Autoxidative degradation of unsaturated fatty acid esters

by

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A Thesis submitted in partial fulfilment
of the requirements of the degree of
Doctor of Philosophy of the University of London

June 1985

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TO MY MOTHER

Acknowledgements

I would like to express my gratitude to my supervisor, Dr R.A. Hancock, for his guidance, encouragement and friendship throughout the course of this work, which was not purely restricted to the research.

Thanks are also due to Dr P.F. Nicks of ICI Paints Division, Slough, for his help and enthusiasm particularly in the industrial aspects of this project. The financial support provided by ICI Paints Division in purchasing specialist chemicals is gratefully acknowledged.

The technical assistance of Messrs B. Smethurst, R. Lane, D. Parkinson, D. Smith, J. Turner, G. Waters and P. Willmore is appreciated as is the help given by Dr. C. Creaser of P.C.M.U. of Harwell, in obtaining the capillary gc-ms results.

Thanks are also due to Mrs E.I. Kearsey for typing this thesis and to Mr D. Ratcliffe for helping to find some of the mistakes.

I would like to thank many of my postgraduate colleagues for their friendship, particularly Alan and Phil. Gratitude is also extended to all those who took part in, and therefore made possible, the series of "NOT THE ROYAL INSTITUTE CHRISTMAS LECTURES".

Finally the financial support from SERC is acknowledged.

Abstract

Autoxidative Degradation of Unsaturated Fatty Acid Esters

The autoxidative degradation of methyl cis-9-octadecenaote, methyl cis-9-cis-12-octadecadienoate and methyl cis-9-cis-12-cis-15 octadecatrienoate promoted by both transition metal ions and photoinitiators produce 'volatile' products. These were collected by cryogenic and chemical traps, then analysed by glc, HPLC and gc-ms. The major products so identified included; 3-heptanone, heptanal and octanal from methyl cis-9-octadecenoate, hexanal, 2-hexenal and 2-heptenal from methyl cis-9-cis-12-octadecadienoate, and propanal, 1-penten-3-ol and 1-penten-3-one from methyl linolenate. Methyl octanoate was found to be a product common to the autoxidation of the three methyl esters. The major products are explained by β-scissions of alkoxy radicals. The quantity of volatile compounds produced was found to depend on both the degree of unsaturation and the type of promotor.

'Volatile products' were observed during the promoted autoxidative crosslinking of polyester resins (alkyd resins). The products so formed corresponded to the fatty acids present in the resins. Time lapse infrared spectroscopy was used to observe chemical changes occurring in the drying resin films. Hydroperoxides are the primary autoxidation products and their rate of formation was shown to depend upon the promotor used.

Benzoyloxyethyl cis-9-cis-12-octadecadienoate, a model alkyd, was synthesised and autoxidised. The 'volatile' products formed were the same as those observed from methyl cis-9-cis-12-octadecadienoate.

Alkyds having a high proportion of non-esterified hydroxyl groups may be crosslinked in the presence of strong acids. This has been shown to be an autoxidative process where the hydroperoxides are decomposed by the acid to give acetal type linkages. 2-Hydroxyethyl linoleate, 2-hydroxyethyllinolenate and a series of 'variable hydroxyl content' alkyds were prepared. The 'volatile products' isolated from the alkyds were similar to those produced using transition metal promotors but the 2-hydroxyethyl esters produced only acetal type compounds.

6,9-Pentadecadiene, 8-methyl-6,9-pentadecadiene and 8,8-dimethyl-6,9-pentadecadiene were synthesised and autoxidised. The composition and quantity of 'volatile products' depended upon the degree of allylic substitution.

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1. Introduction

1.1 Crosslinking in alkyd resin paints

The vulnerability of objects to damage at their surface can often be minimised by applying a protective coating. Paint, and in particular gloss paint, finds many applications for the protection of surfaces in the home. It has the added advantage of improving their decorative appearance. The composition of a gloss paint is often based upon alkyd resins which are the most versatile and economical of all the resin types. The other components are pigment (to provide colour), solvent (typically white spirit), drying promotors and anti-skinning agents.

An alkyd resin has been defined as "the reaction product of a polyfunctional alcohol with a polybasic acid together with a monofunctional acid obtained by a simple esterification reaction."
The name alkyd is derived from the 'al' of alcohol and the 'cid' of acid.

Many acids and alcohols may be used to prepare alkyd resins although the market price of the raw products is often the determining factor in industrial use. The common polybasic acids and polyfunctional alcohols used in alkyd resins are summarised in table 1. The typical fatty acids used are given in table 2.

Table 1

Dibasic acids	Polyhydric alcohols
Phthalic acid (as the anhydride)	ethylene glycol
Isophthalic acid	glycerol
Succinic acid .	pentaerythritol
Adipic acid	diethylene glycol
Sebacic acid	1,2 propylene glycol
	trimethylol propane
	neopentyl glycol

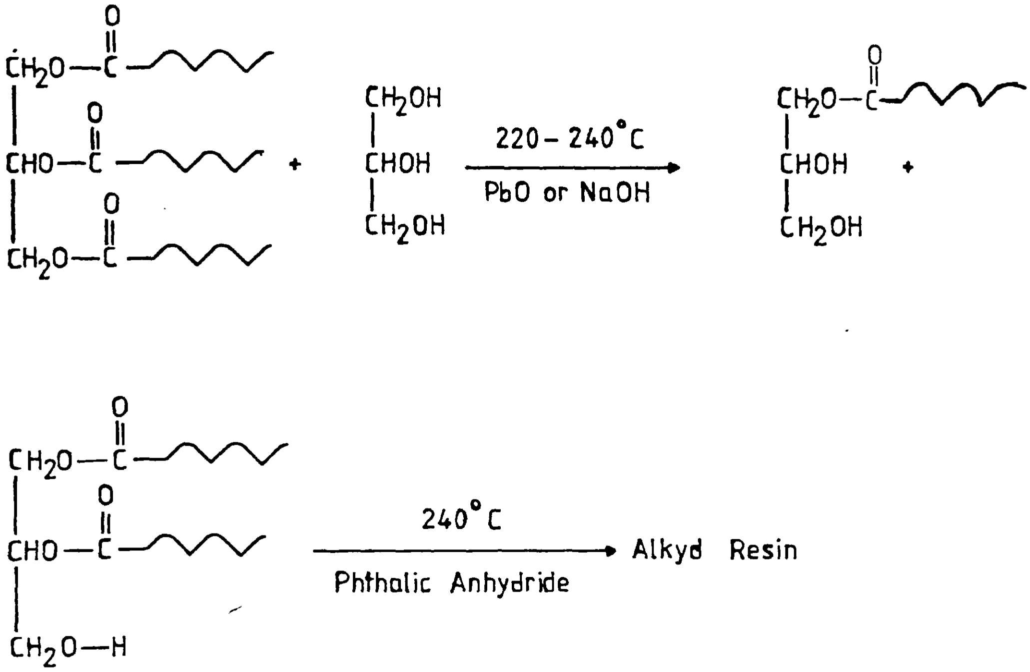
Table 2

Typical fatty acids
Stearic acid
Oleic acid
Linoleic acid
Linolenic acid
β-Eleostearic acid

Originally the use of monofunctional acids, such as oleic or benzoic acid, were used to prevent gelation during resin preparation. These "chain stopped" alkyds actually preceded oil modified alkyds.

The preparation of an alkyd resin is relatively simple, it is that of polyesterification. Two methods may be used to prepare alkyds (i) the fatty acid route, where the polybasic acids, polyhydric alcohols and unsaturated fatty acids are heated at 240°C, under a blanket of nitrogen and the water produced by the esterification process azeotropically removed, (ii) the alcoholysis route, where the natural oil (triglyceride) is heated at 240°C in the presence of the polyhydric alcohol to give a random mixture of glycerol,monoglyceride and diglycerides. This mixture is then reacted with the dibasic acid to produce the alkyd resin, Scheme 1.1.1.

The latter route is used industrially as the natural oils are cheaper than the corresponding fatty acids:



Scheme 1.1.1

The resin preparation has to be carefully monitored to prevent total gelation. Two tests are carried out which are esoteric to alkyd manufacturers, (i) acid value which gives the degree of reaction and amount of residual COOH end groups. This value is expressed as "mgKOH/g non-volatile resin", (ii) viscosity which gives a measure of molecular weight of the resin. This is carried out using a stoppered glass tube almost filled with resin. The time taken for the bubble to pass through the resin when the tube is inverted is recorded. The viscosity is then reported as "X sec bubble test at 25^{o}C at Y% solids in Z solvent". The final constants of the resin are expressed as the acid value, viscosity and % solids.

$$\% \text{Solids} = \frac{\text{weight of resin}}{\text{weight of resin} + \text{solvent}} \times 100$$

Alkyd resins are condensed reproducibly to an acid value and viscosity specification, these values depending on the final use of the resin.

The composition of the resin is expressed by the following general form:

Polyhydric alcohol/dibasic acid/fatty acid

for example:

Pentaerythritol/Phthalic acid/Linseed oil fatty acids.
2 2 3

the numbers represent the molar ratios.

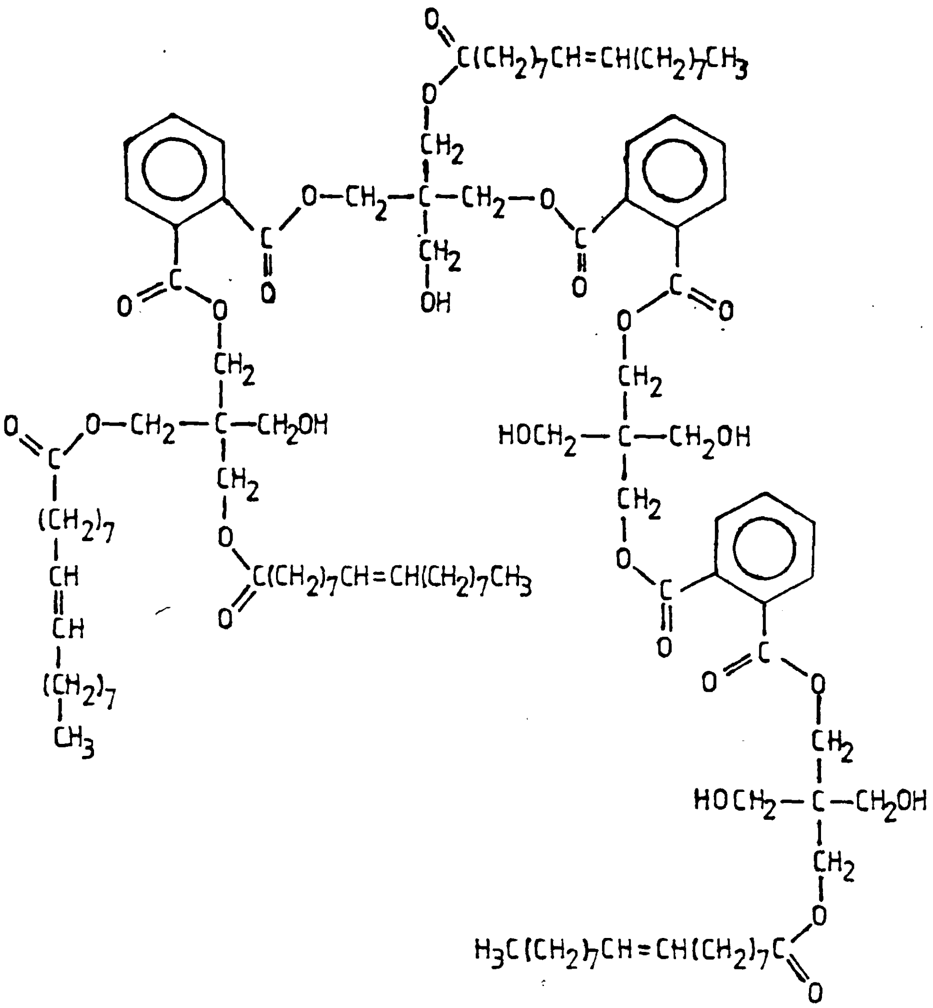
Alkyd resins are also classified by the % weight of oil (i.e. triglycerides) used to make the resin. This is known as the 'oil length', below 45% oil is a 'short oil alkyd', 45-60%, 'medium oil' and above 60%, 'long oil'. 'Long oil alkyds' are soluble in aliphatic hydrocarbons, such as white spirit, whereas 'short oil alkyds' require aromatic hydrocarbons.

Alkyd relative molecular masses are believed to range between 1000 to 5000. Thus a 58% linseed oil glycerol phthalate alkyd contains between two and ten fatty ester chains per alkyd molecule. A simplified alkyd resin is depicted in figure 1.1.1.

The drying of an alkyd based paint occurs by two processes: (i) the evaporation of solvent - termed lacquer drying and (ii) air-drying, which involves autoxidation of the unsaturated fatty esters . forming hydroperoxides

It is believed that the decomposition of these peroxides provides the means for crosslinking.

The chemistry of hydroperoxide formation in the commonly used unsaturated fatty acid derivatives and the mechanism of the various promotors will be reviewed.



Simplified Alkyd Resin

Figure 1.1.1

The natural oils, which are now of increasing importance because of their regeneratable source, will themselves dry and form a film. However, because of their relatively small size numerous crosslinking reactions are required for film formation. In contrast alkyd resins, owing to their greater molecular weight and much higher drying oil functionality require fewer crosslinking reactions to achieve film formation. Hence alkyd resins will dry much faster than natural oils.

This rate of drying for an alkyd resin is however not sufficiently fast, obviously a paint must crosslink (dry) in a reasonable time period to provide a suitable product. To increase rates of drying promotors are added to resins. Several types of promotors have been considered by the paint industry viz: redox catalysts, photoinitiators and strong acids (these will be discussed in sections 1.14, 1.15, 1.16 and 1.17). The essential features for the air-drying of an alkyd paint are the unsaturated fatty acid esters, oxygen and the drying promotors.

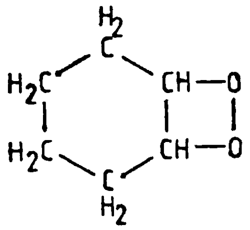
There are two undesirable properties which also accompany the autoxidative drying of paints. These are the production of odourous volatile degradation products and 'yellowing' of the films. The identification of the volatile degradation products and their dependence on ester structure and promotors form the subject of this study.

1.2 Peroxide identification in autoxidation

Priestly first observed the interaction of oxygen with organic compounds. *Inter alia* he showed that linseed oil removed the life giving element oxygen using rats and a bell jar. Currently the term autoxidation is generally used to describe the reaction of a compound with molecular oxygen, usually atmospheric oxygen in the absence of heat and in any case below 120°C.[1]

The formation of peroxides as products in autoxidation was first suggested almost simultaneously in 1897 by Bach[2] and by Engler and Wild.[3] Benzoyl hydroperoxide was identified in 1900 by Baeyer and Villiger,[4] Jornssen and Van der Beck[5] isolated this as the intermediate product in the autoxidation of benzaldehyde.

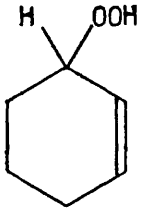
Stephens[6] discovered that cyclohexene, on treating with oxygen in daylight gave a liquid peroxide, $C_6H_{10}O_2$, and presumed it to be a double bond adduct (I) which could be isolated by distillation.



(I)

This peroxide was re-examined by Hock[17] who although obtained seemingly strange results regarding its reactivity agreed with the structure (I) proposed by Stephens.

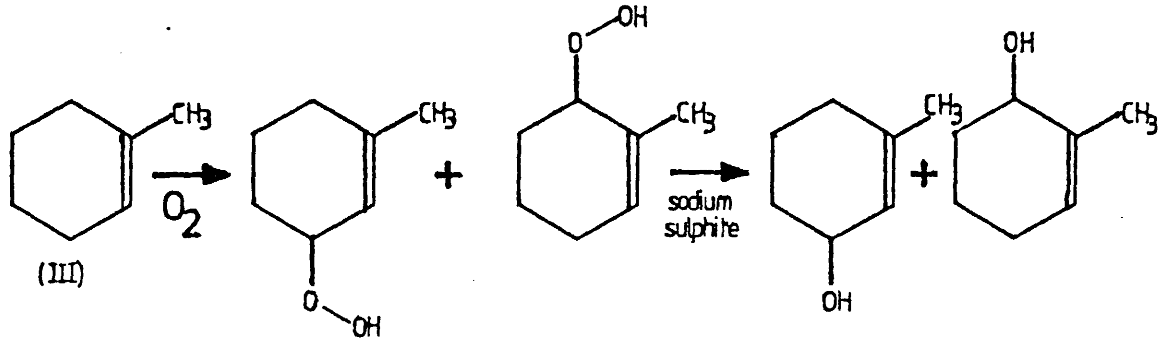
Criegee et al[7] showed that the 'peroxide' formed from cyclohexene in uv light must be a hydroperoxide (II) and still contained a double bond.



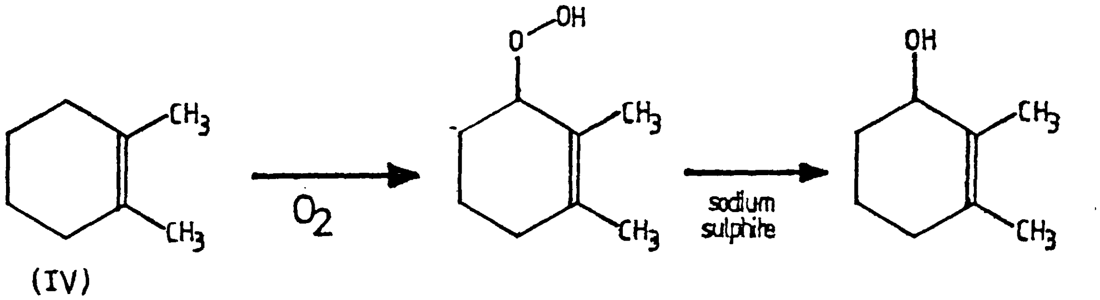
(II)

The evidence provided by Criegee for this structure was: (i) the compound is reducible by sodium sulphite to cyclohexen-3-ol, (ii) it absorbs one mole of bromine per mol and (iii) it contains one atom of reactive hydrogen per mole.

Farmer[8] confirmed Criegee's work by isolating the peroxide (II) and observed that on hydrogenation the peroxide absorbed 2 mols of hydrogen, giving cyclohexanol in almost quantitative yield. Farmer also reacted 1-methyl cyclohexene (III) and 1,2-dimethyl cyclohexene (IV) with oxygen in daylight. These compounds gave products which were determined as hydroperoxides because they yielded the appropriate alcohols. (Schemes 1.2.1 and 1.2.2).



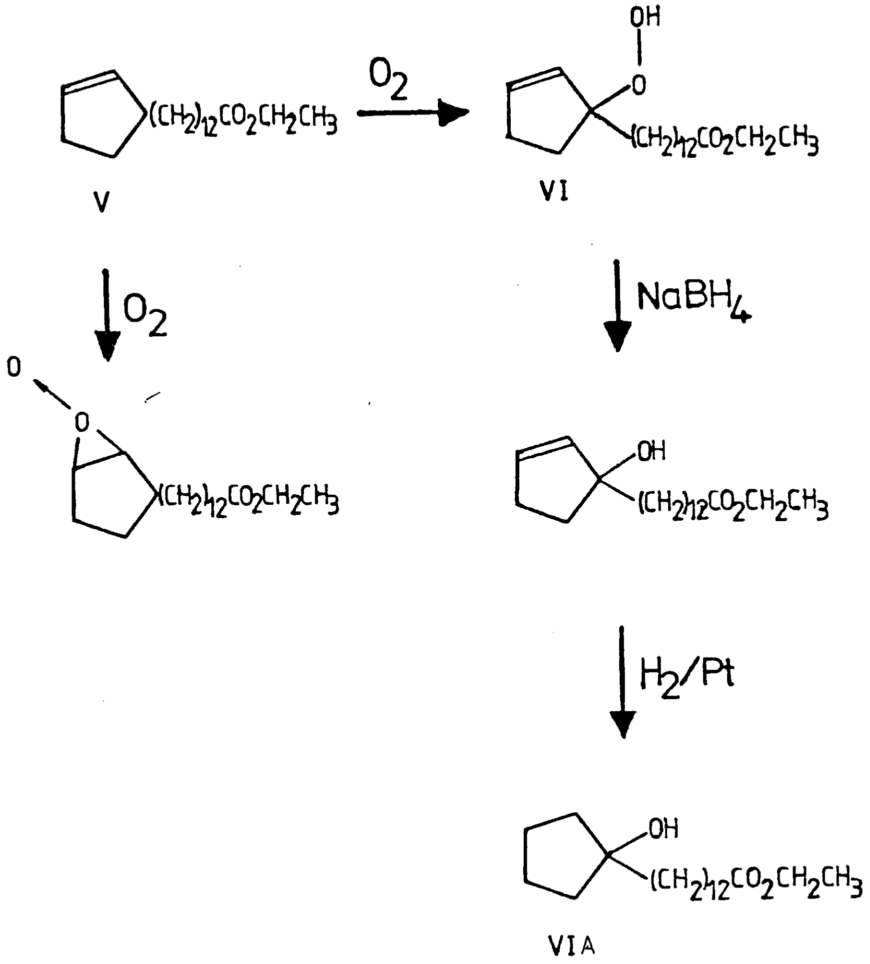
Scheme 1.2.1



Scheme 1.2.2

Cyclic peroxides however have been postulated in olefin autoxidations by several authors,[9,10,11,12,13,14,15] the case appearing strongest in the autoxidation of ethyl-13-(15-cyclopentenyl)tridecanoate.

The majority of evidence was originally based on unisolated and unpurified material. However Davies and Packer[16] isolated the hydroperoxide (VI) by chromatography and Counter Current extraction.



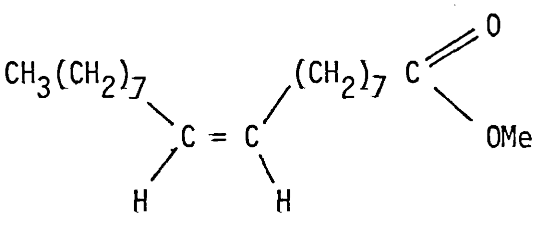
Scheme 1.2.3

The infrared spectrum showed the presence of an OH group (3448 cm^{-1}) which was exchangeable with D_2O to give the OD group (2532 cm^{-1}), a C=C bond (1656 cm^{-1}) with a C=CH group (3067 cm^{-1}). The presence of one olefinic bond was confirmed using Baranger and Marechal's method[11,12] and by quantitative hydrogenation to give a saturated alcohol VIA. Scheme 1.2.3.

The isolation of hydroperoxides from autoxidation reactions has presented many problems. Early workers obtained hydroperoxides by distillation,[18] low temperature solvent crystallisation,[19] and adsorption chromatography.[18,20,21,22] These methods produced low yields of hydroperoxides, probably owing to decomposition during the isolation processes. Purer hydroperoxides were obtained by counter current distribution,[23,24,25,26,27] by fractionation of complexes with urea[28] and by liquid partition chromatography.[29,30,31]

Many hydroperoxides have now been isolated and identified from the autoxidation of olefins, these hydroperoxides are adequately listed[126]

1.3 Hydroperoxide formation in methyl cis-9-octadecenoate (methyl oleate)



VII

Early kinetic studies estimated that hydroperoxides were formed in almost quantitative amounts during the initial stages of autoxidation of methyl cis-9- octadecenoate.[32,33] (VII).

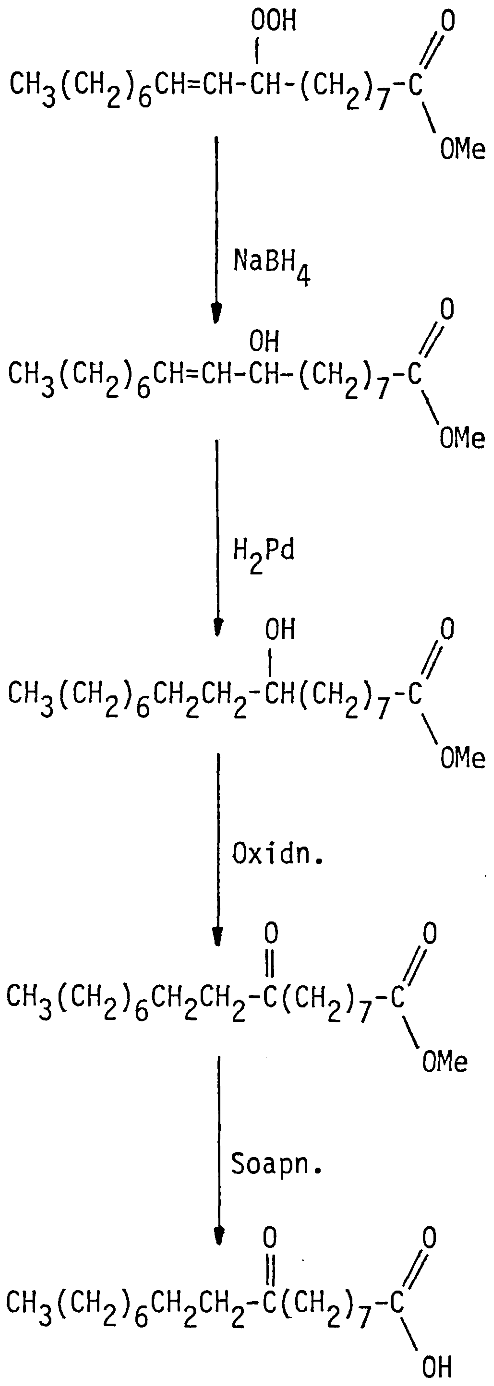
It was also shown that the olefinic bond remained intact and no dimers were formed.[25] The olefinic bond although still intact was shown to isomerise from cis to trans, the more stable isomer.[23,34,35] This isomerisation was identified by infrared spectroscopy using the increases in absorption at 965 cm^{-1} corresponding to trans olefinic unsaturation. A latter study by Hall and Roberts[57] confirmed this isomerisation by infrared and proton nuclear magnetic resonance spectroscopy. The lower stability of the cis isomer led Swern et al[36] to propose that the cis form of the hydroperoxide would probably not be isolated during autoxidation.

In addition to the cis-trans isomerisation, positional isomerisation was observed from the original 9 position.[37] Degradation analysis of the hydroperoxides by scheme 1.3.1 indicated the presence of methyl 9-hydroperoxy-trans-10-octadecenoate and methyl 10-hydroperoxy-trans-8-octadecenoate.

Oxime derivatives of the methyl ketostearates formed by the analysis shown in scheme 1.3.1 were prepared. Hydrolysis of the amides obtained by Beckmann transformation of the oxime gave octanedioic acid and undecanedioic acid indicating the presence of 8- and 11-hydroperoxides, scheme 1.3.2.

Some confusion has occurred in the literature over the quantitative composition of the hydroperoxides arising from methyl cis-9-octadecenoate (table 3). This variation probably results from the long routes for their characterisation, (eg. scheme 1.3.1) which result in low yields of the desired compounds.

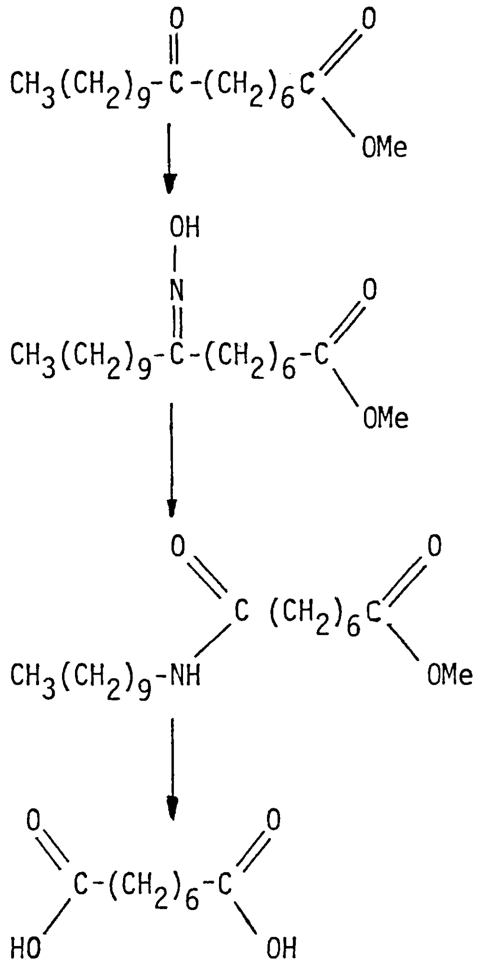
Analysis of Methyl oleate hydroperoxides



Fractional crystallisation to give other isomers

Scheme 1.3.1 using the 9-hydroperoxide as an example

Oxime formation and analysis of Methyl keto stearates formed in scheme 1.3.1



Scheme 1.3.2

TABLE 3

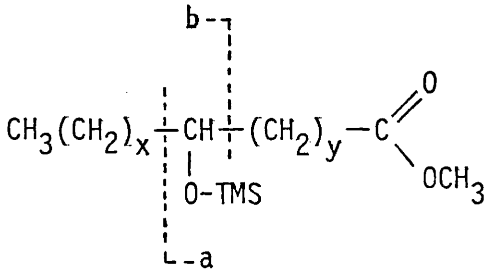
Analysis of the isomeric hydroperoxides of autoxidised methyl oleate

Autoxidation condition	Basis of characterisation	Isomeric distribution	Reference
35^{o}C - UV irradiation	Beckman rearrangement of oximes from keto derivatives.	10-OH > 11-OH > 8-OH > 9-OH	37
35^{o}C	Infrared studies	9-OH = 10-OH	38
Room temperature	Cleavage of acetyl derivatives	8-OH = 9-OH = 10-OH = 11 - OH	39
28^{o}C	Cleavage of hydroxyl derivatives	9-OH = 10-OH	40
Acidic MeOH	Cleavage of di Me acetal derivatives	8-OH > 11-OH > 9-OH > 10-OH	41
40-50^{o}C	$AgNO_3$-TLC	8-OH = 11-OH > 9-OH = 10-OH	42

Mercier[42] in her study of methyl oleate concentrated the hydroperoxides by solvent partition and purified them by either column chromatography or preparative t.l.c. The resultant hydroperoxides were separated into trans (~85%) and cis (~15%) fractions by $AgNO_3$-tlc. The configuration being established by polarography, infrared and ^1H nmr spectroscopy but the relative proportions were not determined by these methods. The trans hydroperoxides after $NaBH_4$ reduction and catalytic hydrogenation were shown by tlc to consist of equal amounts of 8-,9-,10-,11--hydroxy isomers. The cis isomers were shown to consist of equal amounts of 8- and 11-hydroxy isomers. However, the value of tlc to quantify these hydroxy isomers is doubted.

The presence of cis hydroperoxides from methyl oleate contradicts Swerns earlier view, although the cis isomer is apparently less abundant. Piretti[43,44,45] however found evidence for the cis-9- and cis-10- isomers. The oleate hydroperoxides were purified by silica column chromatography, the positional and geometric isomeric composition determined by infrared, $AgNO_3$-tlc, glc and gc-ms. The infrared determination of the total trans unsaturation (based on methyl trans-9-octadecenoate as standard) agreed with the glc analysis of the cis and trans allylic hydroxy derivatives separated by $AgNO_3$-tlc. Gc-ms analysis showed the presence of all four 8-,9-,10-,11-allylic hydroxy derivatives in both the cis and trans tlc fractions. The isomeric composition was estimated by gc-ms using the saturated hydroxy esters as their trimethylsiyl(TMS) derivatives (VIII). The relative intensity of only one ion arising from the α fragmentation of the saturated TMS derivatives, from electron impact mass spectrometry, was assumed to be independent of the position of TMS in the fatty chain.

Frankel[46] checked the gc-ms method of analysis with authentic samples of 8-,9-,10-, and 11-hydroxy octadecanoates. The erroneous results obtained using Piretti's method arose from the assumption that the ion current due to a fragment ion measured at the apex of the chromatographic peak was quantitative. It was subsequently shown that for reliable quantitative results by gc-ms the following two conditions must be met. (i) Summation of all mass spectra within the appropriate gc-peak. (ii) The ion currents of both fragment ions (a) and (b) should be used in the calculation.



$CH_3(CH_2)_x-\underset{\text{O-TMS}}{CH}-(CH_2)_y-C(=O)OCH_3$

TMS derivative of saturated methyl hydroxy octadecanoate

VIII

Fragments a	Fragments b
y = 6 m/z 245	x = 9 m/z 243
y = 7 m/z 259	x = 8 m/z 229
y = 8 m/z 273	x = 7 m/z 215
y = 9 m/z 287	x = 6 m/z 201

Frankel's quantitative analysis was carried out at different temperatures and showed that the 8- and 11-isomers were slightly (8%) but consistently higher than the 9- and 10-hydroxy isomers.

Garwood and fellow workers[47] analysed the stereochemistry of allylic hydroperoxides using ^{13}C nmr. The proportions of cis and trans isomers were determined, after tlc and treatment with $NaBH_4$, using characteristic resonances in the corresponding alcohols arising

Table 4

Variation in isomer distribution with temperature of autoxidation

Temp (°C)	Geometric isomers (%)	Positional isomers (%)				Ref.
		8-OOH Δ9	9-OOH Δ10	10-OOH Δ8	11-OOH Δ9	
20	66.9 trans	7.0	11.0	20.9	28.2	45
	33.1 cis	12.7	1.5	3.6	15.3	
40	71.2 trans	6.9	17.4	16.5	30.3	
	28.2 cis	10.0	5.0	4.7	12.8	
80	76.5 trans	21.5	21.3	22.0	11.8	
	23.5 cis	7.4	4.4	3.5	8.2	
25		26.6	24.3	22.3	26.8	46
40		27.2	23.6	22.0	27.1	
60		26.9	22.5	23.3	27.3	
80		26.5	23.6	23.6	26.3	
25	70.0 trans	12.3	23.1	21.7	12.9	47
	30.0 cis	14.1	1.1	1.1	13.7	
40	76.0 trans	16.0	22.0	21.7	16.0	
	24.0 cis	10.6	1.6	1.7	10.1	
75	82.9 trans	19.0	22.5	22.0	19.5	
	17.1 cis	6.1	2.7	2.9	5.4	
No temps. quoted		26.7	22.3	22.8	28.2	48
		27.2	23.5	22.6	26.5	
		25.5	22.8	23.8	27.7	

from allylic carbon atoms of the cis-trans isomers viz. cis (67.5 ppm) and trans (73.1 ppm). The crude autoxidation mixture and concentrated hydroperoxides were analysed by ^{13}C nmr with the hydroperoxide allylic carbons chemical shifts being assigned as cis (81.1 ppm) and trans (86.9 ppm). It was assumed that the stereochemistry of the hydroperoxides was retained on reduction to the hydroxy compounds. Garwood[47] also carried out gc-ms analysis of the saturated hydroxy stearate compounds obtained by hydrogenation of the hydroperoxides. They employed computer summation of the ion current arising from both the α fissions of the TMS derivatives.

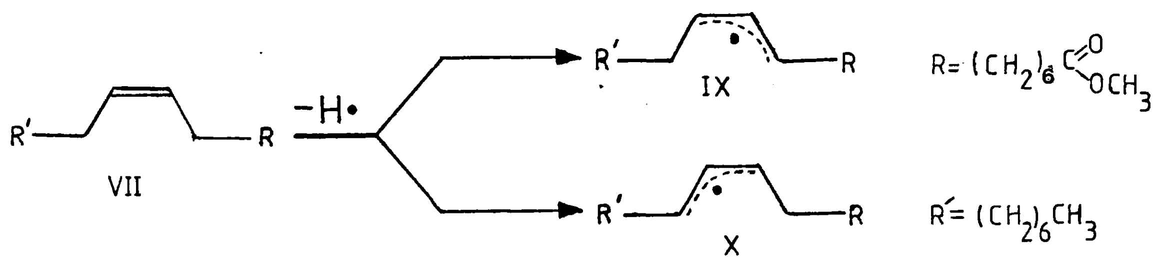
The work of Frankel[46] and Garwood[47] has now been confirmed by Chan and Levett[48] using HPLC. They separated and determined the relative amounts of the saturated 8-,9-,10-, and 11-, hydroxy esters and their results showed that the 8- and 11-isomers were 6.6 to 9.8% higher than the 9- and 10-isomers. Although they carried out 3 analyses no reaction temperatures were reported.

