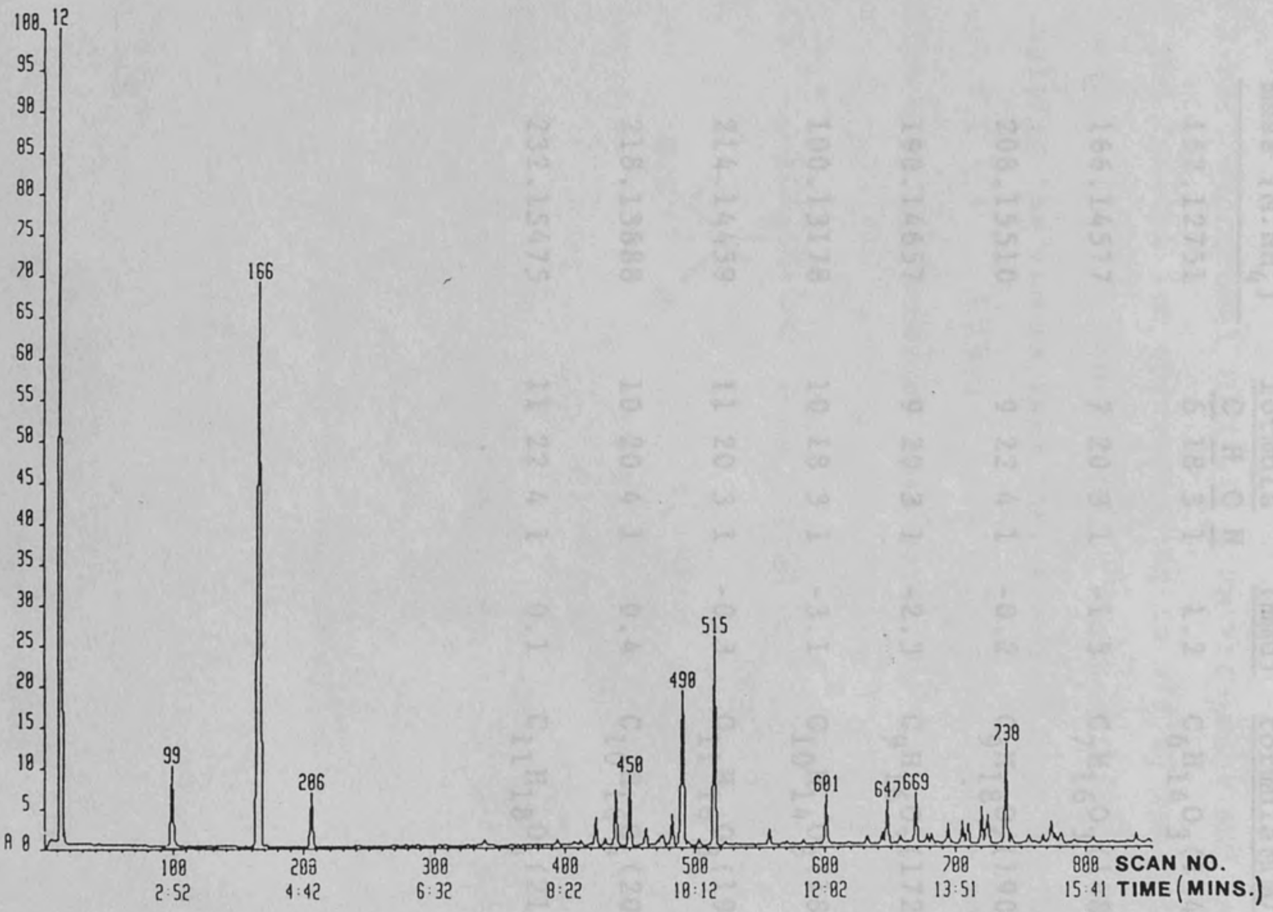
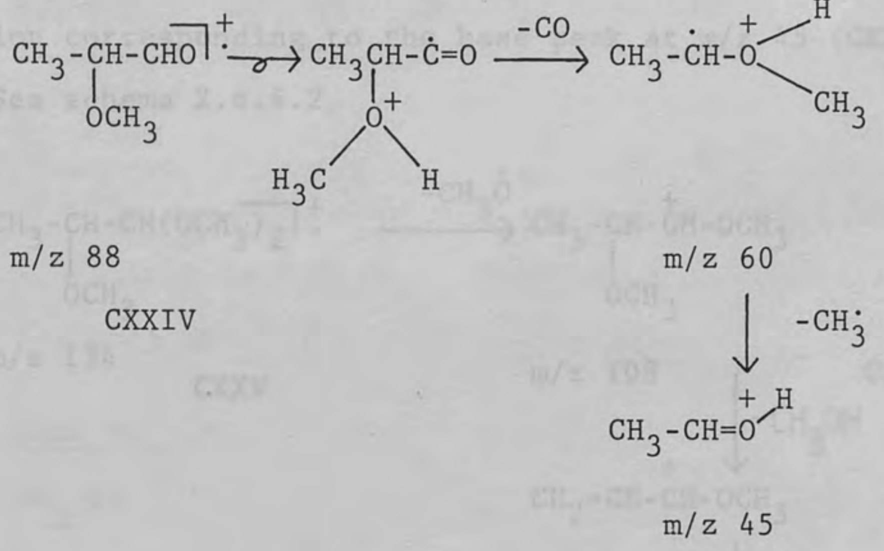


Table 38

Accurate mass measurements for propenal sample

Nominal m/z	Observed mass $[M.NH_4]^+$	Molecular formula				Error (mmu)	Molecular formula M(m/z)
		C	H	O	N		
152	152.12751	6	18	3	1	1.2	$C_6H_{14}O_3$(134)
166	166.14577	7	20	3	1	-1.5	$C_7H_{16}O_3$(148)
208	208.15510	9	22	4	1	-0.2	$C_9H_{18}O_4$(190)
190	190.14657	9	20	3	1	-2.3	$C_9H_{16}O_3$(172)
200	100.13178	10	18	3	1	-3.1	$C_{10}H_{14}O_3$(182)
214	214.14459	11	20	3	1	-0.3	$C_{11}H_{16}O_3$(196)
218	218.13888	10	20	4	1	0.4	$C_{10}H_{16}O_4$(200)
232	232.15475	11	22	4	1	0.1	$C_{11}H_{18}O_4$(214)

The difference between the molecular mass of this compound and that of 2-propenal is 32 daltons. Thus, it would seem that methanol has added across the double bond to give 2-methoxypropanal (CXXIV). Rearrangment and loss of CO by the radical ion corresponding to m/z 88 would lead to the formation of the ion m/z 60. Further loss of $CH_3^{\cdot}$ would result in the ion representing the base peak m/z 45, see scheme 2.6.4.1. However, this molecular formula was not confirmed by the accurate mass data.



Scheme 2.6.4.1.

Scan No. 166

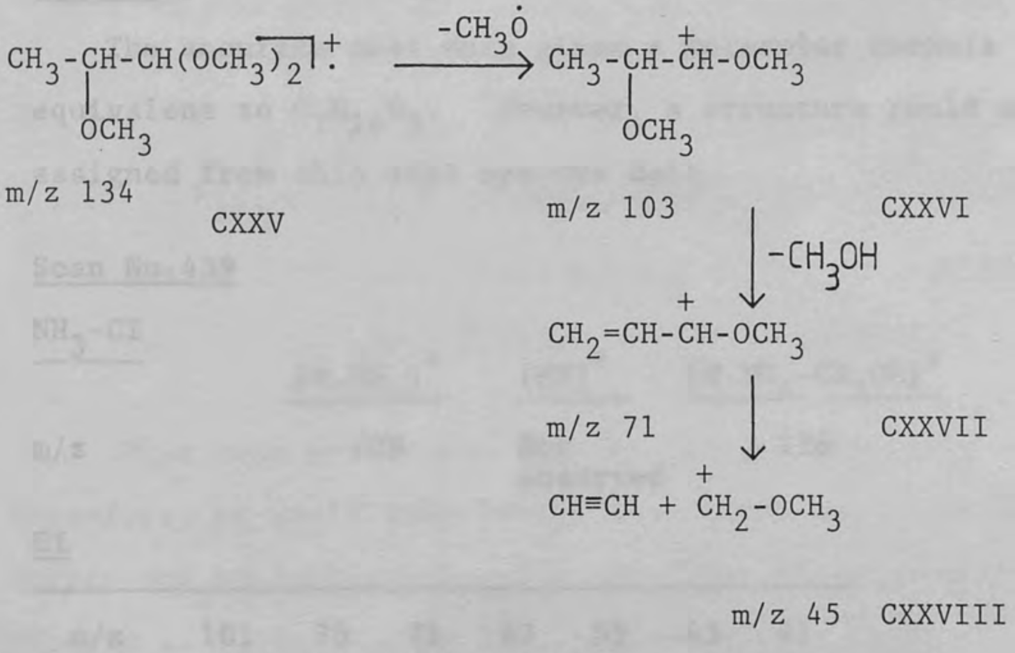
NH_3-CI	$[M.NH_4]^+$	$[MH]^+$	$[M.NH_4-CH_3OH]^+$
m/z	152	not observed	120

EI

m/z	103	75	71	59	47	45
Rel AB%	24	89	25	8	28	100

$M_r = 134$

The accurate mass data gives a molecular formula M equivalent to $C_6H_{14}O_3$. The loss of $CH_3O\cdot$ (M-31) leads to the formation of the ion m/z 103 of composition $C_5H_{11}O_2{}^+$. The ion m/z 75 could be the fragment ion $(CH_3O)_2CH^+$. A suggestion for the structure of this compound is CXXV. See scheme 2.6.4.2. Loss of methanol from the ion m/z 103 (CXXVI) could lead to the formation of the ion m/z 71 (CXXVII). This ion could undergo hydrogen rearrangement followed by further fragmentation to give the ion corresponding to the base peak at m/z 45 (CXXVIII). See scheme 2.6.4.2.



$$CH_3\text{-}\underset{\displaystyle OCH_3}{CH}\text{-}CH(OCH_3)_2]^{+\cdot} \xrightarrow{-CH_3\dot{O}} CH_3\text{-}\underset{\displaystyle OCH_3}{CH}\text{-}\overset{+}{C}H\text{-}OCH_3$$

m/z 134 CXXV

m/z 103 CXXVI

$$\xrightarrow{-CH_3OH} CH_2{=}CH\text{-}\overset{+}{C}H\text{-}OCH_3$$

m/z 71 CXXVII

$$\longrightarrow CH{\equiv}CH + \overset{+}{C}H_2\text{-}OCH_3$$

m/z 45 CXXVIII

Scheme 2.6.4.2.

Using the mass spectra information, it would appear that this compound is 1,1,2-trimethoxypropane (CXXV).

Scan No.206

NH_3-CI

	$[M.NH_4]^+$	$[MH]^+$
m/z	166	149

EI

m/z	103	89	71	61	59	45
Rel AB%	14	59	18	71	9	100

M_r = 148

The accurate mass data gives a molecular formula of M equivalent to $C_7H_{16}O_3$. However, a structure could not be assigned from this mass spectra data.

Scan No.439

NH_3-CI

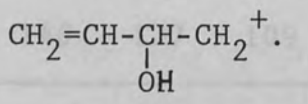
	$[M.NH_4]^+$	$[MH]^+$	$[M.NH_4-CH_3OH]^+$
m/z	208	Not observed	176

EI

m/z	101	75	71	67	55	45	41
Rel AB%	4	100	36	7	8	9	11

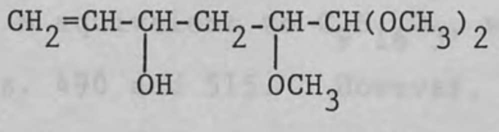
$M_r = 190$

The accurate mass data gives a molecular formula of M equivalent to $C_9H_{18}O_4$.

The base peak at m/z 75 could correspond to $C_3H_7O_2^{\,+}$, which could have the structure $(CH_3O)_2CH^+$. The fragment at m/z 71 could correspond to $C_4H_7O^+$, which could have the structure  $\mathrm{CH_2{=}CH{-}\underset{\displaystyle OH}{\underset{|}{C}}H{-}CH_2^{\;+}}$.

Using this mass spectra data, it would seem that this compound could have two possible structures:-

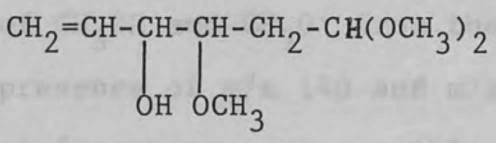
(i) 3-hydroxy-5,6,6-trimethoxyhex-1-ene, (CXXIX)



$\mathrm{CH_2{=}CH{-}\underset{\displaystyle OH}{\underset{|}{C}}H{-}CH_2{-}\underset{\displaystyle OCH_3}{\underset{|}{C}}H{-}CH(OCH_3)_2}$

CXXIX

(ii) 3-hydroxy-4,6,6-trimethoxyhex-1-ene, (CXXX).



$\mathrm{CH_2{=}CH{-}\underset{\displaystyle OH}{\underset{|}{C}}H{-}\underset{\displaystyle OCH_3}{\underset{|}{C}}H{-}CH_2{-}CH(OCH_3)_2}$

CXXX

This scan No.439 and scan No.482 are extremely similar, therefore, it would seem likely that these two scans correspond to two isomers with identical EI fragmentation. Thus it is impossible to distinguish between them.

Scan No.450

NH_3-CI

	$[M.NH_4]^+$	$[MH]^+$
m/z	190	173

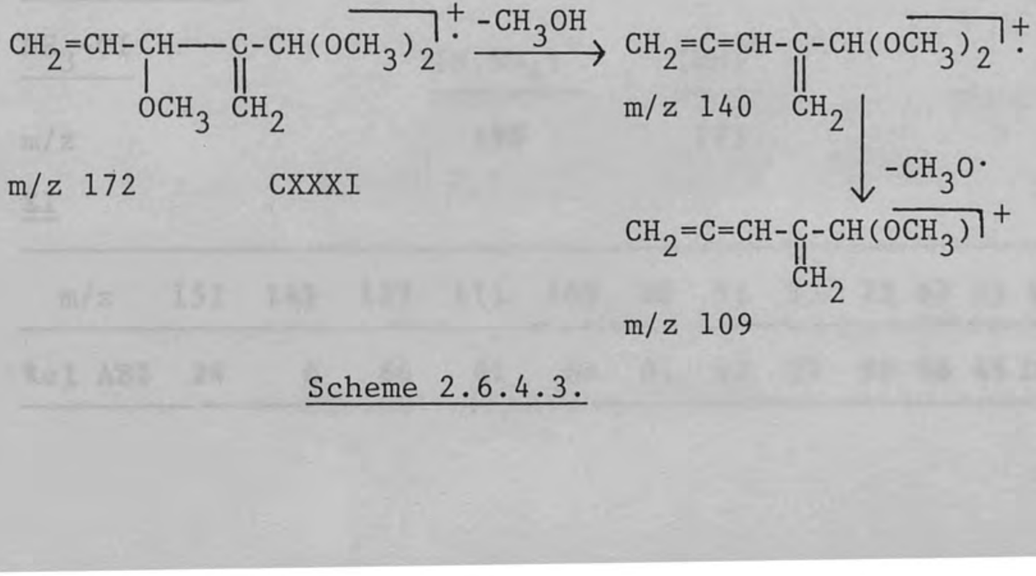
EI

m/z	140	127	109	97	75	67	53	45	41	39
Rel AB%	12	16	100	13	31	17	16	48	26	27

$M_r = 172$

The accurate mass data for this scan gives a molecular formula M equivalent to $C_9H_{16}O_3$, which is the same as for scan nos. 490 and 515. However, the EI and CI spectra for scan No.450 is quite different from the other two scans.

The ion m/z 75 could be the fragment ion $(CH_3O)_2CH^+$. Losses of CH_3OH and $CH_3O\cdot$ from the radical ion are indicated by the presence of m/z 140 and m/z 109. Using all the mass spectra information, one possible structure is CXXXI. See scheme 2.6.4.3.



Scheme 2.6.4.3.

Further fragmentation could lead to the ion at m/z 39, corresponding to $CH_2{=}C{=}\overset{+}{C}H$.

Thus it would seem that this compound could be 3-methoxy-4-(dimethoxymethyl)-1,4-pentadiene, (CXXXI).

Scan No.482

NH_3-CI

	$[M.NH_4]^+$	$[MH]^+$	$[M.NH_4-CH_3OH]^+$
m/z	208	not observed	176

EI

m/z	101	75	71	67	54	45	41
Rel AB%	4	100	31	5	6	9	11

$M_r = 190$

The accurate mass data gives a molecular formula of M equivalent to $C_9H_{18}O_4$. This scan No. is similar to scan No.439. (See scan No.439 for a discussion on the fragmentation of these two isomers).

Scan No. 490

NH_3-CI

	$[M.NH_4]^+$	$[MH]^+$
m/z	190	173

EI

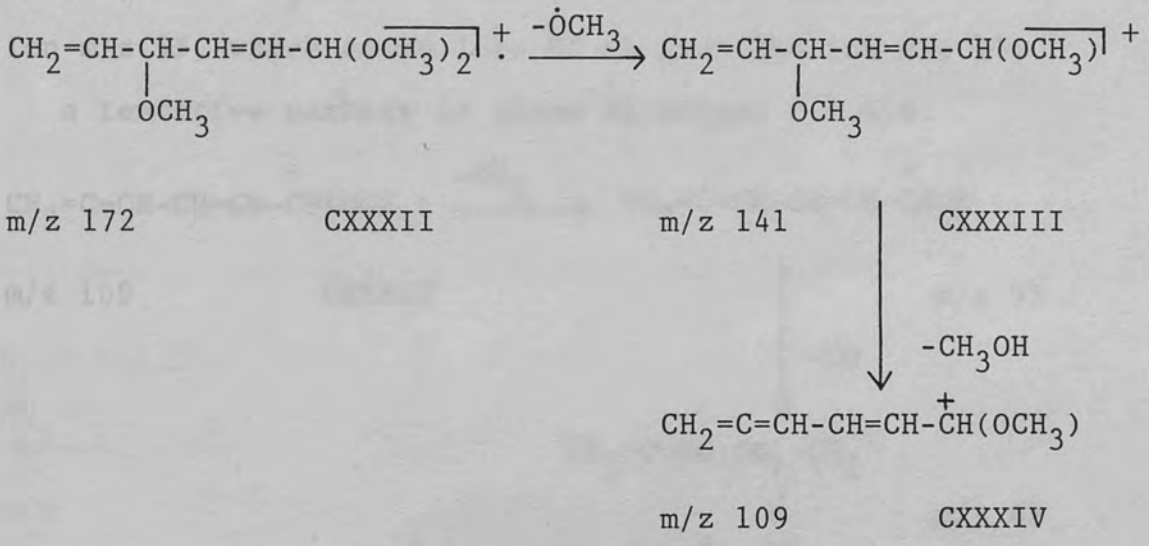
m/z	157	141	127	111	109	96	95	83	75	67	53	45	41	39
Rel AB%	24	6	66	61	64	84	62	27	80	68	49	100	81	98

$M_r = 172$

The accurate mass data for this scan No.490 gives a molecular formula M equivalent to $C_9H_{16}O_3$, which is the same as for scan Nos. 450 and 515. The EI and CI spectra for scan Nos. 490 and 515 are similar, whereas scan No. 450 is quite different.

Using all the mass spectra information, one structure, which may represent this data is CXXXII. Losses of $CH_3O^{\cdot}$(M-31) and further loss of methanol (M-63) would give ions of m/z 141 (CXXXIII) and m/z 109 (CXXXIV). A possible route for this fragmentation pathway is shown in scheme 2.6.4.4.

The peak at m/z 75 probably corresponds to the $(CH_3O)_2CH^+$ fragment.



$$CH_2{=}CH{-}\underset{\displaystyle OCH_3}{\underset{|}{C}}H{-}CH{=}CH{-}CH(OCH_3)_2]^{+\cdot} \xrightarrow{-\dot{O}CH_3} CH_2{=}CH{-}\underset{\displaystyle OCH_3}{\underset{|}{C}}H{-}CH{=}CH{-}CH(OCH_3)]^{+}$$

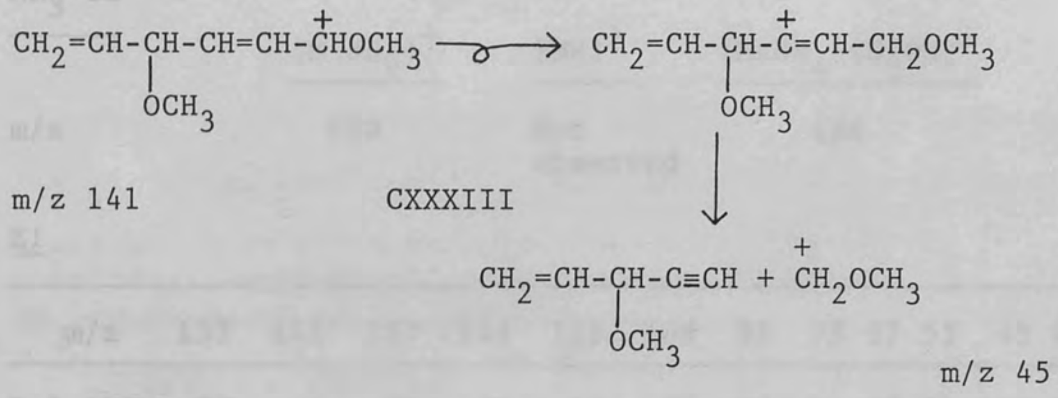
m/z 172 CXXXII m/z 141 CXXXIII

$$\xrightarrow{-CH_3OH} CH_2{=}C{=}CH{-}CH{=}CH{-}\overset{+}{C}H(OCH_3)$$

m/z 109 CXXXIV

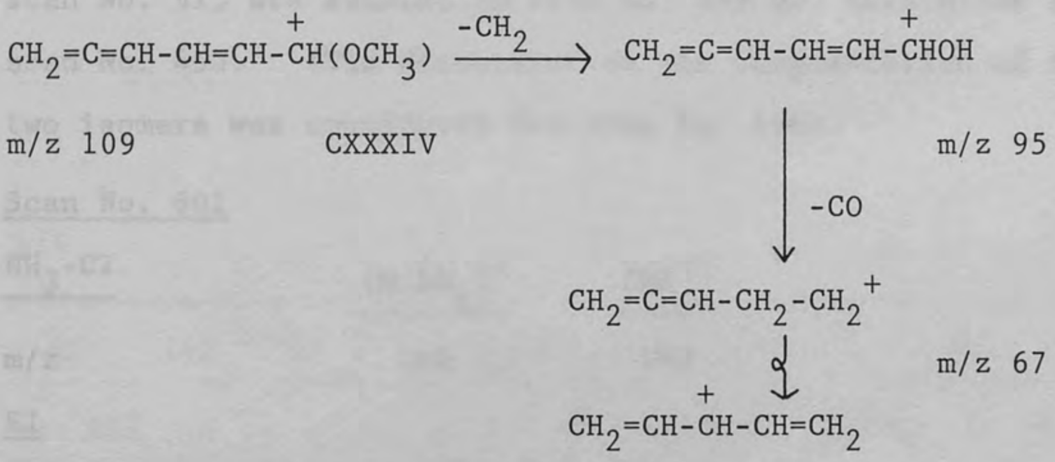
Scheme 2.6.4.4.

The ion m/z 141 (CXXXIII) could undergo a 1,3-hydrogen shift rearrangement, followed by subsequent fragmentation to give the ion corresponding to the base peak m/z 45. See scheme 2.6.4.5.



Scheme 2.6.4.5.

Loss of CH_2 from (CXXXIV) m/z 109, would lead to the ion m/z 95, which could lose CO to give the ion m/z 67; a tentative pathway is shown in scheme 2.6.4.6.



Scheme 2.6.4.6.

From the mass spectra data, it would seem that this compound could be either the cis or trans isomer of

3,6,6-trimethoxy-1,4-hexadiene (CXXXII) and that the compound eluted as scan No. 515 is the other isomer.

Scan No. 515

NH_3-CI

	$[M.NH_4]^+$	$[MH]^+$	$[M.NH_4-CH_3OH]^+$
m/z	190	Not observed	158

EI

m/z	157	141	127	114	110	109	95	75	67	53	45	41	39
Rel AB%	30	4	82	30	40	86	53	94	33	31	100	58	62

$M_r = 172$

The accurate mass data for this scan No. 515 gives a molecular formula M equivalent to $C_9H_{16}O_3$, which is the same as for scan Nos. 450 and 490. The EI and CI spectra for scan No. 515 are similar to scan No. 490 but dissimilar to scan No. 450. (The discussion on the fragmentation of the two isomers was considered for scan No. 490).

Scan No. 601

NH_3-CI

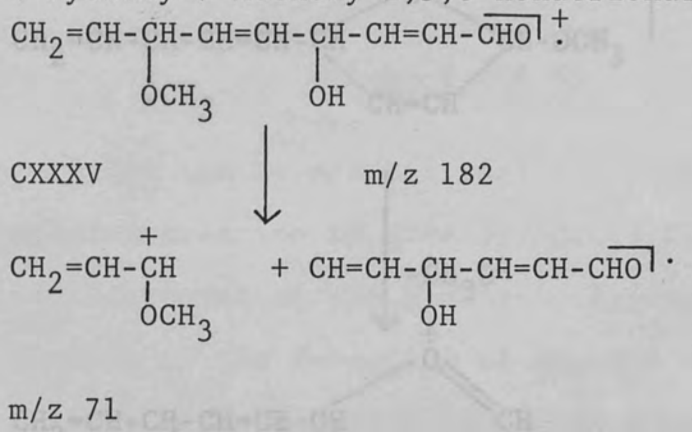
	$[M.NH_4]^+$	$[MH]^+$
m/z	200	183

EI

m/z	127	97	79	75	71	67	55	41
Rel AB%	7	23	56	30	100	30	23	45

M_r = 182

The accurate mass data gives a molecular formula of M equivalent to $C_{10}H_{14}O_3$. The base peak at m/z 71 could correspond to $C_4H_7O^+$. (See scheme 2.6.4.7). The peak at m/z 55 could be due to $C_3H_3O^+$, which could have the structure $CH{=}CH{-}CHO]^+$. Thus piecing these fragments together, a possible structure for this compound is 4-hydroxy-7-methoxy-2,5,8-nonatrienal (CXXXV).



$$CH_2{=}CH{-}\underset{OCH_3}{CH}{-}CH{=}CH{-}\underset{OH}{CH}{-}CH{=}CH{-}CHO]^{+\cdot}$$

$$\downarrow$$

$$CH_2{=}CH{-}\underset{OCH_3}{\overset{+}{CH}} + CH{=}CH{-}\underset{OH}{CH}{-}CH{=}CH{-}CHO]^{\cdot}$$

Scheme 2.6.4.7.

Scan No. 647

NH_3-CI

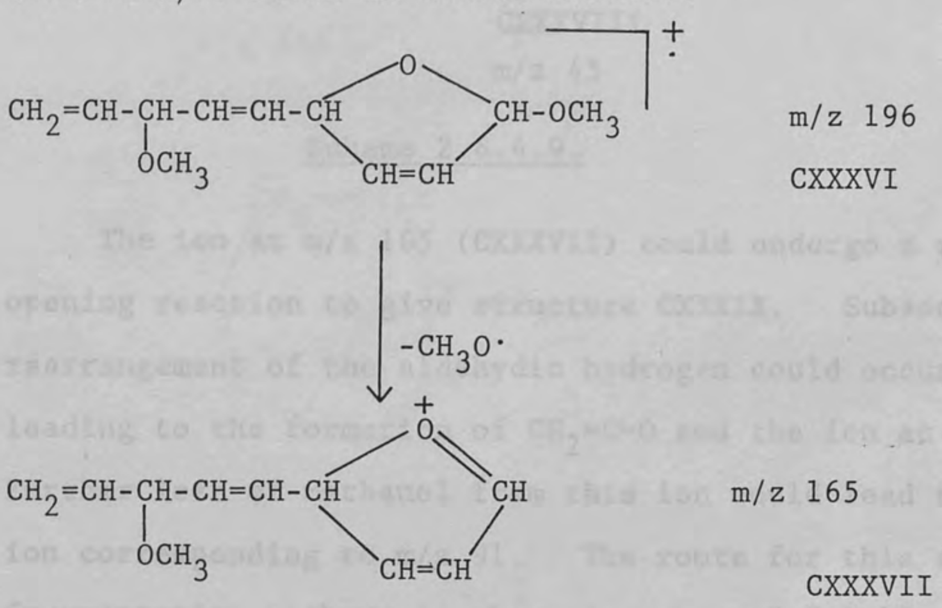
	$[M.NH_4]^+$	$[MH]^+$
m/z	214	197

EI

m/z	165	151	135	123	121	120	104	91	77	65	45	39
Rel AB%	4	7	11	5	22	21	15	91	27	16	100	26

$M_r = 196$

The accurate mass data gives a molecular formula of M equivalent to $C_{11}H_{16}O_3$. This accurate mass data is only 14 daltons (CH_2) higher than the previous scan No. 601, indicating that the structure of the two compounds is probably quite similar. A suggestion for the structure is CXXXVI. Loss of (M-31) could give an ion of m/z 165, (CXXXVII), as shown in scheme 2.6.4.8.

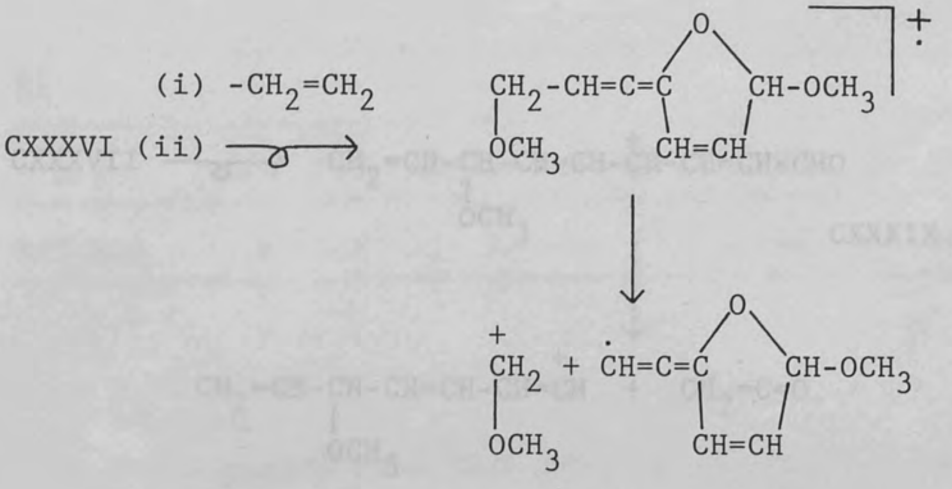


CXXXVI

CXXXVII

Scheme 2.6.4.8.

A tentative suggestion for the formation of the ion corresponding to the base peak at m/z 45, (CXXXVIII), could be the loss of ethene from the radical ion (CXXXVI) followed by hydrogen rearrangement and subsequent fragmentation, scheme 2.6.4.9.



CXXXVIII

m/z 45

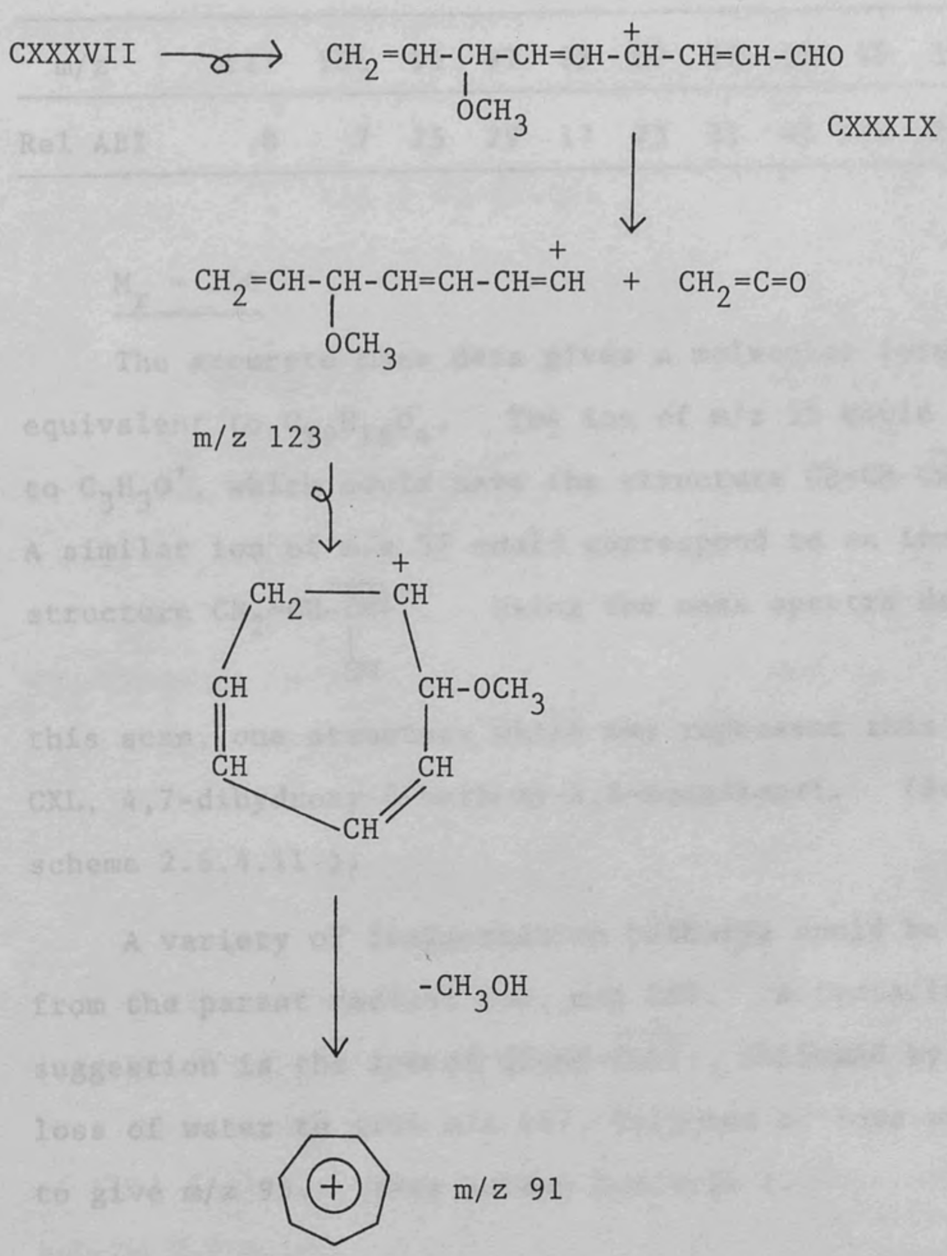
Scheme 2.6.4.9.

The ion at m/z 165 (CXXXVII) could undergo a ring opening reaction to give structure CXXXIX. Subsequent rearrangement of the aldehydic hydrogen could occur leading to the formation of $CH_2=C=O$ and the ion at m/z 123. Further loss of methanol from this ion could lead to the ion corresponding to m/z 91. The route for this suggested fragmentation pathway is shown in scheme 2.6.4.10.

This compound CXXXVI could be 2-(3'methoxypenta-1,4-dienyl)-5-methoxy-2,5-dihydrofuran.

Scan No. 669

NH_3-CI	$[M.NH_4]^+$	$[MH]^+$
m/z	218	201

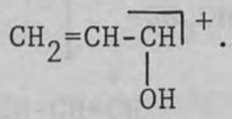


Scheme 2.6.4.10.

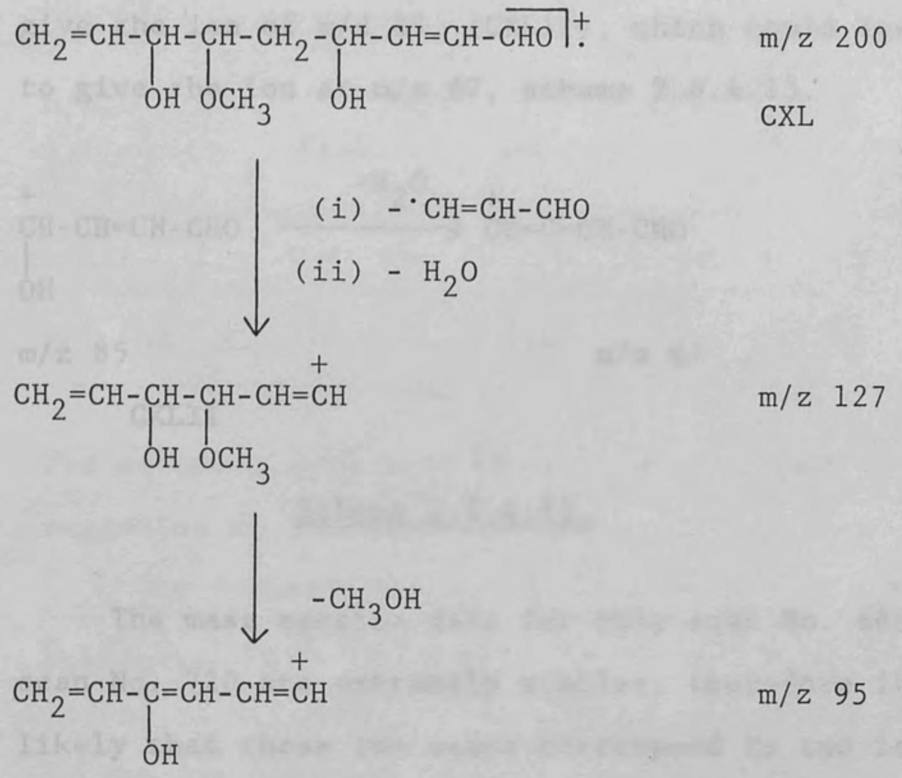
EI

m/z	127	101	95	87	85	67	57	55	45	39
Rel AB%	8	7	25	29	17	73	31	41	100	24

$M_r = 200$

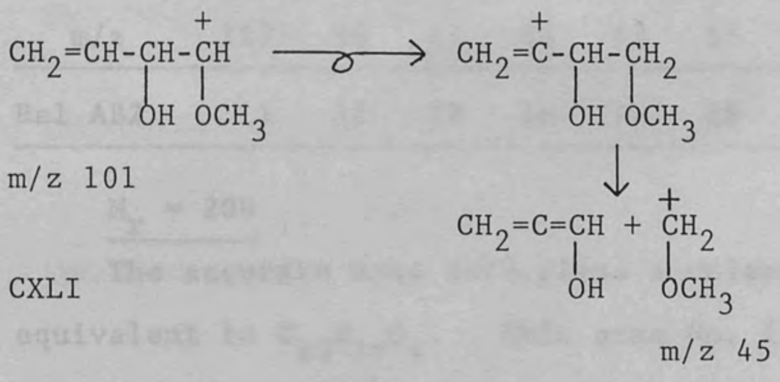
The accurate mass data gives a molecular formula M equivalent to $C_{10}H_{16}O_4$. The ion of m/z 55 could correspond to $C_3H_3O^+$, which could have the structure $CH{=}CH{-}\overline{CHO}\rceil^{+}$. A similar ion of m/z 57 could correspond to an ion of structure  $CH_2{=}CH{-}\underset{OH}{\overline{CH}}\rceil^{+}$. Using the mass spectra data for this scan, one structure which may represent this data is CXL, 4,7-dihydroxy-6-methoxy-2,8-nonadienal. (See scheme 2.6.4.11).

A variety of fragmentation pathways could be followed from the parent radical ion, m/z 200. A tentative suggestion is the loss of $CH{=}CH{-}\overline{CHO}\rceil^{\cdot}$, followed by the loss of water to give m/z 127, followed by loss of methanol to give m/z 95. (See scheme 2.6.4.11).



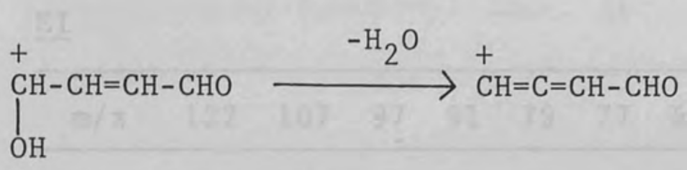
Scheme 2.6.4.11.

Fragmentation of the radical ion (CXL) could possibly lead to the formation of the ion m/z 101, (CXLI). The base peak at m/z 45 could arise from a 1,3-hydrogen shift of CXLI followed by subsequent fragmentation. See scheme 2.6.4.12.



Scheme 2.6.4.12.

An alternative fragmentation of CXL would possibly give the ion of m/z 85, (CXLII), which could lose water to give the ion at m/z 67, scheme 2.6.4.13.



$$\underset{\displaystyle OH}{\overset{+}{C}H}-CH=CH-CHO \xrightarrow{-H_2O} \overset{+}{C}H=C=CH-CHO$$

m/z 85 m/z 67

CXLII

Scheme 2.6.4.13.

The mass spectra data for this scan No. 669 and scan No. 720 are extremely similar, therefore it would seem likely that these two scans correspond to two isomers (cis and trans) with identical EI fragmentation. Thus, it is impossible to distinguish between them.

Scan No. 720

NH$_3$-CI	$[M.NH_4]^+$	$[MH]^+$
m/z	218	201

EI

m/z	127	94	87	85	67	57	55	45
Rel AB%	1	22	29	16	77	28	51	100

$M_r = 200$

The accurate mass data gives a molecular formula M equivalent to $C_{10}H_{16}O_4$. This scan No. is similar to scan No. 669, (see scan No. 669 for a discussion on the fragmentation of the two isomers).