The analysis results of the hydroperoxides formed from the autoxidation of methyl oleate are summarised in table 4.

Park[49] has shown that the positions of hydroperoxide formation in trioleaylglycerol occurs at the 8-,9-,10- and 11-positions and corresponded to those in methyl oleate.

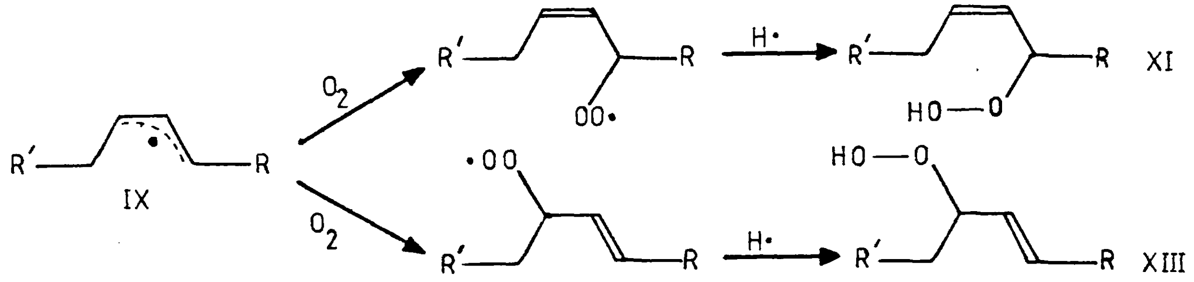
1.4 Mechanism of methyl cis-9-octadecenoate autoxidation

The classical mechanism, first suggested by Farmer[8] involves hydrogen abstraction at carbon numbers 8 or 11. Interaction between the unpaired electron on carbon 8 or 11 and the electrons of the adjacent double bond[77] provides two allylic radicals IX and X. (Scheme 1.4.1).

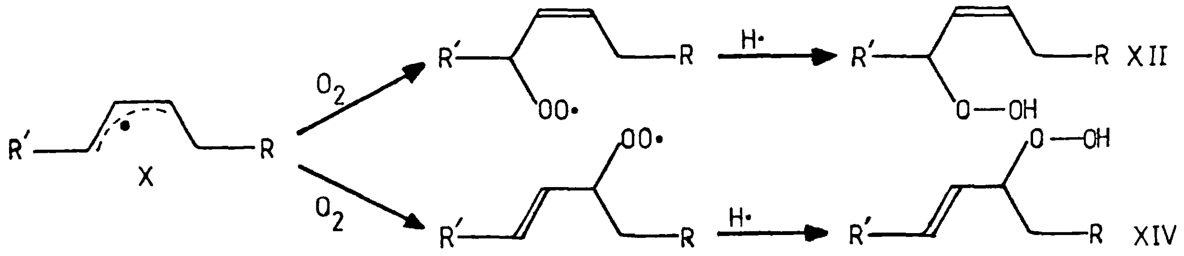


Scheme 1.4.1

Allylic radical IX would be susceptible to oxygen attack at positions 8 and 10 (Scheme 1.4.2) and allylic radical X at positions 9 and 11 (Scheme 1.4.3).



Scheme 1.4.2



Scheme 1.4.3

Mercier[42] explained her results via these allylic radicals. The formation of the new olefinic bond,she stated,would be preferentially trans. The cis isomers are proposed to be formed by direct attack at the initial point of hydrogen abstraction i.e. at the 8 or 11 position. This approach can account for the formation of the following hydroperoxides:

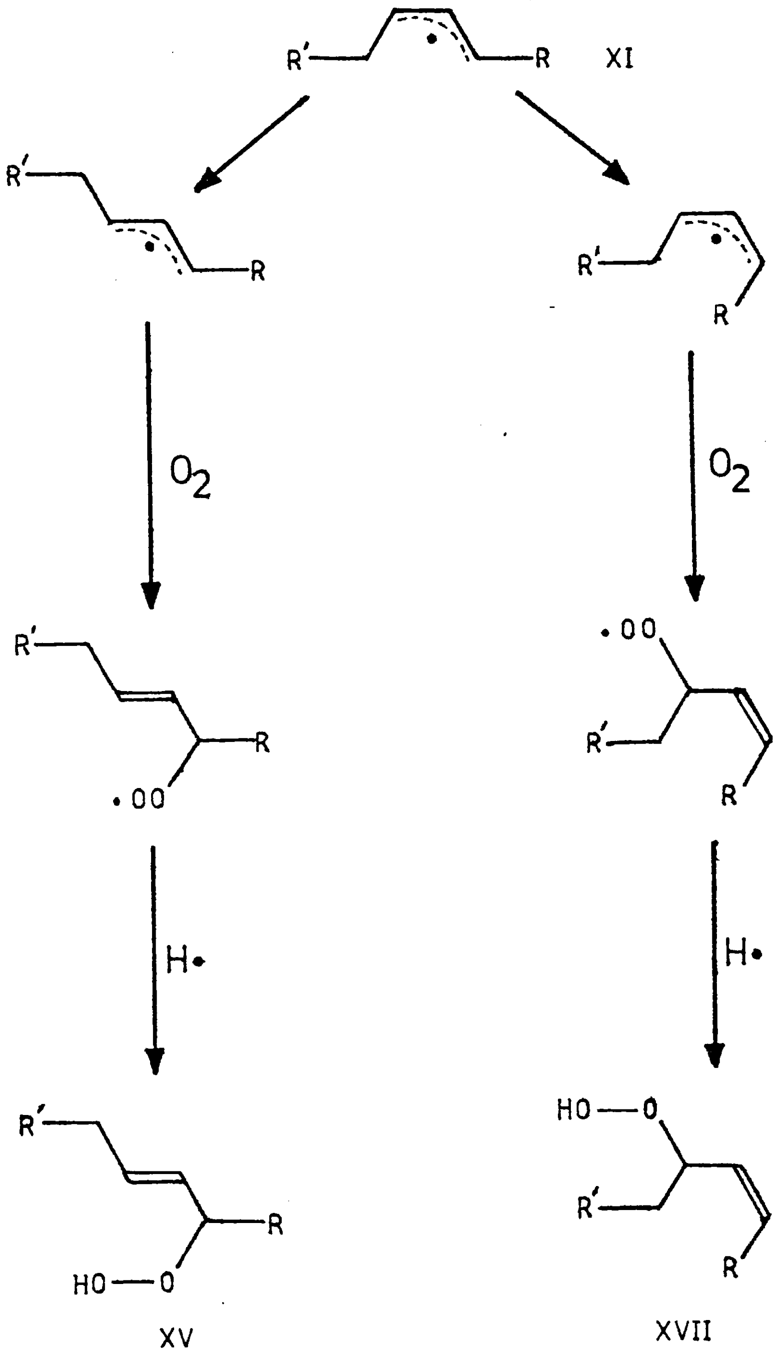
Methyl 8-hydroperoxy-cis-9-octadecenoate	XI
Methyl 11-hydroperoxy-cis-9-octadecenoate	XII
Methyl 10-hydroperoxy-trans-8-octadecenoate	XIII
Methyl 9-hydroperoxy-trans-10-octadecenoate	XIV

but not for the following hydroperoxides observed by Piretti,[43,44,45] Frankel,[46] Garwood[47] and Chan.[48]

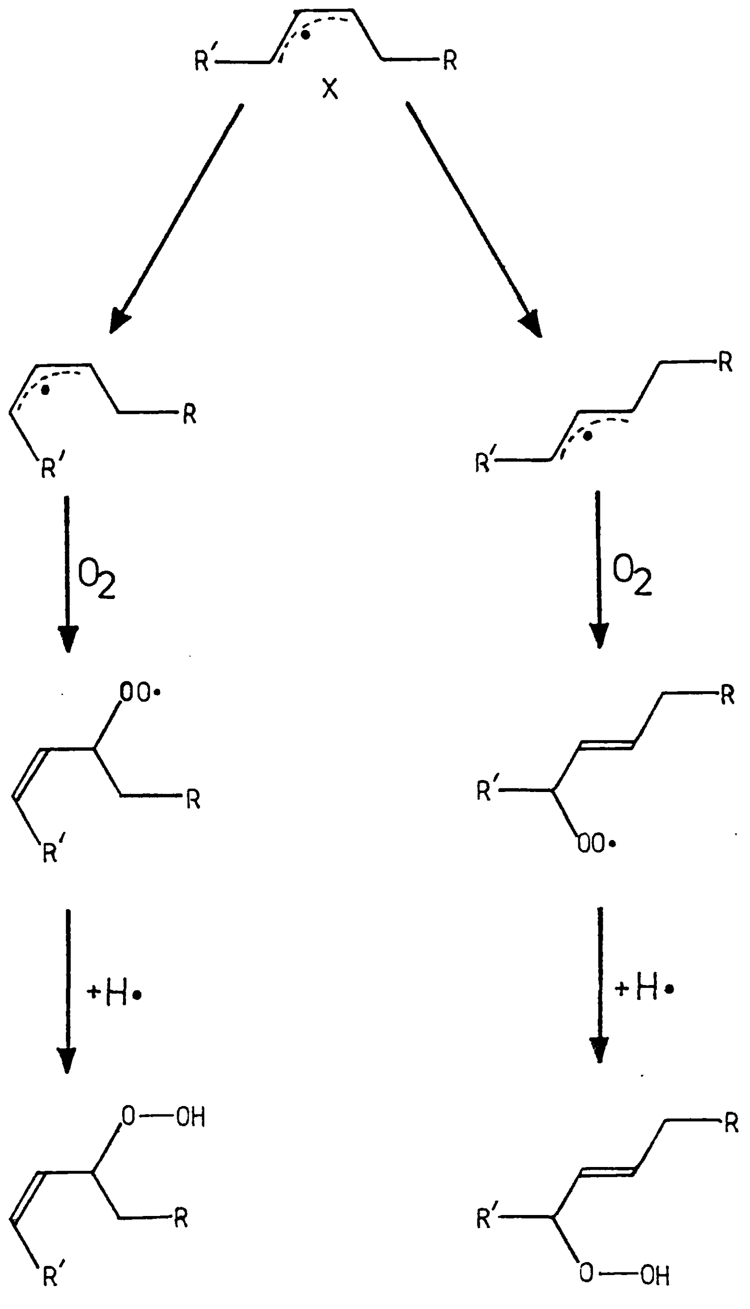
Methyl 8-hydroperoxy trans-9-octadecenoate	XV
Methyl 9-hydroperoxy cis-10-octadecenoate	XVI
Methyl 10-hydroperoxy cis-8-octadecenoate	XVII
Methyl 11-hydroperoxy trans-9-octadecenoate	XVIII

Frankel[59] proposed a route based on Farmer's mechanism[8] but involving configurational isomerisation of the allylic radicals (Schemes 1.4.4 and 1.4.5).

The preference for the trans isomers was explained in terms of steric effects reducing the stability of the cis allylic radicals.[71]



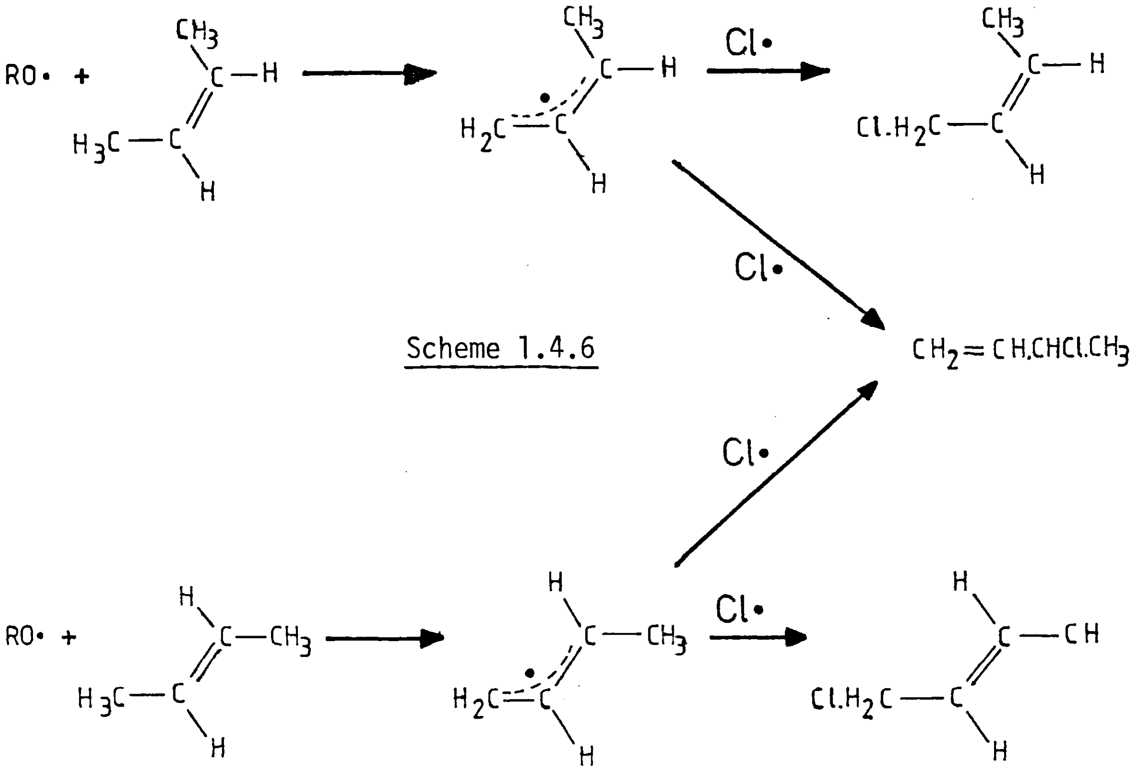
Scheme 1.4.4



XVI XVIII

Scheme 1.4.5

However other workers have shown that the configurational integrity of the allylic radicals is often retained[72] e.g. in the free radical chlorination of the 2-butenes. Scheme 1.4.6 and table 5.



Scheme 1.4.6

Table 5

Chlorination of 2-butenes by tert butyl hypochlorite

Reactant	Products (%)		
	3-chloro-1-butene	1-chloro cis-2-butene	1-chloro trans-2-butene
trans-2-butene	27	0	73
cis-2-butene	37	63	0

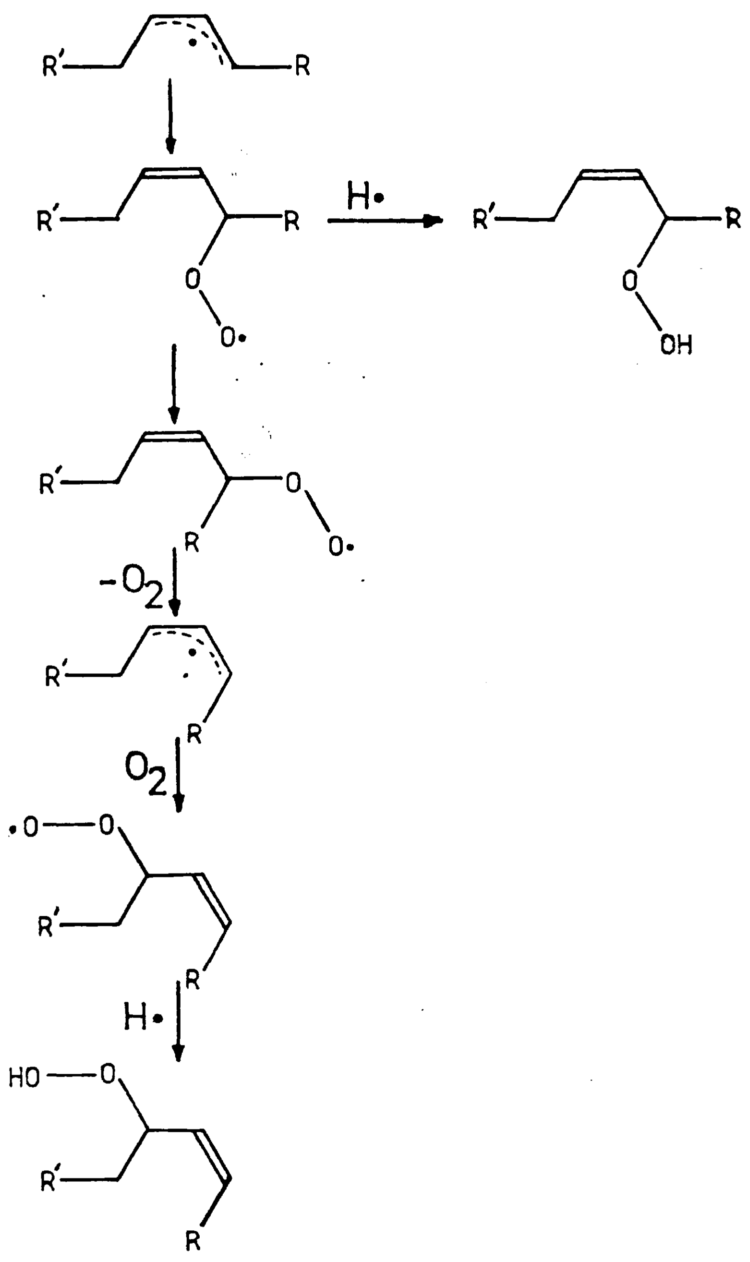
Menguy[78] reported a mixture of 34% cis and 66% trans unsaturated hydroperoxides in the autoxidation of cis-2-butene, whereas the trans-2-butene produced 90% trans unsaturated hydroperoxide. He attributed this to the steric hindrance of the peroxide group, which favours the passage of the cis peroxide radical to the correspondingly less sterically hindered trans form.

Piretti[123] by the use of molecular models demonstrated that if the allyl peroxide group is localised within a long linear chain the two cis- and trans- isomers show practically the same steric hindrance. Therefore Menguy's hypotheis is not applicable to methyl oleate.

The rate of isomerisation of an allyl radical is very low $k = 10^2 sec^{-1}$ [124] in relation to the rate with which the same radical reacts with oxygen during autoxidation $k = 4 \times 10^7$ $l\ mole^{-1} sec^{-1}$ [125] therefore the two schemes 1.4.4 and 1.4.5 proposed by Frankel[59] appear unlikely.

It is therefore suggested the isomerisation process occurs via the following pathway: (see scheme 1.4.7).

The concept of molecular oxygen as a leaving group had been proposed by Chan.[75] He prepared methyl linoleate hydroperoxides with $^{18}O_2$ incorporated in the hydroperoxide group, the level of enrichment was typically 55%, see Table 6.



Scheme 1.4.7

Table 6

^{18}O Hydroperoxides from methyl linoleate

Hydroperoxide		Enrichment
E,Z	$Me(CH_2)_4CH=CH\text{-}CH=CH\ CH(OOH)(CH_2)_7CO_2Me$	81.8%
E,E	$Me(CH_2)_4\ CH=CH\text{-}CH=CH\ CH(OOH)(CH_2)_7CO_2Me$	54.2%
Z,E	$Me(CH_2)_4\ CH(OOH)\ CH=CHCH=CH(CH_2)_7CO_2Me$	56.4%
Z,Z	$Me(CH_2)_4\ CH(OOH)\ CH=CH\text{-}CH=CH\ (CH_2)_7CO\ Me$	53.9%

These isomers were isolated and allowed to isomerise[76] under an atmosphere of $^{16}O_2$ (see section 1.9). The analysis of the oxygen above the hydroperoxide was found to have the following composition (table 7).

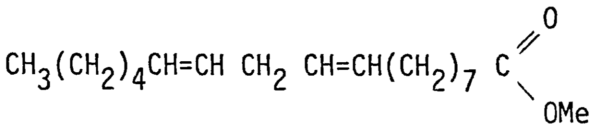
Table 7

Composition of oxygen above methyl linoleate hydroperoxides

	$^{18}O_2$	$^{18}O^{16}O$	$^{16}O_2$	(mole fraction)
Experiment	.330	.004	1.00	
Control	.008	.004	1.00	

The high amount of $^{18}O_2$ in the experimental atmosphere strongly indicates the oxygen present in the hydroperoxide is being exchanged and the lack of any significant amount of $^{18}O^{16}O$ provides evidence for O_2 as a leaving group.

1.5 Hydroperoxide formation in methyl cis-9- cis-12-octadecadienoate (methyl linoleate)



XXI

$$CH_3(CH_2)_4CH{=}CH\ CH_2\ CH{=}CH(CH_2)_7\ C({=}O)OMe$$

The study of methyl linoleate autoxidation was investigated by Treibs[50] who, observing the reaction refractometrically, did not observe the production of any conjugation. However, Farmer[51] deduced conjugation of the double bonds during autoxidation, from the strong absorptions, c.a. 240 nm, which had been attributed to a straight chain conjugated diene by Mitchell[52] i.e. at 234 nm in alkali isomerised linoleic acid. Farmer's observations were supported by Gunstone and Hilditch[53] who determined the presence of conjugation in the course of autoxidation from the absorption bonds at 234 nm and 268 nm. Gunstone observed that diene conjugation followed the formation of peroxides; the amount of conjugation however reaching a maximum before the maximum peroxide value was attained, and thereafter declining steadily. These results are in general agreement with Farmer's proposal viz., that the initial reaction is the loss of a doubly allylic hydrogen atom to give a radical which undergoes rearrangement giving a hydroperoxide and a conjugated diene system.

Bergstorm[20,55] also followed the autoxidation of methyl linoleate by UV spectroscopy and observed an increase in the absorption at 232 nm that parallelled the oxygen uptake. The oxidised ester was separated on alumina yielding two types of peroxides (i) with a strong absorption in the ultraviolet ($\log \varepsilon_{233} = 5$) and (ii) a mixture of peroxides with little absorption above 220 nm. The peroxides in fraction (i) yielded a mixture of monohydroxystearic acids on hydrogenation. Whereas fraction (ii) gave a mixture of hydroxystearic acids which could be split by lead tetraacetate. The two pure monohydroxystearic acids were isolated from fraction (i) and their melting points corresponded to 13-hydroxystearic acid and 9-hydroxystearic acid. Bergstorm therefore concluded that the primary products from methyl linoleate autoxidation are: methyl-9-hydroperoxy-10-, 12-octadecadienoate and methyl-13-hydroperoxy-9-, 11-octadecadienoate. These accounted for 90% of the autoxidation products, and this was confirmed by counter current distribution[23,31,56] and reversed phase partition chromatography[23,31,56] methods of isolation of the peroxides.

The stereochemistry of the olefinic bonds were investigated by Privett[56] using infrared spectroscopy. Two major types were identified, cis, trans conjugated (948 cm^{-1}) and trans,trans conjugated (988 cm^{-1}). Autoxidation at elevated temperatures results in increased proportion of the trans,trans conjugated diene hydroperoxides.[23,55] Hall and Roberts[57] using both ^1H nmr and infrared spectroscopy also observed cis,trans conjugated and trans,trans conjugated diene formation in the autoxidation of methyl linoleate. No isolated trans double bonds were observed based upon the absence of a band at 970 cm^{-1}. Hydroperoxides formation was observed by ^1H nmr with absorptions at 9.0 and 8.8 ppm, and infrared at 3430 and 3460 cm^{-1}. The absorption at 4.2 ppm was assigned to the tertiary proton on the carbon carrying the hydroperoxide group, this having a similar chemical shift to that observed during the autoxidation of methyl oleate (Section 1.3). It should be noted this study was carried out on the unseparated hydroperoxides.

Other workers reported the amount of cis,trans and trans,trans conjugated diene hydroperoxides ranged from 70 - 90%.[21,23,56] To explain these lower than expected values it was suggested that unconjugated[21,55,56] and cis,cis conjugated diene hydroperoxides were formed.[31] These suggestions were discounted by Frankel,[59] using the evidence from Hall's work,[57] and more recently by Chan and Levett.[58]

Although the presence of the isomeric hydroperoxides XXII, XXIII, XXIV and XXV was strongly indicated, no direct separation had been

XXII Methyl-9-hydroperoxy trans-10- cis-12-octadecadienoate

XXIII Methyl-13-hydroperoxy cis-9- trans-11-octadecadienoate

XXIV Methyl-9-hydroperoxy trans-10- trans-12-octadecadienoate

XXV Methyl-13-hydroperoxy trans-9- trans-11-octadecadienoate.

carried out. Measurement of the ratio of the 9 and 13 hydroperoxides involved the conversion of the mixtures of hydroperoxides onto their corresponding hydroxystearates or ketostearates followed by mass spectrometry. Alternatively the mixtures were separated by different chromatographic methods then analysed[60,61,62,63,64] with or without further derivatisation.

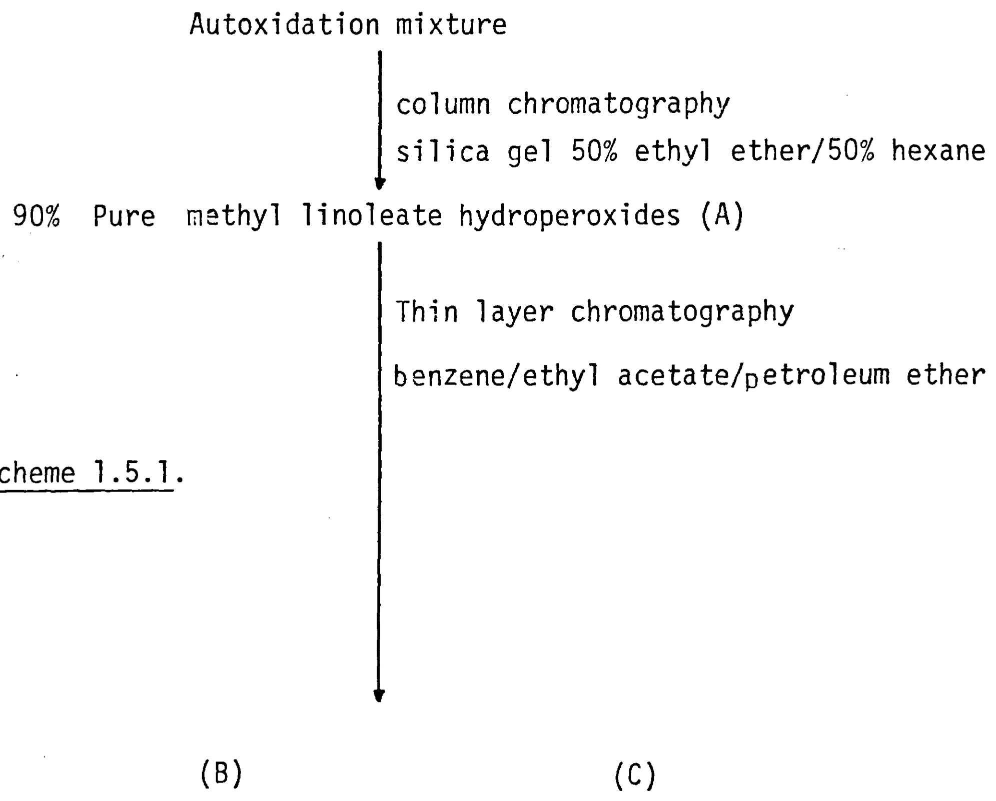
Chan and Prescott[65] separated the 9 from the 13 hydroperoxide by high performance liquid chromatography. This technique did not separate the four isomers (XXII - XXV) expected but merely the positional isomers.

Chan and Levett[66] improved the HPLC conditions and managed to resolve the four linoleate hydroperoxide isomers (XXII - XXV). The structures were then established by (a) mass spectroscopy of the corresponding hydroxystearates giving the position of the OOH group. (b) IR spectroscopy giving the geometry of the olefinic bonds. (c) ^{1}H nmr spectroscopy which confirmed the observations from (a) and (b).

They also established that the trans double bond in the XXII and XXIII isomers was adjacent to the hydroperoxide.

Terao and Matsushita[68] carried out a study at the same time as Chan and Levett. They analysed the hydroperoxides after reduction by gc-ms either directly as the hydroxy stearates or as the TMS derivatives. From the latter method they were able to conclude that the 9 and 13 positional isomers were formed in equal amounts. They subsequently isolated the pure hydroperoxides[69] and carried out their analysis by the method shown in schemes 1.5.1, 1.5.2 and 1.5.3.

Analysis of mixtures of methyl linoleate and methyl linoleate hydroperoxides (MLHPO)



Scheme 1.5.1.

Scheme 1.5.1 (contd)

Separation of positional isomers

$$\begin{tikzcd}[column sep=large] \text{(B)} \arrow[d, "\begin{array}{c} NaBH_4 \\ H_2/Pd \end{array}"] & \text{(C)} \arrow[d] \\ \underline{\text{Methyl-13-hydroxystearate}} & \underline{\text{Methyl-9-hydroxystearate}} \end{tikzcd}$$

Pure methyl linoleate hydroperoxides

$$\begin{tikzcd} & \text{(A)} \arrow[d, "AgNO_3\ \text{T.L.C.}"] & \\ \text{(D)} & & \text{(E)} \end{tikzcd}$$

Scheme 1.5.2.

Separation of cis,trans and trans,trans isomers

Infrared analysis of (D) gave a sharp absorption at 990 cm^{-1} corresponding to a trans,trans conjugated diene.

Infrared analysis of (E) gave two absorptions, one corresponding to trans,trans conjugated diene at 990 cm^{-1} and the other due to a cis,trans conjugated diene at 950 cm^{-1}.

Pure methyl linoleate hydroperoxides

$$\begin{tikzcd} \text{(A)} \arrow[d, "\begin{array}{l} \text{i, } NaBH_4 \\ \text{ii, Trimethyl silyl chloride} \end{array}"] \\ \text{TMS derivatives of methyl hydroxyoctadecadienoate} \arrow[d, "\text{gc-ms}"] \\ \text{(F)} \quad \text{(G)} \quad \text{(H)} \end{tikzcd}$$

Scheme 1.5.3.

The mass spectra obtained from peaks F, G and H provided direct evidence for peak G resulting from a 9-isomer, peak H resulting from a 13-isomer. Peak F corresponded to a mixture of 9- and 13-positional isomers based on the ratio of the ion currents for m/z 225 and m/z 311 recorded at the apex of peak F.

The separation to give B and C were then each subjected to gc-ms analysis. B gave peaks corresponding to F and G, whilst C gave peaks corresponding to F and H. The isomers D and E were also analysed by gc-ms. The trans,trans isomer D gave peaks G and H whilst the cis,trans isomer gave peak F only. The assignment of the T.M.S. derivatives F, G and H separated by scheme 1.5.3. are given in table 8.

Table 8

Conclusion of Terao's analysis of methyl linoleate hydroperoxides

G.C. Peak	Hydroxy compound (as T.M.S. derivatives)
F	Methyl-9-hydroxy-trans-10- cis-12-octadecadienoate Methyl-13-hydroxy cis-9- trans-11-octadecadienoate
G	Methyl-9-hydroxy trans-10- trans-12-octadecadienoate
H	Methyl-13-hydroxy trans-9- trans-11-octadecadienoate

Terao also quantified the amounts of the cis,trans and trans,trans isomers formed at different temperatures and degrees of autoxidation. These are summarised in table 9.

Table 9

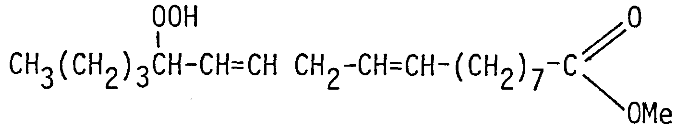
Ratio of conjugated diene hydroperoxide isomers

Temp °C	MLHPO (% w/w based on total autoxidation mixture)	ratio of conjugated diene hydroperoxide isomers	
		cis,trans	trans,trans
37	11	60	40
	24	49	51
60	12	43	57
	23	35	65
90	16	32	68

Chan and Levett[67] improved their HPLC method of separating hydroperoxides and achieved complete separation of the 4 isomers described in the previous study.[66] The structure of the isomers was established by infrared, ^{1}H nmr, and UV spectroscopy and gc-ms of hydroxystearates derived from reduction of the hydroperoxides. Again the presence of the four hydroperoxide isomers was concluded.

More recently Porter[70] studied the autoxidation at various temperatures and ester concentrations. The resulting hydroperoxides were reduced to alcohols by triphenylphosphine and analysed by HPLC. The same four isomers were identified as before.[67] Porter showed that the 9- and 13-positional isomers were formed in equal quantities and this was independent of temperature or concentration. However the proportions of cis-trans isomers depended on both temperature and concentration. The trans,trans conjugated diene increased with temperature and at lower ester concentrations. No dependence on oxygen partial pressure was observed.

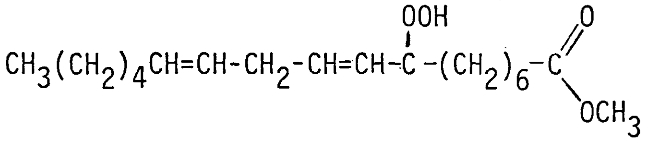
Grosch[78] isolated two unconjugated hydroperoxides by HPLC. The hydroxy products formed by their reduction were separated into major and minor fractions using silica gel/$AgNO_3$. The major fraction contained the 9- and 13-isomers, whilst the minor fraction (~1%) was found to contain methyl 14-hydroxyoctadecadienoate and methyl 8-hydroxyoctadecadienoate providing strong evidence for the formation of hydroperoxides XXVI and XXVII



$$CH_3(CH_2)_3\overset{OOH}{\overset{|}{C}}H\text{-}CH{=}CH\ CH_2\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}C\begin{matrix}{\nearrow\!\!\!\!\nearrow} O \\ \searrow OMe\end{matrix}$$

XXVI

Methyl 14-hydroperoxy-9- ,-13-octadecadienoate



$$CH_3(CH_2)_4CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}\overset{OOH}{\overset{|}{C}}\text{-}(CH_2)_6\text{-}C\begin{matrix}{\nearrow\!\!\!\!\nearrow} O \\ \searrow OCH_3\end{matrix}$$

XXVII

Methyl 8-hydroperoxy-9 -,-13-octadecadienoate

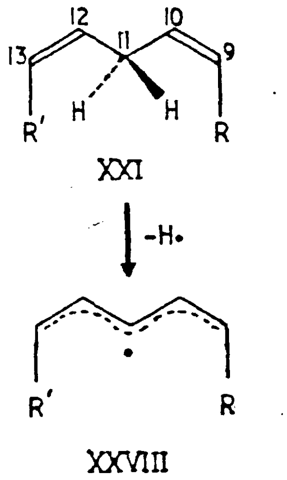
The stereochemistry of both double bonds was suggested to be cis, but based only on chromatographic properties.[97] No evidence for the formation of the 11-hydroperoxide has been found although its formation has been postulated.[98]

The best separation of methyl linoleate hydroperoxides was obtained by Kostras[103] but no quantitative results were quoted.

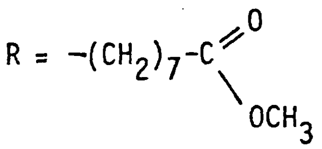
1.6 Mechanism of hydroperoxide formation in methyl cis-9- cis-13- octadecadienoate.

The accepted mechanism of methyl linoleate autoxidation[77] involves hydrogen abstraction at carbon-11- as the initial step.

Interaction of the unpaired electron with the two adjacent π -electron systems produces a bis-allylic radical with delocalisation over 5 carbon atoms, equation 1.6.1. The maximum overlap between the π orbitals of the double bonds and the orbital of the unpaired electron occurs if all 5 carbons lie on the same plane.



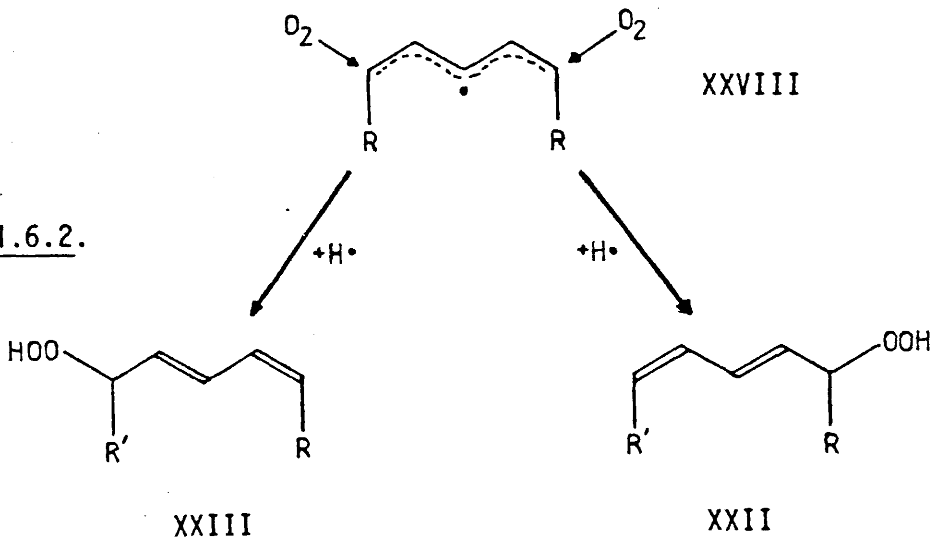
R' = $-(CH_2)_4CH_3$



$$R = -(CH_2)_7-C(=O)OCH_3$$

Equation 1.6.1.

The terminal carbons of the pentadienyl radical, (XXVIII), are equivalent sites for oxygen attachment and results in equal amounts of 9- and 13-hydroperoxides being produced.[70] Scheme 1.6.2.



Scheme 1.6.2.

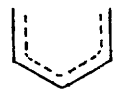
The formation of the cis, trans isomers XXII and XXIII discussed in section 1.5 can be explained simply from radical XXVIII, but the trans,trans isomers XXIV and XXV cannot be explained directly from radical XXVIII, some other isomerisation must occur.

Conformational isomerisation of the pentadienyl radical would provide a means for the formation of the trans,trans isomers.

Sustman[207] studied the conformation of the pentadienyl radicals formed by abstraction of hydrogen from 1,4-pentadiene by t-butoxy radicals. At -115°C a superposition of two spectra ('W' and 'Z' form of the radical) is observed by E.S.R. but at 70°C only the more stable 'W' form remains. The difference in stability

'W'-form

'Z'-form



'U'-form

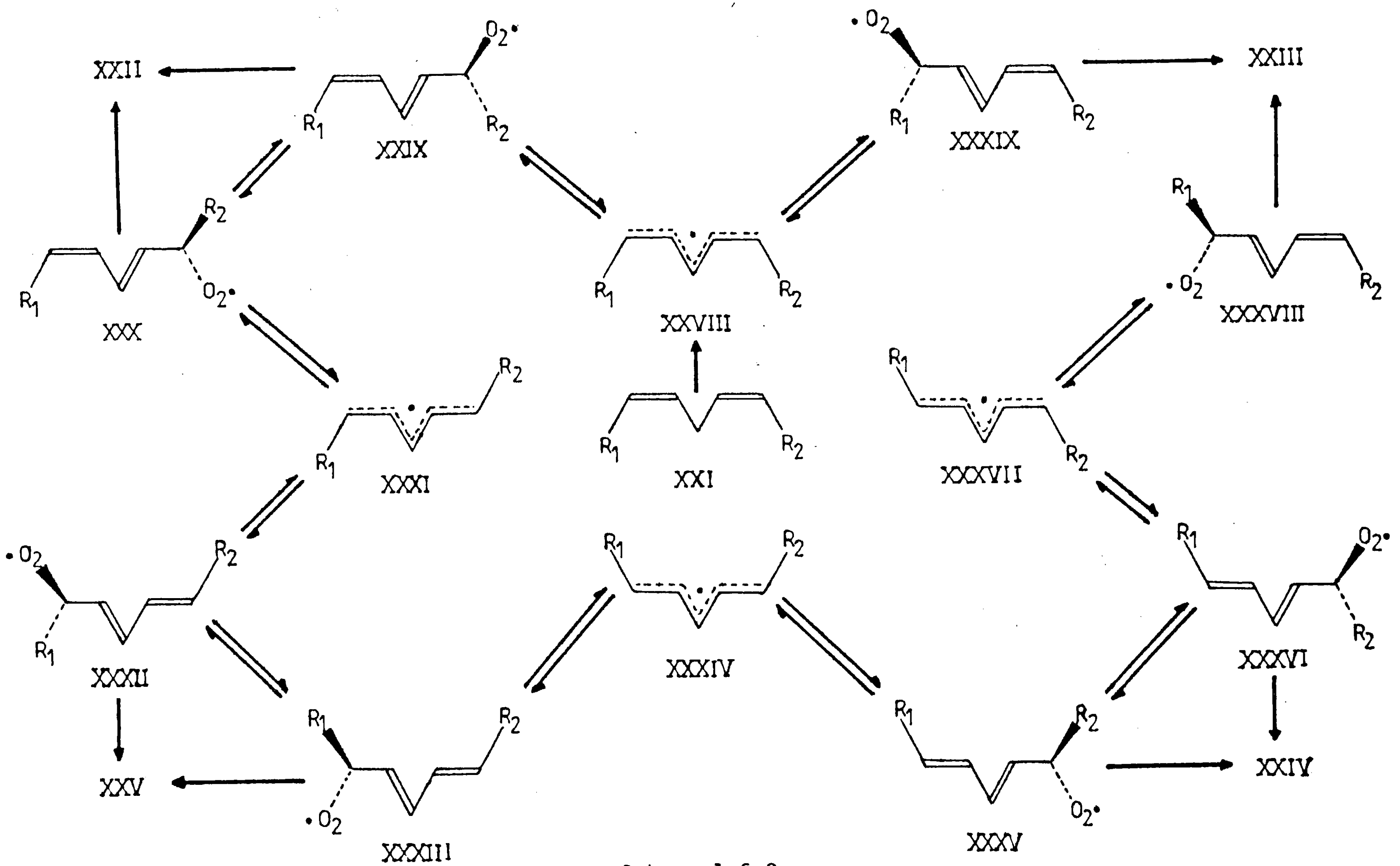
probably results from the strain involved in having three and four cis interactions in the 'Z' and 'U' forms respectively.

Griller[96] also studied the conformation of the pentadienyl radical. 1,4-Pentadiene and di-t-butyl peroxide were photolysed together to give the pentadienyl radical in the E,E conformation. This conformation was found in photolysis experiments carried out from 100°C to -60°C. However when the photolysis was carried out below -60°C a new conformation was observed, which became dominant below -120°C. This was assigned E,Z. Griller abstracted bromine from trans bromo penta 2,4 diene, the radicals formed by this method existed solely on the E,E conformation at temperatures ranging from 180 to -130°C. This proved that at lower temperatures the radicals from 1,4 pentadiene will not be in equilibrium; their relative concentrations would appear to depend on the initial conformation of the pentadiene molecule.

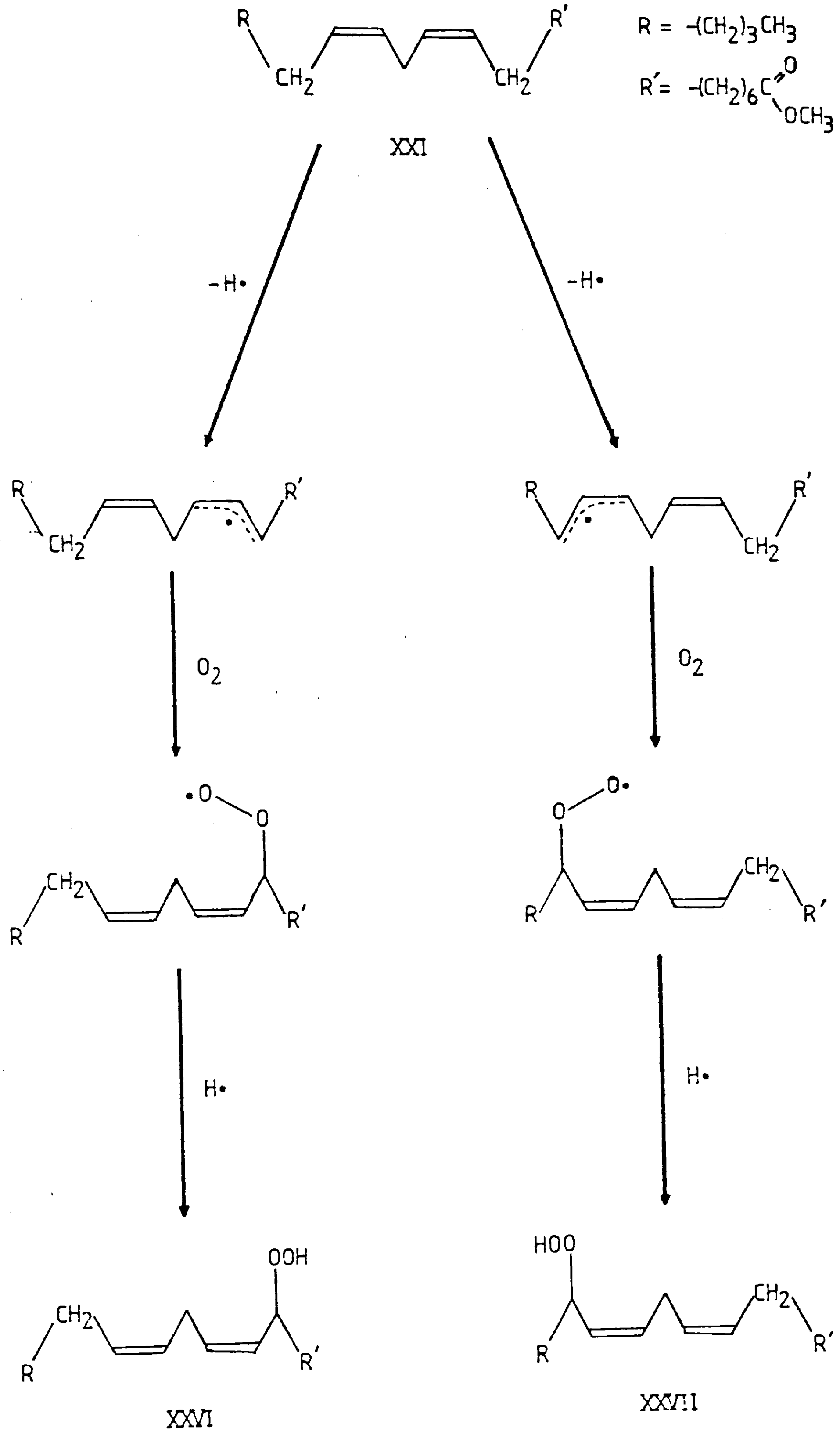
Thus the cis-trans isomerisation to give the trans,trans products in the autoxidation of methyl linoleate must occur after the initial peroxide formation.

Porter[70] explained the formation of all the conjugated diene hydroperoxides by scheme 1.6.3. This involves molecular oxygen as a leaving group (discussed in section 1.4) from a peroxide radical. The mechanism can explain the dependence of the cis,trans/trans,trans isomer ratio on temperature and concentration, viz. it increases in more concentrated solutions and in the presence of excellent hydrogen donors such as cyclohexadiene. This indicates the competition between H-atom abstraction by XXIX, XXX, XXXVIII and XXXIX (cis, trans products) and β fragmentation, leading to radicals XXXI and XXXVII followed by formation of peroxy radicals XXXII, XXXIII, XXXV and XXXVI (trans,trans products). The more easily hydrogens can be abstracted from the medium by radicals XXIX, XXX, XXXVIII and XXXIX the greater the preponderance of compounds XXII and XXIII (cis,trans products). The less easily hydrogens can be extracted from the medium, the more likely radicals XXXII, XXXIII, XXXV and XXXVI will be formed resulting in products XXV and XXIV (trans,trans products).

The formation of the unconjugated diene hydroperoxides XXVI and XXVII can be explained by a similar mechanism to that discussed for the autoxidation of methyl oleate (section 1.4), scheme 1.6.4.


XXII
XXIX
XXXIX
XXIII
XXX
XXVIII
XXXVIII
XXXI
XXI
XXXVII
XXXII
XXXIV
XXXVI
XXV
XXXIII
XXXV
XXIV
R1
R2
O2•
•O2

Scheme 1.6.3.


R
R'
CH2
CH2
XXI
R = -(CH2)3CH3
R' = -(CH2)6C(=O)OCH3
-H•
-H•
O2
O2
•O
O
O•
H•
H•
OOH
HOO
XXVI
XXVII

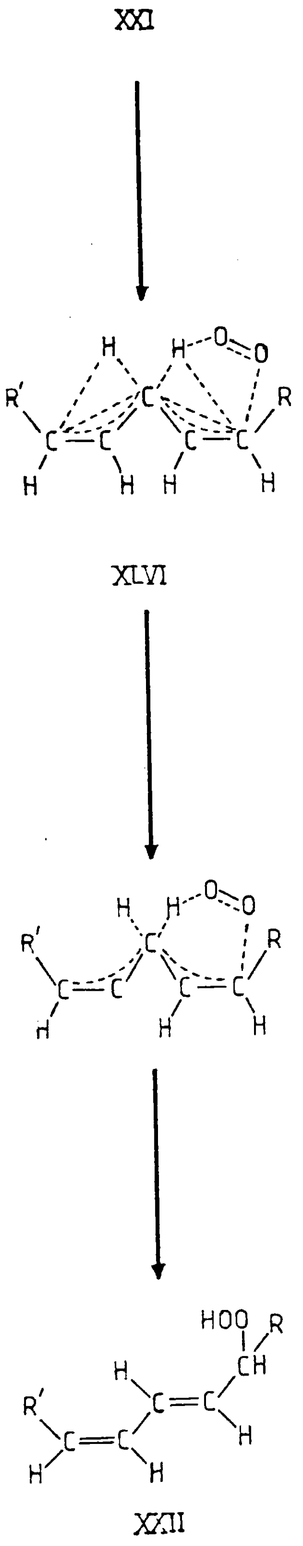
Scheme 1.6.4.

The stereochemistry of XXVI and XXVII have been represented as cis,cis and unconjugated as indicated in Grosch's paper.[97] From the discussion of methyl oleate autoxidation, the presence of the following hydroperoxides would also be expected:

XL methyl 8-hydroperoxy-9-trans -12-cis octadecadienoate
XLI methyl 10-hydroperoxy-8-cis -12-cis octadecadienoate
XLII methyl 10-hydroperoxy-8-trans -12-cis octadecadienoate
XLIII methyl 12-hydroperoxy-9-cis -13-trans octadecadienoate
XLIV methyl 12-hydroperoxy-9-cis -13-cis octadecadienoate
XLV methyl 14-hydroperoxy-9-cis -12-trans octadecadienoate.

In Grosch's analysis of the minor hydroperoxides, several compounds in the HPLC chromatogram were unidentified but they may correspond to the hydroperoxides (XL — XLV).

Other autoxidation mechanisms have been proposed in the past. Khan proposed an 'activated' π complex (XLVI) between oxygen and the electrons of the double bond.[71] This mechanism was proposed on the basis of only cis,trans conjugated isomer formation. Khan did not observe any trans,trans isomers which Privett[56] had observed six years earlier. Khan's mechanism, scheme 1.6.5., 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.[127]



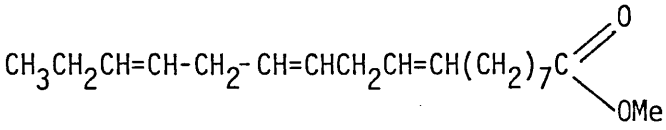
XXI

XLVI

XXII

Scheme 1.6.5.

1.7 Hydroperoxide formation in methyl cis-9- cis-12-cis-15-octadecantrienoate (methyl linolenate)



$$\mathrm{CH_3CH_2CH{=}CH{-}CH_2{-}CH{=}CHCH_2CH{=}CH(CH_2)_7C}\begin{matrix}{/\!\!/}\mathrm{O}\\ \diagdown\mathrm{OMe}\end{matrix}$$

methyl linolenate XLVII

Farmer[51,99] observed that on autoxidation of ethyl linolenate absorption of one mole of oxygen was synchronised with the formation of ½ mole of conjugated diene. This suggested hydroperoxide formation on a α methylenic carbon, followed by double bond rearrangement similar to that in methyl linoleate autoxidation.

Fugger[24] attempted the first isolation of hydroperoxides from autoxidised methyl linolenate using a small 29 tube countercurrent distribution apparatus. They were unable to isolate any monomeric hydroperoxides, and assumed extensive polymerization had occurred. However, significant amounts of diene conjugation was observed in some fractions.

Privett[80] showed the presence of monomeric hydroperoxides in a sample autoxidised at 0°C. They used counter current extraction which on reduction with tin(II) chloride gave an estimated 90% methyl monohydroxy octadecatrienoatewith cis,trans conjugated diene. It was therefore estimated that 90% of the hydroperoxides formed would be with a conjugated cis,trans diene.

Frankel[81] isolated hydroperoxides from an autoxidation experiment at 37°C by partition chromatography and counter current distribution.

The hydroperoxide preparations showed similar chemical and spectral characteristics to those obtained from methyl linoleate hydroperoxides.[25,26,31] Infrared analysis demonstrated that the conjugated system had a predominant cis,trans diene conjugation and a minor (~4%) trans,trans diene conjugation. Quantitative hydrogenation indicated the presence of three olefinic bonds. Frankel also carried a complex characterisation of the isomeric hydroperoxides based on two sequences of reactions:

(i) Reduction with potassium iodide or $NaBH_4$ to the conjugated hydroxylinolenates. The UV and IR spectra of these showed that the diene content corresponded to the theoretical value[23] and the stereochemistry of cis,trans and trans,trans double bonds. Acid dehydration gave a product containing octadecatetraenoic esters,one of which (~50%) was shown to be similar to β paniraric acid (trans-9- trans-11-trans-13-trans-15-octadecatetraenoic acid).

(ii) Catalytic hydrogenation to give a mixture of methyl hydroxystearates which,upon dehydration with boric acid at 200-210°C, gave a mixture of monoenoic esters with the site of unsaturation corresponding to the position of the hydroxy group. Their oxidative fission with permanganate-periodate yielded a mixture of dibasic acids which was examined by liquid chromatography and glc. By assuming an equal amount of monoene is formed on dehydration on each side of the hydroxyl groups, the estimated concentration of methyl hydroxystearates is shown in table 10.

Table 10

Hydroxystearate derivatives formed from the reduction of methyl linolenate hydroperoxides

Methylhydroxy stearates	%
9	30.2
12	10.7
13	9.8
16	48.1

These results have since been confirmed by two entirely different methods. A gc-ms analysis by Frankel[83], who after reduction of the hydroperoxides, managed to identify four isomeric hydroxy allylic trienes with a conjugated diene system. All eight cis,trans and trans,trans diene isomers of the allylic hydroxy compounds were separated and identified by glc as their TMS derivatives. The formation of the following hydroperoxides was indicated:-

XLVIII	Methyl-9-hydroperoxy-10-trans -12-cis -15-cis octadecatrienoate
XLIX	Methyl-9-hydroperoxy-10-trans -12-trans -15-cis octadecatrienoate
L	Methyl-12-hydroperoxy-9-cis -13-trans -15-cis octadecatrienoate
LI	Methyl-12-hydroperoxy-9-cis -13-trans -15-trans octadecatrienoate
LII	Methyl-13-hydroperoxy-9-cis -11-trans -15-cis octadecatrienoate
LIII	Methyl-13-hydroperoxy-9-trans -11-trans -15-cis octadecatrienoate
LIV	Methyl-16-hydroperoxy-9-cis -12-cis -14-trans octadecatrienoate
LV	Methyl-16-hydroperoxy-9-cis -12-trans -14-trans octadecatrienoate

Quantiative gc-ms analysis of the hydroxy octadecanoate derivatives from samples of methyl linolenate autoxidised to different peroxide values (134 to 1839) and at different temperatures (25 to 80°C), showed that the proportion of 9- and 16- hydroxy isomers was consistently higher (75 to 82%), than the 12 and 13-hydroxy isomers (18 to 25%).

Chan et al[84] achieved complete separation of all eight isomers of the methyl hydroxy triene derivatives by HPLC. Mass spectrometry of the hydroxyoctadecenoate derivatives confirmed Frankel's previous studies[81,83] that the 9- and 16- hydroxy isomers were favoured over the 12- and 13- hydroxy isomers in the ratio 3:1. Table 11 shows the complete quantitative analysis results.

Table 11

Isomeric distribution of methyl linolenate hydroperoxides

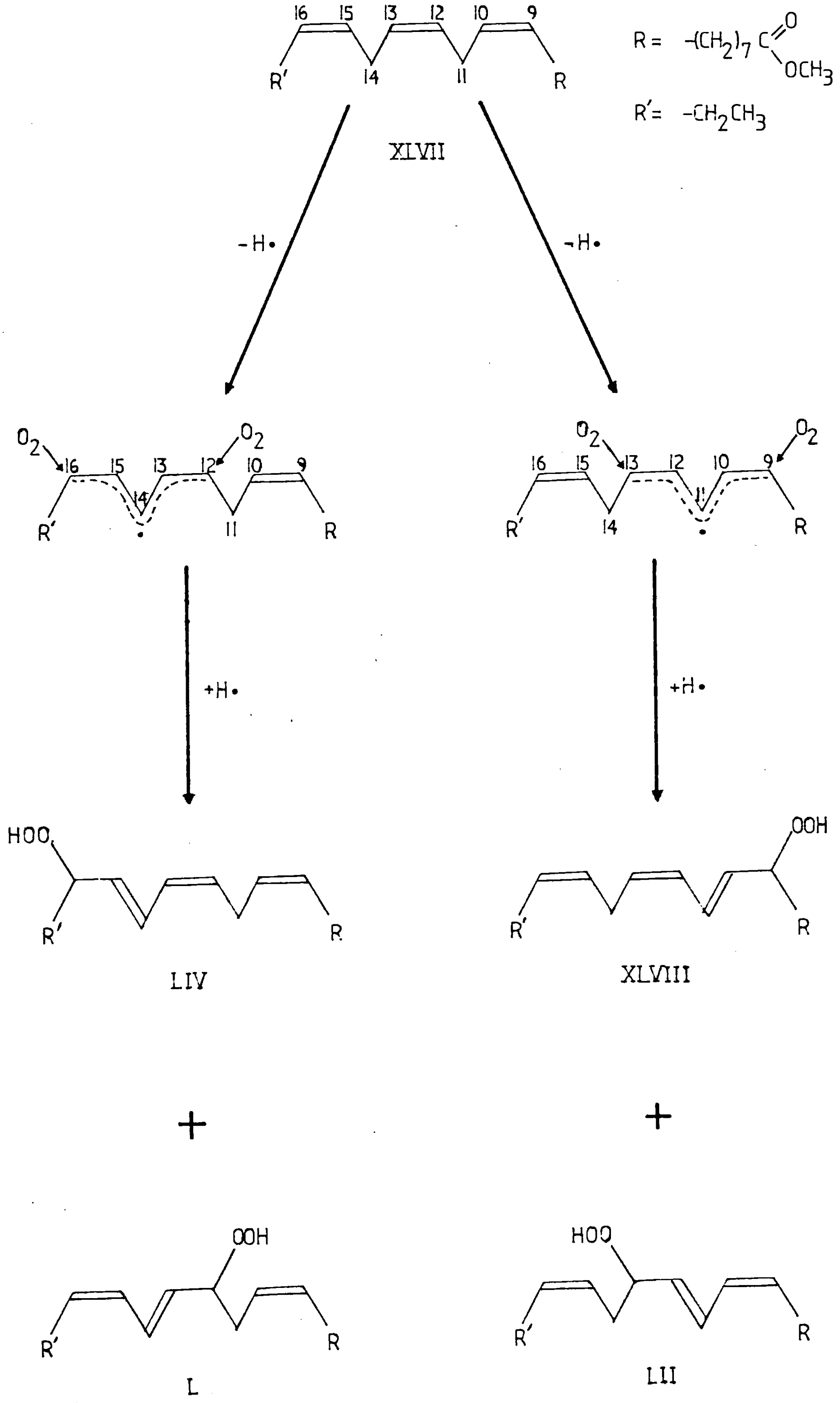
Isomer	Composition %
XLVIII	30.0 ± 1.0
XLIX	3.4 ± 0.5
L	8.2 ± 1.4
LI	1.9 ± 0.4
LII	10.2 ± 1.5
LIII	2.3 ± 0.4
LIV	38.1 ± 2.6
LV	5.8 ± 0.4

The ratio of cis,trans conjugated diene: trans,trans conjugated diene is 6.5 compared to 4.2 in methyl linoleate, indicating less cis-trans isomerisation occurring during the autoxidation of methyl linolenate.

1.8 Mechanism of linolenate autoxidation

The autoxidation of methyl linoleate (section 1.6) involves the abstraction of a hydrogen at carbon 11, the doubly allylic methylene and the formation of a pentadiene radical. Methyl linolenate has two such doubly allylic methylenes at positions 11 and 14. Hydrogen abstraction at carbon 11 would produce a pentadienyl radical over carbons 9, 10, 11, 12 and 13 LVI, whereas abstraction at carbon 14 would produce the radical over carbons 12, 13, 14, 15 and 16 LVII, scheme 1.8.1. The sites for oxygen attack viz. 9, 12, 13 and 16 would all appear to be equal, and an equal distribution of all 4 hydroperoxides should be expected. It is well established that the 9- and 16-isomers predominate over the 12- and 13-isomers, and Frankel[81] has suggested that this may be since the 12- and 13-hydroperoxides decomposed easier. Chan[84] compared the decomposition of 9- and 13-linolenate hydroperoxides (prepared by lipoxygenase oxidation) and found them to decompose at the same rate.

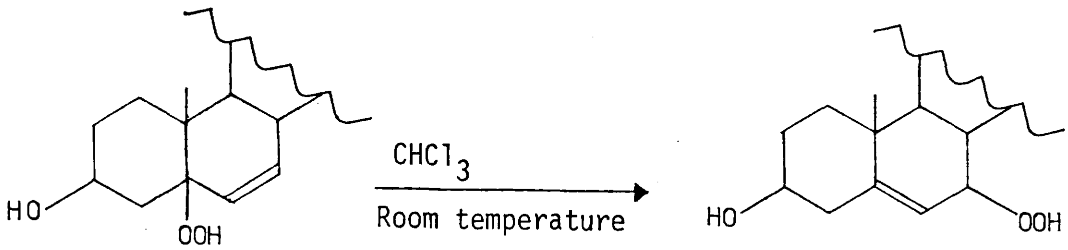
Steric effects might cause greater ease of attachment of oxygen on carbons 9 and 16 than on carbons 12 and 13.[58] A similar geometric isomerisation process probably occurs in methyl linolenate as in methyl linoleate (section 1.6) to give the trans,trans conjugated dienes.


16
15
13
12
10
9
R'
14
11
R
R = $-(CH_2)_7C(=O)OCH_3$
R' = $-CH_2CH_3$
XLVII
-H•
-H•
O_2
O_2
O_2
O_2
+H•
+H•
HOO
OOH
LIV
XLVIII
+
+
OOH
HOO
L
LII

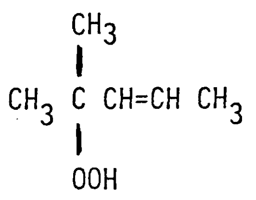
Scheme 1.8.1.

1.9 Isomerisation of hydroperoxides

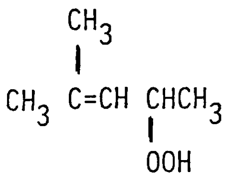
Schenck[100] observed the isomerisation of hydroperoxides in cholesterol; the 5 hydroperoxide on standing in $CHCl_3$ at room temperature was shown to rearrange to 7α hydroperoxy cholesterol.



Brill[101] studied the autoxidation of trans-4-methyl-2-pentene and isolated hydroperoxides LVIII and LIX.


$$CH_3\,\overset{CH_3}{\underset{OOH}{C}}\,CH{=}CH\,CH_3$$

LVIII


$$CH_3\,\overset{CH_3}{C}{=}CH\,\underset{OOH}{CH}CH_3$$

LIX

He demonstrated that either pure LVIII or pure LIX gave 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 LVIII or LIX depends inversely on the total hydroperoxide concentration and the following mechanism was proposed; scheme 1.9.1.

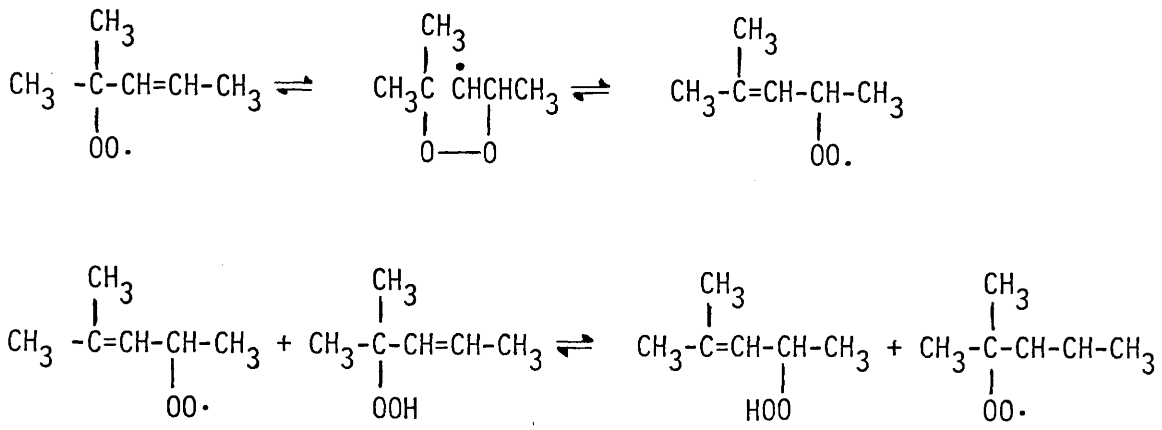
Initiation

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

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

$$ROOH = \text{LVIII or LIX}$$

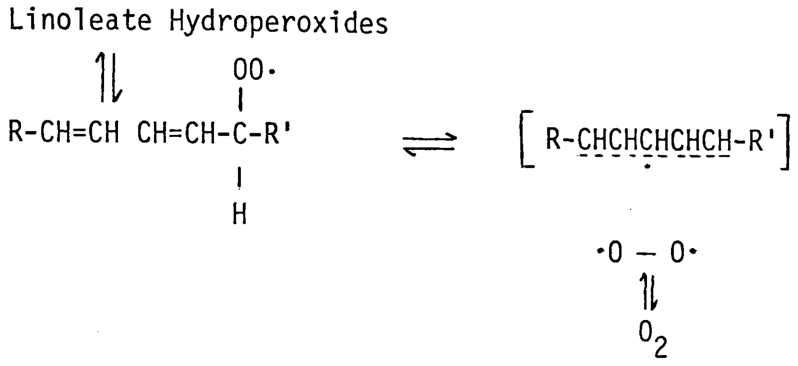
Propagation



Scheme 1.9.1.

Chan[102] 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 observed by gc-ms of the corresponding hydroxystearates and of cis-trans isomerisation by infrared spectroscopy. Chan[76] also studied the interconversion process of individual isomers into products using HPLC.

Chan[75] proposed a mechanism to account for the interconversion (Scheme 1.9.2.). The free radical process was supported by a decrease of reactivity in polar solvent and enhancement by oxygen, metal ions and free radical initiators.

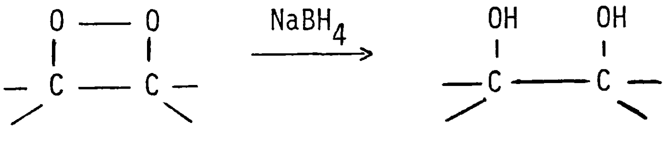


Scheme 1.9.2.

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

1.10 Cyclic peroxides

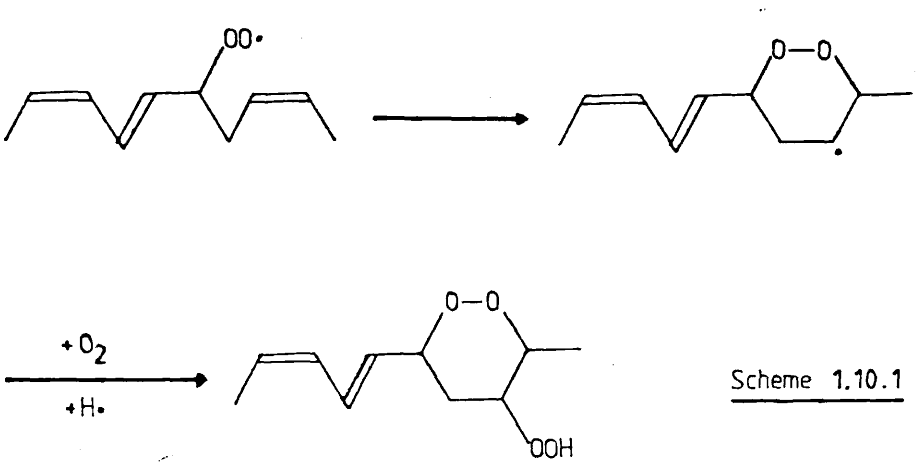
Cyclic peroxide formation has been suggested to explain the difference between total peroxide and hydroperoxide values.[20] Swern[36] suggested as much as 28% of the total peroxides could be not in the form of hydroperoxides, based on polarographic analysis. Any cyclic peroxides should, on reduction, yield α-glycols but the correlation between α-glycol formed and the peroxide value difference was not very good.



α glycol

More recently Begeman[85] identified a cyclic peroxide-hydroperoxide LX from the autoxidation of methyl linolenate.

This provides evidence for Gunstones[86] explanation of the low amounts of 12- and 13-hydroperoxides, (section 1.7) by a 1,4 cyclisation of



LX

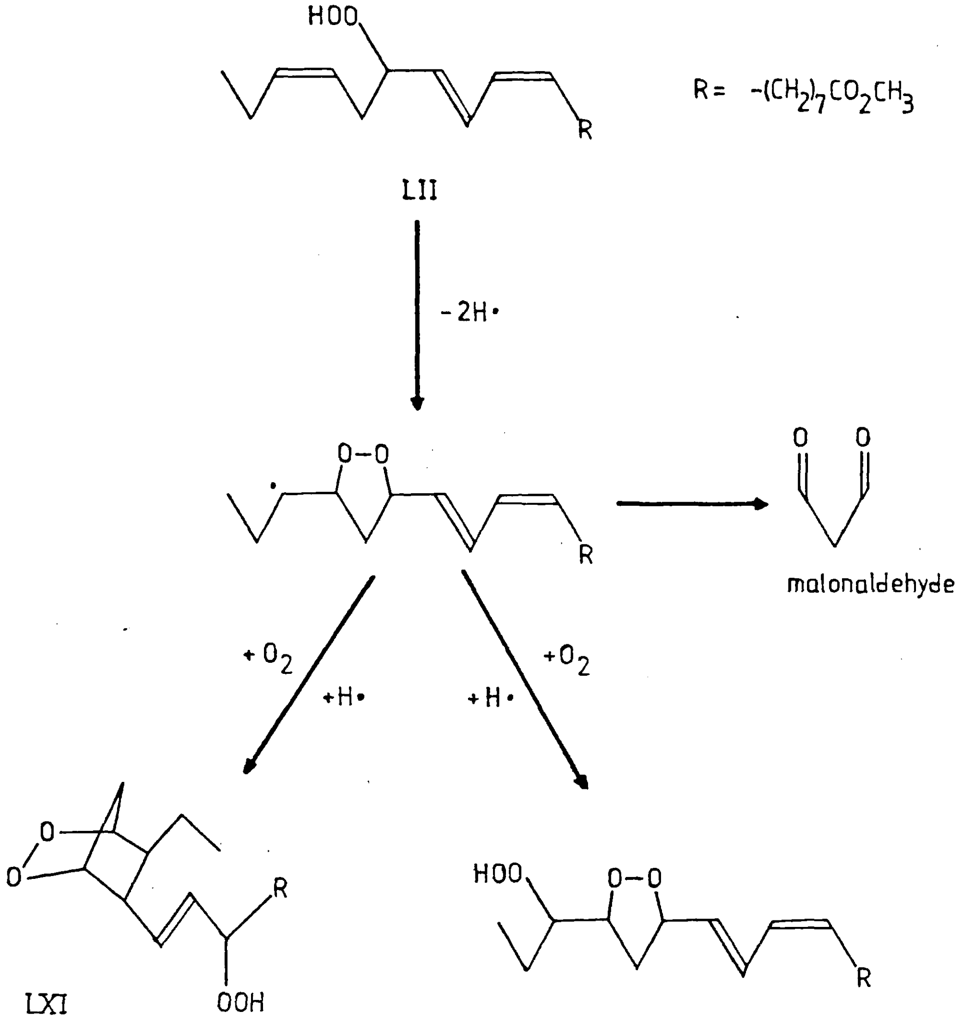
Scheme 1.10.1

the internal peroxides formed in methyl linolenate, scheme 1.10.1.