Scan No. 724

NH_3-CI	$[M.NH_4]^+$	$[MH]^+$
m/z	250	233

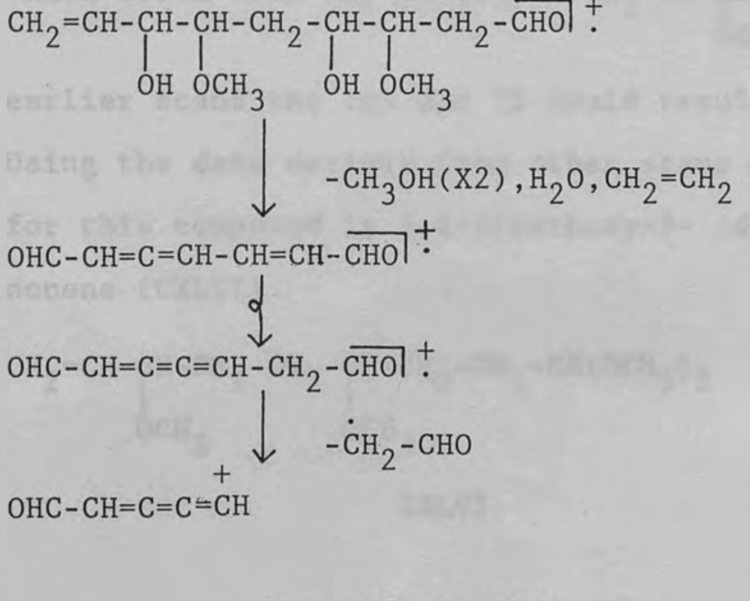
EI

m/z	122	107	97	91	79	77	65	56	40	39
Rel AB%	69	18	28	30	100	65	31	34	47	74

The accurate mass data was not obtained but CI/MS suggested M_r = 232.

The proposed molecular formula for this compound is $C_{11}H_{20}O_5$, which could have the structure CXLIII. Losses of methanol (twice), water and ethene could lead to the ion corresponding to m/z 122, (CXLIV).

Rearrangement of this radical ion followed by subsequent loss of $\cdot CH_2$-CHO could lead to the ion corresponding to the base peak at m/z 79, (CXLV). See scheme 2.6.4.14.



$CH_2=CH-CH(OH)-CH(OCH_3)-CH_2-CH(OH)-CH(OCH_3)-CH_2-CHO^{+\cdot}$ m/z 232 CXLIII

$\xrightarrow{-CH_3OH(X2),H_2O,CH_2=CH_2}$

$OHC-CH=C=CH-CH=CH-CHO^{+\cdot}$ m/z 122 CXLIV

$OHC-CH=C=C=CH-CH_2-CHO^{+\cdot}$

$\xrightarrow{-\dot{C}H_2-CHO}$

$OHC-CH=C=C=\overset{+}{C}H$ m/z 79 CXLV

Scheme 2.6.4.14.

The combined losses of CO and $H\dot{C}O$ from the radical ion CXLIV could also lead to the ion at m/z 65. Therefore, it would seem that this structure could be 4,7-dihydroxy-3,6-dimethoxy-8-nonenal (CXLIII). However the molecular formula of this structure was not confirmed by accurate mass data.

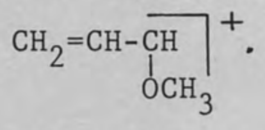
Scan No. 738

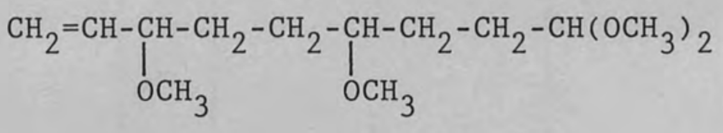
NH_3-CI	$[M.NH_4]^+$	$[MH]^+$
m/z	264	247

EI

m/z	158	103	97	87	75	71	55	45	41
Rel AB%	3	7	8	9	65	100	9	21	17

The CI/MS suggested $M_r = 246$.

The base peak at m/z 71 could correspond to $C_4H_7O^+$, which could have the structure  $\left[CH_2{=}CH\text{-}\underset{\substack{|\\ OCH_3}}{CH}\right]^+$. As with earlier scans the ion m/z 75 could result from $(CH_3O)_2CH.^+$ Using the data derived from other scans a possible structure for this compound is 3,6-dimethoxy-9- (dimethoxymethyl)-1-nonene (CXLVI).



$$CH_2{=}CH\text{-}\underset{\substack{|\\ OCH_3}}{CH}\text{-}CH_2\text{-}CH_2\text{-}\underset{\substack{|\\ OCH_3}}{CH}\text{-}CH_2\text{-}CH_2\text{-}CH(OCH_3)_2$$

CXLVI

The molecular formula corresponding to this structure was not confirmed by accurate mass data. (See also isobaric structures (CLIX - CLXVI) in table 40 in section 2.6.5 and discussion in section 2.6.6).

A summary of all these assignments is made in table 39.

2.6.5 GC-MS analysis of derivatised samples produced under autoxidation conditions of 2-propenal (NH_3-CI spectra only)

Derivatised samples of autoxidised 2-propenal were also examined at PCMU Harwell but using only NH_3-CI. The total ion current chromatogram (scan Nos. 46.P-281.P) obtained from this particular gc-ms analysis is shown in figure 2.6.5.1. The NH_3-CI data is shown in table 40, together with tentative suggestions as to the possible structures.

Table 39

Summary of gc-ms assignments made in section 2.6.4.

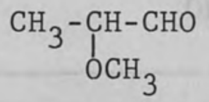
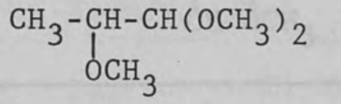
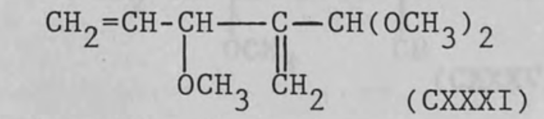
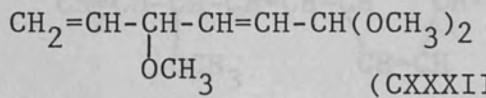
Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Suggested Structure	Notes
99	106	Not observed	88	 $CH_3-\underset{OCH_3}{\underset{\vert}{CH}}-CHO$ (CXXIV)	Accurate mass data not obtained
166	152	Not observed $[M.NH_4-CH_3OH]^+$ present	134	 $CH_3-\underset{OCH_3}{\underset{\vert}{CH}}-CH(OCH_3)_2$ (CXXV)	
450	190	173	172	 $CH_2=CH-\underset{OCH_3}{\underset{\vert}{CH}}-\underset{CH_2}{\underset{\Vert}{C}}-CH(OCH_3)_2$ (CXXXI)	
490	190	173	172	 $CH_2=CH-\underset{OCH_3}{\underset{\vert}{CH}}-CH=CH-CH(OCH_3)_2$ (CXXXII)	Cis or trans isomer See also scan No. 515
515	190	Not observed $[M.NH_4-CH_3OH]^+$ present	172	See structure Scan No. 490 (CXXXII)	

Table 39 (continued)

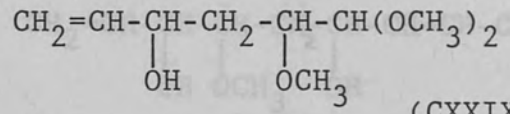
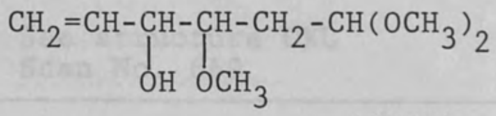
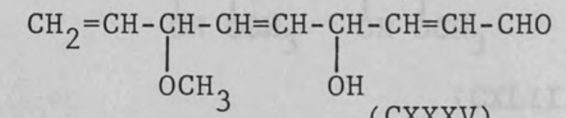
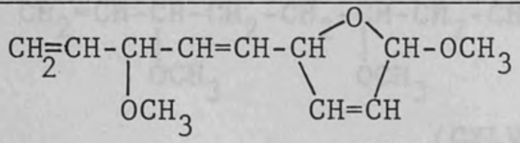
Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Suggested Structure	Notes
439	208	Not observed $[M.NH_4-CH_3OH]^+$ present	190	 $CH_2=CH-\underset{OH}{CH}-CH_2-\underset{OCH_3}{CH}-CH(OCH_3)_2$ (CXXIX)	See also isomer CXXX Scan No. 482
482	208	Not observed $[M.NH_4-CH_3OH]^+$ present	190	 $CH_2=CH-\underset{OH}{CH}-\underset{OCH_3}{CH}-CH_2-CH(OCH_3)_2$ (CXXX)	See also isomer CXXIX Scan No. 439
601	200	183	182	 $CH_2=CH-\underset{OCH_3}{CH}-CH=CH-\underset{OH}{CH}-CH=CH-CHO$ (CXXXV)	
647	214	197	196	 (CXXXVI)	

Table 39 (continued)

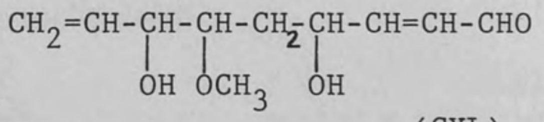
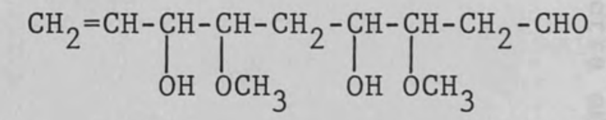
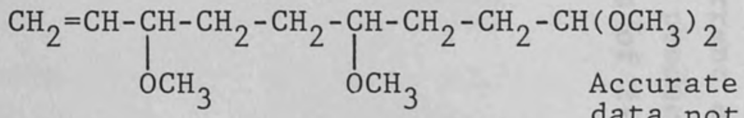
Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Suggested Structure	Notes
669	218	201	200	 $\mathrm{CH_2{=}CH\text{-}\underset{OH}{CH}\text{-}\underset{OCH_3}{CH}\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH{=}CH\text{-}CHO}$ (CXL)	Cis or trans isomer See also Scan No. 720
720	218	201	200	See structure CXL Scan No. 669	
724	250	233	232	 $\mathrm{CH_2{=}CH\text{-}\underset{OH}{CH}\text{-}\underset{OCH_3}{CH}\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}\underset{OCH_3}{CH}\text{-}CH_2\text{-}CHO}$ (CXLIII)	Accurate mass data not obtained
738	264	247	246	 $\mathrm{CH_2{=}CH\text{-}\underset{OCH_3}{CH}\text{-}CH_2\text{-}CH_2\text{-}\underset{OCH_3}{CH}\text{-}CH_2\text{-}CH_2\text{-}CH(OCH_3)_2}$ (CXLVI)	Accurate mass data not obtained

Fig. 2.6.5.1. Capillary total ion current chromatogram of derivatised samples produced under autoxidation conditions of 2-propenal (NH_3-CI spectra only)

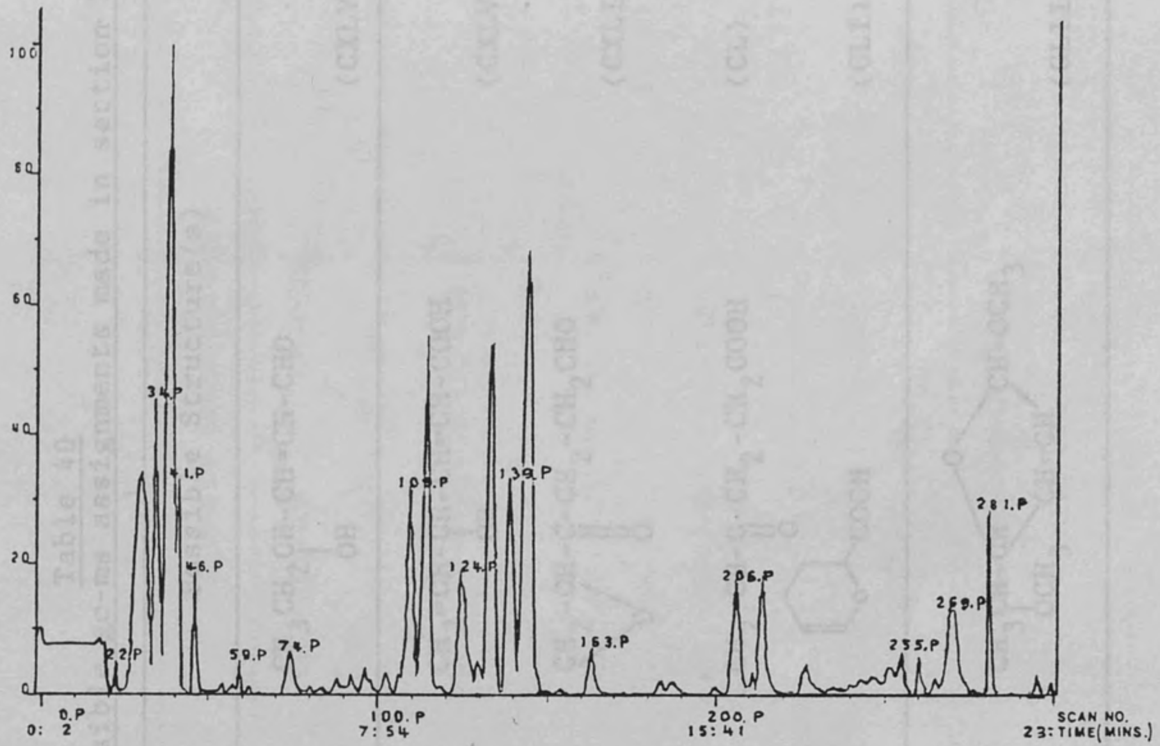


Table 40

Summary of possible gc-ms assignments made in section 2.6.5.

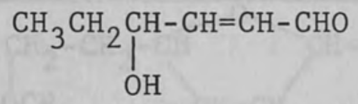
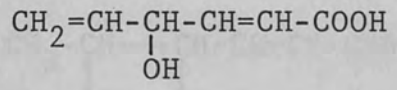
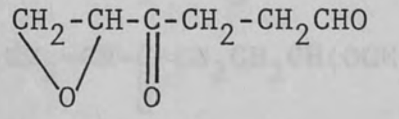
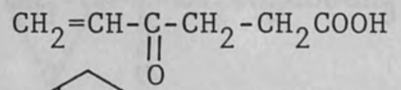
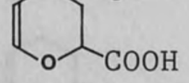
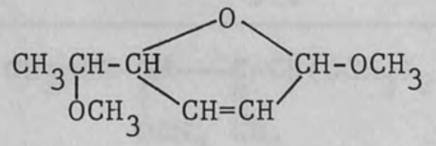
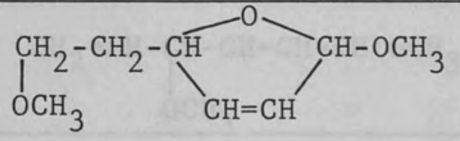
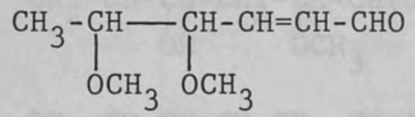
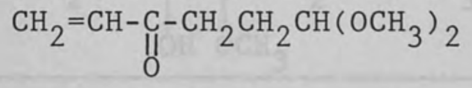
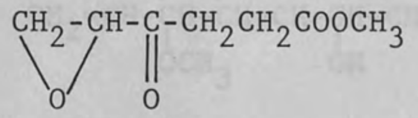
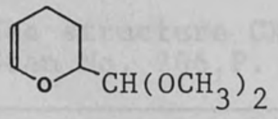
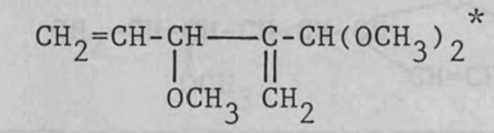
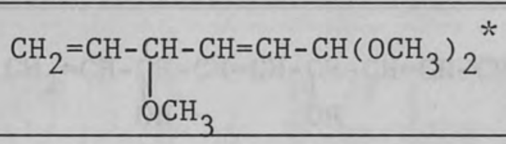
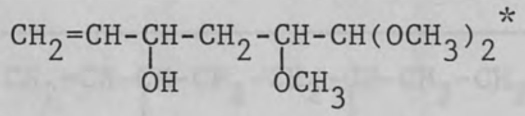
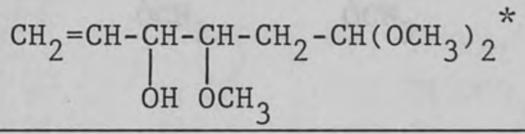
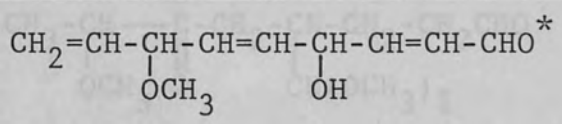
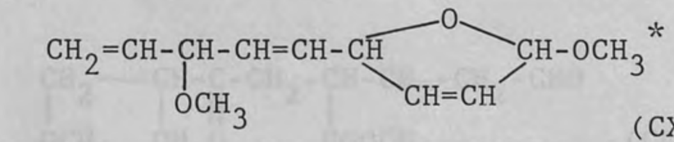
Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Possible Structure(s)		Notes
59.P	132	115	114	 $CH_3CH_2\underset{\mathrm{OH}}{\underset{\vert}{\mathrm{CH}}}\text{-CH=CH-CHO}$	(CXLVII)	
46.P	146	129	128	 $CH_2\text{=CH-}\underset{\mathrm{OH}}{\underset{\vert}{\mathrm{CH}}}\text{-CH=CH-COOH}$	(CXLVIII)	Four alternative structures for one compound eluted
					(CXLIX)	
				 $CH_2\text{=CH-}\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}\text{-}CH_2\text{-}CH_2COOH$	(CL)	
					(CLI)	
74.P	176	159	158		(CLII)	Six alternative structures for four compounds eluted

Table 40 (continued)

Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Possible Structure(s)	Notes
110.P	176	159	158	 (CLIII)	
139.P	176	159	158	 $CH_3-\underset{OCH_3}{CH}-\underset{OCH_3}{CH}-CH=CH-CHO$ (CLIV)	Cis or trans isomer
163.P	176	159	158	 $CH_2=CH-\underset{\overset{\|}{O}}{C}-CH_2CH_2CH(OCH_3)_2$ (CLV)	
				 (CLVI)	
				 (CLVII)	
112.P	190	173	172	 $CH_2=CH-\underset{OCH_3}{CH}-\underset{\overset{\|}{CH_2}}{C}-CH(OCH_3)_2{}^*$ (CXXXI)	Two alternative structures for two compounds eluted

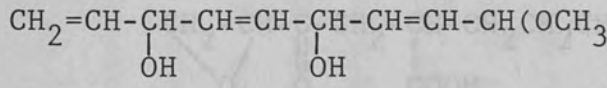
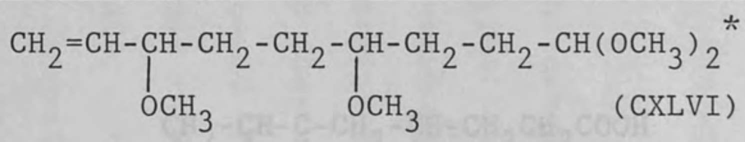
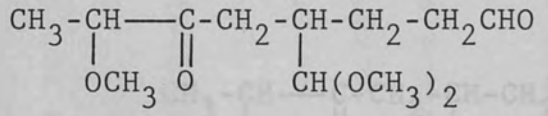
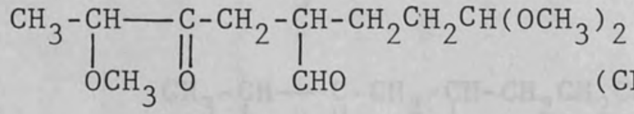
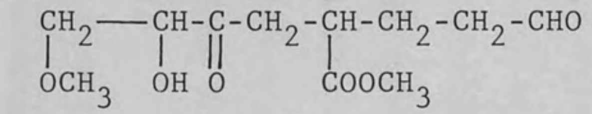
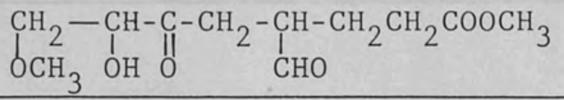
* Structure assigned in 2.6.4.

Table 40 (continued)

Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Possible Structure(s)		Notes
134.P	190	173	172	 $CH_2=CH-\underset{OCH_3}{\underset{\vert}{CH}}-CH=CH-CH(OCH_3)_2{}^*$	(CXXXII)	Cis or trans isomer
124.P	208	Not observed $[M.NH_4-CH_3OH]^+$ present	190	 $CH_2=CH-\underset{OH}{\underset{\vert}{CH}}-CH_2-\underset{OCH_3}{\underset{\vert}{CH}}-CH(OCH_3)_2{}^*$  $CH_2=CH-\underset{OH}{\underset{\vert}{CH}}-\underset{OCH_3}{\underset{\vert}{CH}}-CH_2-CH(OCH_3)_2{}^*$	(CXXIX) (CXXX)	Two alternative structures for two compounds eluted
206.P	200	183	182	 $CH_2=CH-\underset{OCH_3}{\underset{\vert}{CH}}-CH=CH-\underset{OH}{\underset{\vert}{CH}}-CH=CH-CHO^*$	(CXXXV)	Cis or trans isomer
255.P	200	183	182	See structure CXXXV Scan No. 206.P.		
214.P	214	197	196		(CXXXVI)	

* Structure assigned in 2.6.4.

Table 40 (continued)

Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Possible Structure(s)	Notes
227.P	232	Not observed $[M.NH_4-CH_3OH]^+$ present	214	 $CH_2=CH-\underset{\underset{OH}{\vert}}{CH}-CH=CH-\underset{\underset{OH}{\vert}}{CH}-CH=CH-CH(OCH_3)_2$ (CLVIII)	
281.P	264	247	246	 $CH_2=CH-\underset{\underset{OCH_3}{\vert}}{CH}-CH_2-CH_2-\underset{\underset{OCH_3}{\vert}}{CH}-CH_2-CH_2-CH(OCH_3)_2{}^{*}$ (CXLVI)  $CH_3-\underset{\underset{OCH_3}{\vert}}{CH}-\underset{\underset{O}{\Vert}}{C}-CH_2-\underset{\underset{CH(OCH_3)_2}{\vert}}{CH}-CH_2-CH_2CHO$ (CLIX)  $CH_3-\underset{\underset{OCH_3}{\vert}}{CH}-\underset{\underset{O}{\Vert}}{C}-CH_2-\underset{\underset{CHO}{\vert}}{CH}-CH_2CH_2CH(OCH_3)_2$ (CLX)  $\underset{\underset{OCH_3}{\vert}}{CH_2}-\underset{\underset{OH}{\vert}}{CH}-\underset{\underset{O}{\Vert}}{C}-CH_2-\underset{\underset{COOCH_3}{\vert}}{CH}-CH_2-CH_2-CHO$ (CLXI)  $\underset{\underset{OCH_3}{\vert}}{CH_2}-\underset{\underset{OH}{\vert}}{CH}-\underset{\underset{O}{\Vert}}{C}-CH_2-\underset{\underset{CHO}{\vert}}{CH}-CH_2CH_2COOCH_3$ (CLXII)	Nine alternative structures for one compound eluted

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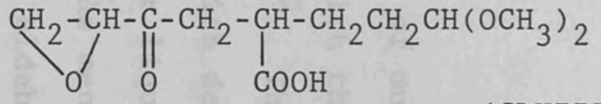
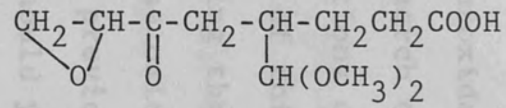
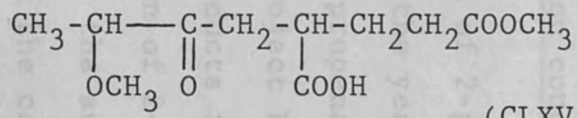
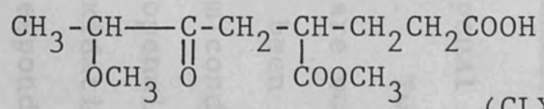
* Structure assigned in 2.6.4.

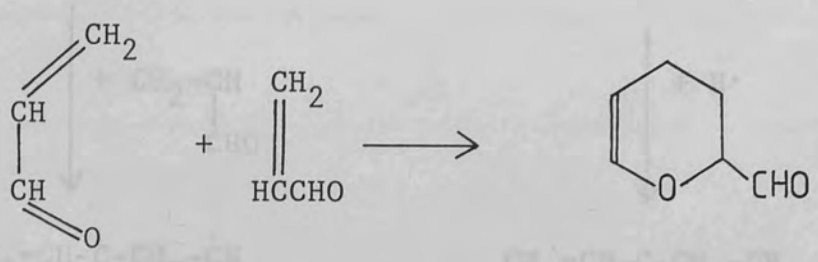
Table 40 (continued)

Scan No.	$[M.NH_4]^+$	$[MH]^+$	M_r	Possible Structure(s)	Notes
				 (CLXIII)	
				 (CLXIV)	
				 $\mathrm{CH_3{-}\underset{OCH_3}{\underset{\vert}{CH}}{-}\underset{O}{\underset{\Vert}{C}}{-}CH_2{-}\underset{COOH}{\underset{\vert}{CH}}{-}CH_2CH_2COOCH_3}$ (CLXV)	
				 $\mathrm{CH_3{-}\underset{OCH_3}{\underset{\vert}{CH}}{-}\underset{O}{\underset{\Vert}{C}}{-}CH_2{-}\underset{COOCH_3}{\underset{\vert}{CH}}{-}CH_2CH_2COOH}$ (CLXVI)	

2.6.6. Mechanistic interpretation of the formation of products revealed by GC-MS of derivatised samples of 'oligomerised' 2-propenal (formed under autoxidation conditions)

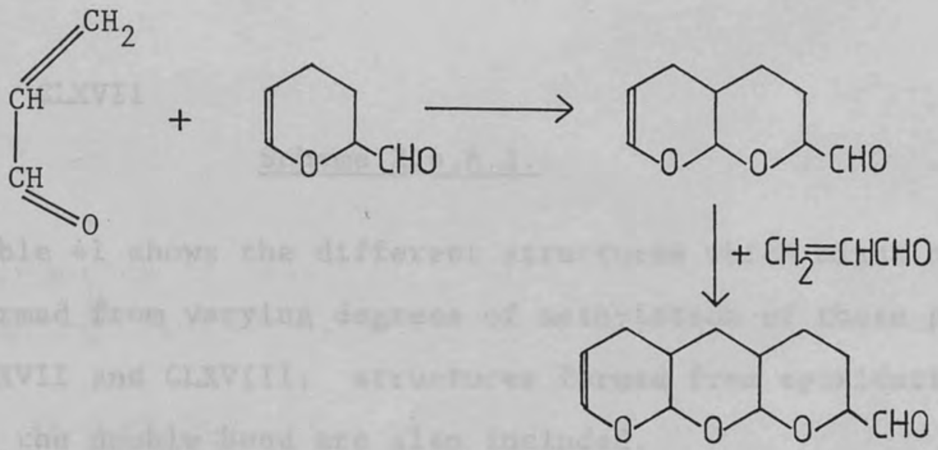
The autoxidation of 2-propenal has been the subject of much research over the years. Two references concerned with the reactions of 2-propenal are worth noting here.[234,235] The work of this project has been concerned primarily with determining the products from conditions suitable for liquid phase oxidation of 2-propenal in the dark at 47°C. As mentioned previously the autoxidation of unsaturated aldehydes should yield the corresponding acid, i.e. 2-propenoic acid. However, this reaction is complicated by the formation of the acyl radical from the aldehyde, which can initiate polymerisation of the acid product; see scheme 2.6.3.8, section 2.6.3. (See also section 2.6.3 for a general discussion on the reactions of the oxidation of aldehydes).

Since its discovery in the mid 1840's, 2-propenal has been known to polymerise very readily in the presence of anionic, cationic or free radical agents.[234] The formation of the 2-propenal dimer was first noted in 1938, by Sherlin and co-workers,[236] who heated 2-propenal containing 1% hydroquinone, for 5 hours at 170°C in the presence of an equal volume of benzene. For this product a Diels-Alder reaction was postulated. See scheme 2.6.6.1.



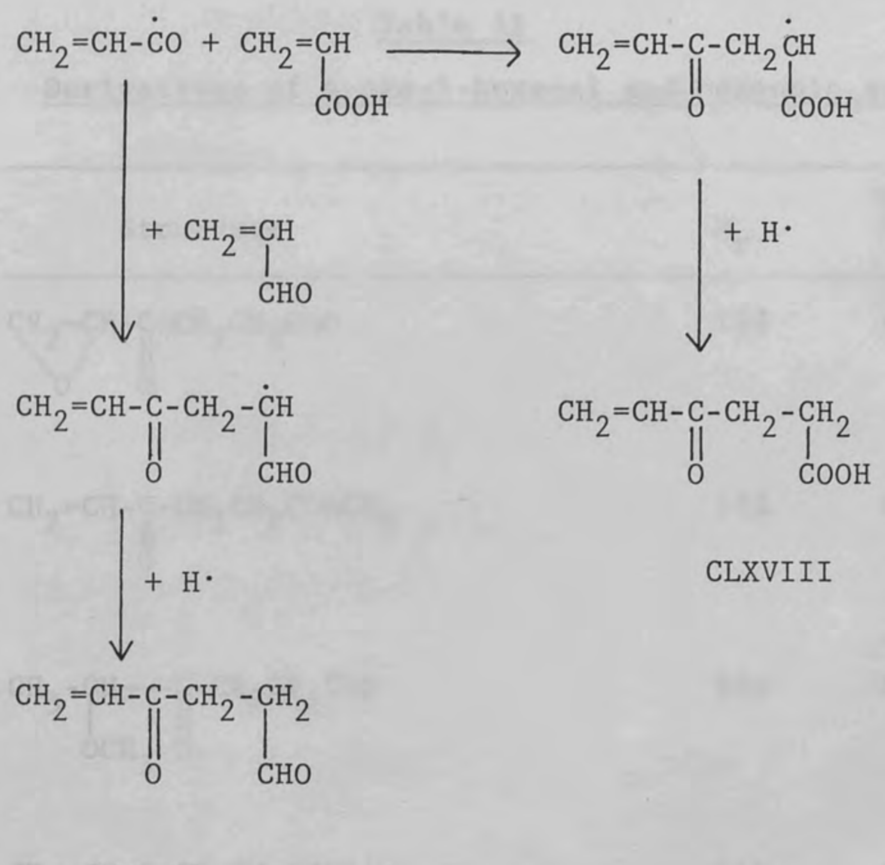
Scheme 2.6.6.1.

Further Diels-Alder reactions as shown in scheme 2.6.6.2 would give higher oligomers.



Scheme 2.6.6.2.

Alternatively the propenoyl radical from 2-propenal could initiate a polymerisation of either the acid product or 2-propenal itself as shown in scheme 2.6.6.3. (Attempts were made to reduce this by inhibition with hydroquinone). Under the conditions of methylation, a variety of compounds could be formed from these products of polymerisation.



CLXVIII

CLXVII

Scheme 2.6.6.3.

Table 41 shows the different structures which might be formed from varying degrees of methylation of these products CLXVII and CLXVIII; structures formed from epoxidation of the double bond are also included.

Only three of the relative molecular masses listed in table 41, namely M_r's 128, 158 and 190, correspond to compounds, which were detected in the gc-ms experiments. (See tables 39 and 40). It is possible that the compound corresponding to M_r 128 was derived from the reaction of 2-propenal with the propenoyl radical followed by epoxidation of the double bond. The compounds of M_r 158

Table 41

Derivatives of 4-oxo-5-hexenal and-hexenoic acid

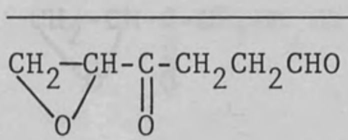
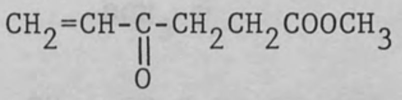
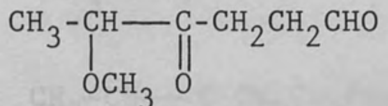
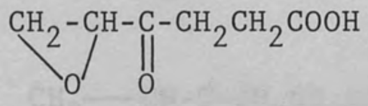
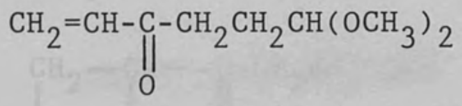
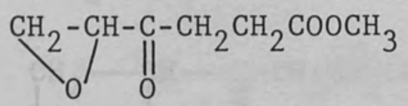
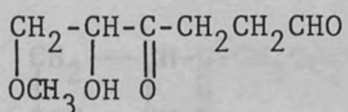
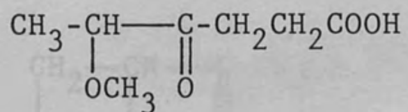
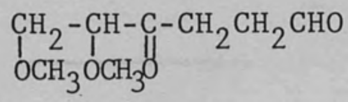
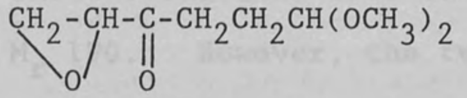
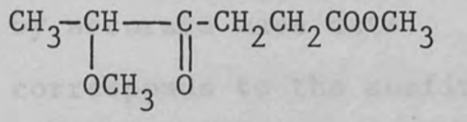
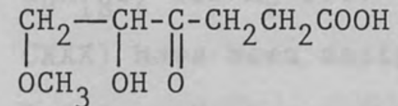
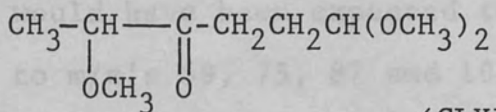
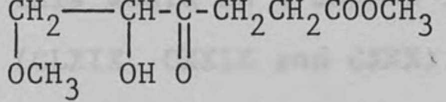
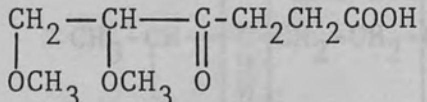
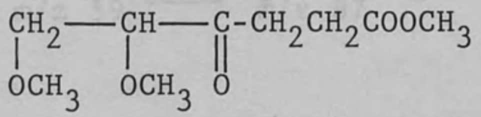
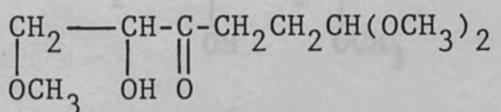
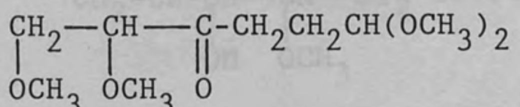
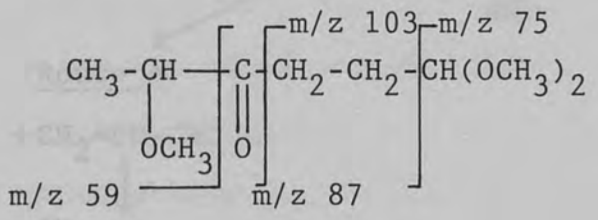
Structure	M_r	Molecular formula
	128	$C_6H_8O_3$
 $CH_2=CH-\underset{\underset{O}{\Vert}}{C}-CH_2CH_2COOCH_3$	142	$C_7H_{10}O_3$
 $CH_3-\underset{\underset{OCH_3}{\vert}}{CH}-\underset{\underset{O}{\Vert}}{C}-CH_2CH_2CHO$	144	$C_7H_{12}O_3$
	144	$C_6H_8O_4$
 $CH_2=CH-\underset{\underset{O}{\Vert}}{C}-CH_2CH_2CH(OCH_3)_2$	158	$C_8H_{14}O_3$
	158	$C_7H_{10}O_4$
 $\underset{\underset{OCH_3}{\vert}}{CH_2}-\underset{\underset{OH}{\vert}}{CH}-\underset{\underset{O}{\Vert}}{C}-CH_2CH_2CHO$	160	$C_7H_{12}O_4$
 $CH_3-\underset{\underset{OCH_3}{\vert}}{CH}-\underset{\underset{O}{\Vert}}{C}-CH_2CH_2COOH$	160	$C_7H_{12}O_4$
 $\underset{\underset{OCH_3}{\vert}}{CH_2}-\underset{\underset{OCH_3}{\vert}}{CH}-\underset{\underset{O}{\Vert}}{C}-CH_2CH_2CHO$	174	$C_8H_{14}O_4$

Table 41 (continued)

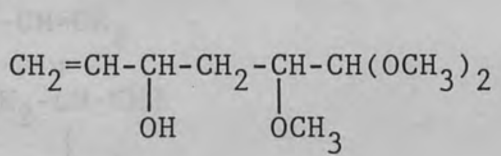
Structure	M_r	Molecular formula
 $\underbrace{CH_2-CH}_{O}-\underset{O}{\underset{\|}{C}}-CH_2CH_2CH(OCH_3)_2$	174	$C_8H_{14}O_4$
 $CH_3-\underset{OCH_3}{\underset{\mid}{CH}}-\underset{O}{\underset{\|}{C}}-CH_2CH_2COOCH_3$	174	$C_8H_{14}O_4$
 $\underset{OCH_3}{\underset{\mid}{CH_2}}-\underset{OH}{\underset{\mid}{CH}}-\underset{O}{\underset{\|}{C}}-CH_2CH_2COOH$	176	$C_7H_{12}O_5$
 $CH_3-\underset{OCH_3}{\underset{\mid}{CH}}-\underset{O}{\underset{\|}{C}}-CH_2CH_2CH(OCH_3)_2$ (CLXIX)	190	$C_9H_{18}O_4$
 $\underset{OCH_3}{\underset{\mid}{CH_2}}-\underset{OH}{\underset{\mid}{CH}}-\underset{O}{\underset{\|}{C}}-CH_2CH_2COOCH_3$	190	$C_8H_{14}O_5$
 $\underset{OCH_3}{\underset{\mid}{CH_2}}-\underset{OCH_3}{\underset{\mid}{CH}}-\underset{O}{\underset{\|}{C}}-CH_2CH_2COOH$	190	$C_8H_{14}O_5$
 $\underset{OCH_3}{\underset{\mid}{CH_2}}-\underset{OCH_3}{\underset{\mid}{CH}}-\underset{O}{\underset{\|}{C}}-CH_2CH_2COOCH_3$	204	$C_9H_{16}O_5$
 $\underset{OCH_3}{\underset{\mid}{CH_2}}-\underset{OH}{\underset{\mid}{CH}}-\underset{O}{\underset{\|}{C}}-CH_2CH_2CH(OCH_3)_2$	206	$C_9H_{18}O_5$
 $\underset{OCH_3}{\underset{\mid}{CH_2}}-\underset{OCH_3}{\underset{\mid}{CH}}-\underset{O}{\underset{\|}{C}}-CH_2CH_2CH(OCH_3)_2$	220	$C_{10}H_{20}O_5$

may have resulted from a similar addition reaction followed by either epoxidation of the double bond and oxidation of the adduct or the formation of the dimethyl acetal. Three structures from table 41 appear to correspond to M_r 190. However, the two structures based on $C_8H_{14}O_5$ may be rejected as the molecular formula was not confirmed by accurate mass data. Thus, only structure CLXIX corresponds to the confirmed molecular formula of $C_9H_{18}O_4$ for M_r 190. Previously, two structures (CXXIX and CXXX) have been assigned corresponding to M_r 190 in section 2.6.4. However, the EI fragmentation of structure CLXIX would have been expected to show ions probably corresponding to m/z's 59, 75, 87 and 103. Only the ion corresponding to m/z 75 was observed, probably due to $(CH_3O)_2\overset{+}{C}H$, but this would be a common ion of the three structures. (CLXIX, CXXIX and CXXX).