Pryor[87], and later Dahle[88], reported the isolation and identification of cyclic peroxide products from the autoxidation of methyl linolenate with structures similar to those of endoperoxides formed biosynthetically from arachidonic acid. They formulated a mechanism involving 1,3 cyclisation of the internal 12- and 13- hydroperoxides and the formation of a five-membered cyclic peroxide hydroperoxide, LXI. See scheme 1.10.2.

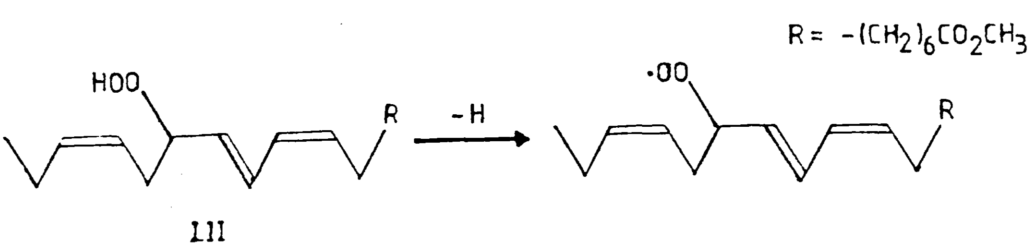
Malonaldehyde was observed in the autoxidation products in 1962 by Dahle[88], and also reported in 1966 by Kwan and Olcott[89]. Both groups of workers used 2-thio barbituric acid to identify the dialdehyde.

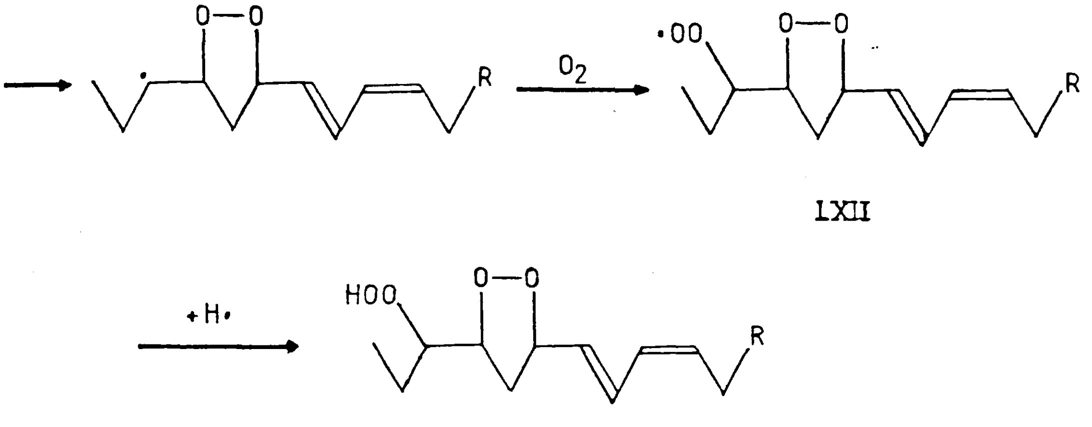
Chan[90] reported ,in 1980 ,hydroperoxy-epidioxide formation during the autoxidation of a hydroperoxide formed from methyl linolenate.



Scheme 1.10.2.

The hydroperoxide LII was autoxidised at 40^{o}Cfor 96 hours and yielded a mixture LII (25.4%) LXIII (31.5%) and a mixture of polar products (43.0%). Preparative HPLC yielded LXIII, the structure being established by UV, Infrared, Mass spectrometry (reduction NaBH$_4$ followed by Pt/H$_2$) and spin decoupling ^{1}H nmr.





LXII

LXIII

Scheme 1.10.3.

Hydrogen abstraction from LII by LXII constitutes progagation of the chain reaction in scheme 1.10.3. When the autoxidation of the hydroperoxide was carried out in the presence of $^{18}O_2$, the oxygen atom at C-13 in LXIII became enriched in ^{18}O (26.1 atom %). This cyclisation of peroxy radicals, the subject of several recent publications,[92-95] has been used to produce prostaglandin like products[91] and can occur when there is a remote double bond in the peroxy radical substrate.

1.11 Peroxide decomposition and polymeric products

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

The basic equations are as follows:

$$\text{Initiation} \longrightarrow 2X\cdot \tag{1}$$

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

$$R\cdot + O_2 \longrightarrow RO_2\cdot \tag{3}$$

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

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

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

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

where R_i the rate of initiation, combining reactions (1) and (2). Experiments show that the relative ease of autoxidation of RH roughly parallels the ease of breaking the C-H bond[113], and for hydrocarbons this increases in the series n-alkanes $<$ branched alkanes $<$ aryl alkanes $\cong$ alkenes $<$ alkynes.[114,115] Thus, both resonance and inductive effects contribute to the stability of the resulting radical, but the subsequent reaction of the alkyl radical with oxygen in reaction (3) is usually never rate limiting.[113]

Alternative termination reactions to (5) may also occur[113]:

$$2R\cdot \longrightarrow R-R \tag{6}$$

$$ROO\cdot + R\cdot \longrightarrow ROOR \tag{7}$$

and it is through 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 weight in oxygen. In non-conjugated oils, oxygen uptake leads to formation of hydroperoxides, and their decomposition accompanies crosslinking reactions.[116] 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[24] appear to be polyperoxides.[104,105,106,107,108,109,110.]

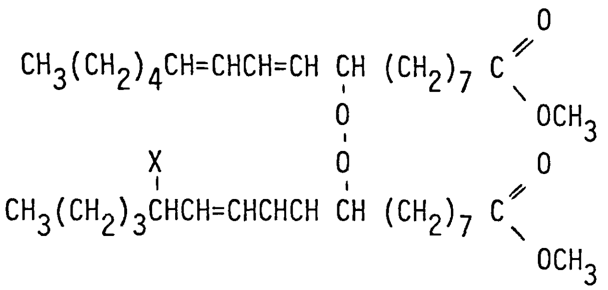
O'Neill[111] has shown that when methyl oleate was heated with methyl oleate hydroperoxides, mainly oxygen bonded products were obtained. Other workers have reported that below 100°C the polymer linkages are mainly through oxygen.[112]

Chang[117] has isolated dimer and trimer fractions by solvent extraction from ethyl linoleate, autoxidised by bubbling with dry air at 30°C for 350 hrs.

More recently, Miyashita[118] studied the formation of dimers in the autoxidation of methyl linoleate at 30°C for 192 hrs. The oxidised ester, separated from the unreacted material by gel chromatography, was separated by HPLC into three components. One was assigned as methyl linoleate hydroperoxides and the others as dimeric, capable of being cleaved by reduction with sodium borohydride and therefore containing the -C-O-O-C- linkage. Miyashita[119] resolved one of the dimer fractions into 4 major fractions by HPLC and determined their mean relative molecular mass, these being 643, 644, 650 and 655 amu. These components could contain two molecules of methyl linoleate together with three to four molecules of oxygen. Their reduction with stannous chloride, silylation and gc-ms analysis gave three components:-

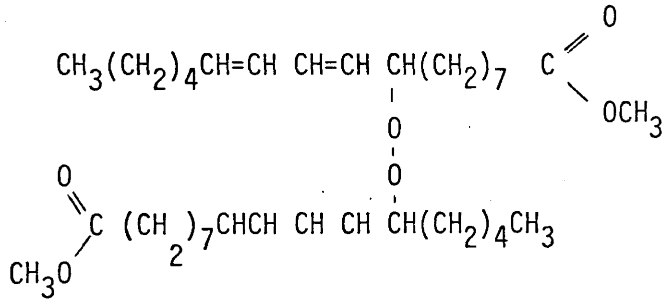
the TMS derivatives of methyl-9-and/or 13 hydroxyoctadecadienoate and methyl -9-,13-dihydroxyoctadecadienoate. The field desorption mass spectrum of the last gave a definite molecular ion at m/z 652. Miyashita has proposed the following structures:

LXIV



$$\begin{array}{rcl} \mathrm{CH_3(CH_2)_4CH{=}CHCH{=}CH} & \mathrm{CH} & \mathrm{(CH_2)_7\,C({=}O)OCH_3} \\ & | & \\ & \mathrm{O} & \\ & | & \\ & \mathrm{O} & \\ & | & \\ \mathrm{CH_3(CH_2)_3\overset{\overset{\textstyle X}{|}}{C}HCH{=}CHCHCH} & \mathrm{CH} & \mathrm{(CH_2)_7\,C({=}O)OCH_3} \end{array}$$

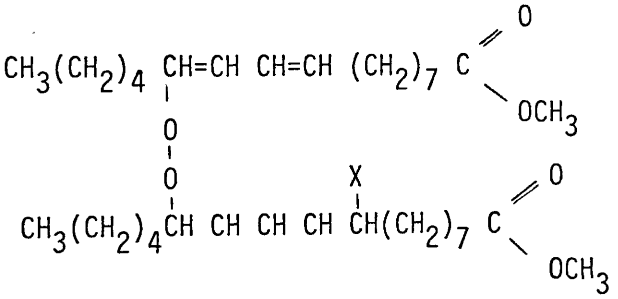
LXV



$$\begin{array}{rcl} \mathrm{CH_3(CH_2)_4CH{=}CH\ CH{=}CH} & \mathrm{CH} & \mathrm{(CH_2)_7\,C({=}O)OCH_3} \\ & | & \\ & \mathrm{O} & \\ & | & \\ & \mathrm{O} & \\ & | & \\ \mathrm{CH_3O(O{=})C\ (CH_2)_7CHCH\ CH\ CH} & \mathrm{CH} & \mathrm{(CH_2)_4CH_3} \end{array}$$

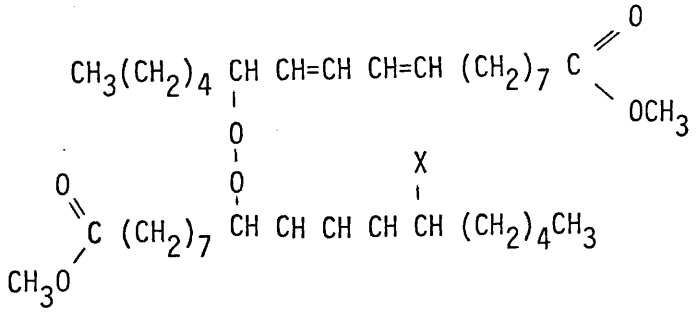
X= OH or OOH

LXVI



$$\begin{array}{rcl} \mathrm{CH_3(CH_2)_4} & \mathrm{CH} & \mathrm{{=}CH\ CH{=}CH\ (CH_2)_7\,C({=}O)OCH_3} \\ & | & \\ & \mathrm{O} & \\ & | & \\ & \mathrm{O} & \\ & | & \\ \mathrm{CH_3(CH_2)_4} & \mathrm{CH} & \mathrm{CH\ CH\ CH\ \overset{\overset{\textstyle X}{|}}{C}H(CH_2)_7\,C({=}O)OCH_3} \end{array}$$

LXVII



$$\begin{array}{rcl} \mathrm{CH_3(CH_2)_4} & \mathrm{CH} & \mathrm{CH{=}CH\ CH{=}CH\ (CH_2)_7\,C({=}O)OCH_3} \\ & | & \\ & \mathrm{O} & \\ & | & \\ & \mathrm{O} & \\ & | & \\ \mathrm{CH_3O(O{=})C\ (CH_2)_7} & \mathrm{CH} & \mathrm{CH\ CH\ CH\ \overset{\overset{\textstyle X}{|}}{C}H\ (CH_2)_4CH_3} \end{array}$$

Two reviews on the drying oil phenomena are worth noting here.[120,121]

1.12 Redox promotors of autoxidation - Industrial application of drying oils

Certain metal compounds have been known for centuries to increase the rate at which oils dry; their first recorded use was primarily in the form of lead linoleates in "paints" for mummification.[128] Litharge or some other oxide of lead was heated with linseed oil to produce *inter alia* lead linoleate. 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 sort of metallic soap." During 1835, zinc oxide replaced white lead as a paint pigment, heralding the problem of drying the vegetable oils used as paint vehicles, however with the synthesis of many metal soaps the paint industries needs could be satisfied.[129,130]

It is now recognised that there are two types of metal promotors. The first group including such metals as cobalt, manganese and iron are known as 'surface driers'. A useful criteria is that they exist in two different oxidation states, the lower being capable of being oxidised to the less stable higher oxidation state by the hydroperoxides formed during the oxidation of the drying oils.[131]

The second group are known as 'through driers' and include metals such as zinc and lead. These assist the drying of the lower layers of the paint film. This is essential as the 'surface driers' used alone produce a 'shrivelled' film.

The promotors typically used in modern paints are cobalt (II) bis-(2-ethyl hexanoate) and lead (II) bis-(2-ethyl hexanoate). The alkyl component of the anion provides solubility for the promotor in the non-polar alkyd resin. These promotors are used at concentrations of 0.04% and 1.5% respectively (described as percentages of the weight of metal present on the catalyst in the weight of the drying oil present).

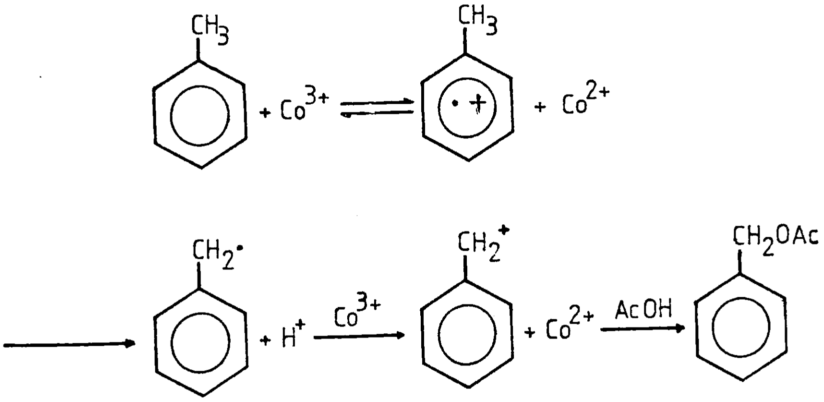
In the presence of these promotors linseed oil will dry in 2 hours[116] (compared to 120 hours unpromoted). This rate of drying is now acceptable for a decorative gloss paint.

The metal ions in their higher oxidation state may generate free radicals directly from an organic substrate, both in polar and non-polar solvents, by a one electron transfer reaction, (equation 1.12.1.

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

Equation 1.12.1

However, this type of initiation is masked by the reaction of accumulated hydroperoxides with the metal ion. Bawn[132,133] however, showed that the cobalt acetate catalysed autoxidation of benzaldehyde in acetic acid proceeded by equation 1.12.1. The most conclusive evidence that this route is important in metal catalysed autoxidations was reported by Heiba.[134] He studied the cobalt acetate catalysed oxidation of alkyl aromatic hydrocarbons in acetic acid in the absence of oxygen. The first step was proposed to be the reversible reaction of Co^{III} with the aromatic hydrocarbon.



The radical cation is then believed to lose an α proton to give a benzyl radical which, in the absence of O_2, is rapidly oxidised by Co^{3+} to the benzyl cation, see scheme 1.12.2. Dessau[135] obtained evidence using ESR for the production of radical cations from several alkyl-aromatic hydrocarbons and Co^{3+}.

The study of hydroperoxides in the presence of metal ions really began when Fenton[136] described the reaction of hydrogen peroxide in the presence of Fe^{2+} ions. It was Haber and Weiss[137] who proposed the free radical process in equation 1.12.3.

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

Equation 1.12.3

Many organic peroxides, such as alkyl, cycloalkyl and arylalkyl hydroperoxides are susceptible to metal ion decomposition. Using Fentons reagent, the analogous reaction in these compounds appears to be the generation of alkoxy radicals, equation 1.12.4.

$$ROOH + m^n \longrightarrow RO\cdot + OH^- + m^{n+1}$$

Equation 1.12.4

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.[138,139,140] In the absence of a reactive substrate the reactions below in Scheme 1.12.5 are indicated, thus providing a catalytic cycle. Hiatt[140] 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%).

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

Scheme 1.12.5

If the metal ions are present in larger quantities the alkoxy radical, (RO·), is reduced as in equation 1.12.6.[141]

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

Equation 1.12.6

The peroxy radicals ROO· undergo a similar reduction,[142,143] equation 1.12.7.

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

Equation 1.12.7

This ion-formation constitutes termination reactions in the free radical processes discussed in section 1.11. This may provide an explanation as to why low concentrations of metal ions give optimum rates for catalyzing autoxidations.[149,145] However it has been reported that the drying time of an alkyd resin increases when the concentration of metal ion is increased.[146]

The choice of metal ion or the gegen ion can effect the reactions given in equations 1.12.5 and 1.12.6 e.g. cobaltic EDTA complex is not reduced by hydroperoxides,[147] although simple cobaltic carboxylates are reduced very rapidly.[140,148] Most Fe (III) salts do not reduce hydroperoxides readily, although the iron phthalocyanine complex does.[140] No apparent correlation between the rate and a relevant property such as oxidation-reduction potential has yet been observed.[149]

The autoxidation of methyl linoleate and methyl linolenate in the presence of cobalt (II) and cobalt (III) cyclohexane carboxylate (naphthenate) in n-heptane solution was published by Hendricks.[150]

He proposed the following reactions, (scheme 1.12.8), to explain the autoxidation of the methyl ester.

Initiation.

$$R_1R_2CH_2 \xrightarrow{h\nu, O_2} R_1R_2HC\cdot + HOO\cdot$$

$$Co^{III} + R_1R_2CH_2 \longrightarrow Co^{II} + R_1R_2HC\cdot + H^+$$

$$Co^{III} + R_1R_2HCOOH \longrightarrow Co^{II} + R_1R_2HCOO\cdot + H^+$$

Propagation.

$$R_1R_2CH\cdot + O_2 \longrightarrow R_1R_2HCOO\cdot$$

$$R_1R_2HCOO\cdot + R_1R_2CH_2 \longrightarrow R_1R_2HCOOH + R_1R_2HC\cdot$$

Termination.

$$Co^{III} + R_1R_2CH \xrightarrow{H_2O} Co^{II} + R_1R_2HCOH + H^+$$

$$Co^{II} + R_1R_2HCOO\cdot \xrightarrow{H^+} Co^{III} + R_1R_2HCOOH$$

$$2R_1R_2HCOO\cdot \longrightarrow R_1R_2HCOH + R_1R_2CO + O_2$$

$$R_1R_2HCOO\cdot + R_1R_2CH\cdot \longrightarrow R_1R_2HCOH + R_1R_2CO$$

$$Co^{III} + HOO\cdot \longrightarrow Co^{II} + H^+ + O_2$$

Co^{II} oxidation.

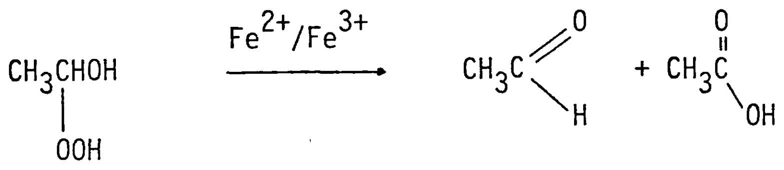
$$2Co^{II} + R_1R_2HCOOH \xrightarrow{2H^+} 2Co^{III} + R_1R_2HCOH + H_2O$$

Scheme 1.12.8

1.13 Decomposition of hydroperoxides in the absence of reactive substrates

This discussion will be restricted to secondary hydroperoxides. The decomposition products of secondary hydroperoxides in the presence of metal ions are mainly alcohols and carbonyl compounds. Hydrocarbons and hydrogen, carbon monoxide and carbon dioxide gas are also found in trace amounts.[151,152]

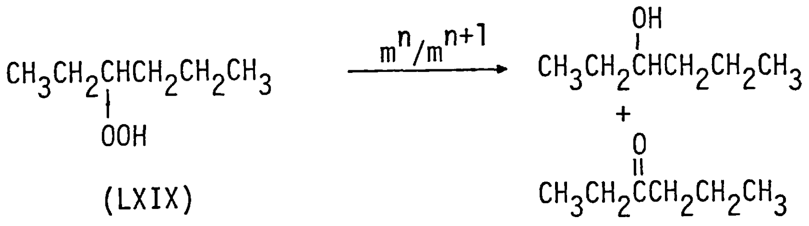
1-Hydroperoxy ethanol (LXVIII) decomposed in the presence of aqueous ferrous sulphate giving ethanal and ethanoic acid[153], equation 1.13.1.



(LXVIII)

Equation 1.13.1

and 3-hydroperoxyhexane (LXIX) decomposes at 80°C in the presence of cobalt, copper, nickel, iron or manganese(II) dodecanoate giving 3-hydroxy hexane (23%) and 3-hexanone (15%) after 20 hrs,[154] equation 1.13.2.



$$\underset{\substack{| \\ OOH}}{CH_3CH_2CHCH_2CH_2CH_3} \xrightarrow{m^n/m^{n+1}} \overset{\substack{OH \\ |}}{CH_3CH_2CHCH_2CH_2CH_3} + \overset{\substack{O \\ \|}}{CH_3CH_2CCH_2CH_2CH_3}$$

(LXIX)

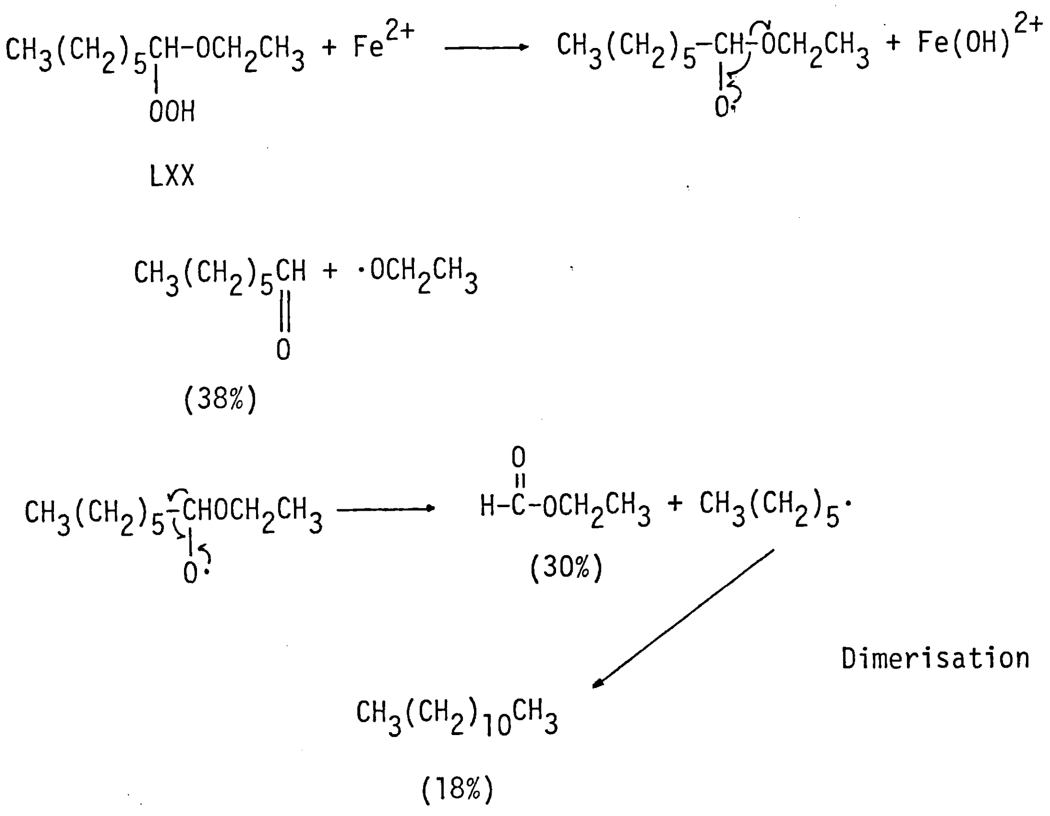
Equation 1.13.2

The decomposition of 2-hydroperoxy,3-hydroperoxy- and 4-hydroperoxy-n-heptane gave the corresponding heptanols and heptanones in 20-40% yields[151] (see table 12).

Table 12

	% Heptanol	% Heptanone
2-hydroperoxy heptane	31	21
3-hydroperoxy heptane	34	24
4-hydroperoxy heptane	40	30

The decomposition of 1-ethoxy-1-hydroperoxy heptane, LXX, in the presence of Fe^{2+} yields ethyl methanoate, n-heptanal and n-dodecane,[155a] scheme 1.13.3.



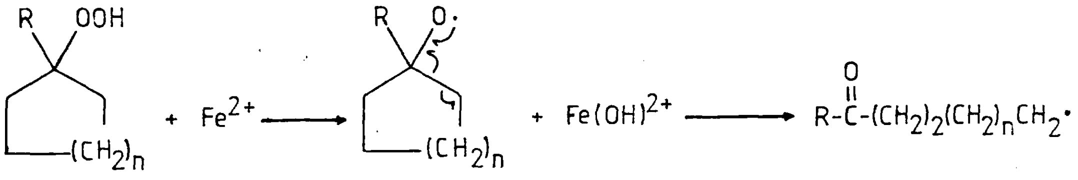
Scheme 1.13.3

When the chlorides of Cu^{I} and Cu^{II} were used to decompose LXX, no n-dodecane was observed. Instead n-hexyl chloride was formed in 20% yield,[155a] equation 1.13.4.

$$CH_3(CH_2)_5\cdot \ + \ CuCl^{+} \longrightarrow CH_3(CH_2)_5Cl$$

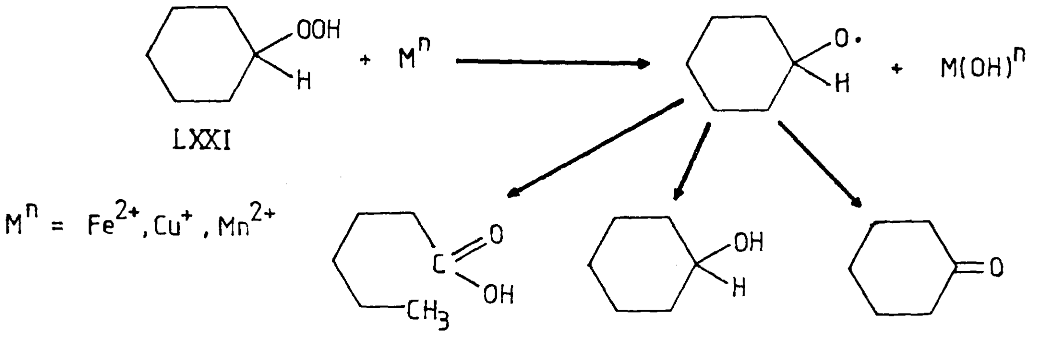
Equation 1.13.4

The ring opening reaction of cyclic hydroperoxides was discovered in the early 1950s. A general reaction route is given in scheme 1.13.5.



Scheme 1.13.5 R = OH, alkyl, alkoxy, aryl, n = 1,2,3.

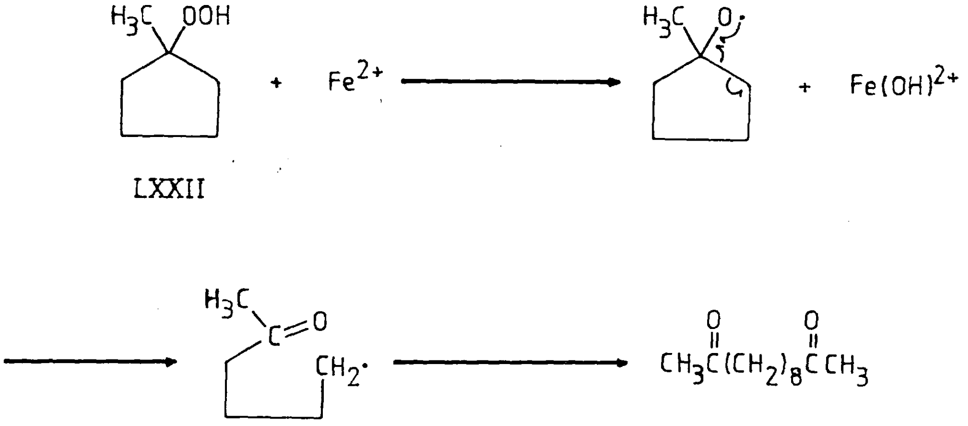
Specific examples are the decomposition of (i) cyclohexylhydroperoxide (LXXI) by metal ions,[154,155b] scheme 1.13.6. and (ii) 1-methylcyclopentylhydroperoxide (LXXII) with ferrous sulphate to give dodecane 2,11-dione,[156,157,158] scheme 1.13.7.



LXXI

$M^n = Fe^{2+}, Cu^+, Mn^{2+}$

Scheme 1.13.6



LXXII

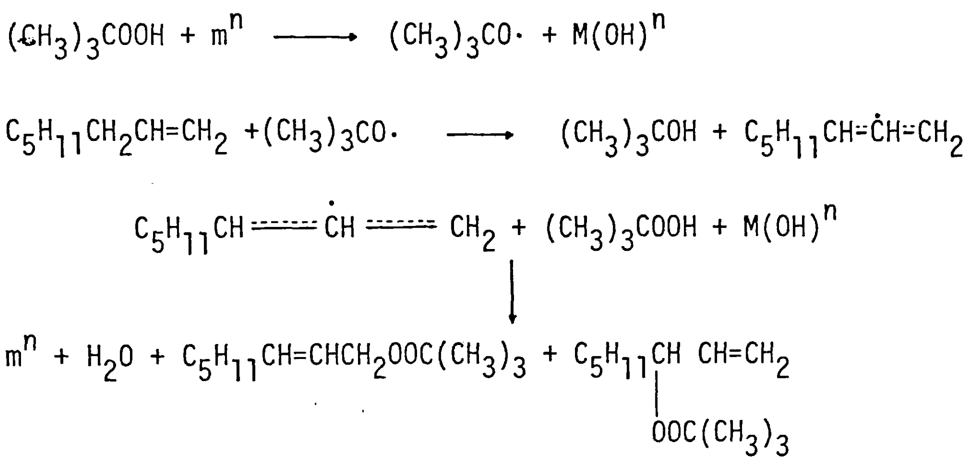
Scheme 1.13.7

Carbon-carbon bond scissions β to alkoxy radicals are also observed in primary[151] and tertiary hydroperoxides[159] and in general the predominant cleavage is that which forms the largest alkyl radical.

Hiatt[160] studied the rates of decomposition of t-butyl hydroperoxide in chlorobenzene with various catalysts and determined the composition of the products. The products being t-butyl alcohol, t-butyl peroxide and 2-propanone. Little variance was found in product composition with anion selection or temperature. However $t_{\frac{1}{2}}$ decreased at higher temperatures and when 2-ethyl hexanoate was the anion. Lead(II) cyclohexane carboxylate also decomposed t-butyl hydroperoxide but at a much slower rate than cobalt(II) stearate.

1.14 Decomposition of hydroperoxides in the presence of alkenes

The reaction of t-butylhydroperoxide in the presence of copper(I) chloride at 70^{0}C with 1-octene gave a mixture of peroxides LXXIII and LXXIV,[161,162] scheme 1.14.1.



$$(CH_3)_3COOH + m^n \longrightarrow (CH_3)_3CO\cdot + M(OH)^n$$

$$C_5H_{11}CH_2CH{=}CH_2 + (CH_3)_3CO\cdot \longrightarrow (CH_3)_3COH + C_5H_{11}CH{\overset{\cdot}{=}}\dot{C}H{=}CH_2$$

$$C_5H_{11}CH \overset{====}{} \dot{C}H \overset{====}{} CH_2 + (CH_3)_3COOH + M(OH)^n$$

$$\downarrow$$

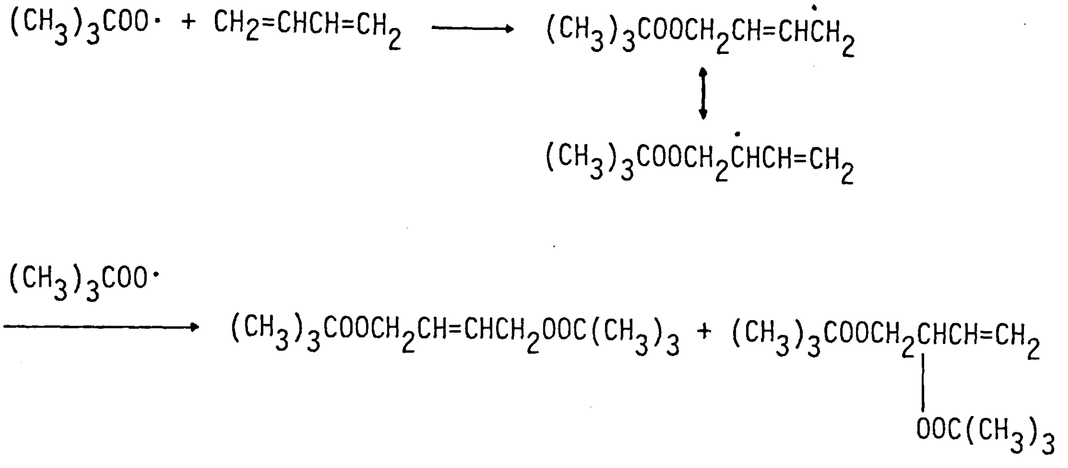
$$m^n + H_2O + C_5H_{11}CH{=}CHCH_2OOC(CH_3)_3 + C_5H_{11}\underset{\displaystyle OOC(CH_3)_3}{\underset{|}{CH}}\,CH{=}CH_2$$

LXXIII LXXIV

Scheme 1.14.1

However it was reported that in the presence of cobalt ethanoate or cyclohexane carboxylate the compound 2-octenal is also formed by the thermal decomposition of LXXIII.

t-Butylhydroperoxide with 1,3-butadiene, in the presence of cobalt(II) cyclohexane carboxylate between-15 and-7^0, gave a mixture of 1,4-di(t-butyl-peroxy)-2-butene (LXXV) and 3,4,di(t-butyl-peroxy)-1-butene (LXXVI) with the following pathway being suggested,[162] scheme 1.14.2 .



$$(CH_3)_3COO\cdot + CH_2{=}CHCH{=}CH_2 \longrightarrow (CH_3)_3COOCH_2CH{=}CH\dot{C}H_2 \updownarrow (CH_3)_3COOCH_2\dot{C}HCH{=}CH_2$$

$$\xrightarrow{(CH_3)_3COO\cdot} (CH_3)_3COOCH_2CH{=}CHCH_2OOC(CH_3)_3 + (CH_3)_3COOCH_2\underset{\displaystyle OOC(CH_3)_3}{\underset{|}{C}}HCH{=}CH_2$$

LXXV LXXVI

Scheme 1.14.2

This reaction gives support to the structure of the dimers formed in the autoxidation of methyl linoleate isolated by Miyashita.[119] (Section 1.11).