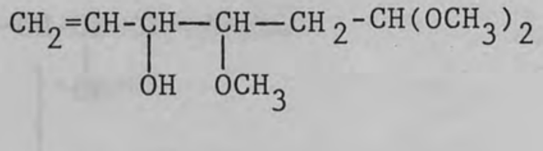
$CH_3-\underset{OCH_3}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-CH_2-CH_2-CH(OCH_3)_2$

CLXIX



$CH_2=CH-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OCH_3}{\underset{|}{CH}}-CH(OCH_3)_2$

CXXIX

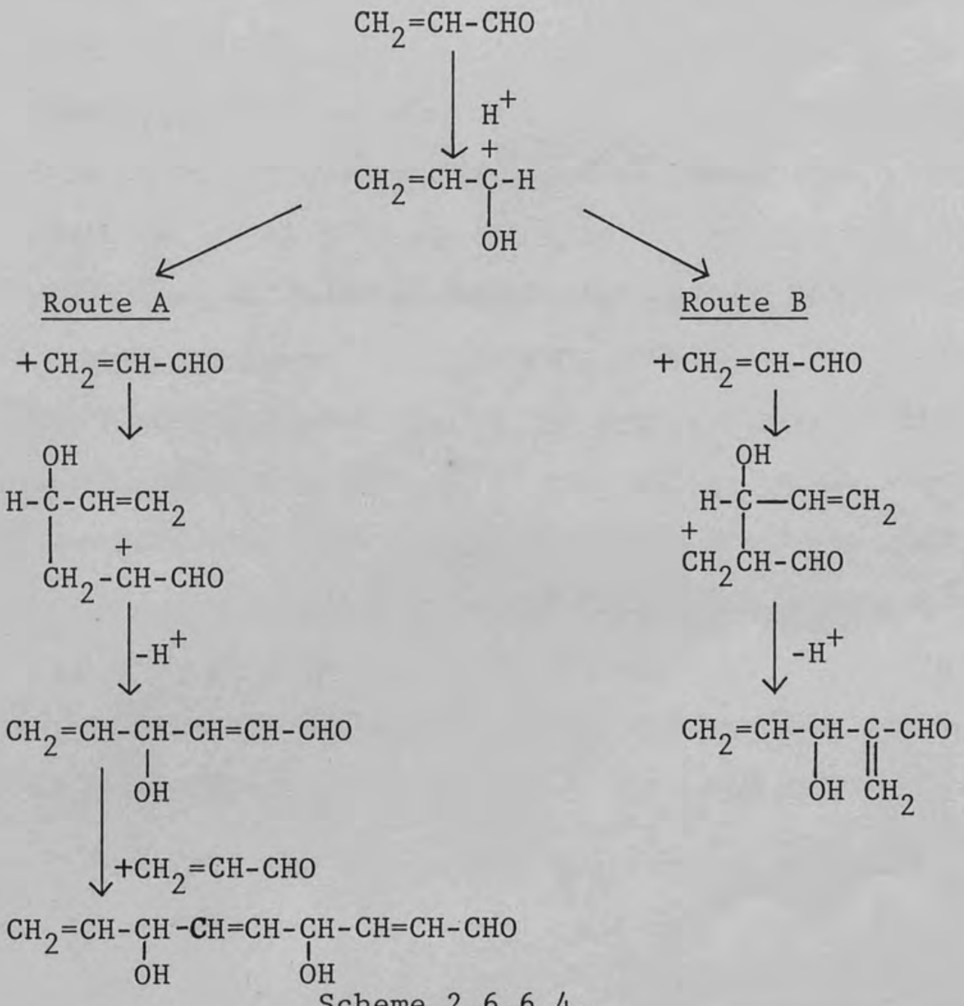


$CH_2=CH-\underset{OH}{\underset{|}{CH}}-\underset{OCH_3}{\underset{|}{CH}}-CH_2-CH(OCH_3)_2$

CXXX

Thus, from the information acquired from the mass spectra data of the derivatised products obtained from conditions suitable for liquid phase oxidation, it would appear that most of the 2-propenal gives a Prins-type reaction,[232,233] (see scheme 2.6.6.4) rather than either oligomerisation initiated by the propenoyl radical or the Diels-Alder reaction.

The results of the gc-ms analysis obtained of the derivatised products of 'oligomerised' 2-propenal will be discussed in two parts, viz. those proposed using: (1) the accurate mass data (section 2.6.4) and (2) the NH_3-CI spectra only (section 2.6.5).



Scheme 2.6.6.4.

Whilst it appears from the mass spectra data, in particular that for which accurate mass data is available, that some methyl esters were produced with the trans-2-hexenal sample vide supra, there seems to be no evidence for the formation of methyl esters with the 2-propenal sample. However, some derivatisation of the carbonyl and hydroxyl groups did occur.

Compound CXXIV in table 39 suggested that addition of methanol across the carbon-carbon double bond in 2-propenal to give 2-methoxypropanal had occurred during derivatisation; however, this molecular formula was not confirmed by accurate mass data. The formation of the compound 1,1,2-trimethoxypropane CXXV, could have arisen as the result of acetal formation of the carbonyl group by the methanol, as well as addition across the double bond. The isomers CXXIX and CXXX (table 39) would seem to have arisen from a Prins type addition (route A in scheme 2.6.6.4) between two 2-propenal molecules, followed by subsequent derivatisation of the carbonyl group and the addition of methanol in both orientations across one of the double bonds. The isomers CXXXI and CXXXII (table 39) also appear to represent compounds, which have been formed by the Prins addition. However, with CXXXII (cis and trans) the mass spectra data suggested the same compound is formed as above, but here there has been derivatisation of the hydroxyl group as well as the carbonyl group to give either cis or trans

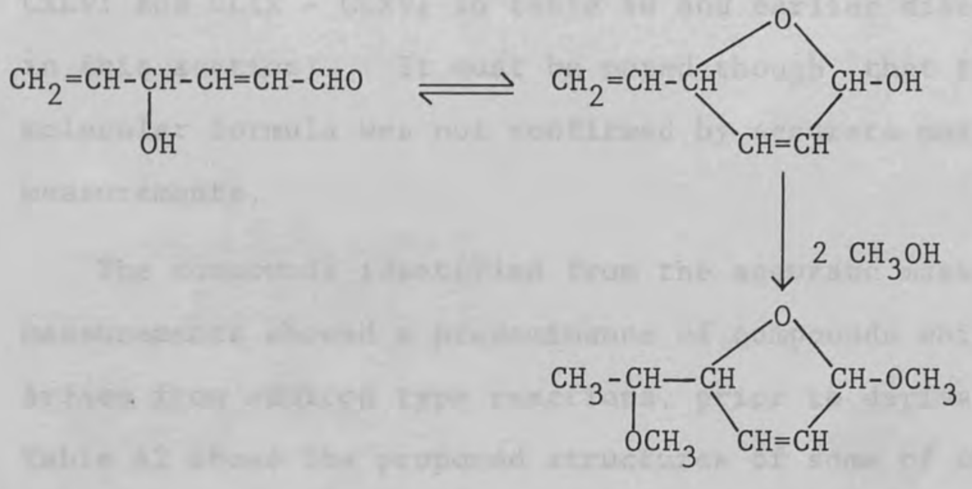
3,6,6-trimethoxy-1,4-hexadiene. Similar derivatisation of the route B adduct (see scheme 2.6.6.4) leads to 3-methoxy-4-(dimethoxymethyl)-1,4-pentadiene (CXXXI).

4-Hydroxy-7-methoxy-2,5,8-nonatrienal (CXXXV) could have resulted from two Prins type additions (route A), followed by derivatisation of one of the hydroxyl groups. Compound CXXXVI probably also resulted from the same Prins addition, but in this case it appeared that the aldehyde group had reacted to form a dihydrofuran type structure followed by subsequent derivatisation of both hydroxyl groups. The formation of the compound 4,7-dihydroxy-6-methoxy-2,8-nonadienal (CXL) could have probably resulted from three molecules of 2-propenal as above; see scheme 2.6.6.4. It is tentatively proposed that during derivatisation methanol adds across the central double bond. As the EI mass spectrum of scan No. 720 (M_r 200) is very similar to scan No. 669, it may be suggested that the two compounds are cis/trans isomers; however, it is impossible to distinguish between them. Compound CXLIII, 4,7-dihydroxy-3,6-dimethoxy-8-nonenal, could probably have arisen as for CXL but with addition of methanol across two of the double bonds. However, the molecular formula was not confirmed by accurate mass data. 3,6-Dimethoxy-9-(dimethoxymethyl)-1-nonene, (CXLVI), if again formed by a Prins type addition requires three molecules of 2-propenal.

The two internal double bonds appear to have become reduced and there is then methylation of the carbonyl and hydroxyl groups. Regrettably the molecular formula was not proven by accurate mass measurements.

The gc-ms analysis of derivatised products of 'oligomerised' 2-propenal, (with NH_3-CI spectra only), section 2.6.5, will now be discussed. Only the tentative structures not already reviewed, for which accurate mass data was obtained, are considered. (See table 40, section 2.6.5).

The tentative structures CXLVII and CXLVIII proposed for scan Nos. 59.P (M_r 114) and 46.P (M_r 128) may have arisen from two 2-propenal molecules, vide supra, but for CXLVIII there would have to have been oxidation of the carbonyl group to the acid. It is also possible that the structure for M_r 128 may have arisen from the addition of the propenoyl radical to 2-propenal, followed by either epoxidation of the double bond or oxidation of the aldehyde group, rather than by a Prins-type addition. The formation of the compound M_r 128 by a Diels-Alder addition may also be considered. (See CXLIX, CL and CLI in table 40 and earlier discussion in this section). However, the common molecular formula $C_6H_8O_3$ was not confirmed by accurate mass measurements. Two structures (CLII and CLIII) considered for M_r 158 could have arisen from the initial Prins adduct, which instead of becoming methylated (see CLIV), undergoes cyclisation to form a dihydrofuran type structure followed by methanol addition across the terminal double bond and methylation of the hemiacetal. See scheme 2.6.6.5.



Scheme 2.6.6.5.

However, as with the previous structure having M_r 128, alternative structures are possible for M_r 158, via either reactions initiated by the propenoyl radical or else a Diels-Alder addition. (See structures CLII - CLVII in table 40 and earlier discussion in this section).

Compound CLVIII could possibly have arisen from a Prins type addition from three molecules of 2-propenal and gives the dimethyl acetal upon methylation.

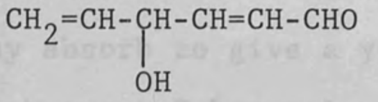
The tentative structure CXLVI proposed for scan No. 281.P may have arisen from the initial addition of three molecules of 2-propenal, as previously mentioned during the discussion of the gc-ms analysis in section 2.6.4. However, it is also possible that the structure for M_r 246 may have arisen from additon reactions of the propenoyl radical to 2-propenal followed by methylation and in some cases epoxidation of the double bond. (See CXLVI and CLIX - CLXVI in table 40 and earlier discussion in this section). It must be noted though that the molecular formula was not confirmed by accurate mass measurements.

The compounds identified from the accurate mass measurements showed a predominance of compounds which had arisen from additon type reactions, prior to derivatisation. Table 42 shows the proposed structures of some of the compounds formed from the autoxidation of 2-propenal in the dark at 47°C, prior to derivatisation by the BF_3/CH_3OH complex, using both the accurate mass data from section 2.6.4 and the NH_3-CI gc-ms from section 2.6.5.

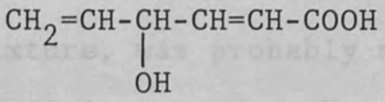
Unlike the gc-ms data from trans-2-hexenal, there appears to be little evidence for the formation of the carboxylic acid group from the 2-propenal. However, the yield of monomeric 2-propenoic acid from liquid phase oxidation has been reported as impractically low.[234] Nevertheless, it must be noted that none of the molecular formulae of the derivatised compounds of structures CLXXI and CLXXII, as well as some molecular formulae of derivatised compounds of the remaining structures, was confirmed by accurate mass measurements. None of the structures shown in table 42 has sufficient conjugation to

Table 42

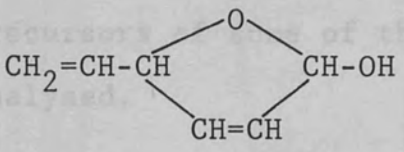
Proposed structures of some of the compounds formed from autoxidation of 2-propenal in the dark at 47°C


$CH_2=CH-\underset{OH}{CH}-CH=CH-CHO$

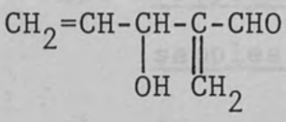
CLXX


$CH_2=CH-\underset{OH}{CH}-CH=CH-COOH$

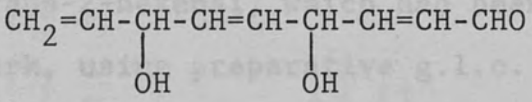
CLXXI



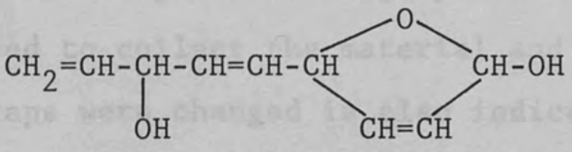
CLXXII


$CH_2=CH-\underset{OH}{CH}-\underset{\overset{\|}{CH_2}}{C}-CHO$

CLXXIII


$CH_2=CH-\underset{OH}{CH}-CH=CH-\underset{OH}{CH}-CH=CH-CHO$

CLXXIV



CLXXV

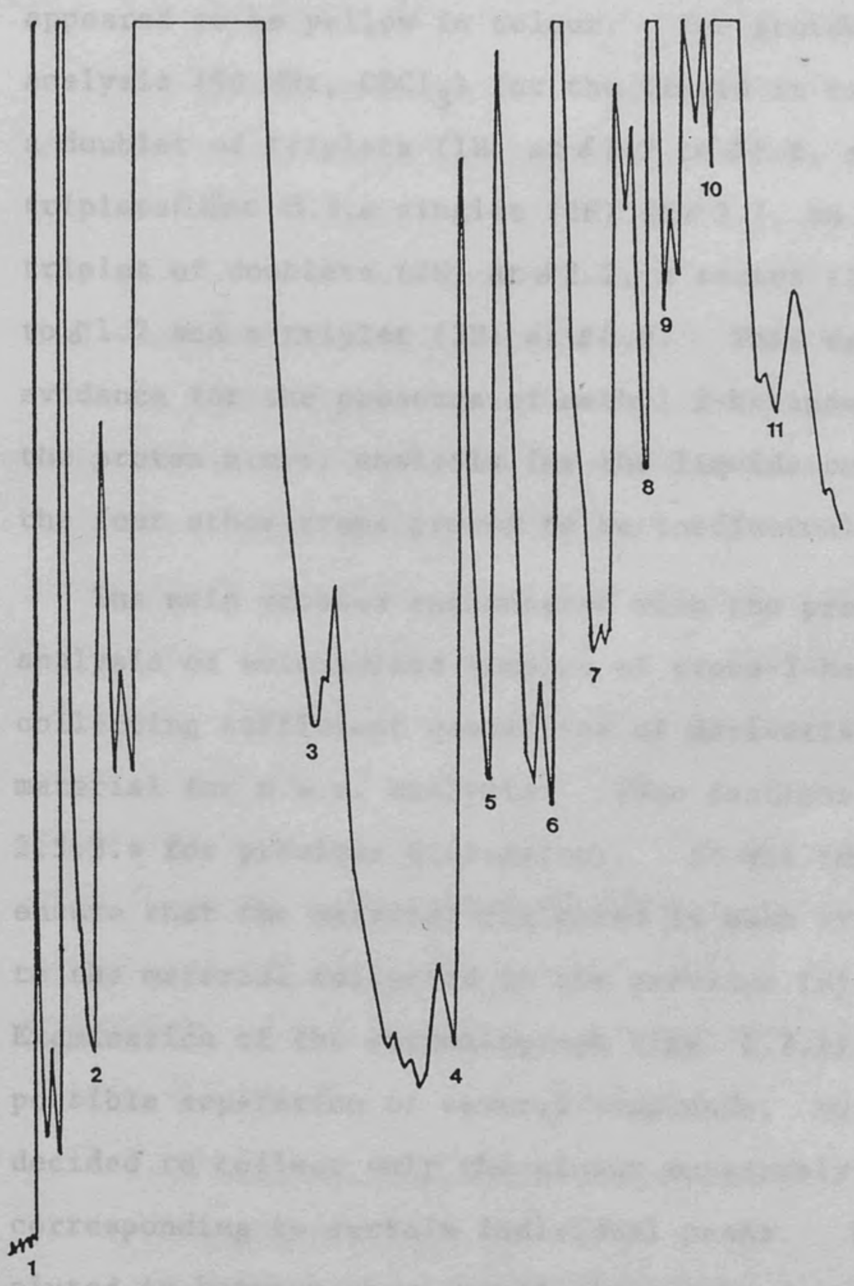
give them a chromophore characteristic of a yellow colour. However, as discussed in section 2.6.3, with trans-2-hexenal, it could be envisaged that some of the structures shown in table 42 could undergo further addition reactions and as the amount of conjugation builds up some products may absorb to give a yellow colouration. Similarly, as with trans-2-hexenal, this type of higher molecular mass material, almost certainly present in the autoxidation mixture, was probably not analysed under the experimental conditions used. However, it seems probable that the precursors of some of these types of yellow compounds were analysed.

2.7 Preparative g.l.c. analysis of autoxidised samples of trans-2-hexenal

An attempt to analyse derivatised samples of trans-2-hexenal, which had been yellowed at 70°C in the dark, using preparative g.l.c. was made. Figure 2.7.1 shows the gas chromatograph obtained. Eleven traps were used to collect the material and the position where these traps were changed is also indicated in fig. 2.7.1. (For experimental details see section 3.18).

The condensed liquid collected in trap 1 was the solvent chloroform. Proton n.m.r. analysis was attempted on each of the liquids collected in traps 2,4,8,10 and 11, as each of these traps contained material assigned from individual peaks as indicated from the chromatograph.

Fig. 2.7.1. Gas chromatograph of derivatised samples of autoxidised trans-2-hexenal using preparative g.l.c. analysis



Trap No. indicates position of trap change

See fig. 2.7.1. The material collected in trap 11 appeared to be yellow in colour. The proton n.m.r. analysis (90 MHz, $CDCl_3$) for the liquid in trap 2 gave a doublet of triplets (1H) at δ 7.2 to δ 6.8, a doublet of triplets (1H) at δ 5.8, a singlet (3H) at δ 3.7, an overlapping triplet of doublets (2H) at δ 2.2, a sextet (2H) at δ 1.7 to δ 1.2 and a triplet (3H) at δ 0.9. This data showed evidence for the presence of methyl 2-hexenoate. However, the proton n.m.r. analysis for the liquids collected in the four other traps proved to be ineffectual.

The main problem encountered with the preparative g.l.c. analysis of autoxidised samples of trans-2-hexenal was collecting sufficient quantities of derivatised yellow material for n.m.r. analysis. (See sections 2.5.1 and 2.5.3.4 for previous discussion). It was important to ensure that the material collected in each trap corresponded to the material collected in the previous injection cycle. Examination of the chromatograph (fig. 2.7.1) showed the possible separation of several compounds, but it was decided to collect only the eluant separately in traps corresponding to certain individual peaks. The materials eluted in between these particular peaks were collected as mixtures in the traps.

Only the presence of methyl 2-hexenoate (obtained from the derivatisation of 2-hexenoic acid) was confirmed by the n.m.r. analysis.

3. Experimental

3.1 Synthesis of cobalt(II) bis(2-ethylhexanoate)[237,238]

2-Ethylhexanoic acid (25.5 g, 0.18 mol) was dissolved in a 10% v/v mixture of 1-butanol and petroleum spirit (100-120°C), (200 cm^3). Cobalt(II) hydroxide (10 g, 0.11 mol) was added and the mixture heated to 120°C and refluxed for 6 hours. On cooling, acetone (100 cm^3) was added to the brown slurry. After shaking well the mixture was filtered using a No.4 sintered glass filter and celite filter aid. The resulting filtrate was reduced in volume under reduced pressure. The remaining solution of cobalt salt in unreacted 2-ethylhexanoic acid was partitioned between water and petroleum spirit; the salt was obtained by evaporating off the water and then dried further by azeotropic distillation with toluene. The cobalt salt was a purple solid with a cobalt content of 16.93% (theoretical 17.07%), as determined by quantitative precipitation of tetrapyridine cobalt dithiocyanate.[238] The yield was 1.63 g (5.24%).

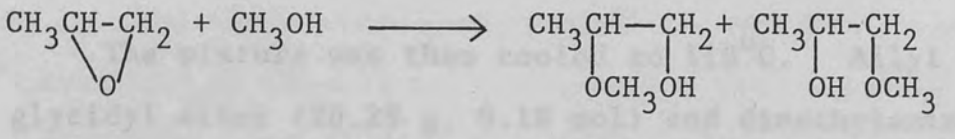
3.2 Synthesis of polymers (used with novel drying systems)

The author is grateful to the staff at ICI Paints Division for their advice on this preparative work. Tables 5 and 6, (section 1.10), show the mass composition of unfunctional polymer and functional polymer respectively, based on 1 kg of non-volatile (NV) charge.

3.2.1. Synthesis of Unfunctional Polymer (UFP) (LXI)

An initiator Genitron AZM, 2,2'-azobis (2-cyanobutane), (8.98 g, added at 5% on the total mass of monomers) was added to the monomers of methyl methacrylate (131.68 g, 1.32 mol), butyl acrylate (30.0 g, 0.23 mol) and methacrylic acid (17.96 g, 0.21 mol). The mixture was added over a period of 3 hours to a solution of Dowanol[*] (179.64 g) maintained at reflux at 120°C and contained in a 750 cm^3 glass reaction vessel with a five necked flanged lid. (Sufficient Dowanol was used to give a 50% solids solution based on the total charge of monomers). Nitrogen was passed through the apparatus and the mixture in the reaction vessel was stirred continuously. After the addition was complete the mixture was refluxed for 15 minutes. A further quantity of initiator, (1.79 g, added at 1% on the total mass of monomers) in Dowanol, (3.58 g), was then added over a period of 1 hour to complete the reaction. The mixture was refluxed for a further 30 minutes.

[*] Dowanol is the name given to the reaction product of 1,2-epoxypropane and methanol in which CLXXVI is predominately formed. See scheme 3.2.1.1.



CLXXVI CLXXVII

CLXXVI (2-methoxypropanol) is predominately formed.

Scheme 3.2.1.1.