1.15 Complexing agents

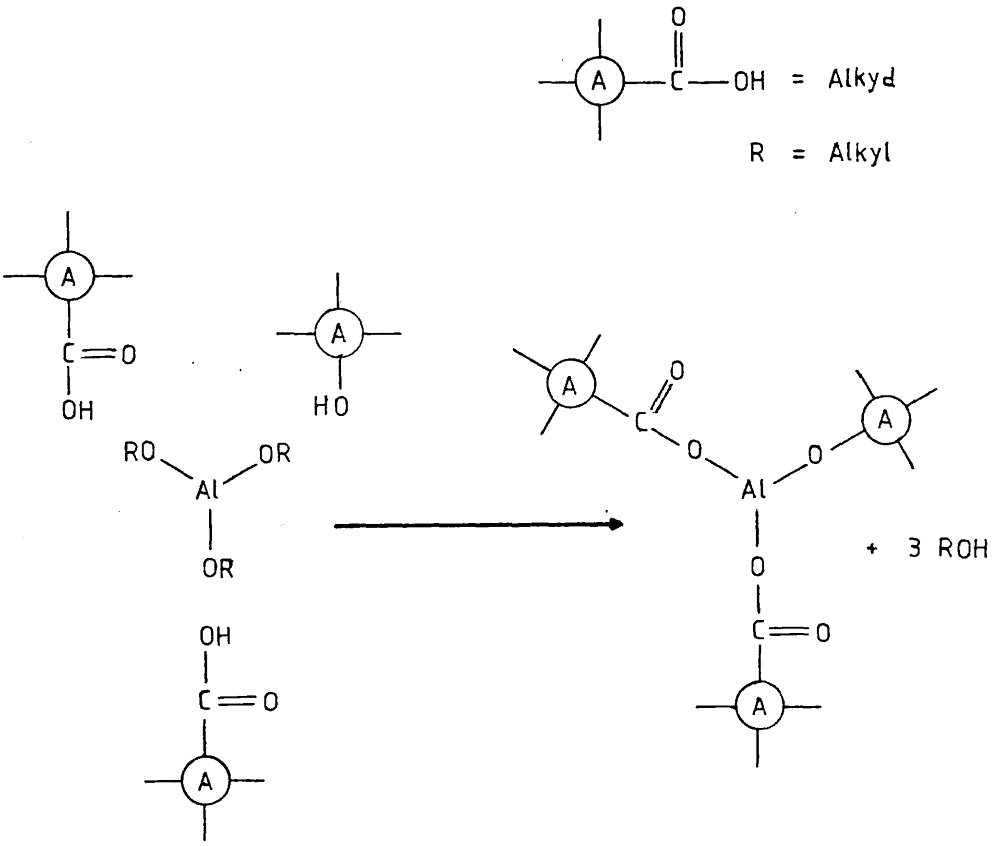
The search for durable paint films coupled with pressure to remove lead driers has recently revived interest in aluminium coordination promotors. The literature contains many patents on the use of organo aluminium compounds in paint. Although Chatfield[164] observed an increase in the viscosity of paints and varnishes in the presence of aluminium soaps, it was left to Weiss[165,166] to develop the final form of the promotor, the use of which is being suggested at the present time.

Weiss reacted aluminium butoxide with an equimolar amount of acetoacetic ester (AAE). The resultant complex was then reacted with Tall oil acids and from, the amount of alcohol liberated, it was concluded that the reaction was an exchange of the two butoxide groups for two acid groups, equation 1.15.1.

$$Al(OBu)_2(AAE) + 2RCO_2H \longrightarrow Al(OCOR)_2(AAE) + 2BuOH$$

Equation 1.15.1

Turner[167] more recently proposed the same type of exchange reaction in the coordination drying of alkyd resins by $Al(OR)_3$, equation 1.15.2.

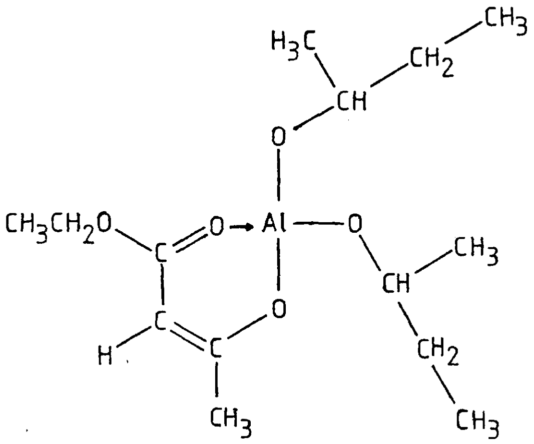


Equation 1.15.2

However a long term storage problem has been encountered with the use of $Al(OR)_3$ in paints; the viscosity of the resin increases to an unacceptable level. The Weiss compound however gave the resin much improved storage properties, but still the viscosity increased.

The use of low acid value alkyds in combination with a Weiss type aluminium compound gives excellent storage properties.

The compound now considered most suitable for incorporation into a paint is aluminium bis(2-butoxide)ethyl acetoacetate. (LXXVII)



LXXVII

Some unpublished work of ICI Paints Division, together with results published by Turner[168] and Love[169] suggest that its complexing reaction is similar to that in scheme 1.15.2, except the complex LXXVII will only combine with two alkyd monomers. The chelating group (ethyl acetoacetate) is believed not to be displaced under ambient conditions.[169]

1.16 Acid catalysed crosslinking of alkyd resins

Recently ICI Paints Division patented the use of acid catalysts to accelerate the drying of alkyd resins.[170] The acid catalyst used for the curing must be a strong acid, such that a solution of the acid in water is fully dissociated i.e. the acid does not have a finite pKa value. Suitably strong aryl and alkyl sulphonic acids include benzene, toluene, methane, ethane, propane, butane and dodecane.

The alkyd resin is formulated as discussed before (section 1.1) but with an excess of polyfunctional alcohol over polycarboxylic acid to give the resin a significant excess "hydroxyl content".

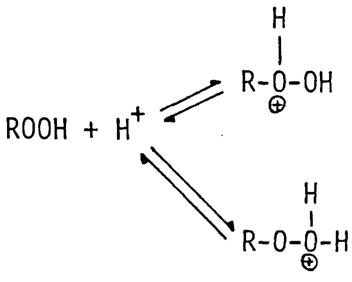
Work at ICI[171] has revealed the following conditions for drying to occur: (i) the presence of oxygen, (ii) the presence of OH groups in the resin, (iii) the presence of unsaturated fatty acids and (iv) the absence of free radical inhibitors.

With 1-6% w/w of the acid catalyst, based on the weight of the film forming material, the rate of drying was comparable to that of conventional driers.[170]

This evidence suggests that oxygen reacts with the unsaturated fatty acids in the resin, i.e. forming hydroperoxides and that their subsequent decomposition may be assisted by the acid.

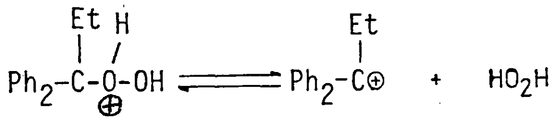
The possibility of acid catalysed addition of alcohols to double bonds in the resin can be disregarded on two counts: (i) for this type of addition to occur the sulphonic acid has to be used as the solvent;[172,173,174,175] (ii) the resin would be expected to crosslink and gel on storage; in practise the viscosity of these alkyd resins often decreases slightly on storage.[171]

The acid catalysed decomposition of hydroperoxides may occur by protonation at either oxygen of the hydroperoxide, see scheme 1.16.1.



Scheme 1.16.1

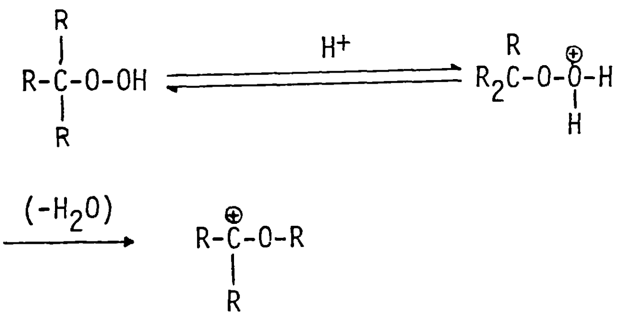
Hydrogen peroxide will become a leaving group with hydroperoxides whose R groups are sufficiently electron donating,[176] equation 1.16.2.



$$Ph_2\overset{Et}{C}\text{-}\underset{\oplus}{\overset{H}{O}}\text{-}OH \rightleftharpoons Ph_2\overset{Et}{C}^{\oplus} + HO_2H$$

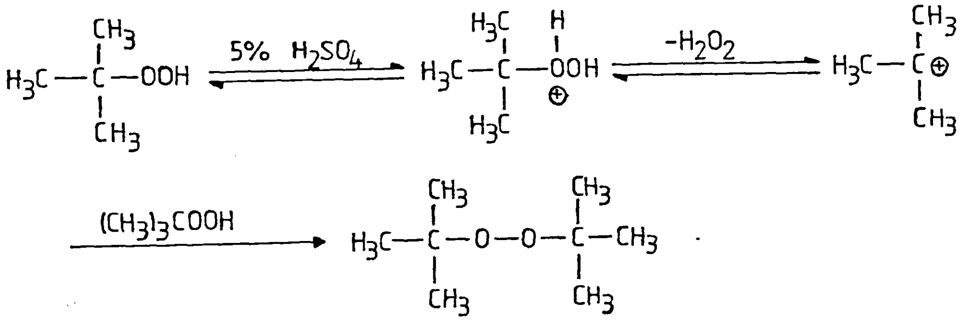
Equation 1.16.2

Alternatively, the protonation of the hydroxylic oxygen leads to O-O heterolysis, followed by nucleophilic rearrangement[177,178,179] with an alkyl or aryl group undergoing a 1,2 shift from carbon to an incipiently positive oxygen, scheme 1.16.3. Experimental evidence



Scheme 1.16.3

suggests that alkyloxonium ions never have a free existence, (a) partial decomposition in ^{18}O labelled water does not yield residual hydroperoxide containing ^{18}O [180,181] and (b) the relative rates for differing R groups show a strong indication of anchimeric assistance in the O-O bond breaking step.[113,182,183,184] Many rearrangement products from aromatic compounds are reported,[182,185] few aliphatic compounds have been studied. However Pritckon[186] reported that secondary alkyl hydroperoxides under acid catalysed conditions rearrange to give ketones, e.g. 1-methylcyclohexyl hydroperoxide gives 7-hydroxy-2-heptanone, and 1-methylcyclopentyl-hydroperoxide produces 6-hydroxy-2-hexanone in 15% yield.[187] March[188] reported that the alkyl migration also occurs in secondary alkyl hydroperoxide decompositions. Deno[189] studied the decomposition of 2-pentyl hydroperoxide by sulphuric acid and obtained 37% isopropyl hydrogen sulphate (n-propyl migration) and 63% 2-pentanone (from H migration). More recently Turner[190] studied the decomposition of t-butyl hydroperoxide and found product dependence on acid concentration, lower concentrations giving di-t-butylperoxide. He did not detect any 2-methylpropene previously reported by Leffler.[179] He explained the di-t-butylperoxide formation by the elimination of hydrogen peroxide from protonated t-butyl hydroperoxide, scheme 1.16.4.



Scheme 1.16.4

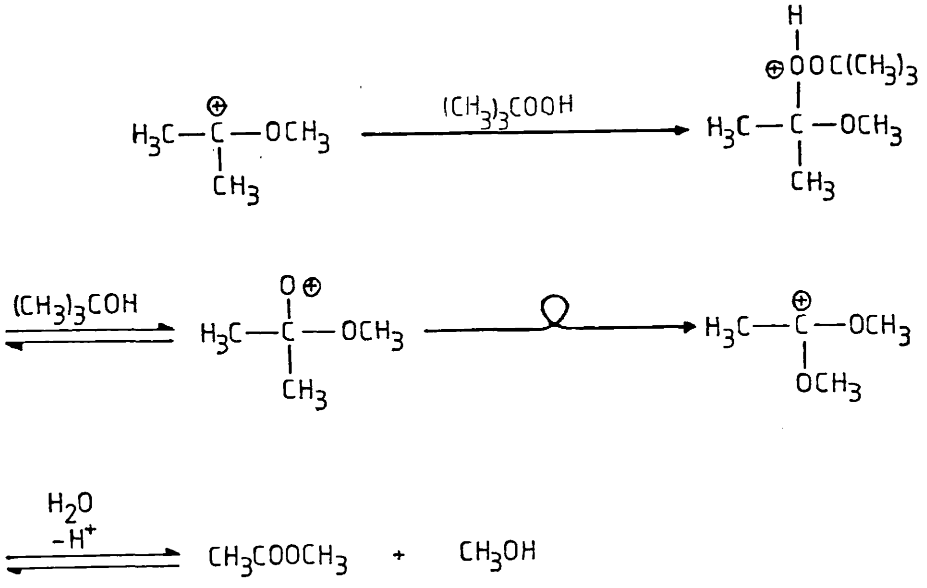
If the decomposition was carried out in the presence of methanol then methyl-t-butyl ether and methyl ethanoate became the major products, schemes 1.16.5 and 1.16.6.

$$(CH_3)_3COOH \rightleftharpoons [(CH_3)_3C{-}OOH_2]^+ \rightleftharpoons (CH_3)_3C^{\oplus} + H_2O + 1/2\,O_2$$

$$(CH_3)_3C^{\oplus} + (CH_3)_3COOH \rightleftharpoons ((CH_3)_3C)_2O_2 + H^+$$

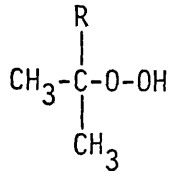
$$(CH_3)_3C^{\oplus} + CH_3OH \rightleftharpoons (CH_3)_3COCH_3 + H^+$$

Scheme 1.16.5



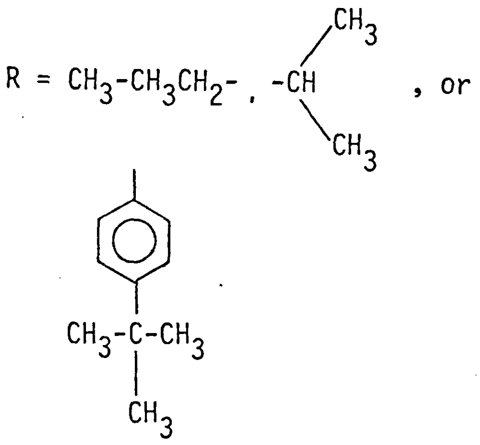
Scheme 1.16.6

Sheldon[191] studied the acid catalysed decomposition of several hydroperoxides (LXXVIII) by $FSO_3H:SbF_5$ (5:1) at -40°C.

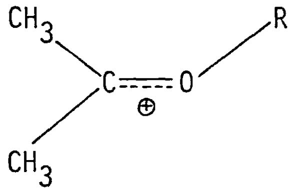


$CH_3-\overset{R}{\underset{CH_3}{C}}-O-OH$

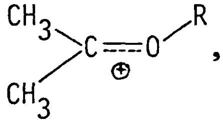
LXXVIII



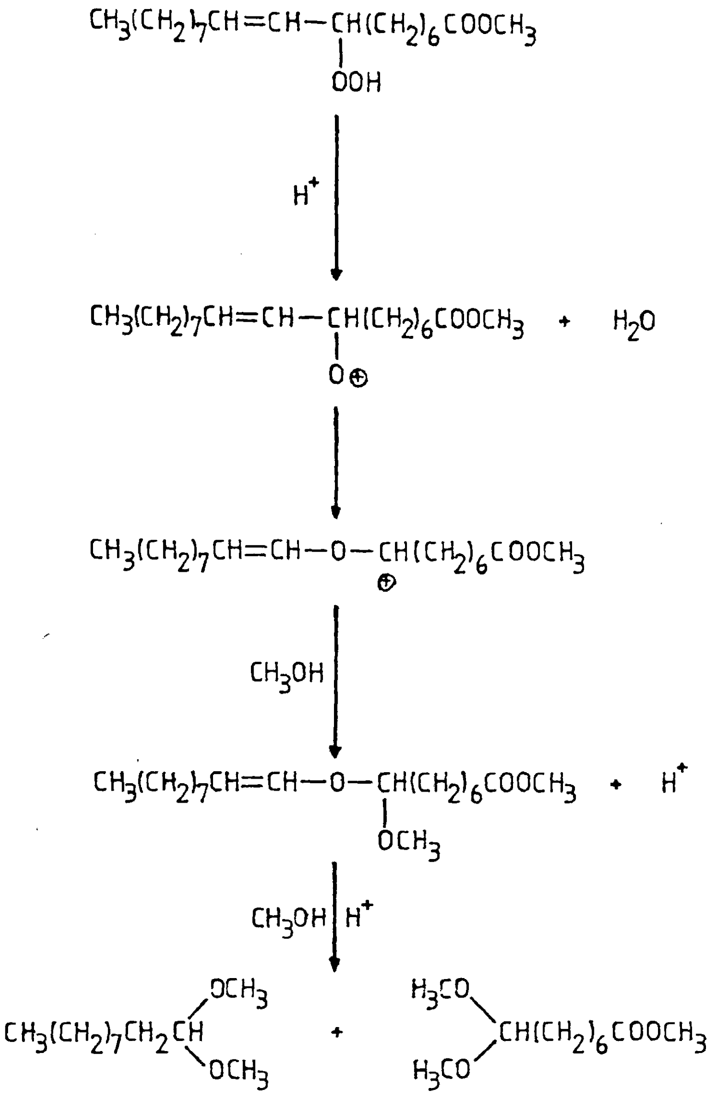
Spectra obtained by ^1H n.m.r. were interpreted to show the formation of alkoxycarbonium ion of the structure (LXXIX)



LXXIX

The chemical shift of the α- hydrogens on the R group being downfield from those α to an ether linkage (e.g.  , R = CH_3 4.89 ppm).

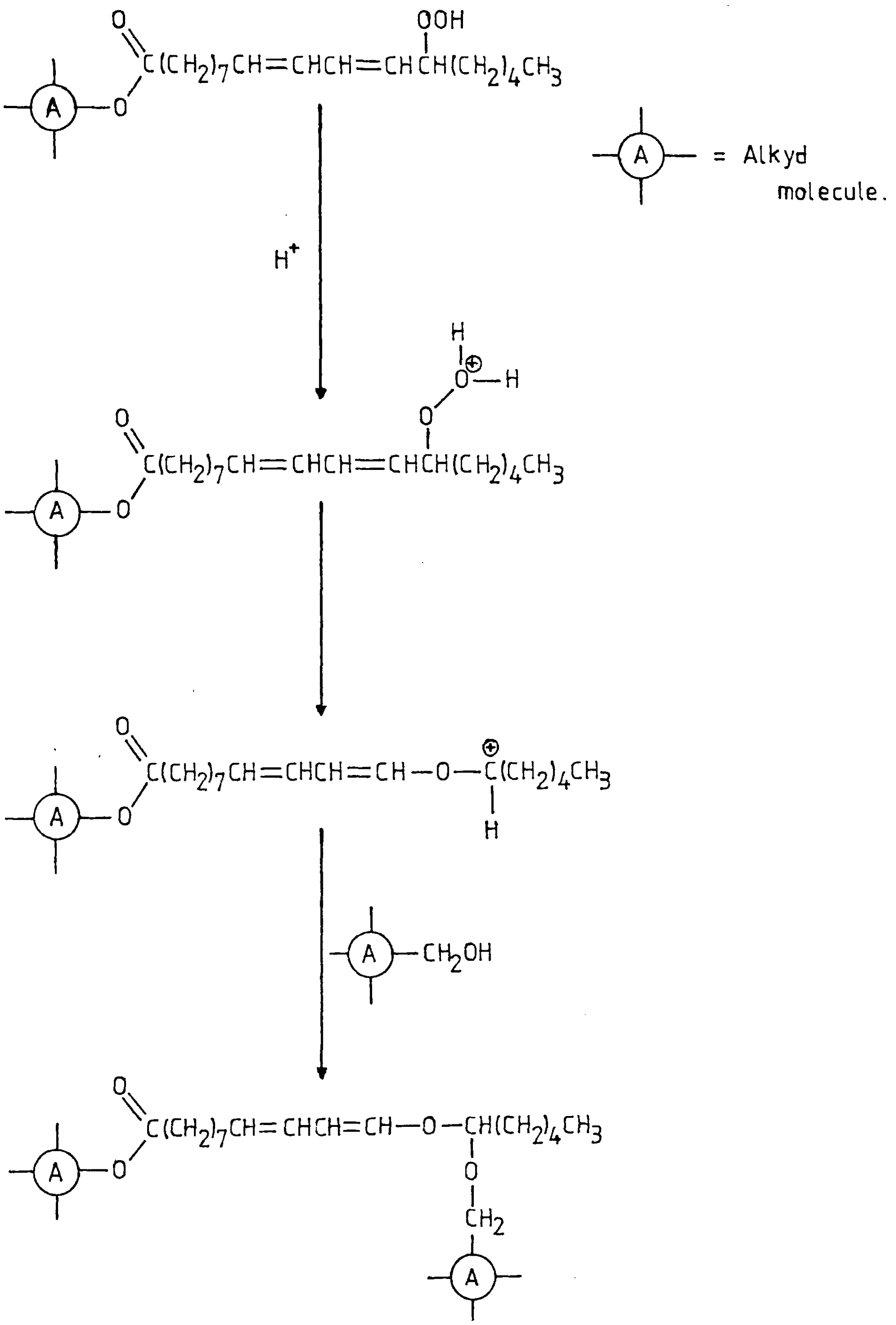
Schoellner studied the autoxidation of methyl oleate[192] and methyl linoleate[193] in the presence of methanol and strong acid. Evidence was found for the formation of dimethoxy acetals and these was determined by fractional vacuum distillation (no boiling points quoted) and 2,4 dinitrophenylhydrazine derivatives. The acetals were formed on the carbon atom that corresponded to the position of hydroperoxide formation in the esters. The following mechanism was proposed, scheme 1.16.7.



Scheme 1.16.7

The rearrangement of the oxenium cations can be compared with the Wagner-Meerwein rearrangement. It is known from the Wagner-Meerwein rearrangement that nucleophilicity will show the greatest migratory aptitude. For this reason the migration of the unsaturated group to the oxygen atom is preferred, as the vinyl group is considerably more nucleophilic than a saturated alkyl group.

The peroxide "content" of these autoxidised esters is much lower than an ester autoxidised in the normal manner. Methyl



Scheme 1.16.8

oleate with uv irradiation at 50^{o}C showed a 25% peroxide content after 48 hours, whereas under the same conditions, in the presence of methanol and sulphuric acid, this same level of peroxides was obtained only after 36 days.

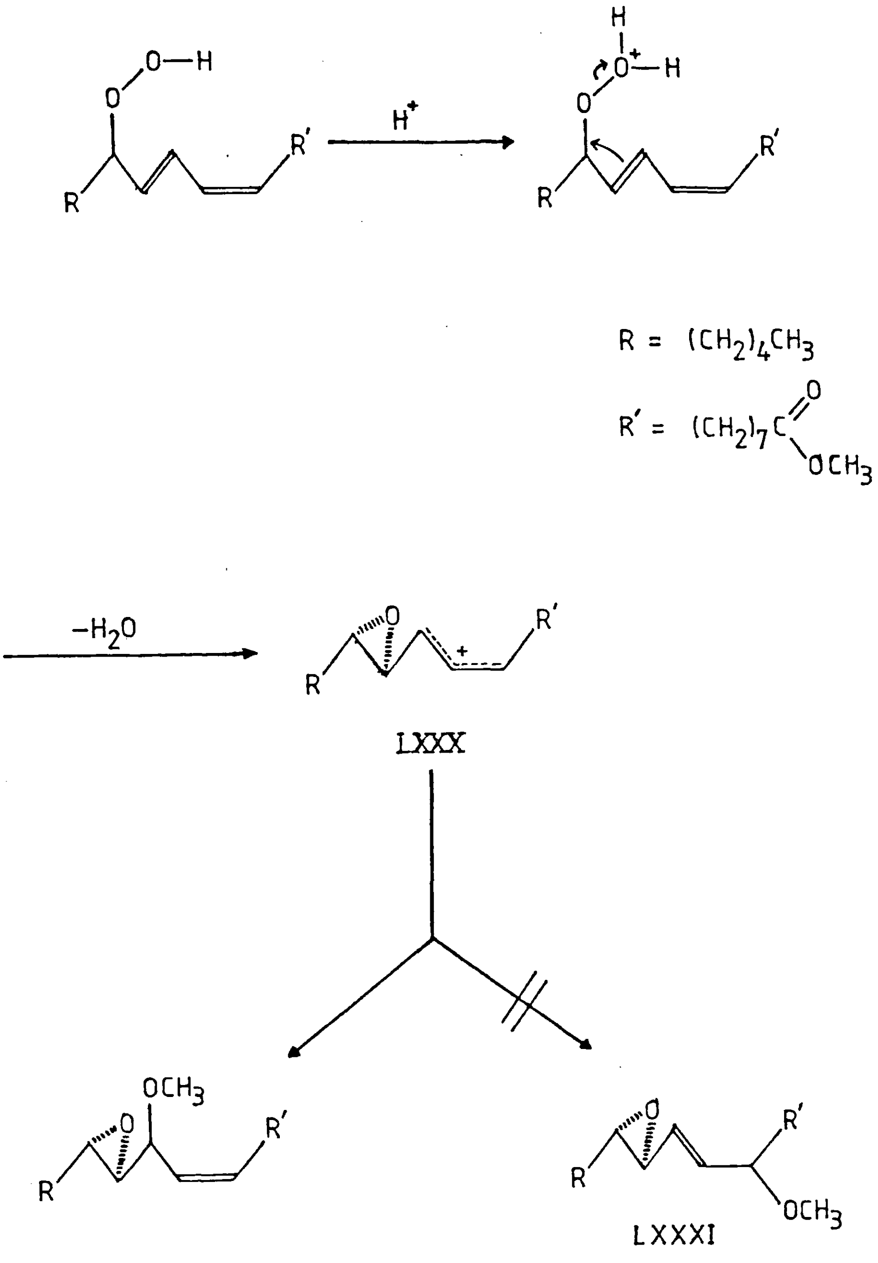
A possible mechanism of crosslinking in an alkyd resin using methane sulphonic acid could involve hydroperoxide formation on the fatty acid chain, its acid catalysed decomposition, alkoxy carbonium ion formation and nucleophilic attack by a hydroxyl group attached to another alkyd molecule, see scheme 1.16.8.

Gardner[194] in 1984 studied the acid catalysed decomposition of 13-hydroperoxy-cis-9-trans-11-octadecadienoic acid in the presence of $MeOH/H_2O$ (9:1 v/v). The rather complex mixture of products was separated by column chromatography and then HPLC and 18 compounds were identified by ^{1}H n.m.r., infrared spectroscopy and mass spectrometry. The type of compounds identified included isomeric epoxymethoxyoctadecenoic and hydroxy dimethoxyoctadecenoic acids. The compounds identified are listed in table 13.

Table 13

Methyl 12,13 epoxy-11-methoxy 9-cis-octadecenoate
Methyl 12,13 epoxy-11-hydroxy 9-cis-octadecenoate
Methyl 12 hydroxy -11,13-dimethoxy 9-cis-octadecenoate
Methyl 13 hydroxy -9,12-dimethoxy 10-trans octadecenoate
Methyl 13 hydroxy -9,10-dimethoxy 11-trans octadecenoate
Methyl 12,13 dihydroxy-11-methoxy-9-cis-octadecenoate
Methyl 11,13 dihydroxy-12-methoxy-9-octadecenoate
Methyl 12,13 dihydroxy-9-methoxy-10-octadecenoate
Methyl 12-oxo-10-trans dodecenoate
Methyl 9,13 dihydroxy-12-methoxy-10-octadecenoate

The formation of the epoxides was explained by electrophilic attack on the hydroperoxide along with the elimination of water to form LXXX and subsequent methanolysis, scheme 1.16.9.



Scheme 1.16.9

The formation of methyl 12,13-epoxy-9-methoxy-trans-10-octadecenoate (LXXXI) would be expected but no evidence was given for its presence.

The hydroxy and methoxy compounds result from solvolysis of the parent epoxides, although the formation of the 9-methoxy compounds suggest the intermediacy of LXXXI.

Thus there appears to be two routes for crosslinking on the acid catalysed drying of alkyd resins, (i) the Hock rearrangement of hydroperoxides and (ii) intramolecular rearrangement of the hydroperoxides into epoxides, with the accompanying addition by an alcohol.

1.17 Photoinitiated autoxidation and crosslinking reactions

The absorption of energy by organic compounds in the visible and ultraviolet region of the spectrum involves the promotion of electrons from their ground state occupation of σ, π and n orbitals to higher states. In the case of carbonyl compounds, the transitions requiring the lowest absorptions of energy correspond to eitheran n-electron being transferred to the π-antibonding orbital (π^*) or a π-electron being transferred to the π^* orbital. These are referred to as $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions respectively and the former usually has the lowest energy and therefore corresponds to absorption at longer wavelengths. Normally ground state electrons are paired and this is termed the 'singlet state'. When an electronic transition occurs the spin of the electron is conserved and the initial photoexcited state is also a singlet. This species is very short lived (about 10^{-8} secs) and usually the spin of the promoted electron is reversed by a process known as intersystem crossing giving a 'triplet state'. From Hund's rules this state is lower in energy and longer lived (10^{-4} secs). It is from this state that most of the subsequent photochemistry occurs.

With aliphatic ketones we are normally concerned with an $n \rightarrow \pi^*$ transition. An electron previously wholly associated with the oxygen atom becomes excited to an antibonding orbital and associated with both nuclei. The oxygen atom is then electron deficient and there are radical centres at both the carbon and oxygen atoms. With the $\pi \rightarrow \pi^*$ transition the electron distribution is not so greatly perturbed and the oxygen does not become electron deficient. In aromatic ketones mixing of the two states occurs and excitation energy may be delocalised into the π system and may not be available for reaction at the carbonyl moiety.

Autoxidation of alkenes can be initiated either directly by uv irradiation or by using photo initiators. There are two pathways for photo-sensitized oxidations.[195] In type 1 the sensitiser reacts, after absorption, with the substrate (A) to form intermediates which then in turn react with ground state (triplet) oxygen to yield the oxidation products. In type 2 photo-sensitised oxidation, molecular oxygen rather than the substrate is the species which reacts with the sensitiser after light absorption. In both cases more than one intermediate may be involved, scheme 1.17.1.

Type 1

$$\text{Sens} \xrightarrow{h\nu} \text{Sens}^*$$
$$\text{Sens}^* + \text{A} \longrightarrow \text{intermediates}$$
$$\text{intermediates} + O_2 \longrightarrow \text{Products} + \text{Sens.}$$

Type 2

$$\text{Sens}^* + O_2 \longrightarrow \text{intermediates}$$
$$\text{intermediates} + \text{A} \longrightarrow \text{Products} + \text{sens.}$$

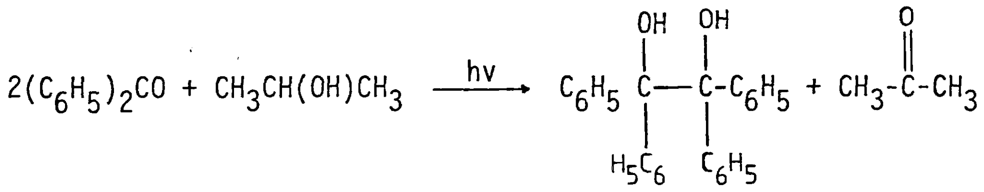
Scheme 1.17.1

In the case of type 2 photo-sensitized oxidation, singlet oxygen is generally regarded as the reactive species responsible for oxygenation of the substrate. Here the reaction is between singlet oxygen and olefinic bonds, and does not involve conjugated free radicals, but proceeds via a spin-allowed addition i.e. the ene-reaction.[196] This is a concerted reaction in which the oxygen molecule is inserted at either carbon atom of the carbon-carbon double bond which shifts to yield an allylic hydroperoxide. An example of "type 1" mechanism is the riboflavin photo-sensitized autoxidation of methyl linoleate, which yields the same isomeric hydroperoxides as autoxidation i.e. the 9 and 13 conjugated diene hydroperoxides. The formation of a diene radical is thus suggested. The riboflavin sensitised autoxidation of methyl oleate gave the 8,9,10 and 11 isomeric allylic hydroperoxides and methyl linolenate the expected 9,12,13 and 16 conjugated diene hydroperoxides.[197]

However erythrosine sensitized autoxidation on the other hand is an example of the 'type 2' mechanism which involves singlet oxygen as the oxygenating species. Methyl oleate oxidation gave rise to a mixture of only the 9 and 10 positional hydroperoxide isomers. The methyl linolenate oxidation gave the 9,12,13 and 16 conjugated diene hydroperoxides along with hydroperoxide groups at the 10 and 15 positions.[197]

The photo-initiator system patented by ICI[198] uses the combination of a ketone, and a reducing agent that is capable of reducing the photo excited state of the ketone. The ketones covered include aliphatic, benzenoid and non-benzenoid aromatic, alicyclic and mixed mono and poly ketones. The reducing agents which have been shown to have activity include both aliphatic and aromatic amines, phosphines, thioureas and sulphinates. The most useful system for drying unsaturated polyesters (alkyd resins) was reported to be the combination of benzil and a tertiary aliphatic amine. More recently ICI discovered that the drying of alkyd resins can be initiated using benzil alone and in daylight.[171]

The electrophilic nature of the $n\rightarrow\pi^*$ photo-excited state of carbonyl containing compounds is reactive towards hydrogen abstraction. The photoreduction of ketones in solution has been the subject of many investigations [199] and can be illustrated by the photoreduction of benzophenone in 2-propanol to give a quantitative yield of benzopinacol and acetone (equation 1.17.2). The photoreduction is

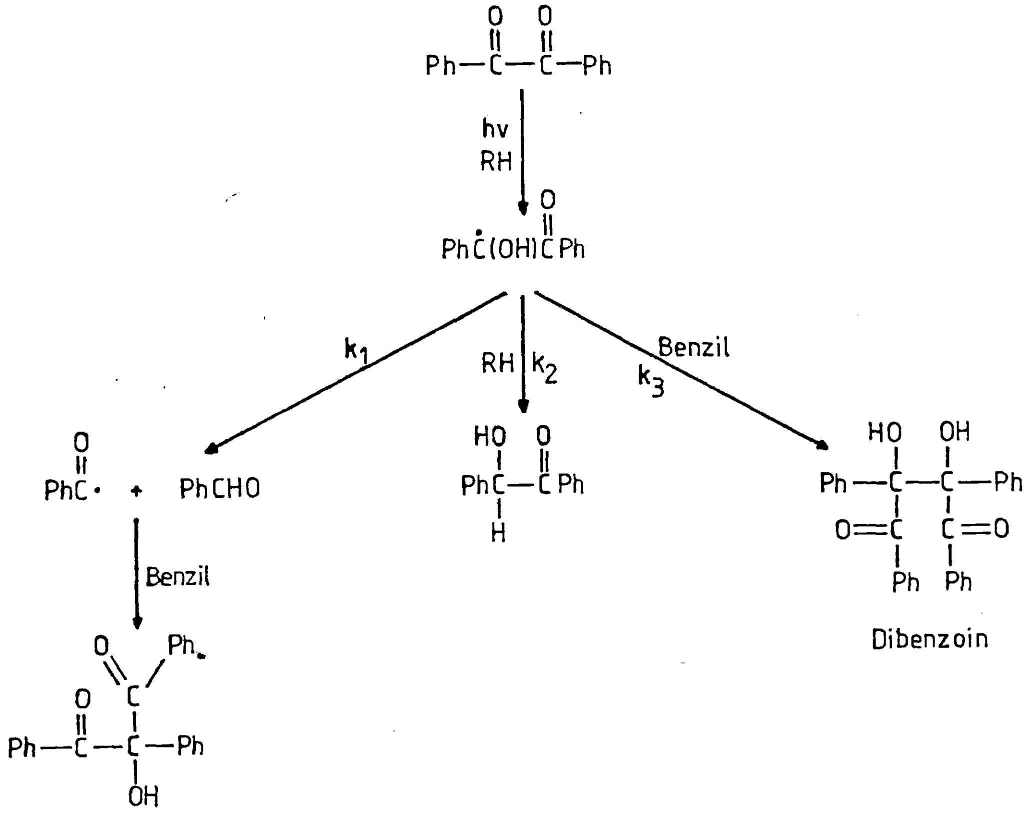


$$2(C_6H_5)_2CO + CH_3CH(OH)CH_3 \xrightarrow{h\nu} C_6H_5\,\overset{OH}{\underset{H_5C_6}{C}}-\overset{OH}{\underset{C_6H_5}{C}}-C_6H_5 + CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Equation 1.17.2

believed to occur by hydrogen abstraction by the ketone triplet from the carbinol carbon.

The photochemistry of the diketone benzil has been studied.[200] The resemblance between the absorption spectra of benzil and benzaldehyde suggest a similarity both in their ground states and in their first excited singlet states. Benzil in its ground state has its individual benzoyl groups planar but generally these lie at approximately 90° to each other. There is little configurational interaction between the two halves of the molecule in the ground state and the n $\longrightarrow \pi^*$ absorption takes place in individual carbonyl groups. The energy of the triplet state, which is formed with nearly 100% efficiency is however decreased by a strong interaction between the two carbonyl groups. The photoreduction of benzil by 2-propanol does however occur and the reaction is believed to be represented by scheme 1.17.3.[201]



Scheme 1.17.3

The hydrogen abstraction[202] by benzil from cyclohexane has also been reported, again the abstraction is thought to take place by the ketone triplet.

It is believed[203] that benzil in its triplet state abstracts a methylenic hydrogen from unsaturated fatty acids and this production of radicals provides a means for the crosslinking of alkyd resins. Hence benzil would appear to act by a type I mechanism. Benzil is used at a level of 1% w/w on the resin. Hydroperoxide formation is observed during resin drying suggesting that oxygen reacts with the radicals resulting from the hydrogen abstraction process. It is doubted that these peroxides contribute signficantly to the drying process. This is evidenced by the fact that if peroxy and alkoxyl radical scavengers, such as t-butyl catechol, are added to a resin, the rate of drying is reduced only slightly. However if an effective alkyl radical scavenger, such as galvinoxyl or diphenylpicryl hydrazyl, is added, then the rate of drying is substantially retarded.[203] The addition of hydroperoxides, for example cumene hydroperoxide, to the resin also had no effect on the rate.[203]

Armstrong[203] reported that benzil will decompose hydroperoxides in its excited state and in the absence of oxygen, however no experimental evidence or references were quoted. Fluorenone decomposes hydroperoxides via a ketyl-radical mechanism but did not photo-sensitise the decomposition of acyl peroxides.[204,205]

2. Results and Discussion

2.1 Autoxidation of methyl cis-9-octadecenoate

The volatile degradation products formed during the autoxidation of methyl oleate were collected in a cold trap. They were analysed by both packed column and capillary column glc. After having determined the conditions for good chromatographic separations, the products were identified by gc-ms. Carbonylic volatile compounds collected by the chemical trap were analysed by HPLC. The retention times and their 2,4-dinitrophenylhydrazine derivatives were compared to those of standard samples.

2.1.1 Autoxidation promoted by Cobalt(II) bis(2-ethyl hexanoate) and lead(II) bis(2-ethyl hexanoate)

2.1.1.1 Determination of volatile products by gc-ms

The total ion current chromatogram obtained from the capillary gc-ms analysis is shown in figure 2.1.1.1.1 with the spectra being obtained at the apex of each chromatographic peak. The relative abundances of ions were expressed as percentages of the base peak in each spectrum.

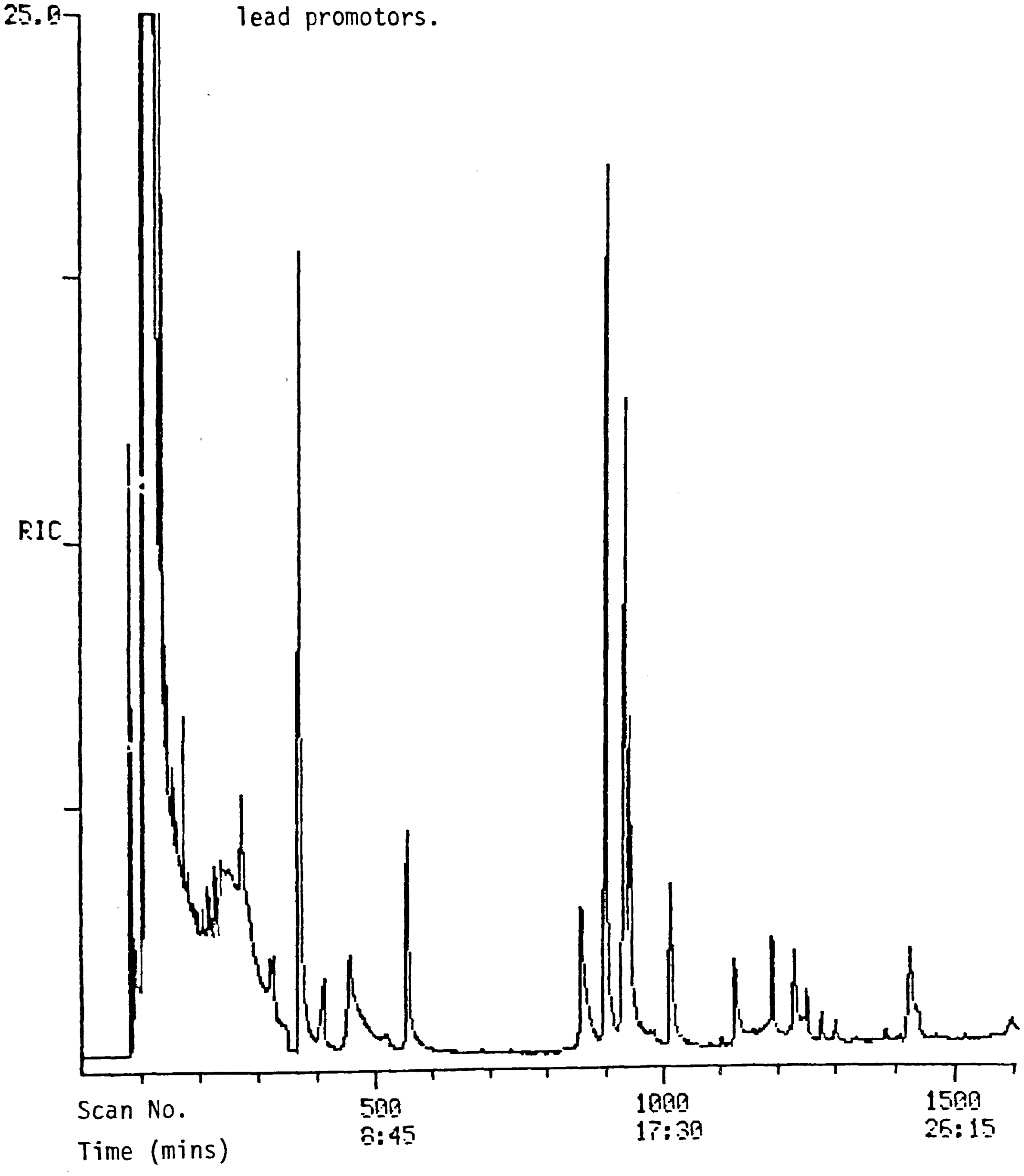
Scan No.135

m/z	70	55	42	40	39	38	30	27
Rel AB %	36	42	100	13	40	8	13	32

The largest relative molecular mass and the retention time of the compound suggests a hydrocarbon of formula C_5H_{10}.

Figure 2.1.1.1.1.

Capillary total ion current chromatogram of the volatile products from the autoxidation of methyl oleate in the presence of cobalt and lead promotors.

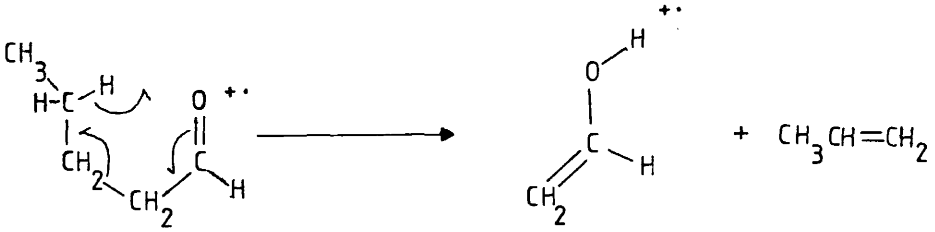


2-Pentene has a base peak at m/z 55 and is therefore ruled out. Two other possibilities exist, viz. cyclopentane and 1-pentene both of which have a base peak at m/z 42. Owing to their very similar fragmentation patterns no distinction can be made.

Scan No. 272

m/z	86	68	58	57	45	44	43	42	41	38	29	27
Rel AB %	1.4	1.4	28	22	11	100	26	14	50	26	99	75

A base peak at m/z 44 is characteristic of straight chain aldehydes (C_4 - C_7); this ion arises from a McLafferty rearrangement of the parent ion, (equation 2.1.1.1.1).



Equation 2.1.1.1.1

The loss of water (M-18) and ethene (M-28) also provides evidence for the aldehyde structure. Comparison with standard spectra[206] confirmed this compound as pentanal.

Scan No. 370

m/z	46	45	44	29
Rel AB %	93	89	23	100

The molecular ion m/z 46 can arise from methoxy methane, ethanol or methanoic acid. The loss of 17 daltons from the molecular ion suggests the presence of a hydroxyl group. Thus methoxy methane is ruled out and since ethanol gives a base peak at m/z 31, it appears that this compound is methanoic acid. Comparison with the standard spectrum^{206} gave a fairly good match.

Scan No. 415

m/z	60	45	44	43	42	41	31	29
Rel AB%	37	80	6.8	100	19	4.7	7.4	23

The losses of 15 and 17 daltons from the molecular ion indicate the presence of a methyl and a hydroxyl group respectively.

Possible molecular formulae are C_3H_8O and $C_2H_4O_2$. Alcohols corresponding to C_3H_8O are not applicable because the base peak for 1- and 2-propanol are at m/z 31 and m/z 45. However ethanoic acid ($C_2H_4O_2$) is therefore the most probable compound and comparison with its standard spectrum^{206} gave a fairly good match.

Scan No. 458

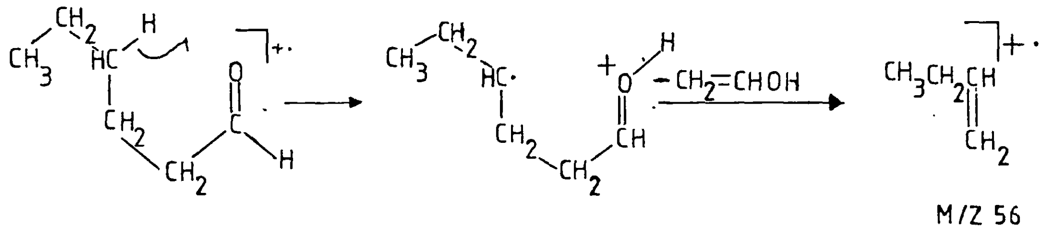
m/z	88	70	51	56	55	45	44	43	42	41	40	39	31	29	27
Rel AB	0.2	29	14	10	60	5	7	25	100	79	6.8	31	80	86	67

Here the loss of 18 daltons from the molecular ion suggests a hydroxy group in the compound. The loss of 33 daltons (CH_5O), an ion at m/z 31 of high abundance and the presence of an ion m/z 45 also suggest an oxygen containing compound. Taking M_r = 88 the molecular formula is $C_5H_{12}O$. There is no unsaturation present and the evidence indicates an alcohol. 1-, 2- and 3-pentanols have base peak ions at m/z 42, 45 and 59 respectively. Comparison with the standard spectrum of 1-pentanol[206] gave excellent agreement. It is therefore concluded that this compound is 1-pentanol.

Scan No. 558

m/z	100	82	72	71	69	67	58	57	56	55	45	44	43	42	41	40	39	29
Rel AB %	0.3	7.5	10.6	4	0.7	6.8	5.6	35	50	14	16	100	58	17.4	88	7.	44	88

The base peak at m/z 44, an ion corresponding to loss of 18 daltons from the molecular ion and an abundant ion (88% of base peak) at m/z 29 suggests a straight chain aldehyde. The presence of an ion at m/z 56 which results from a McLafferty-type rearrangement Scheme 2.1.1.1.2 indicates again the aldehyde structure. A comparison of this spectrum with the standard spectrum of hexanal[206] confirms this assignment.

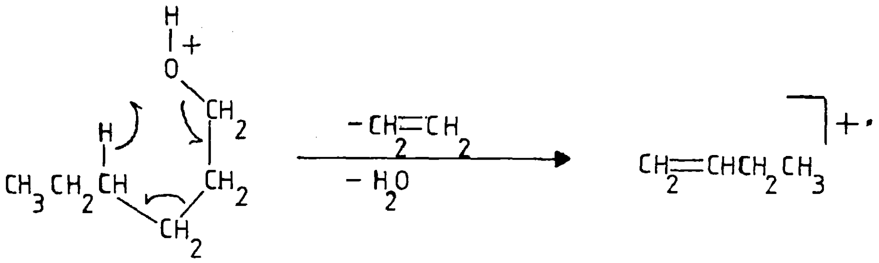


Scheme 2.1.1.1.2

Scan No. 857

m/z	102	84	70	69	57	56	55	54	53	44	43	42	41	40	39	31	29	27
Rel AB %	0.8	4	2	29	9	100	59	4	4	9	84	64	85	7.3	43	81	77	85

The presence of ions resulting from (M-18), (M-33) and the ion m/z 31 (CH_2OH^+) indicates an oxygen-containing molecule.
The base peak at m/z 56 can result from the loss of water and ethene from the parent ion (equation 2.1.1.1.3).



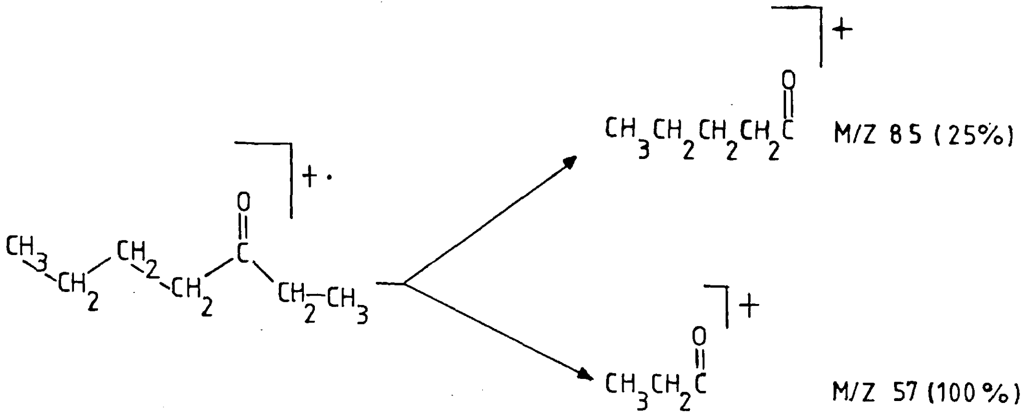
Equation 2.1.1.1.3

This suggests again a primary alcohol structure and comparison with the standard spectrum of 1-hexanol[206] confirmed this assignment.

Scan No. 903

m/z	114	85	72	58	57	55	43	42	41	39	29	27
Rel AB %	8	25	19	4.7	100	5.3	19	8	48	18	72	53.3

Loss corresponding to the loss of 29 and 57 daltons from the molecular ion suggests the presence of CH_3CH_2- and $CH_3CH_2CH_2CH_2$- respectively and the rearrangement ion at m/z 72, suggests an oxygen-containing ion. These types of fragmentation suggest a ketone structure with the larger alkyl group being eliminated preferentially over the smaller group, (Scheme 2.1.1.1.4).



Scheme 2.1.1.1.4

3-Heptanone was confirmed by comparison with its standard spectrum.[206]

Scan No. 936

m/z	116	98	87	70	69	59	58	57	56	55	45	44	43	42	41	39	31	29	27
Rel AB %	0.4	3	24	4	73	100	11	20	4	8	12	7	25	7	81	21	69	61	63

The expulsion of water from the molecular ion coupled with a base peak at m/z 59 tends to indicate a secondary alcohol. The loss of 29 daltons from the parent ion implicates the presence of at least a CH_3CH_2 group and while the loss of 57 daltons to form the base peak ion indicates the presence of $CH_3CH_2CH_2CH_2$-. 3-Heptanol was confirmed[206] as the compound present.

Scan No. 944

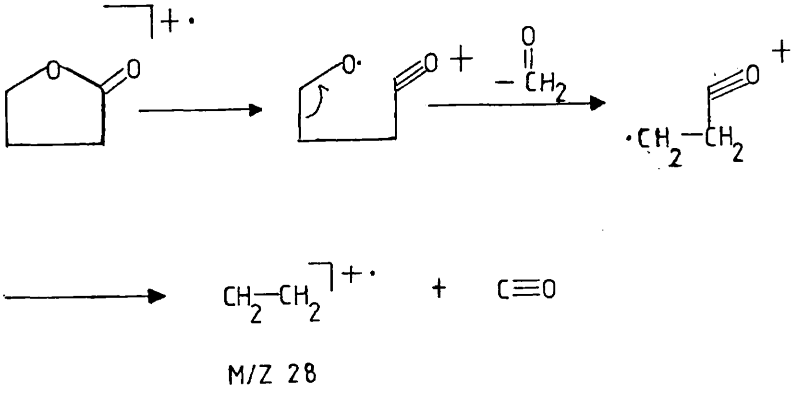
m/z	114	96	86	85	81	72	71	70	68	67	57	56	55	54	53	45	44	43	42	41	39	29	27
Rel AB %	0.2	46	7	2	11	5	12	42	9	6	28	4	35	5	4.3	1.3	100	67	48	84	44	82	78

The base peak at m/z 44, an abundant ion at m/z 29 (82%) together with the loss of 18 daltons from the molecular ion and the presence of the rearrangement ion peak m/z 70 point to an aldehyde of the formula $C_7H_{14}O$. Comparison with the standard spectrum of heptanal[206] confirms this assignment.

Scan No. 1014

m/z	86	85	57	56	55	43	42	41	40	39	29	28	27
Rel AB %	8.7	6.0	6.7	11	5	4	73	42	12	17.5	72	100	59

An ion of m/z 86 could be formed from the compound having molecular formulae C_6H_{14}, $C_5H_{10}O$, $C_4H_6O_2$ and $C_3H_2O_3$. The retention time of the compound suggested a fairly polar species and on this basis those molecules corresponding to C_6H_{14} or $C_5H_{10}O$ were considered less likely. The base peak at m/z 28 probably results from $C_2H_4^{+\cdot}$ formation. 2(3H) Dihydrofuranone has m/z 28 as its base peak, (Scheme 2.1.1.1.5). Comparison with the standard spectrum of 2(3H) dihydrofuranone[206] gave excellent agreement with scan 1014.



Scheme 2.1.1.1.5

Scan No. 1126

m/z	98	83	70	69	68	57	56	55	45	44	43	42	41	40	39	31	29	27
Rel AB %	1.9	4.9	57	31	9	16	60	54	4	7	65	49	100	6.5	33.5	66	72	76

A computer search of the spectra library for this spectrum produced heptyl methanoate as the best fit. The molecular ion (m/z 156) of this compound is also absent in the standard spectrum[206] and the match between them is very good.

Scan No. 1191

m/z	128	110	100	94	85	84	82	81	69	68	67	57	56	55	45	44	43	42	41
Rel AB %	.1	2.5	4	3	6	19	10	10.2	10	11	11	37	34	33	12	51	74	35	92

m/z	39	29	27
RelAB%	45	100	93

The molecular ion loses water, so together with the large abundances of the ions m/z 44 and 29, an aldehydic structure is likely. Octanal has $M_r = 128$. The expected base peak of m/z 44 is not seen, the base peak of 1-octanal is at m/z 43. Although the base peak obtained here was at m/z 29 this spectrum is still interpreted as being octanal.

The lower mass ions are of higher intensity than expected, probably owing to the start of the recording of the spectrum being just after the apex of the total ion current peak. The higher mass ions were consequently recorded at a lower source concentration.

Scan No. 1250

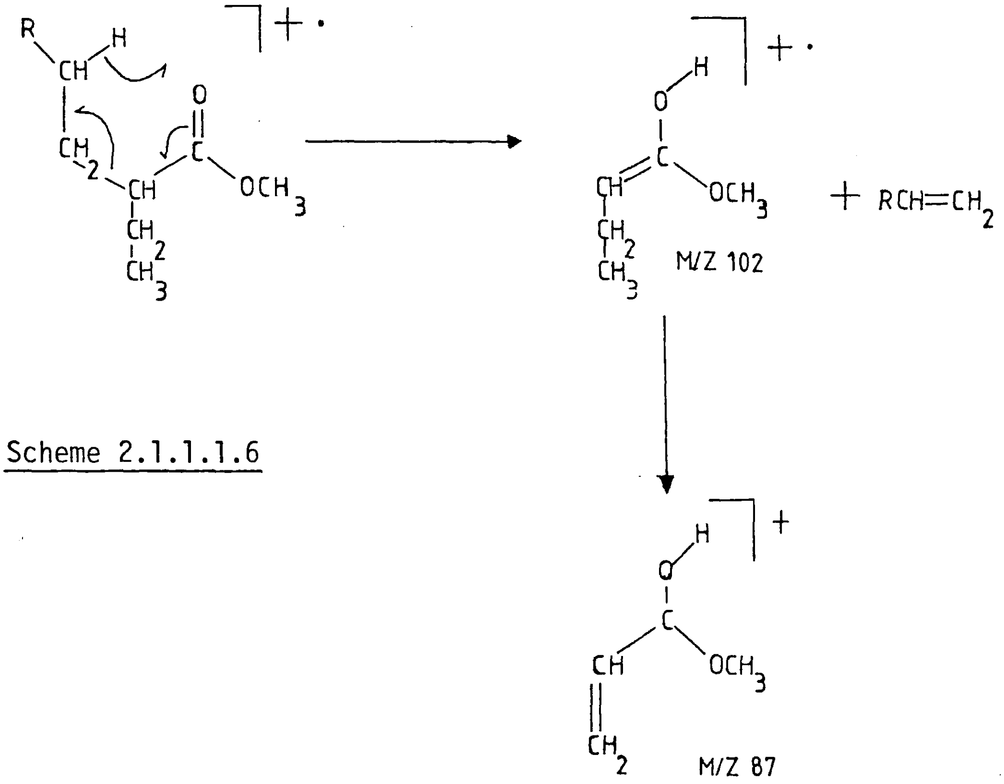
m/z	128	113	99	85	71	57	43	42	39	29	27
Rel AB %	0.6	0.6	43	2	13	14	100	7.5	6	53	44

The losses of neutral fragments of 29 and 71 daltons from the molecular ion shows the presence of CH_3CH_2- and C_5H_{11}-. Compositions of the ion m/z 43 can be CH_3CO^+ or $C_3H_7^+$. Similarly the neutral fragments of 57 daltons lost from the molecular ion can be either $CH_3CH_2\overset{O}{\overset{\|}{C}}$ or C_4H_9. The retention time of this compound dictates against the hydrocarbon structures. Octanal ($C_8H_{16}O$) was identified earlier in the chromatogram hence ketone isomers have to be considered. Neither 2- or 4-octanones give an ion corresponding to m/z 99 whereas 3-octanone does. The standard spectrum of 3-octanone[206] confirms this assignment.

Scan No. 1275

m/z	158	143	130	129	127	115	102	101	87	73	69	59	57	55	45	43	42	41	39	29	27
Rel AB %	0.3	0.7	9.3	7	53	8	69	16	100	12	14	21	65	52	73	35	16	82	36	83	68

Ions (M-15), (M-30) and (M-31) suggest a methyl ester. However base peaks for straight chain methyl esters occur at m/z 74 resulting from a McLafferty rearrangement. However if the ester is also branched at the α-position then the rearrangement ion is altered, e.g. if the α-side chain is an ethyl group then the expected rearrangement ion is m/z 102, (Scheme 2.1.1.1.6).



Scheme 2.1.1.1.6

The subsequent loss of a methyl group gives the base peak at m/z 87. Confirmation of this fragmentation was provided by the observation of a peak at m/z 74.3, resulting from the fragmentation of metastable ions at m/z 102.

From the relative abundance of the(M+1) ion, arising from heavy isotopes, the presence of nine carbons was indicated i.e. $C_9H_{18}O_2$.

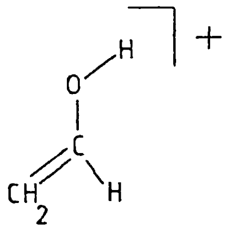
Comparison with the standard spectrum of methyl 2-ethyl hexanoate[206] confirmed this as the compound produced.

Scan No. 1386

m/z	142	113	98	96	95	82	81	70	69	68	67	57	56	55
Rel AB%	0.2	2.6	12	6	6.7	12	11.3	13.3	13.7	11.7	12	44.5	34.5	31.5

m/z	44	43	42	41	39	29
Rel AB%	36	50	25	78	33	100

The tentative assignment of this compound as nonanal is based on the molecular ion at m/z 142. The ion of m/z 44 can result from a McLafferty rearrangement of the parent ion to give



However the base peak in the 70 eV electron impact mass spectrum of nonanal is m/z 57, whereas in this spectrum m/z 57 is only 44.5% of the base peak (m/z 29). A computer search using the database at P.C.M.U. Harwell gave nonanal as the compound of best fit.

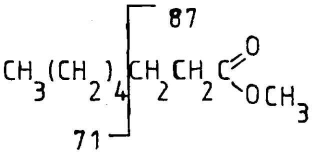
The packed column gc-ms analysis of the volatile compounds provided evidence for two compounds in addition to those analysed above.

m/z	158	127	115	87	83	74	59	57	55	43	42	41	39	29	27
Rel AB	1.0	11	7	36.1	10	100	13	17.5	24	25	9	27	11	17	15.3

The base peak m/z 74 eliminates the possibility of a straight chain aldehyde, carboxylic acid or ketone. A base peak at m/z 74 is characteristic of methyl esters and carboxylic acids with a methyl on the β-carbon atom and results from McLafferty rearrangements.

The loss of 31 daltons (OCH_3) from the parent ion and the absence of ions corresponding to M-17, M-18 and m/z 45 (CO_2H^+) supports the methyl ester structure.

The fragmentation giving m/z 87 from the parent ion could result from a simple fragmentation (as below). Comparison with the



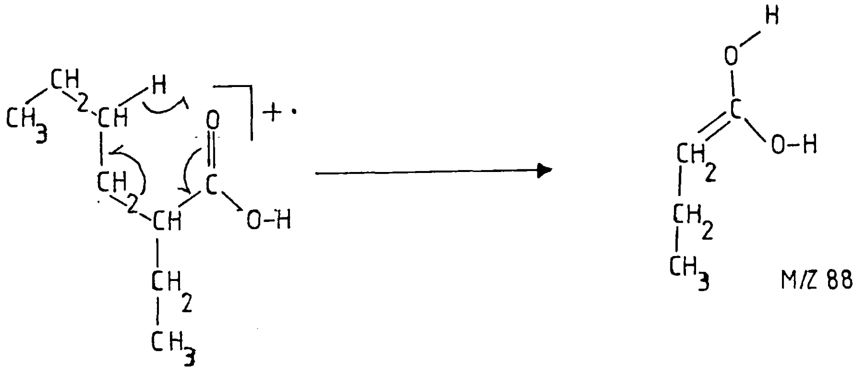
$$CH_3(CH_2)_4CH_2CH_2C(=O)OCH_3$$

standard spectrum of methyl octanoate[206] confirmed the analysis.

m/z	144	127	116	115	101	88	87	73	60	57	55	45	43	41
Rel AB	2.0	3.0	17.2	11.9	17.0	100.0	21	87	10	35	17.0	9.7	21.1	29.0

The base peak at m/z 88 must result from a rearrangement process. The relative molecular mass of ethylhexanoic acid is 144.

A Mclafferty rearrangement of the 2-ethylhexanoic acid molecular ion would result in the formation of an ion m/z 88. Equation 2.1.1.1.7.



Equation 2.1.1.1.7

A subsequent fragmentation with the loss of a methyl group resulting in an ion m/z 73 is confirmed by the presence of an ion at m/z 60.6 arising from metastable decomposition.

The presence of an ion having m/z 45 together with an ion corresponding to M -17 confirms the acid structure. It was concluded,after comparison with the standard spectrum[206], that the compound was 2-ethyl hexanoic acid.

The compounds identified by gc-ms from the autoxidation of methyl oleate are summarised in table 14.

Table 14

Volatile products formed during the autoxidation of methyl oleate in the presence of cobalt and lead promotors

Compound	% composition determined on freshly autoxidised ester
3-Heptanone	18.7
3-Octanone	
2(3H) Dihydrofuranone	2.7
Pentanal	
Hexanal	1.8
Heptanal	20.0
Octanal	14.1
Nonanal	4.2
1-Pentanol	
1-Hexanol	
3-Heptanol	1.3
Methyl-2-ethylhexanoate	20.4
Methyl octanoate	3.1
Heptyl formate	
Formic acid	
Acetic acid	
2-Ethyl hexanoic acid	1.3

The total amount of volatile material collected in the cold trap, from 5 g of methyl oleate, autoxidised under the standard conditions (Section 3.4.5), was determined to be 1.1 x 10^{-3}g (using dodecanal as the internal standard).

2.1.1.2 Determination of volatile products by HPLC

The volatile products trapped as their 2,4-dinitrophenylhydrazones were identified by HPLC. The retention times of the standard 2,4-dinitrophenylhydrazones, using conditions set out in Section 3.5.3.3., are given in table 15.

Table 15

Retention times of standard 2,4 DNPH derivatives

2,4-dinitrophenylhydrazone derivative	Retention Time (Minutes)
Methanal	6.6
Ethanal	9.4
Propanone	12.0
Propanal	12.4
Methyl vinyl ketone	15.0
Methyl ethyl ketone	16.2
2-Butenal	16.6
Butanal	17.4
3-Penten-2-one	18.6
Diethyl ketone	19.8
Pentanal	20.8
Hexanal	24.6

The retention times of the compounds collected in the chemical trap are given in table 16 along with their assignments.

Table 16

Retention time (minutes)	Compound assigned
9.5	Ethanal
12.4	Propanal
17.2	Butanal
20.0	Diethyl ketone

2.1.2 Autoxidation promoted by cobalt (II) bis(2-ethyl hexanoate) and aluminium bis(2-butoxide) ethyl acetoacetate

2.1.2.1 Determination of volatile products by gc-ms

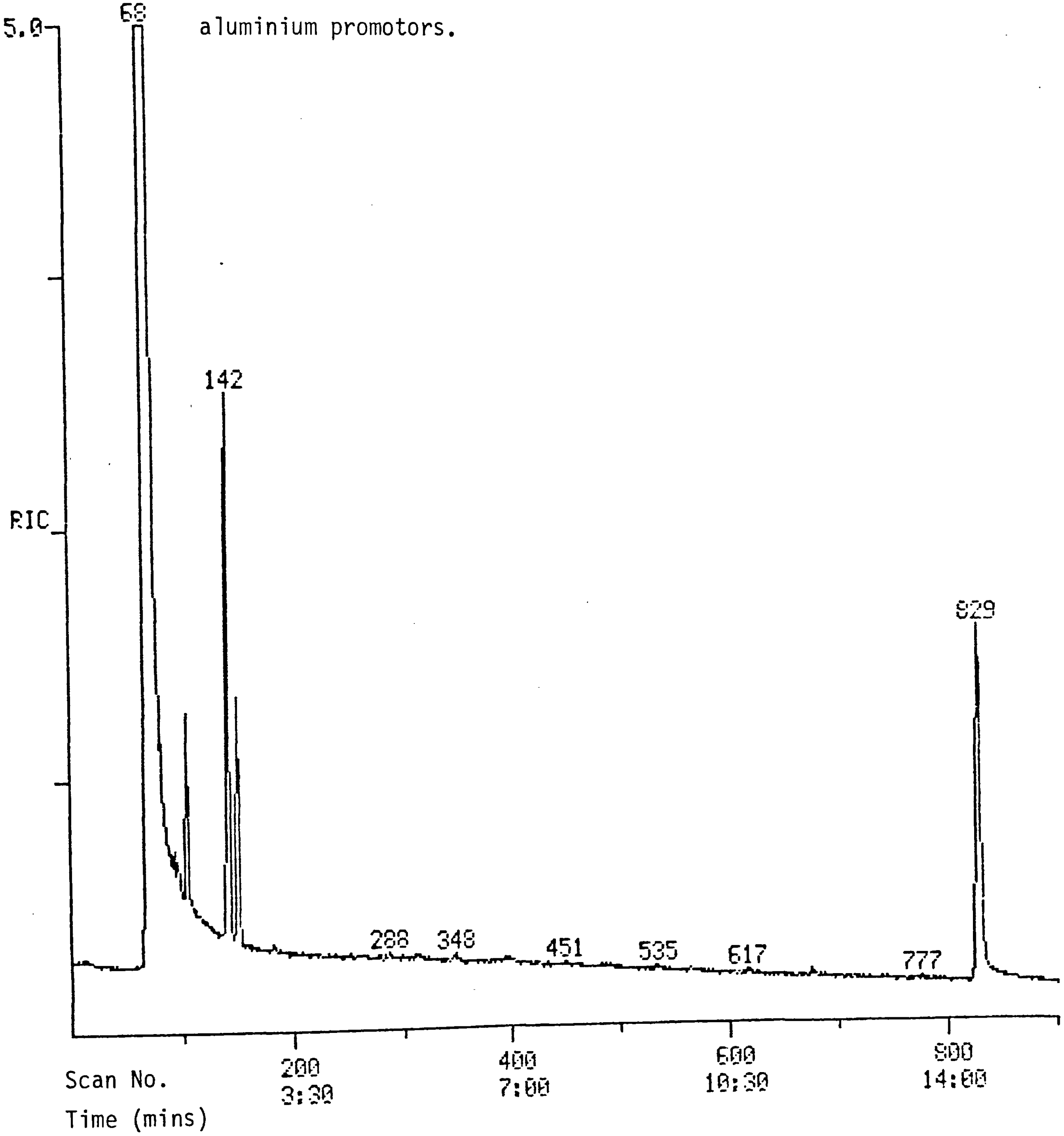
The total ion current chromatogram obtained from the capillary gc-ms analysis is shown in diagram 2.1.2.1.1. Again the spectra used for analysis were obtained at the apex of the chromatographic peak.

Scan No. 106

m/z	46	45	43	41	31	30	29	27	26
Rel AB %	11	28	8.1	2.5	100	8.0	35	30	16

Figure 2.1.2.1.1

Capillary total ion current chromatogram of the volatile products from the autoxidation of methyl oleate in the presence of cobalt and aluminium promotors.