3.2.2. Precipitation of unfunctional polymer (UFP)

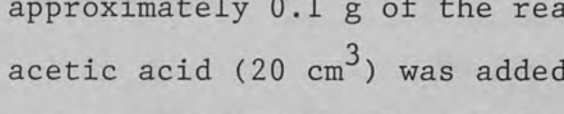
The UFP in Dowanol solution (20 g), as prepared in section 3.2.1, was diluted with approximately 27 g of dowanol and added dropwise to water (4 dm^3), which was stirred vigorously. The polymer precipitated as a white solid, was filtered off, washed with water and air-dried.

3.2.3. Synthesis of functional polymer (FP) (LXII)

The preparation was carried out as for the UFP (see section 3.2.1) but using the following quantities: initial Genitron AZM (7.8 g), methyl methacrylate (95.29 g, 0.95 mol), butyl acrylate (30.0 g, 0.23 mol), methacrylic acid (30.88 g, 0.36 mol), Dowanol (176.46 g) and final Genitron AZM (1.56 g) in Dowanol (3.12 g).

The mixture was then cooled to 110°C. Allyl glycidyl ether (20.29 g, 0.18 mol) and dimethylaminoethanol (DMAE) (0.71 g), acting as a catalyst, were added to the mixture, which was brought back to reflux at 120°C; the DMAE was added at 3.5% of the total mass of AGE used. The reaction was monitored by measuring the 'epoxide value' (EV), vide infra, while the mixture was under reflux, until the EV was below 10. Final EV 4.5 (92% reacted).

The epoxide value (EV) of a resin gives a measurement of the epoxide groups remaining and thus the degree of reaction. The EV is expressed in 'mgKOH/g NV resin sample'. The epoxide value[151,239], of the above reaction was determined for an aliquot of known mass of approximately 0.1 g of the reaction mixture. Glacial acetic acid (20 cm^3) was added to the sample followed by cetyl trimethyl ammonium bromide (2 g). A few drops of crystal violet indicator was added to the sample which was then titrated against 0.1M perchloric acid in glacial acetic acid; the end point was taken as the change from a blue/purple to a yellow/green colour. In this titration, hydrogen bromide generated in situ by the addition of perchloric acid to the quaternary ammonium halide rapidly opens the epoxide ring. See equation 3.2.3.1.



Equation 3.2.3.1.

The large excess of bromide and the higher acid strength of perchloric acid gives a rapid epoxide titration with a sharp end-point. The EV is calculated as follows:-

$$EV = \frac{\text{molarity of perchloric acid} \times \text{titre}}{\text{Mass of aliquot}} \times 56.1$$

mg KOH/g NV sample

The EV at the start of the reaction is given by:-

$$\text{EV at start} = \frac{\text{No. of moles of AGE} \times 56{,}100}{\text{Total charge (g)}}$$

The % reaction is given by:-

$$\%\ \text{reaction} = \frac{\text{EV (at start)} - \text{Residual EV}}{\text{EV (at start)}} \times 100$$

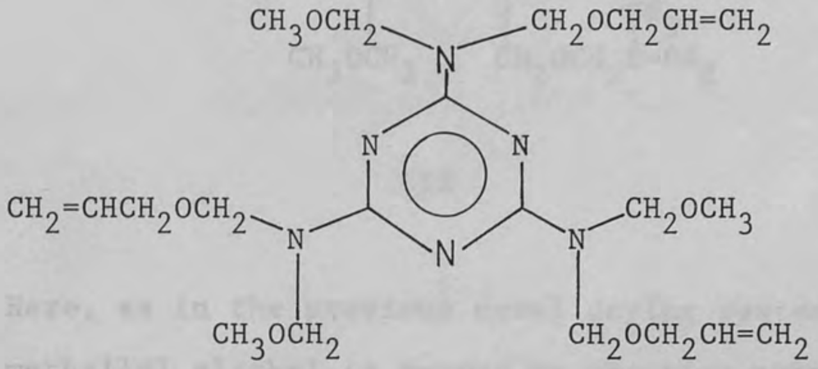
3.2.4. Precipitation of functional polymer (FP)

The functional polymer was precipitated using the same method as for the UFP, (see section 3.2.2). The FP precipitated as a white solid, which was filtered, washed with water and air-dried.

3.3 Novel drying systems[151]

The novel drying systems used in these experiments were supplied by ICI Paints Division; these particular compounds are listed below:-

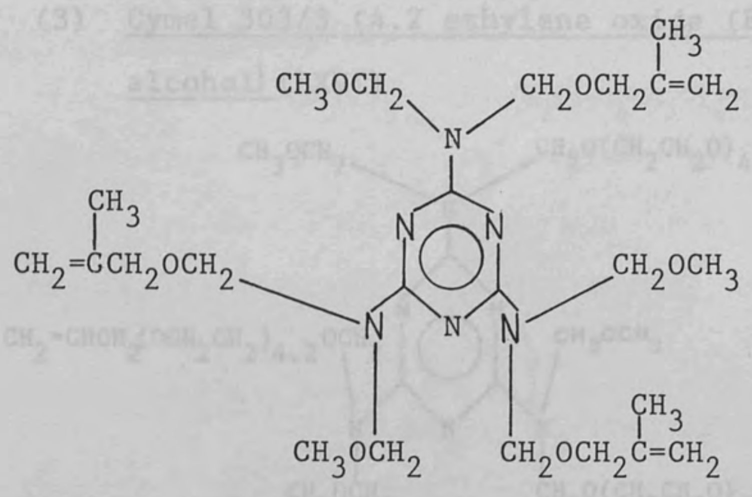
(1) Cymel 303/3 allyl alcohol (LVIII)



LVIII

This drying system is formed by reacting cymel 303 [hexa(methoxymethyl)melamine] with allyl alcohol in the presence of p-toluene sulphonic acid to give a compound containing approximately three allyl groups per cymel 303 molecule. The reaction mixture supplied probably contained some cymel 303 molecules with both more than and less than three allyl groups attached. As stated in section 1.10, LVIII, shows only an idealised structure. The reaction mixture supplied by ICI Paints probably contained some dimeric cymel 303 molecules, as discussed in section 2.4, see fig. 2.4.1.

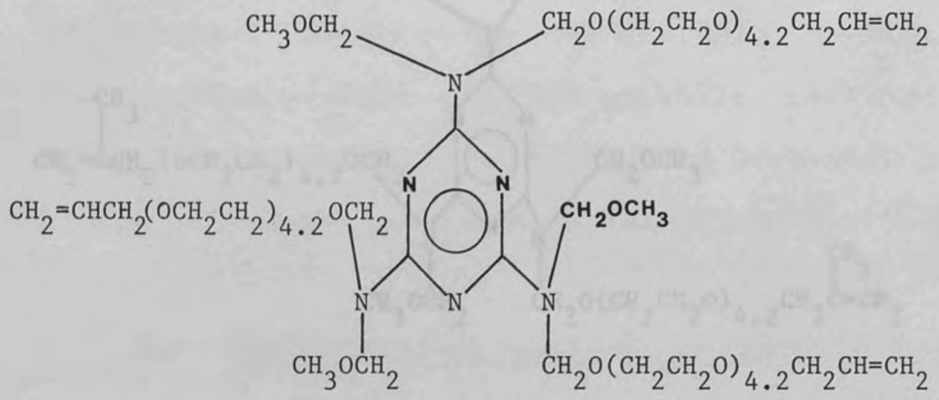
(2) Cymel 303/3 Methallyl alcohol (LIX)



LIX

Here, as in the previous novel drying system, cymel 303/3 methallyl alcohol is formed by reacting cymel 303 with 3 equivalents of methallyl alcohol. LIX shows an idealised structure of this drying system. Again, some cymel 303 molecules will have more than three or less than three methallyl groups attached and, as mentioned in (1) above some dimeric cymel 303 material may be present.

(3) Cymel 303/3 (4.2 ethylene oxide (EO) + allyl alcohol) (LXVI)

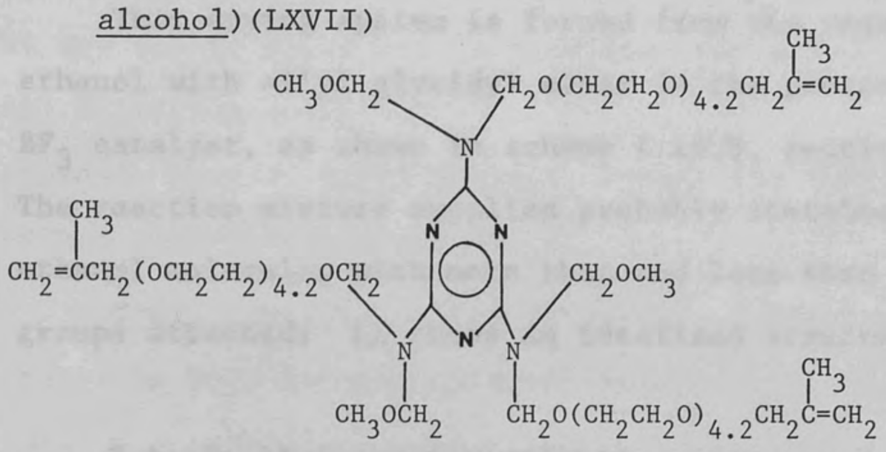


LXVI

This drying system is formed by reacting allyloxy PEG, (where PEG is polyethylene glycol), with the cymel 303 compound. The allyloxy PEG is initially formed by adding allyl alcohol to ethylene oxide (EO) in the presence of a base catalyst, and then adding the required amount of EO. An average of 4.2 EO groups are added to each allyl group present.

As discussed previously in (1) some cymel 303 molecules will have more than three or less than three modified allyloxy groups attached; LXVI shows only an idealised structure.

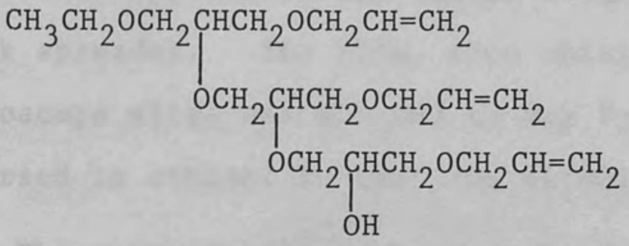
(4) Cymel 303/3 (4.2 ethylene oxide (EO) + methallyl alcohol)(LXVII)



LXVII

This drying system is formed in a similar manner to the previous drying system (3), except that methallyl alcohol is used instead of allyl alcohol. LXVII shows only an idealised structure.

(5) Ethanol/3 AGE (allyl glycidyl ether) (LX)



LX

This drying system is formed from the reaction of ethanol with allyl glycidyl ether in the presence of BF_3 catalyst, as shown in scheme 1.10.5, section 1.10. The reaction mixture supplied probably contained some ethanol molecules with more than and less than 3 AGE groups attached; LX shows an idealised structure.

3.4 Preliminary investigations concerned with novel drying systems, based upon allyl ethers and either functional or unfunctional polymers (non-quantitative)

Separate solutions were prepared for (1) cymel 303/3 allyl alcohol (LVIII), (2) cymel 303/3 methallyl alcohol (LIX), (3) ethanol/3 AGE (EtOH/3 AGE) (LX), (4) functional polymer (FP), (LXII), (5) unfunctional polymer (UFP), (LXI), by dissolving approximately 10 g of each of the above in ethanol (2g). These were applied to microscope slides using a 150 μm block spreader. The film, thus obtained, on each microscope slide was allowed to dry for 24 hours and then immersed in ethanol to test the solubility of the film.

The above materials were prepared again but cobalt (II) bis (2-ethyl hexanoate), (0.06 g), was added as a promoter; the cobalt catalyst was added at 0.1% cobalt metal on the non-volatile material present in the blend, (17% cobalt metal). Microscope slides were

spread with the films of these blends, which were allowed to dry for 24 hours before immersing for a few minutes in the following solvents:-
ethanol, hexane, ethyl acetate, carbon tetrachloride, toluene and dichloromethane.

The solubility of the films from each blend was tested in both hot and cold solvent.

Experimental details for some other preliminary investigations were as follows:-

(1) Films of cymel 303/3 allyl alcohol on five microscope slides were allowed to dry for 12 hours at room temperature ($20^{o}C$) and then extracted using soxhlet extraction apparatus with ethanol for 1 hour. Weighings were taken of the extractable material (a) and compared with the amount of material applied to the slides before extraction and after solvent evaporation (a+b); the amount of non-extractable material (b) was determined by subtraction.

(2) The cymel 303/3 allyl alcohol, cobalt promoted in ethanol, films were allowed to dry at room temperature for 24 hours and then extracted as before with hot ethanol for 1 hour. This experiment was repeated, extending the soxhlet extraction time to 18 hours. Weighings were recorded as in (1) above.

(3) The FP, cobalt promoted and UFP, cobalt promoted blends, both in ethanol, were similarly spread on to five separate microscope slides using the same block spreader.

The films so obtained were allowed to dry at room temperature for 24 hours, 48 hours and 1 week in the case of FP blend; 24 hours and 48 hours in the case of the UFP blend. After extractions for 1 hour as before, weighings were recorded as in (1) above.

3.5 Preparation of drying systems based upon allyl ether compounds for crosslinking investigations

The following allyl ether compounds were used in the blend preparation of the drying systems, described in sections 3.5.1, 3.5.2 and 3.5.3:-

(i) cymel 303/3 allyl alcohol (LVIII), (ii) cymel 303/3 methallyl alcohol (LIX), (iii) cymel 303/3 (4.2 ethylene oxide (EO) + allyl alcohol) (LXVI), (iv) cymel 303/3 (4.2 ethylene oxide (EO) + methallyl alcohol) (LXVII), (v) ethanol/3 AGE (LX).

3.5.1. Preparation of blends based upon allyl ether compounds, cobalt promoter and solvent

A separate blend was prepared for each of the allyl ether compounds listed in section 3.5. The allyl ether (10 g) was weighed out in a suitable paint tin with a lid. The solvent (ethanol/toluene in 4/1 ratio), (6.67 g), was added to the allyl ether with frequent stirring, to give a 60% solids solution.

Cobalt (II) bis (2-ethylhexanoate), (0.06 g) was added to the mixture at 0.1% cobalt metal on the mass of allyl ether used (17% cobalt metal).

3.5.2. Preparation of blends based upon allyl ether compounds, FP, cobalt promoter and solvent

A separate blend was prepared for each of the allyl ether compounds listed in section 3.5. These blends were made up using a 1/1 blend (N.V.) of allyl ether/FP at 60% final solids. The actual masses of material used are shown in table 43.

Table 43

Blend mixture	Mass (g)
Allyl ether compound	30.0
FP	30.0
Solvent (ethanol/toluene in 4/1 ratio)	40.0
Total	100.0
Cobalt (II) bis (2-ethylhexanoate)	0.35
(added at 0.1% cobalt metal based on 60% solids, 17% cobalt metal)	

Initially, the FP was dissolved in approximately 30 g of the solvent mix, in a suitable paint tin with a lid. The novel drying system was then added slowly to this mixture with frequent stirring. The cobalt promoter was dissolved in approximately 4 g of solvent mix and added to the above mixture with careful stirring. The remaining solvent was used to rinse out the container into which the required amount of allyl ether compound had been measured; this solvent was then added to the prepared blend with thorough mixing.

3.5.3. Preparation of blends based upon allyl ether compounds, UFP, cobalt promoter and solvent

A separate blend was prepared for each of the allyl ether compounds listed in section 3.5. The preparation of these blends was carried out as for those in section 3.5.2, but UFP (30.0 g) was used in place of FP (30.0 g).

3.5.4. FTIR studies of the non-extractable film formed from drying systems based upon allyl ethers

Only the allyl ether compounds (i) - (iv) as described in section 3.5 were used in this study.

The FP and UFP blends of the different allyl ether compounds, as prepared in sections 3.5.2 and 3.5.3, were each spread separately onto five clean microscope slides using a 150 μm block spreader. The films thus obtained, on each set of five microscope slides, were allowed to dry at ambient temperature for given time periods of 24 hours, 48 hours, 1 week and 5 weeks. The film on the slides was then extracted using soxhlet extraction apparatus, (thimble size approx. 75 mm x 30 mm (i.d.)), and ethanol (250 cm^3) as the extracting solvent. After 1 hour of extraction, samples of each non-extractable film still present on the slides were removed and ground with pure potassium bromide to give a KBr disc using the standard procedure. Spectra for each KBr disc were obtained by FTIR spectroscopy, using a Perkin-Elmer 1710 Infrared Fourier Transform spectrometer with a model PP1 Plotter Printer.

FTIR spectra of the non-extractable film from each allyloxy ether compound (i) - (iv) alone with cobalt promoter and solvent, as prepared in section 3.5.1, were obtained in a similar manner as described above, after either 24 hours or 48 hours drying time. This was to provide the correction term (C) for the contribution to the carbonyl absorption from the autoxidation of each allyloxy ether compound.

3.5.5. Investigations concerned with the extent of film formation from drying systems based upon allyl ethers

The fifteen different blends, as prepared in sections 3.5.1, 3.5.2 and 3.5.3 were each spread onto five separate clean microscope slides using a 150 μm block spreader. The films, thus obtained, on each set of five microscope slides were allowed to dry at room temperature for given time periods of 24 hours, 48 hours, 1 week and 5 weeks. The film on the slides was then extracted using soxhlet extraction apparatus and ethanol (250 cm^3), as the extracting solvent. The slides were arranged carefully in the soxhlet thimble, (approx. size 75 mm x 30 mm (i.d.)), back to back so that the film on each slide would be exposed to the ethanol. These soxhlet extractions were carried out for 1 hour from the start of reflux, after which time the ethanol used for extraction was evaporated off under reduced pressure and the amount of extractable material ascertained. Weighings were taken of the amount of extractable material (a) and as previously compared with the amount of material applied to the slides before extraction, but after solvent evaporation, (a + b). The non-extractable or crosslinked material (b) was determined by subtraction.

3.6 Synthesis of radioactive butyl acrylate

3.6.1. Synthesis of radioactive butyl acrylate (^{14}C labelled) using methyl acrylate,[240] scheme 3.6.1.1.

$$CH_2{=}CHCOOCH_3+CH_3(CH_2)_2\overset{*}{C}H_2OH \longrightarrow CH_2{=}CHCOO\overset{*}{C}H_2(CH_2)_2CH_3+CH_3OH$$

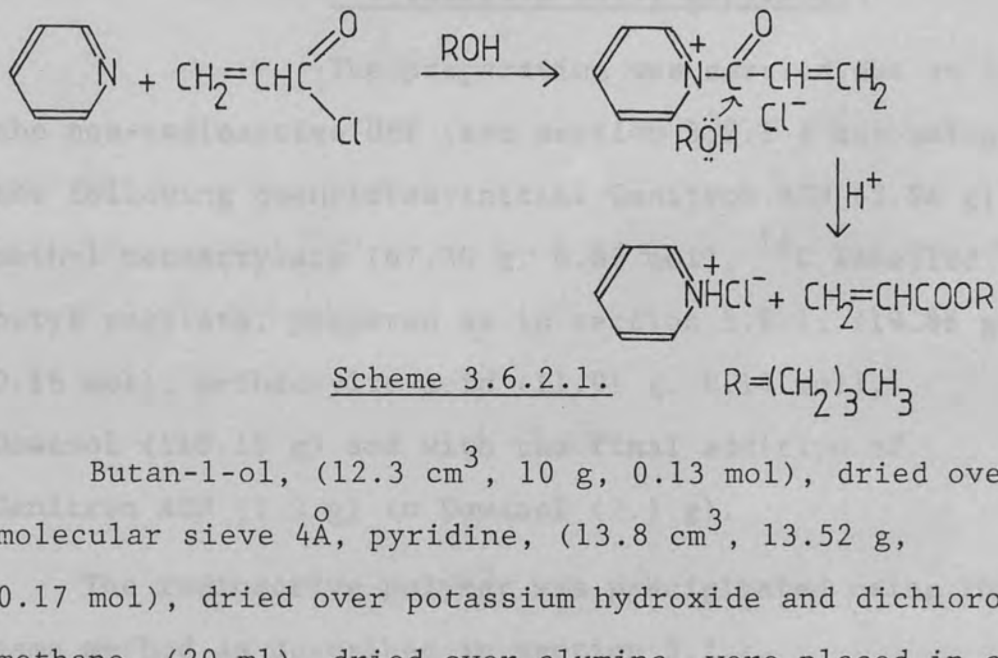
Scheme 3.6.1.1.