The base peak at m/z 31 (CH_2OH^+) suggests a primary alcohol. The relative molecular mass of this compound is 46 daltons and comparison with the standard spectrum[206] of ethanol confirmed this in the chromatogram.

Scan No. 142

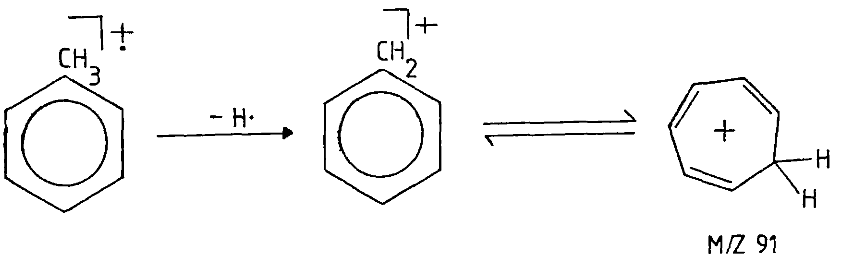
m/z	74	73	60	59	57	55	46	45	44	43	42	41	39	31	29	27	26
Rel AB %	0.6	1.2	0.6	18	3.7	3.1	2.5	100	11	18.6	4	19	8	32	34	37	10

The base peak of m/z 45 could result from a secondary alcohol. The molecular formulae possible for this compound are $C_4H_{10}O$, $C_3H_6O_2$ and $C_2H_2O_3$. The loss of 15 daltons (CH_3) from the molecular ion rules out any compound with the formula $C_2H_2O_2$ the base peak of propanoic acid ($C_3H_6O_2$) is at m/z 28 thus leaving only $C_4H_{10}O$ to be considered. Comparison with standard spectra[206] confirmed 2-butanol.

Scan No. 151

m/z	92	91	65	63	62	61	51	50	45	39	38	37	27	26
Rel AB %	58	100	17	15	6.8	4	15	12	5	34	9.3	4.9	11	5.6

The loss of a proton from the molecular ion to give the base peak at m/z 91 is indicative of toluene which was easily confirmed, (Scheme 2.1.2.1).



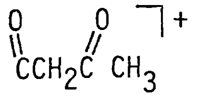
Scheme 2.1.2.1

Scan No. 829

m/z	130	115	102	88	87	85	84	73	69	61	60	58	45	43	42	31
Rel AB %	4	1.2	3	10	3.7	10	1.8	1.2	6	3	7.5	2	5	100	24	6.2

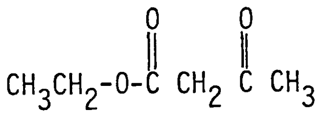
m/z	29	27	26
Rel AB %	4.2	34	11

The base peak at m/z 43 can arise from the following ions, $C_3H_7^+$ or $C_2H_3O^+$ and the ions at m/z 45 and m/z 31 suggest the presence of oxygen in this molecule. Thus the base peak ion appears to be $C_2H_3O^+$. Analysis of the (M+1) heavy isotope ion suggested $C_6H_{10}O_3$ as the molecular formula. The ions of m/z 85 and 86 can be explained by the elimination of CH_3CH_2O and CH_3CHO. The ion at m/z 85 may have the structure



$$\left[\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}\,CH_3\right]^+$$

. Thus piecing these fragments together suggests a structure LXXXII



$$CH_3CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\,CH_2\,\overset{O}{\overset{\|}{C}}\,CH_3$$

Ethyl acetoacetate LXXXII

Comparison with the standard spectrum of ethylacetoacetate[206] confirms this assignment.

The volatile compounds identified by gc-ms from this autoxidation experiments are summarised in table 17.

Table 17

Volatile compounds detected from the autoxidation of methyl oleate in the presence of cobalt and aluminium promotors

Compound	% composition
Ethanol	11.3
2-butanol	47.4
Ethyl acetoacetate	39.6

The total quantity of these compounds produced under the standard conditions is 1.7×10^{-2} g, based on dodecanal as the internal standard.

2.1.2.2 Determination of volatile products by HPLC

In the analysis of the compounds retained by the chemical trap great difficulty was encountered in detecting any carbonyl compounds. However at high sensitivity settings two compounds could be detected (Table 18).

Table 18

Retention time (minutes)	Compound assigned
9.4	Ethanal
12.4	Propanal

2.1.3 Autoxidation promoted by Benzil

2.1.3.1 Determination of volatile products by gc-ms

The total ion current chromatogram obtained from the capillary gc-ms study of these volatiles closely resembles that obtained in section 2.1.1.1 (figure 2.1.1.1.1). The differences that occur are the absence of a peak at scan No.1275 (methyl-2-ethyl hexanoate) and the formation of a new compound at scan No. 892.

Scan No. 892

m/z	106	105	78	77	74	52	51	50	39	38	37	29	27
Rel AB %	71	83	19	100	10	19	72	45	10.1	12	9.3	13	6

The base peak at m/z 77 represents a loss of either CH_3CH_2 or CHO from the molecular ion. The high abundance of an ion corresponding to (M-1) indicates a labile hydrogen. The molecular formula was established, again from the heavy isotope ratio (M+1)/M, to be C_7H_6O suggesting the compound to be aromatic. The ion m/z 77 probably represents $C_6H_5^+$. Thus this compound appears to be benzaldehyde. This was confirmed by comparison with its standard spectrum.[206]

The packed column gc-ms analysis confirmed the similarity of the products with the absence of both methyl-2-ethylhexanoate and 2-ethylhexanoic acid. Table 19 lists the volatile compounds determined.

Table 19

Volatile compounds detected from the autoxidation of methyl oleate in the presence of benzil

Compound	% composition
3- Heptanone	26.1
2(3H) Dihydrofuranone	3.4
Hexanal	2.5
Heptanal	27.4
Octanal	18.5
Nonanal	3.2
Benzaldehyde	9.6
1-Hexanol	-
3-Heptanol	1.7
Methyl octanoate	4.2

The total amount of volatile material produced was 0.26 x 10^{-4} g, based on dodecanal as the internal standard, from 5 g methyl oleate autoxidised under the standard conditions section 2.4.5.

2.1.3.2 Determination of volatile products by HPLC

The analysis of the 2,4-dinitrophenylhydrazones obtained from the chemical trap are summarised in table 20.

Table 20

Rentention time (minutes)	Compound assigned
6.5	Methanal
9.5	Ethanal
12.1	Propanone

2.1.4 Mechanistic interpretation

The formation of carbonyl compounds during the autoxidation of olefins was reported as early as 1913 by Willstatter[208] who observed the formation of cyclohexan-1-ol-2-one in the autoxidation of cyclohexene. The formation of ketones in the autoxidation of 1-methylcyclohexene, 1,2-dimethylcyclohexene, α-pinene, β-pinene, limonene and tetralin along with the appropriate alcohols were reported by Farmer.[8] He showed that the ketones did not result from direct oxidation of the alcohols, but explained them by mechanisms involving cyclic peroxides.

The volatile products observed in the thermal autoxidation of methyl oleate was reported by Deatherage.[209] The volatile products were collected in a dry ice trap and consisted of water and water soluble substances along with a water phobic fraction. Swift[210] reported the identification of 2-undecenal from the thermal decomposition of methyl oleate hydroperoxides. He proved this by isolating its 2,4-dinitrophenylhydrazone and semicarbazone derivatives from the decomposition mixture. Fritsch and Deatherage[211] extended their earlier study and identified methanoic and ethanoic acid along with traces of propionic and higher carboxylic acids in the volatile products. Tai[212] and his co-workers studied the volatile decomposition products from methyl oleate resulting from open air heating at 200^{o}C. They showed,based upon glc retention times, the presence of C_8 and C_9 aldehydes, methyl oxo esters, C_7 and C_8 hydrocarbons, methyl esters of fatty acids, several fatty acids, mono-methyl esters of dibasic acids and some alcohols. Withycombe[213] studied the volatiles from the autoxidation of methyl oleate, by trapping them on anthracene crystals coated with silicone oil and then subsequently analysing by gc-ms. The compounds so identified are given in table 21.

Table 21

Volatile products, identified by gc-ms, from the thermal degradation of methyl oleate

Compounds identified	
Heptane	Methyl octanoate
Octane	2-Decanone
Benzene	Methyl 7-oxoheptanoate
Methyl hexanoate	Methyl 8-oxooctanoate
O-Xylene	Methyl 9-oxononanoate
Methyl heptanoate	

The most complete study of the thermal degradation of methyl oleate hydroperoxides was reported by Frankel[214] who compared the volatile products from autoxidation with those from photosensitised oxidation. The hydroperoxides were decomposed in the injector port of a gas chromatograph and identified by gc-ms. The results they obtained are summarised in table 22.

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 carbon-carbon bond scission to form the 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}.[216]) Evidence that has been collected for the existence of alkoxy radicals, includes the pyrolysis of ether and detection of alkoxy radicals by mass spectrometry.[217]

Table 22

Gc-ms analysis of volatiles from thermally decomposed methyl oleate hydroperoxides

Compound	Autoxidation (rel %)	Photosensitised oxidation (rel %)
Heptane	4.4	4.6
Octane	2.7	10.0
Heptanal	0.5	0.5
1-Heptanol	0.4	0.4
Octanal	11.0	3.8
Methyl heptanoate	1.5	4.9
1-Octanol	0.4	1.0
Nonanal	15.0	10.0
Methyl octanoate	5.0	9.7
2-Nonenal	0.5	0.7
Decanal	3.9	2.0
Methyl nonanoate	1.5	0.8
2-Decenal	5.4	12.0
2-Undecenal	1.7	7.1
Methyl 8-oxooctanoate	3.5	3.0
Methyl 9-oxononanoate	15.0	11.0
Methyl 10-oxodecanoate	12.0	1.7
Methyl 10-oxo-8-decenoate	3.4	5.0
Methyl 11-oxo-9-undecenoate	5.8	4.6

The fluorescence spectra of certain molecules containing alkoxy groups have also been studied.[216] Methyl nitrite, nitrate, and chloroformate all show the same band system (330 - 350 nm). The emitter is probably the methoxyl group. Chemical evidence has been obtained, for example, in the presence of a molecule (H - X) with a weakly attached hydrogen atom. The hydrogen is abstracted by alkoxy radicals and the corresponding alcohols produced. (Scheme 2.1.4.1.). If the alkoxy radical is optically active, then this activity is retained.[218]

$$R - O\cdot + H - X \longrightarrow ROH + X\cdot$$

$$2X\cdot \longrightarrow \text{dimer}$$

Scheme 2.1.4.1

Alkoxy radicals have been observed by electron spin resonance spectroscopy from the irradiation of compounds at low temperatures.[219-223]

Alkoxy radicals cannot be detected in solution by ESR owing to extreme line broadening, although they can often be trapped by $CH_2{:}NO_2^-$ and analysed as the adduct $ROCH_2NO_2^{-}$. Gilbert,[224] using this method, studied the secondary reactions of alkoxy radicals arising from the one electron reduction, by titanium (III) ion, of secondary alkyl hydroperoxides and hydroperoxides of cyclic alkenes typically formed by autoxidation.

The reactions of alkoxy radicals can generally be classified as follows:

1. Bimolecular radical association.
2. Displacement.
3. Rearrangement.
4. Hydrogen abstraction.
5. Addition.
6. Fragmentation.

Reaction types 4,5 and 6 will now be discussed in further detail. Hydrogen abstraction by alkoxy radicals from organic substances is fairly common (equation 2.1.4.2). The tendency

$$R'O\cdot + RH \longrightarrow R'OH + R\cdot$$

Equation 2.1.4.2

for alkoxy radicals to react by hydrogen abstraction is in the general order $CH_3O\cdot > CH_3CH_2O\cdot > (CH_3)_3CO\cdot$; this being based on the decomposition of peroxydicarbonates in solution. However the relative rates of hydrogen abstraction from a series of hydrocarbons appears to be virtually independent of the attacking radical, and whether the reaction is carried out in solution or in the gas phase, although the absolute rates differ,[226] (table 23).

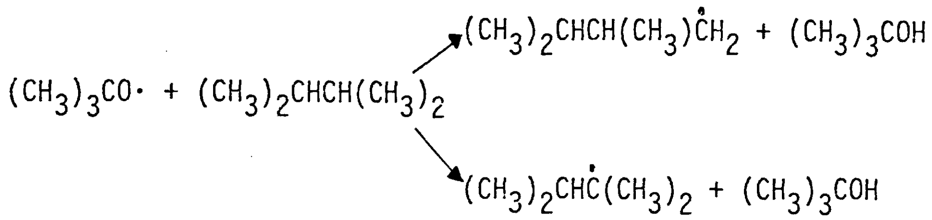
Table 23

Reactivity (average) of C-H bonds to alkoxy radicals at 40°C

	Paraffinic		Benzylic	Allylic*
	$(CH_3)_3CO\cdot$	$CH_3O\cdot$	$(CH_3)_3CO\cdot$	$(CH_3)_3CO\cdot$
Primary	1.0	1.0	10	12(p) 20(s)
Secondary	12.2	14	32	61(p) 93(s)
Tertiary	44	46	69	375 (cyclic) 176(p)

* Letter in parentheses indicates substitution on 3-carbon centre.

The effect of solvents on the reactivity of t-butoxy radicals was observed by the competitive removal of the primary and tertiary hydrogens from 2,3-dimethylbutane,[227] (scheme 2.1.4.2).



$$(CH_3)_3CO\cdot + (CH_3)_2CHCH(CH_3)_2 \begin{array}{l} \nearrow (CH_3)_2CHCH(CH_3)\dot{C}H_2 + (CH_3)_3COH \\ \searrow (CH_3)_2CH\dot{C}(CH_3)_2 + (CH_3)_3COH \end{array}$$

Scheme 2.1.4.2

Walling in this study reported the relative rates and their activation parameters. There is a change in selectivity which parallels approximately the solvent polarity and which may be interpreted in terms of the t-butoxy radicals partially losing their solvation in the transition state for hydrogen abstraction.

As mentioned earlier in this section, alkoxy radicals will add to olefinic bonds. Using the reaction of t-butoxy radicals, derived from t-butyl hypochlorite, with simple alkenes, addition appears to be favoured by a cis configuration and asymmetrical substitution about the double bond.[72]

The structure of the alkene can give rise to different relative rates of addition by the t-butoxy radicals.[228] The rates, at 40°C and quoted in table 24, are relative to the hydrogen abstraction from the methyl group of butane.

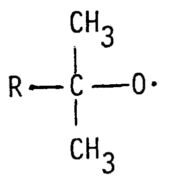
Table 24

Relative rates of addition to alkenes by t-butoxy radical

Olefin	k_{add}(relative)
$PhCH = CH_2$	105.0
cis-$CH_3CH = CHCH_3$	25.9
$(CH_3)_2\ C = CH_2$	14.6
$(CH_3)_2\ CH\ CH = CH_2$	4.7
trans-$CH_3CH = CHCH_3$	4.4
$CH_3CH_2CH = CH_2$	4.2

However the important reaction in this study relates to the β-scission of alkoxy radicals to form carbonyl compounds. The volatile compounds produced by the thermal degradation of oleate hydroperoxides have been proposed to be formed by homolytic cleavage of the hydroperoxide to form alkoxy radicals. The alkoxy radicals then undergo β-scission of carbon-carbon bonds to give volatile carbonyl products. 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.

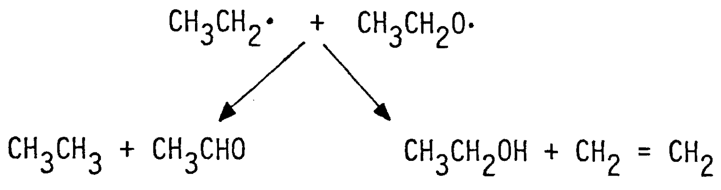
The majority of alkoxy radical studies have been conducted on t-alkyl radicals (LXXXIII).



$$R-\overset{CH_3}{\underset{CH_3}{C}}-O\cdot$$

(LXXXIII)

The rupture of the C_α - H bond of both primary and secondary alkoxy radicals is rarely competitive with the unimolecular fragmentation by scission of the C_α - C_β bond. When it is observed, it has to be distinguished from disproportionation which is a bimolecular process[229] (Scheme 2.1.4.4).



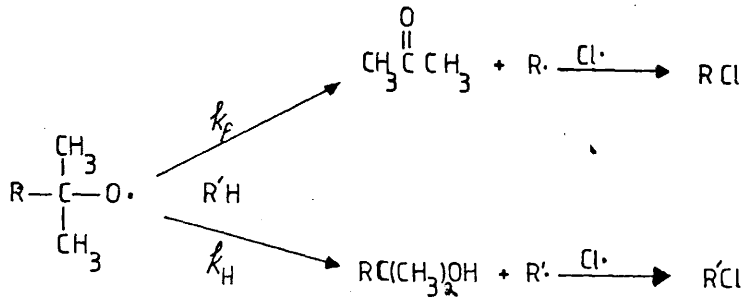
Scheme 2.1.4.4

The relative rates of β-scission have been obtained from the radical chain decomposition of t-alkyl hypochlorites in which the competition is measured relative to hydrogen abstraction from cyclohexane. It is assumed that the hydrogen abstraction k_F/k_H rate is invarient of R in the radical LXXXIII, thus comparisons of the k_F/k_H ratios will give the relative rates of the β-scissions involved (see Table 25 and scheme 2.1.4.5.)

Table 25

Fragmentation of alkoxy radicals $R(CH_3)_2CO\cdot$ at 40°C

R	k_F/k_H
CH_3	0.021
$ClCH_2$	0.121
$C_6H_5CH_2$	1.98
CH_3CH_2	2.09
$(CH_3)_2CH$	76.4
$(CH_3)_3C$	300.0



Scheme 2.1.4.5

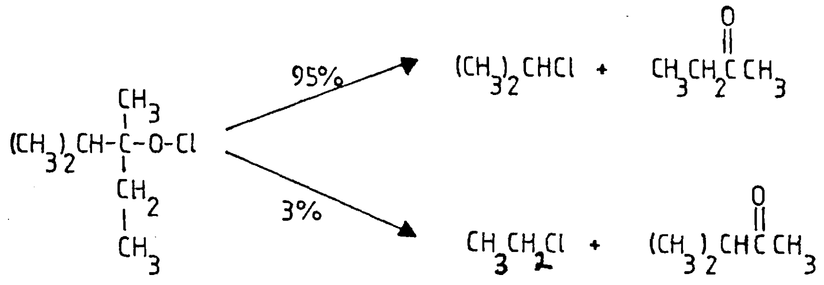
The ratios being determined by equation 2.1.4.6.

$$\frac{k_F}{k_H} = [R'H]\frac{[RCl]}{[R'Cl]}$$

Equation 2.1.4.6

The results obtained by Walling[230] presented in table 25 clearly show a cleavage sequence methyl<ethyl<isopropyl<t-butyl, which is explained by the increased stability of the departing radicals. The k_F/k_H ratio for the expulsion of the benzyl radical would be expected, on the earlier criteria, to be much larger than that reported. Walling[231] explained this anomalous result in terms of a small PZ factor. Another surprising result is in the case where R = phenyl. It is observed that the methyl group rather than the phenyl group is lost. One plausible explanation is that the acetophenone has enhanced stability, compared to acetone, owing to overlap between the orbitals of the carbonyl group and the benzene ring.

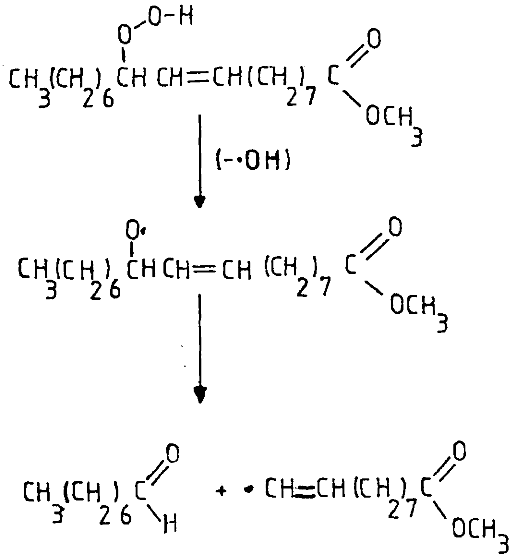
The difference in rates of elimination of primary relative to secondary alkyl radicals is emphasised in the product distribution shown in scheme 2.1.4.7.[231]



Scheme 2.1.4.7

The similarity of the volatile products observed from the autoxidation promoted by cobalt (II) and lead (II) octoates,or the photoinitiator benzil,suggests a similar degradation pathway. The similarities between the volatile compounds from the promoted autoxidations (tables 14 and 19) and those products previously observed in the thermal decomposition of the oleate hydroperoxides (table 22) again suggest a common mechanism of formation.

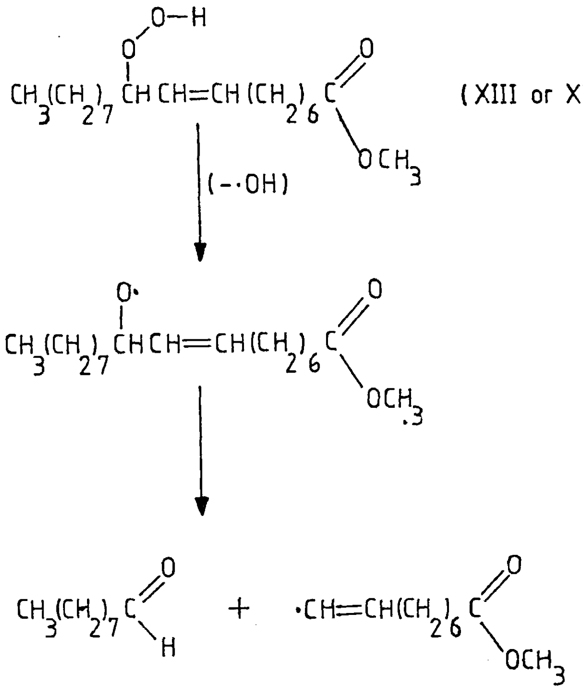
The proposed mechanism of volatile product formation from the promoted autoxidations of methyl oleate are shown in schemes 2.1.4.8, 2.1.4.9 and 2.1.4.10.



(XII or XVIII)

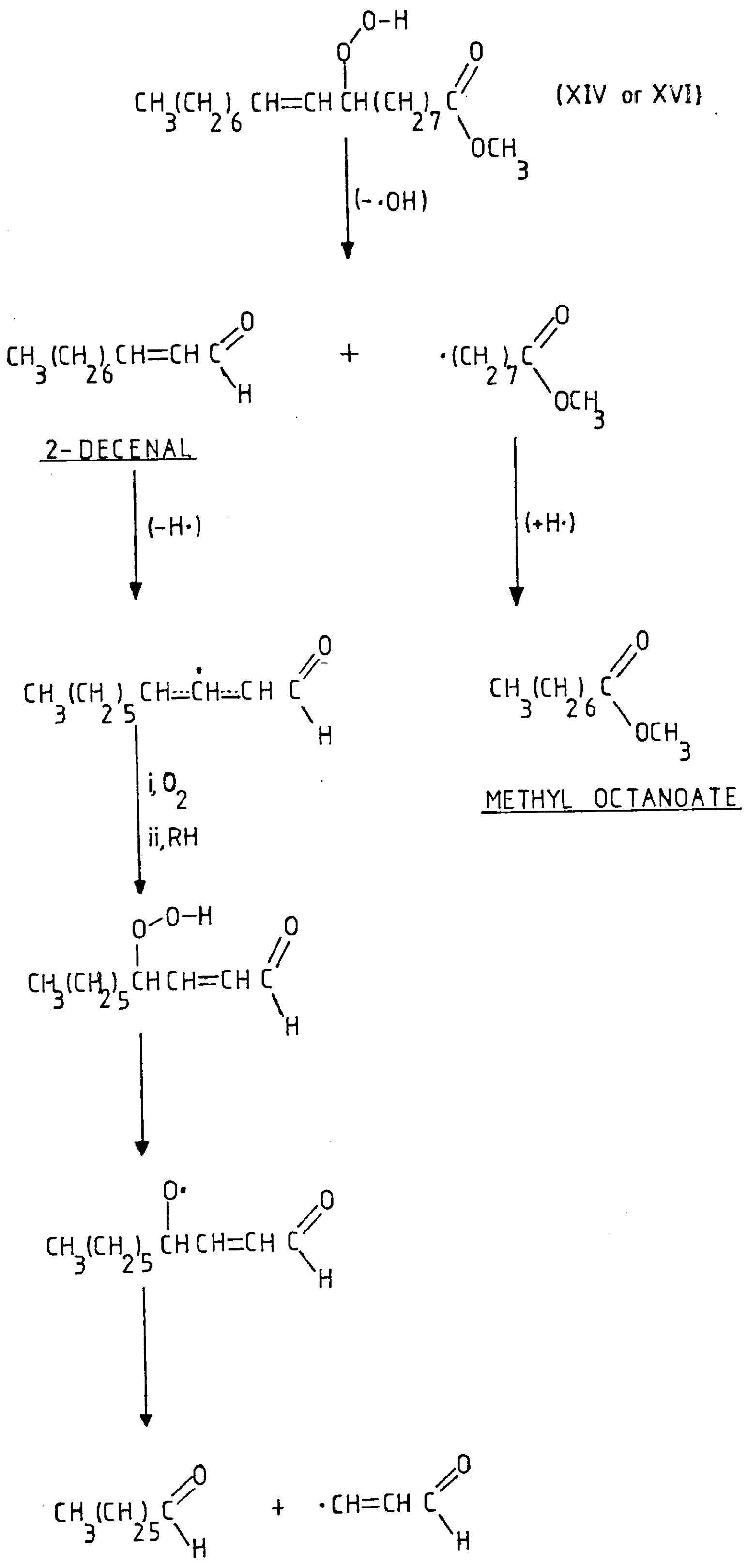
Scheme 2.1.4.8 Formation of octanal

One of the expected major volatile compounds is nonanal, resulting from the decomposition of the 10-hydroperoxides XIII and XVII (Scheme 2.1.4.9). Nonanal however constitutes only ~4% of the mixture of volatiles from the . promoted autoxidation of methyl oleate. The hydroperoxides XIII and XVII are formed in smaller quantities than the 11-hydroperoxides XII and XVIII, so this with the lower volatility of nonanal may explain the lower 'observed' yield.



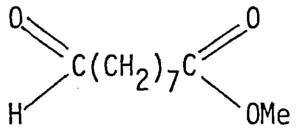
Scheme 2.1.4.9 Formation of nonanal

The aldehydes pentanal and hexanal probably result from hydrogen abstraction further down the hydrocarbon chain resulting in hydroperoxide formation at the 13 and 14 carbon positions thus providing the potential for alkoxy radical formation and carbon-carbon bond scission.

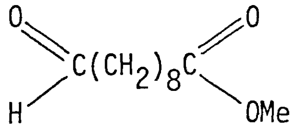


Scheme 2.1.4.10 Formation of heptanal and methyl octanoate

There are however some major discrepancies between the compounds in table 22 and those identified from the promoted autoxidations at ambient temperatures, (tables 14 and 19). The compounds formed in the thermal decomposition of the oleate hydroperoxides in the gc injector port include higher molecular weight compounds such as methyl 9-oxononanoate (LXXXIV) and methyl 10-oxodecanoate (LXXXV). These compounds



(LXXXIV)

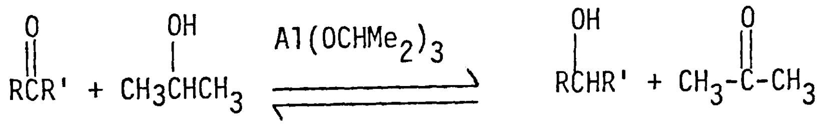


(LXXXV)

are probably formed in the promoted autoxidation of methyl oleate but owing to their lower volatility are not transported to the cold trap. Some differences also occur between the redox promoted and photoinitiated autoxidations, namely the identification of methyl 2-ethylhexanoate amongst the volatile compounds from the cobalt and lead promoted reactions but its total absence in the benzil promoted autoxidation. The origin of this ester is discussed in section 2.10.1. The reverse is true of benzaldehyde which is found solely in the benzil promoted reactions. This results from the decomposition of the initiator via a ketyl-radical (scheme 1.17.3, section 1.17).

The quantity of volatile material produced appears dependent on the initiator, the cobalt and lead system produces approximately 42 times as much as the benzil system. This probably reflects the difference in the ability of the promotors to reduce hydroperoxides to alkoxy radicals. This inability of benzil is illustrated in section 1.17 viz the addition of cumene hydroperoxide to an alkyd resin did not increase the rate of crosslinking in the presence of benzil. If the peroxide was reduced by benzil,the rate of drying would be expected to increase. However the absence of any detectable volatile compounds from methyl linoleate bubbled with oxygen in the absence of a promotor (section 2.10.4) does suggest some influence by benzil. The most likely effect is that the formation of hydroperoxides is aided, thus providing a greater probability of obtaining their decomposition products.

The absence of any degradation products from the cobalt (II) bis(2-ethylhexanoate) and aluminium bis(2-butoxide) ethylacetoacetate may suggest that the complexing agent either hinders the degradation process or reacts with the carbonyl products. The latter has been proposed by ICI Paints[171] i.e. the Meerwein-Ponndorf-Verley reduction, equation 2.1.4.11. However the absence of the degradation products could be due to their low concentration in the 2-butanol/ethyl acetoacetate solution. This will be discussed later in section 2.2.4.



$$\mathrm{R\overset{\overset{O}{\|}}{C}R' + CH_3\overset{\overset{OH}{|}}{C}HCH_3 \xrightleftharpoons{Al(OCHMe_2)_3} R\overset{\overset{OH}{|}}{C}HR' + CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3}$$

Equation 2.1.4.11

The more volatile aldehydes such as ethanal, propanal and butanal were collected and analysed as their 2,4-dinitrophenylhydrazones. The presence of these aldehydes is explained by hydrogen abstraction further down the hydrocarbon chain (at carbon numbers 15, 16 and 17) with hydroperoxide formation, and carbon-carbon bond cleavage with carbonyl formation.
The detection of carbonyl compounds, as their 2,4-dinitrophenylhydrazones, from methyl oleate autoxidised in the presence of the cobalt and aluminium promotors provides evidence that autoxidative degradation is occuring. This method of analysis has the advantage of being selective to carbonyl compounds thus excluding the preponderance of 2-butanol from the analysis.

2.2 Autoxidation of methyl cis-9- cis-12-octadecadienoate

2.2.1 Autoxidation promoted by cobalt (II) bis(2-ethylhexanoate) and lead (II) bis(2-ethylhexanoate)

2.2.1.1 Determination of volatile products by gc-ms

The total ion current chromatogram, obtained from capillary gc-ms, of the volatile compounds collected using the cold trap is shown in figure 2.2.1.1.1.

Scan No. 150

m/z	70	56	55	53	43	42	41	40	39	38	29	27
Rel.AB %	35	4	60	53	29	100	63	17	56	93	19	51

This spectrum is as in section 2.1.1.1 scan No. 135 and again no distinction can be made between cyclopentane and 1-pentene.

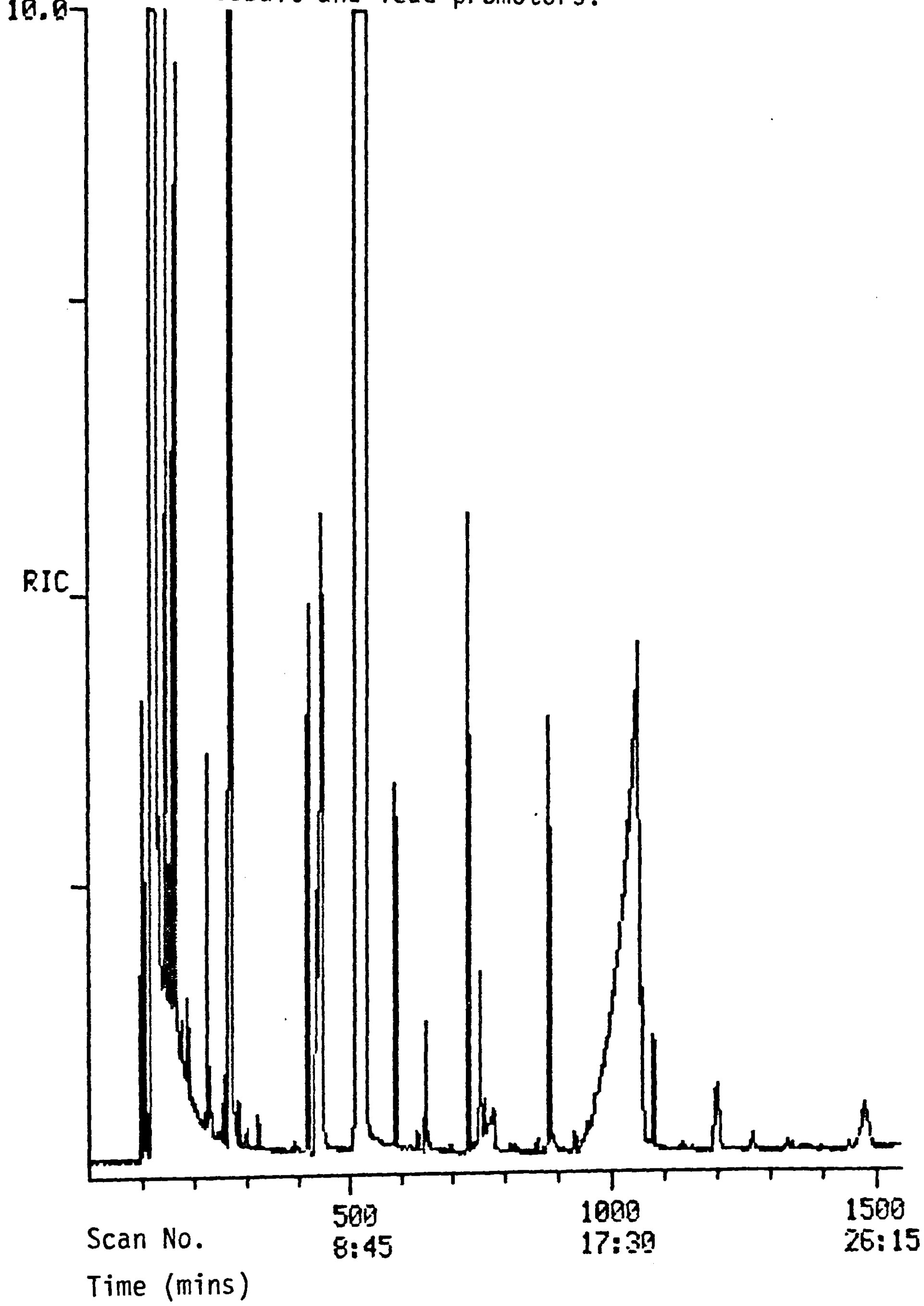
Scan No. 163

m/z	72	57	44	43	42	41	40	39	29	27
Rel. AB %	213	147	100	61	21	60.7	4	33	62	51

The loss of 15 daltons from the molecular ion together with one abundant ion m/z 29 suggests a hydrocarbon chain. The base peak ion at m/z 44 however is indicative of a straight chain aldehyde. The relative molecular mass of 72 (C_4H_8O) corresponds to that of butanal. This assignment was confirmed by reference to the standard spectrum of butanal.[206]

Figure 2.2.1.1.1

Total ion current chromatogram of the volatile products from the autoxidation of methyl Linoleate in the presence of the cobalt and lead promotors.



Scan No. 169

m/z	73	59	45	44	43	42	41	39	31	29	27
Rel AB %	1.3	19	100	93	13	3.0	16	7	33	28	28

The base peak at m/z 45 can arise from a secondary alcohol, and this compound has a similar spectrum to that obtained in section 2.1.2.1 Scan No. 142, and it is again concluded that this compound is 2-butanol.