Butan-1-ol, ^{14}C labelled at carbon atom 1,[*] (20 cm^3, 16.2 g, 0.22 mol), methyl acrylate, freshly distilled, (79.25 cm^3, 75.76 g, 0.88 mol), hydroquinone (1 g) and p-toluene sulphonic acid, (0.42 g), were placed in a two-necked round-bottomed flask which had a capillary ebullator in one neck, through which nitrogen was introduced during the reaction. The flask was attached to a Vigreux column. The column was operated under total reflux until the temperature of the vapours at the still head fell to 62 - 63°C, which is the boiling point of the methanol-methyl acrylate azeotrope. This azeotrope was then distilled as rapidly as it was formed; the temperature of the still head was not allowed to exceed 65°C. When the production of methanol had become very slow (6 - 10 hours), the excess methyl acrylate and any remaining butan-1-ol were removed by distillation at room pressure. The butyl acrylate was distilled under reduced pressure at 47°C/ 20 mm Hg; the yield was 19.89 g (70.53%). The structure of butyl acrylate was confirmed by proton n.m.r. of a non-radioactive sample prepared under the same reaction conditions using AnalaR butan-1-ol. Proton n.m.r. (60 MHz; $CDCl_3$) for this non-radioactive product gave a complex multiplet (3H) at δ6.7 to 5.75 ppm, a triplet (2H) at δ4.3, a multiplet (4H) at δ2.15 to 1.4 ppm and a triplet (3H) at δ1.15.

[*] The butan-1-ol, ^{14}C labelled, was obtained from ICN Radiochemicals; 8.7 mg, total activity 1mCi, specific activity 8.52 mCi/mmol. The labelled butan-1-ol was diluted with AnalaR butan-1-ol, which had been dried over molecular sieve 4Å to give a solution of activity 1mCi per 100 cm^3. An aliquot of this solution was further diluted to give a solution of 400 μCi per 100 cm^3, 20 cm^3 of which was used in the above reaction.

3.6.2. Synthesis of butyl acrylate (non-radioactive) using acryloyl chloride

Although the synthesis of butyl acrylate from acryloyl chloride and butanol was attempted (scheme 3.6.2.1), this method was abandoned owing to low yields in favour of the method described above, see section 3.6.1, for the synthesis of the ^{14}C labelled butyl acrylate.



Scheme 3.6.2.1. $R = (CH_2)_3CH_3$

Butan-1-ol, (12.3 cm^3, 10 g, 0.13 mol), dried over molecular sieve 4Å, pyridine, (13.8 cm^3, 13.52 g, 0.17 mol), dried over potassium hydroxide and dichloromethane, (20 ml), dried over alumina, were placed in a round-bottomed flask in an ice-bath. The reaction mixture was stirred during the addition of the acryloyl chloride, (11.6 cm^3, 12.94 g, 0.14 mol), and then stirred for 4 hours. At the end of which time, it was poured onto dilute hydrochloric acid (0.2 M, 50 cm^3) and extracted with dichloromethane (2 x 20 cm^3). The organic layer was washed with dilute sodium hydroxide

(0.2 M), water and dried with anhydrous magnesium sulphate. The resulting liquid was distilled at room pressure to remove the dichloromethane and then at reduced pressure, after the addition of a few crystals of hydroquinone. Butyl acrylate was obtained at 47°C/20 mm Hg; the yield was 0.76 g (4.56% yield).

3.7 Synthesis of radioactive polymers

3.7.1. Synthesis of radioactive UFP (using ^{14}C labelled butyl acrylate)

The preparation was carried out as for the non-radioactive UFP (see section 3.2.1) but using the following quantities:initial Genitron AZM (5.96 g), methyl methacrylate (87.30 g, 0.87 mol), ^{14}C labelled butyl acrylate, prepared as in section 3.6.1, (19.86 g, 0.16 mol), methacrylic acid (11.91 g, 0.14 mol), Dowanol (119.10 g) and with the final addition of Genitron AZM (1.2 g) in Dowanol (2.4 g).

The radioactive polymer was precipitated using the same method as described in section 3.2.2.

3.7.2. Synthesis of radioactive FP (using ^{14}C labelled butyl acrylate)

The preparation was carried out as for the non-radioactive FP (see section 3.2.3) but using the following quantities: initial Genitron AZM (7.1 g), methyl methacrylate (86.65 g, 0.87 mol), ^{14}C labelled butyl acrylate, prepared as in section 3.6.1, (27.28 g, 0.21 mol), methacrylic acid (28.08 g, 0.33 mol), Dowanol (160.46 g), final Genitron AZM (1.42 g) in Dowanol (2.84 g), AGE (18.45 g, 0.16 mol) and DMAE (0.65 g). Final EV 6.62.

The radioactive polymer was precipitated using the same method as described in section 3.2.4.

3.8 Preparation of radioactive blends

3.8.1. Preparation of radioactive blend based upon cymel 303/3 allyl alcohol, FP (^{14}C labelled), cobalt promoter and solvent

The preparation was carried out as for the non-radioactive blend (see section 3.5.2). The following quantities were used:cymel 303/3 allyl alcohol (30 g), ^{14}C labelled FP, prepared as in section 3.7.2, (30 g), ethanol/toluene, (4/1), (40 g) and cobalt (II) bis (2-ethyl hexanoate) (0.35 g).

3.8.2. Preparation of radioactive blend based upon cymel 303/3 allyl alcohol, UFP (^{14}C labelled), cobalt promoter and solvent

The preparation was carried out as for the non-radioactive blend (see section 3.5.3). The following quantities were used cymel 303/3 allyl alcohol (30 g), ^{14}C labelled UFP, prepared as in section 3.7.1, (30 g), ethanol/toluene, (4/1), (40 g) and cobalt (II) bis (2-ethyl hexanoate), (0.35 g).

3.9 Crosslinking investigations of radioactive blends based upon cymel 303/3 allyl alcohol, ^{14}C labelled polymer (either FP or UFP), cobalt promoter and solvent

The two different radioactive blends, as prepared in sections 3.8.1 and 3.8.2 were each spread onto five separate clean microscope slides using a 150 μm block spreader. The films, thus obtained, on each set of five microscope slides were allowed to dry at room temperature for given time periods viz., 0 hr, 12 hr, 24 hr, 48 hr, 72 hr, 5 days, 1 week, 18 days and 4 weeks. The film on the slides was then extracted following the procedure in section 3.5.5. However, the extractable material in the ethanol was concentrated to 25 cm^3 under reduced pressure. 1 cm^3 of this mixture was mixed in a small vial with the scintillation cocktail Ready-solv HP/b (10 cm^3). The solution was then counted using a Beckman LS1800 liquid scintillation system connected to an Apple IIe microcomputer and Epson printer LX80. Each sample vial was wiped with an antistatic cloth and kept in the machine overnight before measuring the activity to reduce the random counts. The mass of material applied to the slides before extraction, after solvent evaporation, (a + b) was also measured.

During the preparation of the radioactive compounds and subsequent liquid scintillation counting, care was exercised to ensure that the radioactive experiments were carried out in a well-contained area and that standard radioisotope laboratory techniques were followed.[241,242,243,244]

The activity of known masses (0.1 g, 0.1751 g and 0.2 g) of ^{14}C labelled FP and UFP was also measured, as well as known masses of the non-radioactive polymers and cymel 303/3 allyl alcohol.

3.10 Gel Permeation Chromatography (G.P.C.) of the extractable and non-extractable portions of films formed from blends based upon purified cymel 303/3 allyl alcohol

3.10.1. Distillation of cymel 303/3 allyl alcohol for use in G.P.C. studies

Initially ether (100 cm^3) was added to the viscous cymel 303/3 allyl alcohol, (46.75 g), to make the liquid more mobile. The liquid was extracted with 0.5 M KOH (2 x 20 cm^3), washed with water, dried with anhydrous magnesium sulphate and filtered. This procedure was followed in an attempt to remove any remaining acid catalyst from the preparation of cymel 303/3 allyl alcohol, (see section 3.3). The ether was then removed by evaporation under reduced pressure. Cymel 303/3 allyl alcohol was distilled as a clear liquid at 212 - 216°C, 0.01 mm Hg, using a diffusion pump. The presence of the purified compound was confirmed by G.P.C., see figure 2.4.1, section 2.4.

3.10.2. Preparation of blends based upon purified cymel 303/3 allyl alcohol, cobalt promoter and solvent, with the addition of either FP or UFP

The preparation of these blends was carried out as for the blends in section 3.5.1, 3.5.2 and 3.5.3, using the purified cymel 303/3 allyl alcohol, see section 3.10. The actual masses of material are shown in table 44.

These three different blends were each spread separately onto two clean microscope slides using a 150 μm block spreader. The films, thus obtained, on each set of two microscope slides were allowed to dry at ambient temperature for given time periods of 12 hr, 24 hr, 48 hr, 72 hr and 1 week. The film on the slides was then extracted by placing the slides in hot ethanol (25 cm^3) for 5 - 10 minutes. The ethanol was filtered, placed in a R.B. flask (50 cm^3) and evaporated to dryness under reduced pressure. The flask containing this extractable material was flushed with nitrogen prior to G.P.C. analysis.

Any material remaining on the microscope slides was classified as the non-extractable material and was also kept in a container under nitrogen. The drying of the

Table 44 (Mass/g)

Materials used	Cymel 303/3 allyl alcohol, Co promoter, and solvent	Cymel 303/3 allyl alcohol, FP, Co promoter and solvent	Cymel 303/3 allyl alcohol, UFP, Co promoter and solvent
Cymel 303/3 allyl alcohol (purified)	6.00	6.00	6.00
FP	-	6.00	-
UFP	-	-	6.00
Solvent (ethanol/ toluene in 4/1 ratio	4.00	8.00	8.00
Cobalt (II) bis (2-ethylhexanoate)	0.04	0.07	0.07

films was arranged so the G.P.C. analysis of the films from all three blends at different time intervals occurred on the same day. Care was taken to remove traces of vacuum grease from the apparatus used.

3.10.3. G.P.C. Analysis

The G.P.C. determinations of the extractable and non-extractable portions of the films formed from the blends prepared in section 3.10.2. were carried out at ICI Paints Division.

A Perkin Elmer Series II pump was used together with a LC 420 auto injector and a LC 100 column oven. The RI detector used was an ERMA ERC/7510. The equipment was interfaced to a Waters 380 data system (version 4). The three columns used in series for the G.P.C. analysis were Polymer Lab columns (lengths 30 cm) of pore size 10^6 Å , 10^4 Å and 500 Å . The column packing used was PL gel (10 micron).

Initially, the samples were dissolved in THF, (~20 cm^3), Fisons HPLC grade (unstabilised), which had been degassed using an ERMA ERC-3310. The extractable and non-extractable material were filtered through Millex-SR Millipore membranes (0.5 micron) prior to injection (100 µl). The G.P. chromatographs were printed out using a Digital LVPL6 plotter.

One problem encountered during the preparation of the G.P.C. samples was the partial solubility of the non-extractable film in the THF, whereas the extractable material appeared soluble in THF. However, all samples were treated in exactly the same manner in order to minimise experimental error.

3.11. Paint preparation and formulation

The author is grateful to the staff at ICI Paints Division for their advice in this preparative work.

3.11.1. Synthesis of oleic acid alkyd

A 500 ml three necked flask was charged with pentaerythritol (PE) 42.1 g, (0.31 mol), phthalic anhydride (PA) 49.1 g, (0.33 mol) and Sigma Grade (approximately 99%) oleic acid 124.8 g (0.44 mol) ; toluene (12.9 g) was added at 6% on the total charge mass. The mixture was heated under reflux with constant stirring in an atmosphere of nitrogen; the water produced was azeotropically removed and collected in a Dean and Stark apparatus. During the reaction a sample of the alkyd was removed every hour and the 'acid value' determined by titration with 0.1M ethanolic potassium hydroxide. The term acid value (AV) refers to the measurement of carboxyl end groups expressed as AV = mg KOH/g non-volatile (NV) resin and is calculated from the following equation 3.11.1.1.

$$AV = \frac{\text{Vol. of titre (cm}^3\text{) x molarity KOH x 56.1}}{\text{mass of alkyd sample}} \text{ mg KOH/g (NV) resin}$$

Equation 3.11.1.1.

(The weighed alkyd sample was dissolved in approximately 10 - 20 cm^3 of toluene/ethanol (5/2) prior to titration).

When the 'acid value' of the mixture decreased to between 12 and 14 mg KOH/g NV resin, the reaction was stopped. Toluene, 25 g, was added and mixed into the resin. The final 'acid value' and 'solids content' were then determined. The 'solids content' is calculated as the percentage of the non-volatile material in the final resin, (see section 1.2).

PE /PA /oleic acid
2.1/2.25/3

Final AV = 13.84. % solids = 87.15%.

3.11.2. Synthesis of linoleic acid alkyd

Pentaerythritol 42.2 g, (0.31 mol), phthalic anhydride 49.2 g, (0.33 mol), linoleic acid 124.2 g, (0.44 mol), and toluene (12.9 g), added at 6% on the total charge mass were refluxed together following the same experimental procedure as described in the above section 3.11.1.

PE /PA /linoleic acid
2.1/2.25/3

Final AV = 10.54. % solids = 79.3%.

3.11.3. Paint formulation of alkyd based paints

A series of alkyd based paints were made up from oleic, linoleic and soya bean oil alkyds. (The soya bean oil alkyd was supplied by ICI Paints Division but see sections 3.11.1 and 3.11.2 for preparation of oleic and linoleic alkyds).

The pigment rutile, TiO_2, was made so as to become 15% by volume in the dried film, (ρ of TiO_2 = 4.1). The resin (non-volatile) was made to be 85% by volume in the dried film, (ρ of resin = 1). TiO_2 was added to the paint in the form of "millbase", (a proprietary pigment dispersant), which contained 69.1% TiO_2. Resin was added to the millbase with stirring and then the driers which were (1) cobalt (II) bis(2-ethylhexanoate), added at 0.05% on resin solids (10% cobalt content), and (2) lead (II) bis(2-ethylhexanoate), added at 1.2% on resin solids (36% lead content). Finally the viscosity of the paint was adjusted using toluene. The exact paint formulations are shown in table 45.

3.11.4. Synthesis of cymel 303/3 allyl alcohol[151] (LVIII)

Cymel 303 (97.5 g, 0.25 mol), allyl alcohol, (2-propen-1-ol), (57 g, 0.98 mol) and p-toluene sulphonic acid (0.3 g), added at 0.3% on the mass of cymel used, were placed in a glass reaction

Table 45

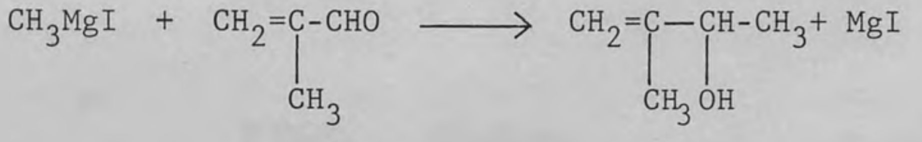
	Oleic acid alkyd paint	Linoleic acid alkyd paint	Soya bean oil alkyd paint
Millbase (g) (a proprietary pigment dispersant)	44.50	44.50	44.50
Alkyd (g)	48.75 (87.15% solids)	53.60 (79.3% solids)	56.60 (75.18% solids)
Co drier (g)	0.21	0.21	0.21
Pb drier (g)	1.42	1.42	1.42
Viscosity (centipoise at 10,000 sec^{-1})	4	4	4

vessel with a five necked lid. The mixture was stirred in an atmosphere of nitrogen and refluxed for two hours, (b.p. of cymel 303 96 - 98^{o}C); the methanol produced in the reaction was then removed by distillation. The reaction mixture was neutralised with lithium hydroxide and any remaining allyl alcohol was removed under reduced pressure.

There are six potential sites for the allyl alcohol to become attached to the cymel 303 but on average the allyl alcohol becomes attached to only three of these sites. However, some of the lower and higher analogue material may also be formed in the reaction mixture.

3.11.5. Synthesis of 3-methyl-3-buten-2-ol[245]

Initially the Grignard reagent, methyl magnesium iodide CH_3MgI (1 mole) was prepared in 450 cm^3 of sodium dried ether; this reagent was then reacted with 2-methylprop-2-enal (methacrolein) to give 3-methyl-3-buten-2-ol (CLXXVIII), see scheme 3.11.5.1.



$$CH_3MgI + CH_2{=}\underset{CH_3}{\underset{|}{C}}\text{-}CHO \longrightarrow CH_2{=}\underset{CH_3}{\underset{|}{C}}-\underset{OH}{\underset{|}{CH}}\text{-}CH_3 + MgI$$

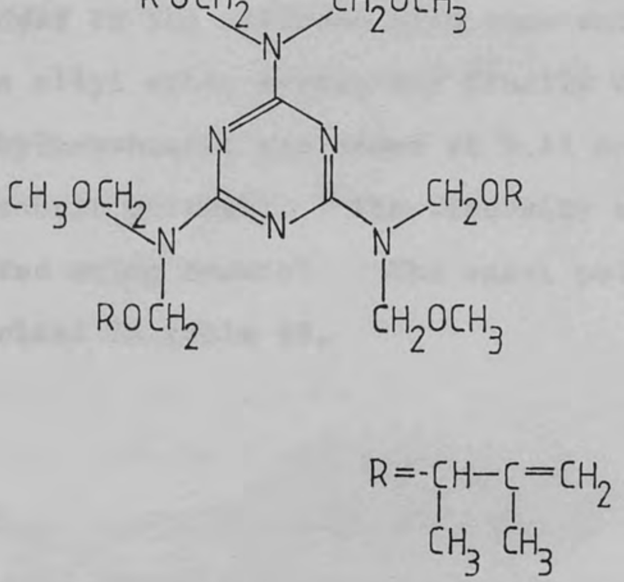
CLXXVIII

Scheme 3.11.5.1.

CH_3MgI was prepared according to the standard method.[246]

2-Methylprop-2-enal (56.07 g, 0.8 mol) in 250 cm^3 of ether, which had previously been purified by fractional distillation through a short Vigneux column under nitrogen, was added during 1 hour to a prepared solution of methyl magnesium iodide at 0°C. The mixture was stirred for 3 hours at room temperature and then poured on to ice in a saturated ammonium chloride solution; the ether layer was separated, washed, dried and the ether removed under reduced pressure. The alcohol was obtained from the crude product by vacuum distillation under nitrogen; 3 methyl-3-buten-2-ol distilled as a clear liquid at 28 - 30°C, 37 - 38 mm Hg,(lit. b.p. 116 - 117°C). The yield was 20.95 g (30.45%). Proton n.m.r. (60 MHz; $CDCl_3$) for the product gave a doublet (2H) at δ 4.7, a multiplet (2H) at δ 4.3 to 3.75 ppm $(-\underset{\mid}{\overset{}{C}}H-)$ with OH below, a singlet (3H) at δ1.63 and a doublet (3H) at δ 1.2.

3.11.6. Synthesis of cymel 303/3 (3-methyl-3-buten-2-ol)(CLXXIX)



CLXXIX

Cymel 303 (97.5 g, 0.25 mol), 3-methyl-3-buten-2-ol (62.2 g, 0.72 mol) and p-toluene sulphonic acid (0.3 g) were refluxed together following the same experimental procedure as described in section 3.11.4.

The synthesis of 3-methyl-3-buten-2-ol is described in section 3.11.5.

3.11.7. Paint formulation of allyl ether based paints

Two paints were formulated using (1) cymel 303/3 allyl alcohol and (2) cymel 303/3 (3-methyl-3-buten-2-ol) as the drying system in each case, (see sections 3.11.4 and 3.11.6 for preparation details). A 1/1 blend by mass was prepared of acrylic polymer/allyloxy system. The pigment was added as a millbase, 100 g of which contained pigment (43.19 g), acrylic polymer (32.30 g) and Dowanol (24.51 g). Acrylic polymer was added to the millbase with constant stirring, followed by the allyl ether system and finally cobalt (II) bis (2-ethylhexanoate) was added at 0.1% on the solids present, (10% cobalt content). The viscosity of the paint was adjusted using Dowanol. The exact paint formulations are summarised in table 46.

Table 46

	cymel 303/3allyl alcohol paint	cymel 303/3(3-methyl 3-buten-2-ol) paint
millbase (g) (a proprietary pigment dispersant)	89.91	89.91
acrylic solution polymer (g)	1.56	1.56
allyloxy system (g)	30.60	30.60
Co drier (g)	0.60	0.60
Viscosity (centipoise at 10,000 sec^{-1})	4	4

3.11.8 'Yellowing tests' of traditional alkyd based paints and paints based on allyloxy systems (novel drying systems)

Tin plate panels were spread with each of the paints listed below using a 200 μm block spreader:-

(i) soya bean oil alkyd,
(ii) oleic acid alkyd,
(iii) linoleic acid alkyd,
(iv) cymel 303/3allyl alcohol,
(v) cymel303/3(3-methyl-3-buten-2-ol),
(vi) a commercially available white alkyd gloss paint (used as a standard).

For paint preparation details see sections 3.11.3 and 3.11.7.

These panels were subjected, for 1 week, to several different environments, viz. (1) ammonia atmosphere (2) 40°c in the dark (3) 70°C in the dark (4) room temperature (22°C) in the light. The panels spread with the different paints were allowed to dry at room temperature for 4 days before being placed under test conditions. Any change in the yellowing of the paint was detected by measuring the reflectance of the spread paint in order to determine the colour index (CI)[182], both before and after being placed in the test environment. The reflectance was measured using a Zeiss spectrometer coupled with a 'Reflectance Storing' program with specular correction. Increasing positive values of CI indicate an increase in the yellow tone of the paint.

3.12. Investigations concerned with the 'yellowing' of trans-2-hexenal

This experimental section refers mainly to the initial investigations concerned with the yellowing of trans-2-hexenal.

3.12.1. Yellowing of aldehydes in oxygen at 70°C

The following aldehydes were obtained from the Aldrich Chemical Co. Ltd., and then freshly distilled prior to use:-

hexanal b.p. 128°C, (lit. value 128°C),
trans-2-hexenal b.p. 32°C at 14 mm Hg, (lit. value 47°C at 17 mm Hg),

2,4-hexadienal b.p. 48°C at 8 mm Hg, (lit. value 76°C at 30 mm Hg) and
2-butenal b.p. 102°C, (lit. value 104 - 105°C).

Approximately, 5 cm^3 of each aldehyde was placed separately in a 25 cm^3 two-necked round-bottomed (RB) flask. Each flask was wrapped in silver foil, fitted with a reflux condenser, drying tube and then placed in an oil bath at 70 ± 1°C. Dry oxygen gas was bubbled, using a capillary bleed, through each aldehyde, which was examined after 15 hours and after 39 hours for any noticeable colour changes.

Trans-2-hexenoic acid (0.5 g), Lit. m.p. 32°C, was treated similarly.

3.12.2. Effect of free radical initiator and inhibitor on trans-2-hexenal

The radical initiator and inhibitor, Perkadox 16 N (bis(4-t-butylcyclohexyl)peroxydicarbonate) and POM (primary octyl mercaptan) respectively, were used as supplied by ICI Paints Division.

Trans-2-hexenal (~5 cm^3), freshly distilled as in section 3.12.1, was placed in two sample tubes to which was added either initiator (1 microspatula) or inhibitor (a few drops); the sample tubes were then sealed. A third sample tube was prepared which contained trans-2-hexenal alone as a control. All three samples were placed in the light at room temperature (~21°C) and examined for any observable colour change after 1 week and 2½ months.

The experiment was repeated except that the samples were placed in glass ampoules, (approximate size 5 mm x 3 mm (i.d.)), which were sealed and placed in the dark in a container at 70 ± 1°C. These samples were also examined for any observable colour change after 16 days.

3.12.3. Yellowing of trans-2-hexenal in the dark at 70°C

The 'yellowing' investigations were carried out mainly using the following procedure. Trans-2-hexenal, freshly distilled, (10 - 15 cm^3), was placed in a 25 cm^3 RB flask, which was wrapped in silver foil, fitted with a reflux condenser and drying tube. This apparatus was then placed in an oil bath at 70 ± 1°C and kept under these conditions for approximately 3 weeks.

3.12.4. Base extraction of yellowed samples of trans-2-hexenal

The yellowed trans-2-hexenal, as prepared in section 3.12.3, was initially diluted with ether (30 - 40 cm^3), which was then extracted with 1 M KOH (3 x 10 cm^3). This aqueous layer was back extracted with ether (2 x 20 cm^3). The aqueous layer was then acidified with 1M HCl and extracted with ether (3 x 15 cm^3) and this dried with magnesium sulphate. The ether was then removed under reduced pressure, leaving the base extractable yellow components.

3.12.5. T.L.C. analysis of 'yellowed' trans-2-hexenal

Solvent systems used to analyse solutions of the yellowed trans-2-hexenal, as prepared in section 3.12.3, were:-

chloroform, methanol and chloroform (using a range of methanol concentrations from 1 - 7.5%), hexane, petroleum spirit/ethyl acetate (4:1, 3:1, 2:1), and petroleum ether/acetone (4:1, 3:1, 2:1).

A silica gel (60 7733) column was also run of yellowed trans-2-hexenal (2 g) using 5% methanol in chloroform as the solvent system. Flash chromatography[247] of the yellowed sample (0.35 g) was also attempted using petroleum ether/ethyl acetate (3:1) as the solvent system.

3.13. Trapping of volatile products from autoxidation of ethanol/3AGE and preparation of trapping agent

This section deals with the preparation of the trapping agent, 2,4-dinitrophenylhydrazine on silica gel, and the formation of 2-4 dinitrophenylhydrazones used corresponding to the volatile products formed from the autoxidation of ethanol/3AGE.

3.13.1. Preparation of 2,4-dinitrophenylhydrazine (DNP) coated silica gel[248]

Silica gel (35 - 70 mesh), (12.5 g) was placed in a 100 cm^3 (RB) flask to which was added 6M HCl (12.5 cm^3). DMF (40 cm^3) was added to a 50 cm^3 volumetric flask containing 2,4-DNP (5 g). The mixture was swirled (10 - 15s), then quickly diluted to the mark with more DMF and immediately poured through a glass wool plug in a funnel into the flask containing the silica gel and acid. (The 2,4-DNP and DMF mixture was unstable and needed to be used quickly). The volumetric flask and glass wool were rinsed with an additional 5 cm^3 DMF, and this was added to the RB flask. The mixture was allowed to stand for 30 min with occasional swirling before vacuum filtration. The silica gel was rinsed sparingly with DMF (2 - 3 cm^3) and left on the filter paper with continued suction for 1-2 min. The silica gel was then transformed quickly to a 100 cm^3 RB flask and dried under vacuum at 55°C for 1 hour with brief turning every 10 minutes.

3.13.2. Preparation of 2,4-dinitrophenylhydrazones (DNPH) of aldehydes

The 2,4-DNPH derivatives listed below were prepared using the following procedure.[249]

2,4-DNP (1 g), 6M HCl (2 cm^3) and ethanol (15 cm^3) were warmed in a beaker until a clear solution was obtained. Aldehyde (0.5 g) was added to this warm solution, which was heated just to boiling. The solution was allowed to stand until a precipitate formed. After cooling further to room temperature, the 2,4-DNPH derivative was filtered off and then recrystallised from ethanol.

The prepared 2,4-DNPH derivatives gave the following melting points:-
methanal (166°C, lit. 167°C), ethanal (143-145°C, lit.146°C), propanal (142-143°C, lit.142-148°C),
2-propenal (162-164.5°C, lit. 165°C),
butanal (123-124°C, lit. 123°C), 2-butenal (191-193°C, lit. 196-197°C), and pentanal (106-108°C, lit. 106-107°C).

3.13.3. Trapping of volatile products from autoxidation of ethanol/3AGE

Ethanol/3AGE (5 g) and cobalt (II) bis(2 -ethyl hexanoate), (0.029 g), added at 0.1% on the mass of EtOH/3AGE, (17% cobalt metal), were placed in a 25 cm^3 RB flask. Dry oxygen gas was bubbled through the mixture at 8-10 cm^3/min. The exit tube from the flask passed into a glass tube containing the 2,4-DNP coated silica gel (0.7 g), which was held in place by glass wool plugs. (The dimensions of the glass tube were 10 cm x 4 mm i.d.). Oxygen was bubbled through the apparatus for 5 hours. The coated silica gel was then placed in acetonitrile (1-2 cm^3) for 1 hour and the supernatant analysed by T.L.C. using (1) silica gel plates with methanol/chloroform (5/95) as the solvent system and (2) reverse phase KC_{18} plates with acetonitrile/water (80/20) as the solvent system. The R_f values obtained for this coated silica gel were compared to those obtained for the 2,4-DNPH derivatives prepared in section 3.13.2.

3.14 'Yellowing' of 2-propenal in the dark

The 'yellowing' of 2-propenal, obtained from the Aldrich Chemical Co. Ltd., and inhibited with 200 ppm hydroquinone, was carried out in a similar method to trans-2-hexenal, section 3.12.3.

2-Propenal (3 cm^3), which was pale yellow in colour was placed in a 5 cm^3 RB flask. Silver foil was wrapped around the flask, which was fitted with a reflux condenser and drying tube. The apparatus was then placed in an oil bath at 47 ± 1^oC. The 2-propenal was kept under these conditions for approximately 1 week.

If the 2-propenal was kept in the oil bath for much longer than 1 week, then, although the 2-propenal 'yellowed' in colour, polymerisation of the material occurred in spite of the presence of hydroquinone.

3.15 Derivatisation of the 'yellowed' trans-2-hexenal for GC-MS studies

The acid components of 'yellowed' trans-2-hexenal, extracted as described in section 3.12.4, were derivatised using the following methods.

3.15.1. Derivatisation of base extracted 'yellowed' trans-2-hexenal using boron trifluoride/methanol complex[250,251] (BF_3/CH_3OH)

The acid components of the yellowed trans-2-hexenal (100-200 mg) were placed in a 10 cm^3 RB flask to which was added boron trifluoride methanol complex, $BF_3 \cdot CH_3OH$ (~12 wt.%), (3 cm^3). The mixture was refluxed for 20 minutes and then poured onto water (20 cm^3). The derivatised acidic components of the yellowed material were extracted with chloroform (3 x 10 cm^3) and washed with aqueous potassium bicarbonate (3 x 5 cm^3). The chloroform layer was dried with magnesium sulphate and then concentrated under reduced pressure.

3.15.2. Derivatisation of base extracted 'yellowed' trans-2-hexenal using chloroacetone

The derivatisation of the acid components of 'yellowed' 2-hexenal using chloroacetone was also attempted following the given method[252] to give the acetonyl esters. (For GC analysis the stationary phase used was 10% carbowax 20M coated on gas chrom Q mesh size 80/100). However, the resolution of these derivatised components was poor, and it was thought that the chloroacetone, in spite of purification[253] gave several compounds as determined by the peaks on the gas chromatograph. This method of derivatisation was abandoned in favour of the $BF_3 \cdot CH_3OH$ reagent, section 3.15.1.

3.16. Derivatisation of 'yellowed' 2-propenal for GC-MS studies

The derivatisation of 2-propenal,which had been 'yellowed' (see section 3.14), was attempted directly rather than after an initial base extraction, as with yellowed trans-2-hexenal.

BF_3 in methanol was used as the derivatising agent and the first part of the method given in section 3.15.1 was followed. However, after refluxing for 20 minutes the mixture was poured onto water and extracted with chloroform (3 x 10 cm^3). The chloroform layer was dried with magnesium sulphate and then concentrated under reduced pressure.

3.17. Packed column g.l.c. and gc-ms analysis of derivatised samples of autoxidised trans-2-hexenal and 2-propenal

The derivatised samples of autoxidised trans-2-hexenal and 2-propenal were each subjected to the same packed column and gc-ms conditions. (See sections 3.15.1 and 3.16 for the derivatisation details).

3.17.1. Packed column g.l.c. analysis

Initially packed column g.l.c. analysis of these derivatised samples was carried out using a Pye 104 gas chromatograph; the conditions used are shown in table 47.

3.17.2. GC-MS analysis (with accurate mass measurements)

This gc-ms analysis was obtained from the SERC Mass Spectrometry Centre at the University College of Swansea.

After having determined the conditions for good chromatographic separations, section 3.17.1, capillary column gc-ms analysis using EI and NH_3-CI was carried out. The EI and NH_3-CI data was obtained using a VG 12-253 Quadrupole GC-MS instrument coupled to a Hewlett Packard Model 5890 microprocessor controlled gas chromatograph.

Table 47

Packed column glc analysis

Stationary phase	10% SP1000 coated on gas chrom Q mesh size 100/120
Column dimensions	1.45 m x 3 mm (i.d.)
Carrier gas	Nitrogen
Carrier gas flow rate	40 $cm^3 min^{-1}$
Oven temperature	110°C isothermal for 30 min. then rising 2°C min^{-1} to 200°C isothermal for 30 min.
Injection volume	1 µl
Detector	Flame ionisation detector
Injector temperature	200°C
Detector temperature	250°C

The conditions used for the capillary column analysis are shown in table 48.

The accurate mass measurements of ions produced by NH_3-CI were obtained by distilling the complete mixture directly off the probe using a VG ZAB-E high resolution instrument.

3.17.3. GC-MS analysis (NH_3-CI only)

This gc-ms analysis was obtained from PCMU, Harwell.

After having determined the conditions for good chromatographic separations, section 3.17.1, capillary column gc-ms analysis using NH_3-CI was carried out. The NH_3-CI data was obtained using a VG Micromass ZAB-2F and ZAB-1F system with VG Datasystem (2000) coupled to a Pye Unicam Series 204 Chromatograph. The conditions used for capillary column analysis are shown in table 49.

3.18 Preparative g.l.c. analysis of autoxidised samples of trans-2-hexenal

This preparative g.l.c. analysis of derivatised samples of autoxidised trans-2-hexenal was carried out using a Pye 105 chromatograph. (See sections 3.12.3, 3.12.4 and 3.15.1 for details of yellowing and derivatisation). The conditions used are shown in table 50.

Table 48

Capillary column g.l.c. analysis (with EI and NH_3-CI)

Column	
liquid phase	XE-60
length	25 m
i.d.	0.32 mm
film thickness	0.5 μm
Carrier gas	helium
flow rate	$\sim$40 cm^{3}s^{-1}
head pressure	5 psi
Injector system	split
Injector temperature	200°C
Interface temperature	220°C
Oven temperature	50°C isothermal 2 min. then rising 10°C min^{-1} to 220°C isothermal for 5 min.

Table 49

Capillary column glc analysis (with NH_3-CI only)

Stationary phase	SP1000
Column length	25 m
Carrier gas	Helium
Carrier gas flow rate	30 $cm^3 min^{-1}$
Oven temperature	110°C isothermal for 4 min. then rising to 220°C isothermal for 10 min.
Injector volume	0.5 µl
Injector temperature	200°C
Detector temperature	250°C

Eleven traps were used on the preparative gas chromatograph to collect the material, as indicated by the g.l. chromatograph, from either individual peaks or mixtures of peaks. (See fig. 2.7.1, section 2.7 showing the positions when the trap was changed.)

Proton n.m.r. analysis, using a Jeol 90 MHz was attempted on the liquid collected in traps 2,4,8, 10 and 11.

Table 50

Preparative column g.l.c. analysis

Stationary phase	10% SP1000 coated on gas chrom Q mesh size 100/120
Column dimensions	4.5m x 5 mm (i.d.)
Carrier gas	Nitrogen
Carrier gas flow rate	60 cm^3/min
Oven temperature	110°C isothermal for 30 min. then rising to 210°C isothermal for 30 min.
Injection volume	150 µl (x12)
Detector	Flame ionisation detector
Injector temperature	200°C
Outlet heater	220°C

4. Conclusions

This study has fallen into two main areas viz. the crosslinking ability of the novel drying systems based upon allyloxy compounds and attempts to characterise the yellow products derived from trans-2-hexenal, which had been identified as an autoxidative degradation product of alkyds incorporating linoleic and linolenic acids. The novel drying systems have been developed in part to minimise two undesirable features of autoxidative drying of traditional alkyd resin paints:- (i) the production of odourous volatile degradation products and (ii) the 'yellowing' of the films, (particularly under the influence of heat, drying in the dark or the presence of foul atmospheres). Since 2-propenal was identified as a by-product of the autoxidative degradation of the new drying systems attempts were made to characterise the yellow compounds that could be derived from this. The conclusions from these separate investigations will be considered in two parts. The crosslinking ability of the novel drying systems will be considered first.

It appeared that ethanol/3 AGE showed the best crosslinking ability of all the five allyloxy systems studied,followed by the cymel 303/3 allyl alcohol. Cymel 303/3 methallyl alcohol showed a much less efficient film formation and the long term stability of the allyl ether compounds modified with ethylene oxide appeared poor. The effect of the unfunctional polymer (UFP) appeared to slow the rate of film formation, as did the functional polymer (FP) but the effect was not quite so apparent with the latter compound. The only exception to this trend was the blend containing cymel 303/3 methallyl alcohol and FP. Here, this blend produced more non-extractable material after a given drying time than the allyl ether compound alone. The FP, having an allyl functionality, probably undergoes crosslinking reactions with the allyloxy compound and itself, whereas the UFP cannot participate in the free radical crosslinking of the allyloxy compound but merely becomes entrapped in the crosslinked matrix of the dried blend.

FTIR showed that more of the FP becomes incorporated into the film than UFP with cymel 303/3 allyl alcohol, and even more of the FP is to be found in the film with blends incorporating cymel 303/3 methallyl alcohol. The ethylene oxide modified cymel 303 systems appeared to show the FP and UFP incorporated equally into the non-extractable films. (Although it must be noted, from the weighing experiments, that the long term stability of the ethylene oxide modified cymel 303 systems is poor).

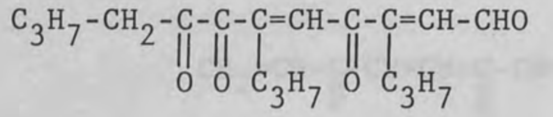
Radioactivity studies showed that a mixture of cymel 303/3 allyl alcohol and FP, dried for 4 weeks, gave a non-extractable film composed of slightly more of the former than the latter.

In the initial stages of drying the composition of the film showed a much larger proportion of allyloxy compound present than FP. However, with the cymel 303/3 allyl alcohol and UFP blend, the composition of the dried film after 4 weeks drying time appeared to contain a much larger proportion of allyloxy compound than UFP, and the initial stages of drying gave a film consisting of virtually allyloxy compound alone.

The G.P.C. analysis of the extractable and non-extractable portions of films formed from blends based upon purified cymel 303/3 allyl alcohol provided another method of examining the crosslinking ability of the drying system. Although the information obtained was not as quantitative as the FTIR, weighing and radioactivity data, the same pattern of crosslinking of the cymel 303/3 allyl alcohol was observed. Again the film appeared to be dominated by the polymerised cymel 303/3 allyl alcohol in the early stages of drying.

Whilst any further study could be to produce more data on the crosslinking ability of the other allyloxy drying systems by using radioactive ^{14}C labelled polymers, alternatively ^{14}C labelled ethanol/3 AGE could be used but with unlabelled polymers.

Although a second objective of this work was to attempt to characterise the yellow components of both autoxidised trans-2-hexenal and 2-propenal, difficulty was experienced in that the quantities of these yellow compounds was extremely small and separation proved to be not straightforward. Analysis by gc-ms with EI and NH_3-CI and accurate mass measurement of the alkali soluble products, which had been derivatised with BF_3/ methanol complex, and derived by 'yellowing' trans-2-hexenal in the dark at 70°C, showed not unsurprisingly that the major component to be the methyl ester of trans-2-hexenoic acid. The analysis of the other compounds of the autoxidation mixture, which although not coloured could be precursors of chromophoric compounds, showed a predominance of epoxide type compounds prior to derivatisation, with possible rearrangement to carbonyl compounds. Their formation was accompanied by a variety of addition reactions between either propanal or propenal, as well as the mutual addition of trans-2-hexenal with itself to produce the compounds determined from the gc-ms data. As discussed in section 2.6.3 (table 37), none of the suggested structures for the compounds formed during the autoxidation of trans-2-hexenal in the dark had sufficient conjugation to give them a chromophore characteristic of a yellow colour. However, it could be envisaged that some of the structures shown in table 37 could undergo further addition reactions and as the amount of conjugation builds up some products may absorb to give a yellow colouration. A speculative suggestion for this type of higher molecular mass compound is shown in structure CLXXX.



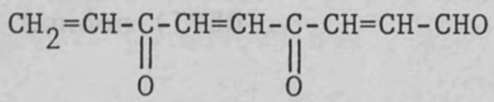
$$C_3H_7-CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-\underset{\underset{C_3H_7}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-\underset{\underset{C_3H_7}{|}}{C}=CH-CHO$$

CLXXX

Compounds, such as the structure CLXXX, if present in the autoxidation mixtures, would not have been analysed under the experimental conditions used. However, it seems likely that precursors of some of the types of yellow compounds were analysed.

Confirmation of the precursors would require their synthesis and gc-ms analysis.

Similar gc-ms analysis of the products obtained by yellowing 2-propenal in the dark at 47°C showed a predominance of compounds, which appeared to have arisen from two or more Prins type addition reactions prior to derivatisation. Unlike trans-2-hexenal there appeared to be very little evidence for the formation of 2-propenoic acid. Again, none of the suggested structures for the compounds, (see table 42), possess sufficient conjugation to give them a chromophore characteristic of a yellow colour. Structure CLXXXI shows a possible suggestion for higher molecular mass material, that could result from further addition reactions of 2-propenal and which would have sufficient conjugation to absorb to give a yellow colouration.



$CH_2{=}CH{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH{-}\underset{\underset{O}{\|}}{C}{-}CH{=}CH{-}CHO$

CLXXXI

Synthesis of the precursor compounds is necessary to confirm their structure and higher molecular mass material needs to be collected in sufficient quantity to prove the yellowing theory.

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