Scan No. 226

m/z	56	55	45	44	43	42	41	40	39	33	31	29	27
Rel AB %	58	13	5.3	5.3	56.7	29	74	6	13	6.7	100	40	63

No conclusion was made regarding the assignment of this spectrum.

Scan No. 274

m/z	86	85	71	70	58	57	56	55	45	44	42	41	40	39	29	27
Rel AB %	13	13	16	67	37	43	15	153	213	100	33	55	107	44	57	56

The base peak at m/z 44 is indicative of straight chain aldehydes, and a molecular formula consistent with the ion of largest relative molecular mass is $C_5H_{10}O$. Comparison with the standard spectrum of pentanal[206] confirmed the identity of this compound.

Scan No. 420

Toluene impurity from the slush bath used for the cold trap.

Scan No. 448

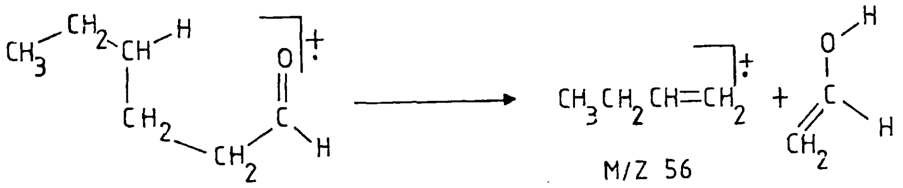
m/z	70	69	57	56	55	43	42	41	39	31	29	27
Rel.AB %	27	5	16	12	63	28	100	63	29	88	96.7	61

The facile loss of 15 daltons indicates the presence of a methyl group but the retention time of this compound suggested that it was not a hydrocarbon. The presence of CH_3 rules out a molecular formula of C_3H_2O but C_4H_6O is possible with the fragment at m/z 55 corresponding to $C_4H_3O^+$. The abundant ion at m/z 31 can only be CH_3O^+. No structure was assigned to this spectrum.

Scan No. 536

m/z	100	82	72	71	67	58	57	56	55	45	44	42	41	40	39	29	27
Rel.AB %	1.4	18	20	11	15	12	70	54	30	30.1	100	29	55	14	46	52	57

The base peak at m/z 44, for the ion formed in a Mclafferty rearrangement, is indicative of a straight chain aldehyde. An ion from the loss of 18 daltons from the parent ion (m/z 72) and the formation of an ion m/z 56 (equation 2.2.1.1.1) provides more evidence for this initial assignment. Comparison with the standard spectrum of hexanal[206] confirmed this assignment.



Equation 2.2.1.1.1

Scan No. 591

m/z	88	87	71	70	55	45	43	42	41	39	31	29	27
Rel.AB %	0.7	3.3	3	44	69	6.7	24	100	57	28	59	85	55

The losses of 18 daltons (H_2O) and 33 daltons (CH_5O) from the parent ion along with the presence of ions at m/z 45 (C_2H_5O) and m/z 31 (CH_3O^+) indicate a primary alcohol. Comparison with the standard spectrum of 1-pentanol[206] confirms the identification of this compound.

Scan No. 650

m/z	98	97	83	80	70	69	68	57	56	55	43	42	41	39	29	27
Rel.AB %	6.7	4	33	6.7	14.7	46.7	5.3	28	11	64	22	55	100	86	89	83

The molecular ion (Rel. Ab. 7%) and the base peak ion at m/z 41 indicates an unsaturated species. The ion at m/z 55 could have the composition of $C_4H_7^+$ or $C_3H_3O^+$ associated with the losses of $C_2H_3O\cdot$ or $C_3H_7\cdot$ respectively. The positive charge will probably remain on the heteroatom containing fragments. It is therefore believed that the ion at m/z 55 is $C_3H_3O^+$. Both the loss of 29 daltons from the parent ion and the predominant ion at m/z 29 suggest that an aldehyde group is present in this molecule. The molecular ion (m/z 98) demonstrating the presence of unsaturation and a heteroatom (oxygen) suggests its molecular formula is $C_6H_{12}O$. Comparison with the standard spectrum of 2-hexenal[206] confirmed the presence of 2-hexenal.

Scan No. 734

m/z	114	85	72	57	43	42	41	39	29	27
Rel. AB %	6	23	15	95	16	6	33	13	100	46.7

The fragmentation pattern of this compound resembles very closely that observed in Section 2.1.1.1. Scan No. 903 and is concluded to be 3-heptanone.

Scan No. 755

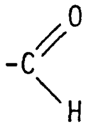
m/z	116	115	98	87	70	69	59	58	57	56	55	45	43	41	39	31	29	27
Rel. AB %	0.5	0.5	2.7	20	53	73	100	9.3	10.7	4	9.3	12	21	60	17	49	51	41

The loss of 18 daltons from the parent ion along with the ions at m/z 45 and 31 indicate the presence of oxygen in this compound. The loss of water (M-18) also suggests a hydroxyl group. This spectrum is similar to that for 3-heptanol and comparison with its standard spectrum[206] confirmed this.

Scan No. 886

m/z	112	83	70	69	68	57	56	55	41	39	29	27
Rel. AB %	15	77	46	31	38	65.5	61	69	100	53.5	31	53.5

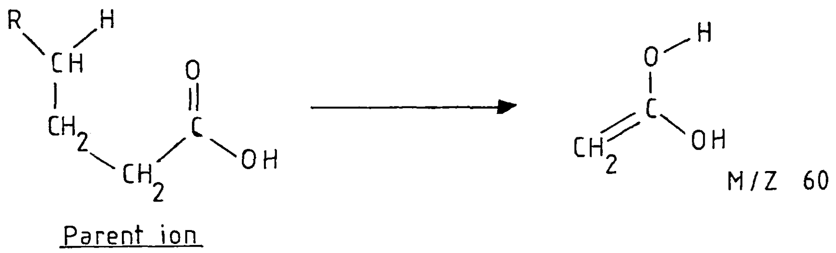
The base peak ion at m/z 41 indicates unsaturation. The abundant ion at m/z 55 indicates the possibility of $\overset{\oplus}{C}H=CHCH=O$.

The loss of 29 daltons indicates either CH_3CH_2- or  $-C(=O)H$ being extruded. From the relative molecular mass 2-heptenal seemed plausible and comparison with standard spectrum[206] confirmed this.

Scan No. 1053

m/z	74	73	70	61	60	56	55	45	43	42	41	39	29	27
Rel. AB%	47	43	3	11	100	92	16	28	31	23	45	25	28	61

The base peak at m/z 60 is indicative of straight chain carboxylic acids and arises from a Mclafferty rearrangement of the parent ion (equation 2.2.1.1.2).



Equation 2.2.1.1.2

Butanoic acid is the first member of the carboxylic acid series to undergo such a rearrangement. The parent ion could not be distinguished in the capillary gc-ms analysis therefore no conclusion was reached except that this was a carboxylic acid.

Scan No. 1056

m/z	158	143	130	129	127	115	102	101	87	83	70	69	59	57	55	43	41	39	29	27
Rel AB %	1	1.6	12	8.5	5.4	13	78	15	100	4	5	12	24	53	27	19	47	13	32	21.2

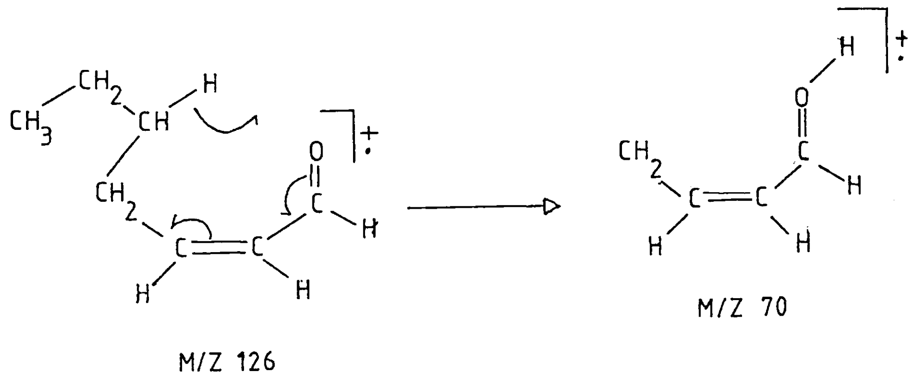
This spectrum is very similar to the one obtained in section 2.1.1.1 Scan No. 1275 and is therefore concluded to be methyl-2-ethyl hexanoate.

Scan No. 1061

m/z	126	111	108	97	84	83	82	71	70	69	58	57	56	55	43	42
Rel.AB%	1.4	2.0	2.4	14.1	18	62	36	12.7	90	38	17	60.6	18.3	85.9	18.3	42

m/z	41	39	29	27
Rel.AB %	100	45	73	45.1

The ion at m/z 41, giving rise to the base peak, and the relative molecular mass of 126 daltons gives some evidence for an unsaturated compound. The loss of 18 and 29 daltons and the ion at m/z 55 provides evidence for an α,β unsaturated aldehyde. The rearrangement ion giving a large peak at m/z 70 could result from a Mclafferty-type rearrangement(equation 2.2.1.1.3).



Equation 2.2.1.1.3

A similar rearrangement was also observed in the spectrum of 2-heptenal. It is concluded that this compound is either cis or trans 2-octenal.

Scan No. 1081

m/z	126	111	108	98	97	93	84	83	82	71	70	69	68	67	58	57
Rel. AB %	0.7	1.5	1.5	4.7	6.0	6.0	8	31	15	5.3	45	24	9.3	16	8	29

m/z	56	55	53	43	42	41	39	29	27
Rel. AB %	9	61	11	17	29.3	77.3	59	100	64

This spectrum has a similar fragmentation to Scan 1061 and is therefore concluded to be the other isomeric 2-octenal.

Scan No. 1204

m/z	158	127	115	87	83	74	59	57	55	43	42	41	39	29	27
Rel. AB %	1.7	10.2	6.8	35	10	100	11.9	18.6	23.7	25.4	8.5	27.1	11.2	17	13.6

The base peak ion at m/z 74 and the loss of 31 daltons ($M-OCH_3$) from the parent ion suggests a straight chain methyl ester. Comparison with the standard spectrum of methyl octanoate[206] confirmed the presence of this compound.

Scan No. 1480

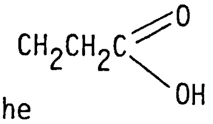
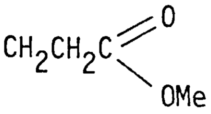
m/z	172	171	170	107	100	99	98	87	83	82	72	71	69	60
Rel. AB %	2.7	20	4.7	2·0	8·0	72	2.7	1.3	28	12	4.7	37	10.7	13.3

m/z	57	56	55	51	45	44	43	39	29	27
Rel. AB %	43	14	31	2.7	9.3	14.7	100	16	51	33

The base peak ion at (m/z 43) indicates the presence of hydrocarbon chain containing little or no unsaturation. A hydrocarbon chain is also indicated by the series of ions 14 daltons apart (CH_2) i.e. m/z 71, 57, 43 and 29. The ion at m/z 99 may also result from a hydrocarbon fragment (C_7H_{15}) by the fragmentation of the molecular ion through the loss of 73 daltons. The composition of this neutral fragment could be C_4H_9O or $C_3H_5O_2$ the two other possible compositions C_6H and C_2HO_3 being excluded. However no conclusive analysis has been possible.

Packed column gc-ms analysis revealed the presence of two additional compounds.

m/z	116	99	87	74	73	60	57	56	55	45	43	41	29	27
Rel AB %	2.9	1.5	11.8	5.9	44	100	10.3	8.8	8.8	8.9	11.8	20.6	11.8	15.0

The base peak ion at m/z 60 is characteristic of a straight chain carboxylic acid and the loss of 17 daltons (M-OH) from the parent ion and the presence of an ion at m/z 45 (CO_2H^+) support this argument. The abundant ion at m/z 43 (44% of the base peak) can be explained by the formation of a  $CH_2CH_2C(=O)OH$ ion. This type of fragment was also observed in the spectra of methyl octanoate i.e.  $CH_2CH_2C(=O)OMe$.

Analysis of the standard spectrum of hexanoic acid[206] (relative molecular mass 116) confirmed this assignment.

The presence of 2-ethylhexanoic acid was also confirmed, the analysis of this spectra was discussed in section 2.1.1.1.

The compounds identified by gc-ms from the autoxidation of methyl linoleate are summarised in table 26.

Table 26

The volatile products formed during the autoxidation of methyl linoleate in the presence of cobalt and lead promotors

Compound	% composition
3-Heptanone	0.9
Butanal	4.71
Pentanal	3.82
Hexanal	72.46
2-Hexenal	0.24
2-Heptenal	1.57
2-Octenal	-
2-Butanol	-
1-Pentanol	-
3-Heptanol	0.68
Methyl heptanoate	0.23
Methyl octanoate	0.68
Methyl 2-ethylhexanoate	0.46
Hexanoic acid	-
2-Ethylhexanoic acid	0.77

The total quantity of volatile material produced is 2.59×10^{-3}g based on dodecanal as the internal standard.

The autoxidation of methyl linoleate was carried out in the presence of cobalt (II) bis(2-ethylhexanoate) alone, and lead (II) bis(2-ethylhexanoate) alone. The same volatile products were identified in each case and were found to be identical to those in table 26. However the quantity of the volatile material produced differed, the results are summarised in table **27**.

Table **27**.

Promotor	Quantity of volatiles produced
Co	2.34×10^{-3}g
Pb	0.78×10^{-3}g
Co/Pb	2.59×10^{-3}g

2.2.1.2 Determination of volatile products by HPLC

The volatile products trapped as their 2,4-dinitrophenylhydrazone derivatives were identified by HPLC; (the retention times of the standard 2,4-dinitrophenylhydrazones prepared are given in table 15). Their retention times and the assignments of the compounds are given in table 28.

Table 28

Retention time (minutes)	Compound assigned
6.7	Methanal
9.4	Ethanal
12.3	Propanal
16.4	2-Butenal
17.1	Butanal
20.9	Pentanal

2.2.1.3 Collection of volatile products under reduced pressure. Autoxidation promoted by cobalt (II) bis(2-ethylhexanoate) and lead (II) bis(2-ethyl hexanoate)

The volatile products collected in the cold trap at point G in diagram 3.7.1 were analysed by packed column gc-ms. The chromatography conditions were altered to accommodate the higher boiling point compounds. The compounds previously identified in section 2.2.1.1 were identified in the early part of the chromatogram. However several other compounds were identified in the latter part, these being carboxylic acids. The identification of these compounds will be discussed.

Component 1

m/z	60	45	43	42	29
Rel. AB %	61.8	76	100	16.4	14.5

This mass spectrum is similar to the one obtained from the autoxidation of methyl oleate (see section 2.1.1.1, Scan No.415) and is therefore concluded to be ethanoic acid.

Component 2

m/z	88	73	60	46	45	44	43	42	41	29	27
Rel. AB %	4.2	33.3	100	26.7	32.5	16.7	24.2	20	25	22.5	25.8

The base peak ion at m/z 60 is indicative of a straight chain carboxylic acid; the largest relative molecular mass (88 daltons) indentifies this compound to be butanoic acid and comparison with the standard spectrum[206] confirmed this.

Component 3

m/z	102	87	85	83	74	73	60	55	45	43	42	41	29	27
Rel. AB %	2.7	3.6	1.8	2.8	45	40	100	9.1	10	11	8.2	16.3	16.3	18.3

The base peak ion at m/z 60 is again indicative of a straight chain carboxylic acid and the relative molecular mass of 102 daltons allows this compound to be pentanoic acid. Again comparison with the standard spectrum[206] confirmed this assignment.

Component 4

m/z	116	99	87	74	73	61	60	55	45	43	42	41	39	29	27
Rel. AB %	3.1	8.6	14.3	5.7	47.6	9.5	100	12.4	13.8	17.1	11.4	30.9	15.2	13.8	19.0

Again the base peak ion at m/z 60 can result from a carboxylic acid in which case the relative molecular mass of 116 daltons corresponds to hexanoic acid. The standard spectrum of hexanoic acid[206] contains this assignment.

Component 5

m/z	130	115	101	87	73	60	55	45	43	41	29	27
Rel. AB %	3.3	4.2	15	26.7	83.3	100	30	20	35	49	30	26.6

The parent ion of a carboxylic acid at m/z 130 fits the formula of $C_7H_{14}O_2$ (heptanoic acid). Comparison with its standard spectrum[206] confirms this assignment.

Component 6

m/z	128	110	99	73	68	56	55	45	43	41	29	27
Rel. AB %	8.0	17.0	50	100	50	81.2	37	21.0	50.0	92.0	32.0	51.0

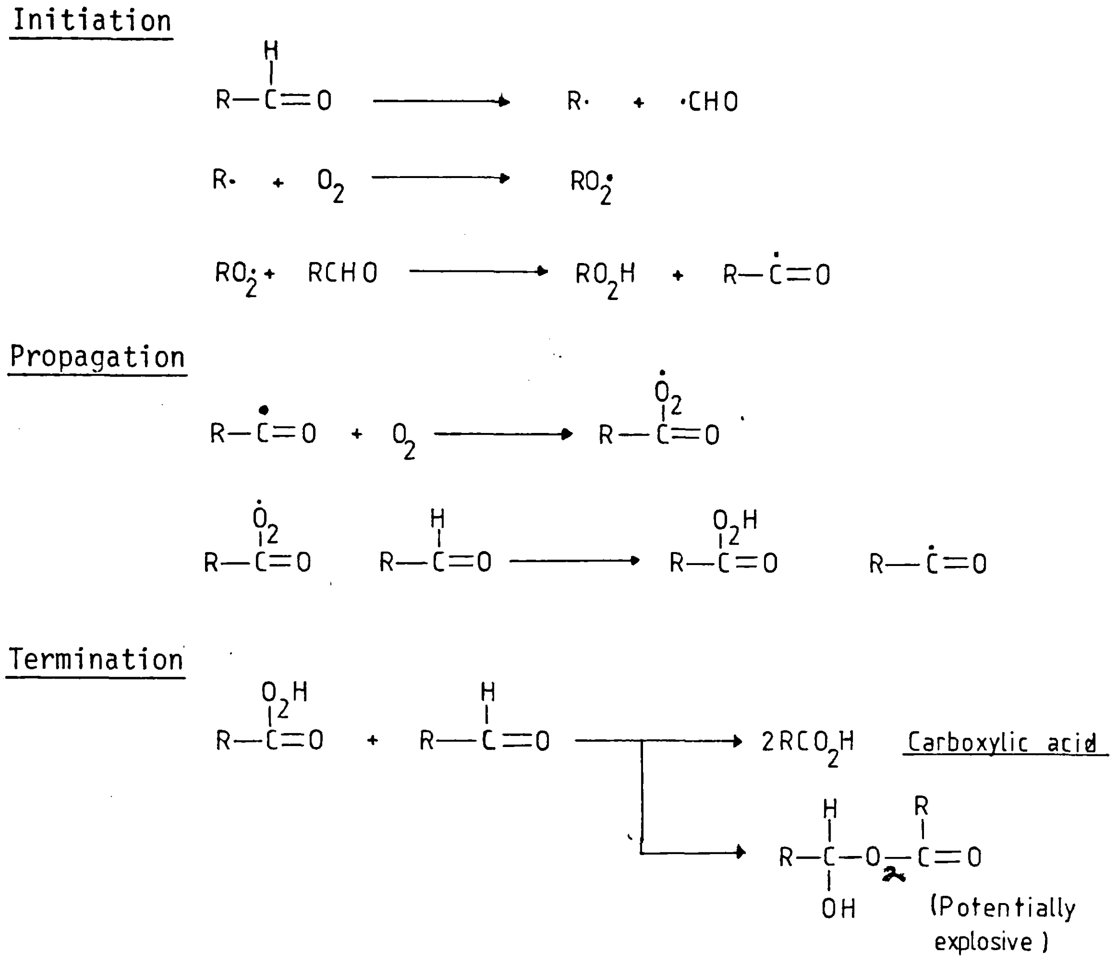
The loss of 18 daltons from the parent ion indicates the presence of an OH group and that of 29 daltons, the presence of CH_3CH_2. The presence of an ion at m/z 45 (21%) provides some evidence for the presence of the carboxylicacid functionality. The prominent m/z 41 ion also indicates some degree of unsaturation as does the parent ion.

The new compounds identified by collection under reduced pressure are: ethanoic, butanoic pentanoic, hexanoic and heptanoic acids.

The object of this experiment was to try and isolate the expected degradation products, resulting from the 9-hydroperoxides of methyl linoleate (XXII and XXIV) - specifically methyl-9-oxo-nonanoate. This compound would be expected as a mechanism for its formation corresponds to that of hexanal from the 13-hydroperoxides (XXIII and XXV). However this compound was not identified. Its formation is not really under doubt as it has been isolated from the thermal degradation of methyl oleate hydroperoxides (see previous section) and long-term uncatalysed autoxidations of the methyl esters XXI and XLVII.[215]

Consideration has to be given to the effect of the method of isolation upon the nature of the volatile products. Heating of the reaction mixture to aid volatility, could induce thermal homolysis of hydroperoxides. To be able to identify the presence of methyl -9-oxo nonanoate some prior extraction may be necessary before gc-ms analysis.

The presence of the carboxylic acids shows that additional oxidation has occurred. The autoxidation of aldehydes to form the corresponding acid is one of the older reactions in organic chemistry,[232] it is proposed to be free radical chain reaction,[233,234,235,236] see scheme 2.2.1.3.1.



Scheme 2.2.1.3.1

It is proposed that the carboxylic acids formed in the autoxidation reactions result from the corresponding peroxy acids and their reaction with aldehydes.

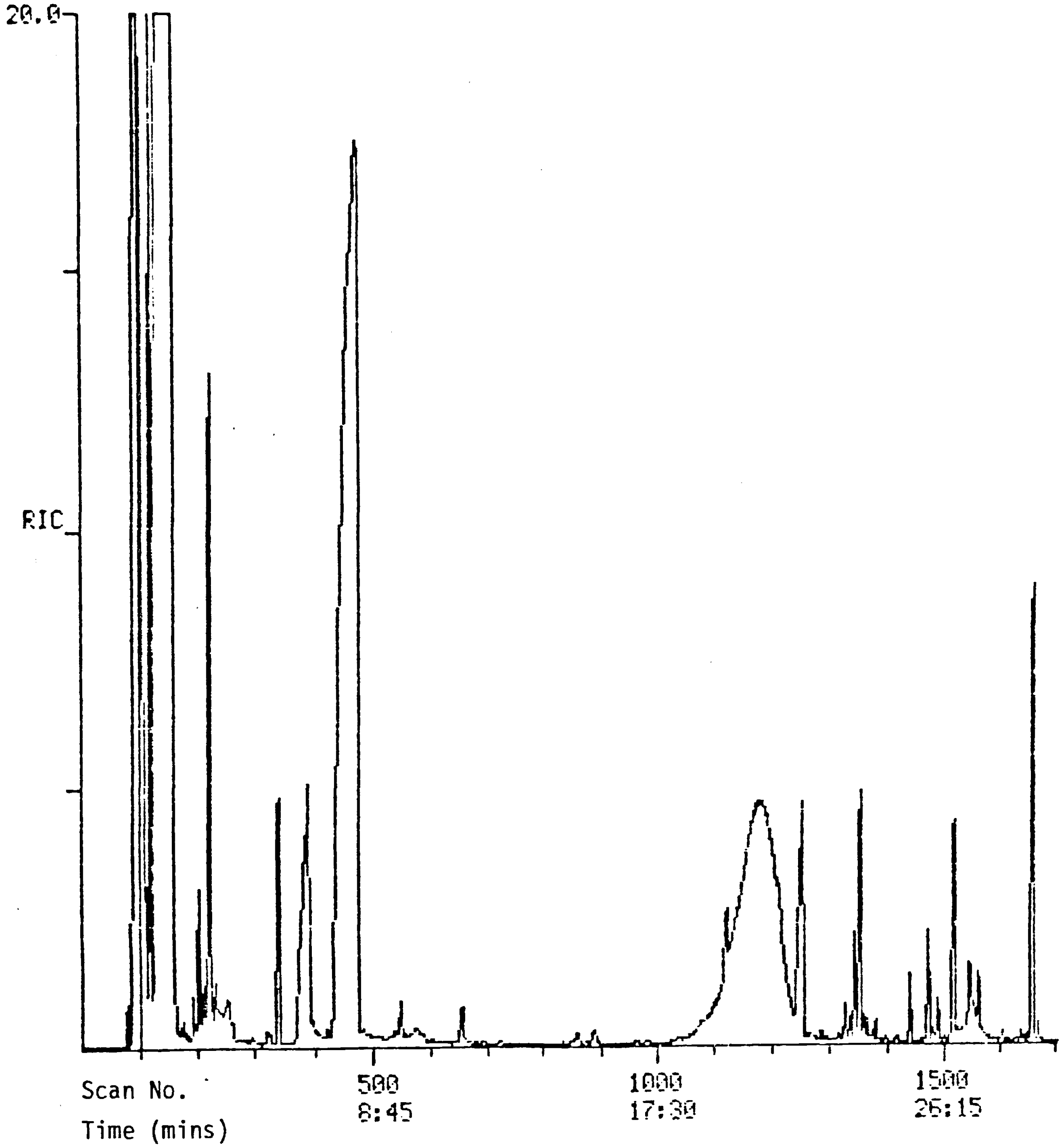
2.2.2 Autoxidation promoted by cobalt (II) bis(2-ethyl hexanoate) and aluminium bis(2-butoxide) ethyl acetoacetate

2.2.2.1 Determination of volatile products by gc-ms

The total ion current chromatogram obtained from the gc-ms study of the volatiles closely resembled that obtained in section 2.2.1.1. (figure 2.2.1.1.1.). The difference that

Figure 2.2.1.1.1

Capillary total ion current chromatogram of the volatile products from the autoxidation of methyl linoleate in the presence of cobalt and aluminium promotors.



occurred was the absence of the following: butanal, methyl 2-ethyl hexanoate, hexanoic and 2-ethylhexanoic acid, but with the additional presence of 2-butanol, ethyl acetoacetate, 2-pentylfuran, 3-octen-2-one and methyl hexanoate. The identification of 2-butanol and ethyl acetoacetate has been discussed in section 2.1.2.1. The identification of 2-pentylfuran, 3-octen-2-one and methyl hexanoate follows.

Scan No. 1354

m/z	138	109	95	94	82	81	67	53	52	51	43	41	39	29	27
Rel. AB %	14.3	2.5	6.2	5.6	28.6	100	7.5	46	8	11	7.1	29	38	36	71.4

The loss of 57 daltons to form the base peak ion coupled with the loss of 29 and 43 daltons suggest a hydrocarbon chain. The relative molecular mass of 138 daltons can have the following molecular formulae; $C_{10}H_{18}$, $C_9H_{14}O$, $C_8H_{10}O_2$ and $C_7H_6O_3$. The use of the heavy isotope ratio ((M+1)/M) determined it as $C_9H_{14}O$ and thus the base peak ion to have the composition C_5H_5O through the loss of 57 daltons corresponding to C_4H_9. The presence of an ion at m/z 39 could result from C_3H_3, a common fragment in furans, and the base peak could be composed of a furan type structure

Comparison with the standard spectrum of 2-pentylfuran[206] confirmed the presence of this compound.

Scan No. 1476

m/z	126	111	97	83	79	71	69	68	56	55	53	51	43	41	39	29	27
Rel. AB %	3.7	21	10	43	1.9	5.6	11	6.2	5.0	100	8.7	43	76	42	37.9	24.0	55

The base peak ion at m/z 55 results from the loss of 71 daltons from the parent ion. The composition of the ion at m/z 55 could be C_4H_7 or C_3H_3O with the loss from the molecular ion being either C_5H_{11} or C_4H_7O. If the base peak ion is $C_3H_3O^+$, an unsaturated ketone structure is suggested. The loss of 15 daltons from the parent ion suggests that it is a methyl ketone. Thus the proposed compound is 3-octen-2-one and this was confirmed by analysis of the standard spectrum.[206]

Scan No. 1124

m/z	130	101	99	88	87	75	74	71	59	57	55	45	43	42	41	39	31	29	27
Rel. AB %	0.4	6.8	15	3.7	28.6	37	86.3	9.9	34	6.2	25	6.0	100	37	52	38.5	6.8	64	72

The loss of 31 daltons from the parent ion suggests the presence of OCH_3 and the large m/z 74 indicates a straight chain methyl ester.

The relative molecular mass of 130 daltons prompted comparison of this spectrum with the standard spectrum of methyl hexanoate.[206] From the fairly good match it is concluded that this compound is methyl hexanoate.

The compounds identified by both capillary and packed column gc-ms are summarised in Table 29.

Table 29

Volatile products formed during the autoxidation of methyl linoleate in the presence of cobalt and aluminium promotors

Compound	% Composition*
3-Heptanone	0.7
3-Octen-2-one	0.4
Pentanal	4.7
Hexanal	76.4
2-Hexenal	0.3
2-Heptenal	2.3
2-Butanol	-
1-Pentanol	-
Methyl hexanoate	0.3
Methyl heptanoate	0.4
Methyl octanoate	1.1
Ethyl acetoacetate	
Pentylfuran	3.7

* 2-butanol and ethyl acetoacetate are not included.

The total amount of material collected was 2.15×10^{-2}g, but excluding 2-butanol and ethyl acetoacetate 2.37×10^{-3}g.

2.2.2.2 Determination of volatile products by HPLC

The volatile products trapped chemically by the silica gel coated with 2,4-dinitrophenylhdrazine were identified by their retention times on a C_{18}-reversed phase HPLC column. The retention times and assignments of the compounds are given in table **30**.

Table **30**

Retention time (minutes)	Compound assigned
9.5	Ethanal
12.3	Propanal
17.4	Butanal

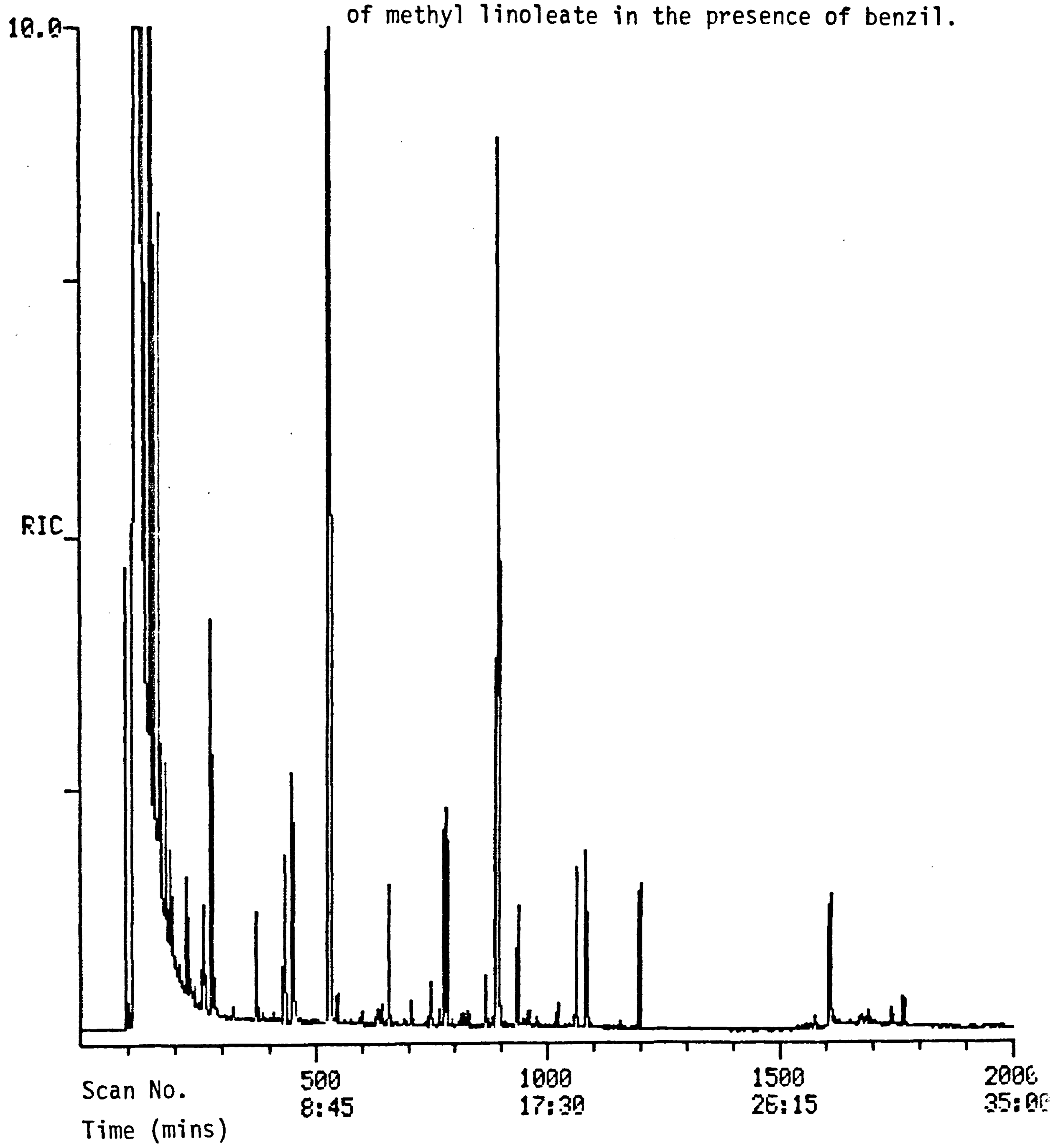
2.2.3 Autoxidation promoted by benzil

2.2.3.1 Determination of volatile products by gc-ms

The compounds identified from this autoxidation experiment, total ion current chromatogram from capillary gc-ms figure 2.2.3.1.1, again resembled closely those obtained from the autoxidation of methyl linoleate in the presence of cobalt and lead promotors (figure 2.2.1.1.1) the major product again being hexanal, but with fewer compounds being detected. The vast majority of the compounds identified by gc-ms have been identified before, with the exception of that having scan No.229.

Figure 2.2.3.1.1.

Capillary total ion current chromatogram of the volatile products from the autoxidation of methyl linoleate in the presence of benzil.



Scan No. 229

m/z	84	69	68	63	56	55	52	51	50	43	42	41	39	29	27
Rel. AB %	13	9	1.3	5	10	72	15	31	27	11	28	100	58	17	40

The base peak ion at m/z 41 indicates a compound with olefinic unsaturation present, the low retention time suggests a compound that is not very polar i.e. an alkene with a molecular formula C_6H_{12}. Comparison with the standard spectrum of 1-hexene[206] identified this as the compound.

The compounds identified by gc-ms are concluded in table 31. The total amount of volatile material collected was 2.3×10^{-4}g based on dodecanal as the internal standard.

Table 31

Volatile compounds formed during the autoxidation of methyl linoleate in the presence of benzil

Compound	% composition
1-Hexene	-
2-Hexanone	1.4
Pentanal	4.2
Hexanal	67.2
2-Hexenal	0.9
2-Heptenal	6.4
2-Octenal	-
Benzaldehyde	2.6
1-Pentanol	0.7
Methyl octanoate	2.1

2.2.3.2 Determination of volatile products by HPLC

The volatile products trapped chemically by the silica gel coated with 2,4-dinitrophenylhydrazine were identified by their retention times by HPLC. The retention times and assignments of the compounds are given in table 32.

Table 32

Retention time (minutes)	Compound assigned
6.3	Methanal
12	Propanone
12.5	Propanal

2.2.3.3 Destruction of benzil during autoxidation

In the autoxidation of methyl linoleate promoted by benzil the reaction was monitored at 388 nm, corresponding to the $n \longrightarrow \pi^*$ transition in benzil. The decrease in the concentration of benzil, with reaction time is shown in figure 2.2.3.3.1 and table 33.

A limit to any further reduction in concentration from 0.0165mol dm^{-3} occurred after 21.5 h.

2.2.4 Mechanism of volatile product formation in the autoxidation of methyl linoleate

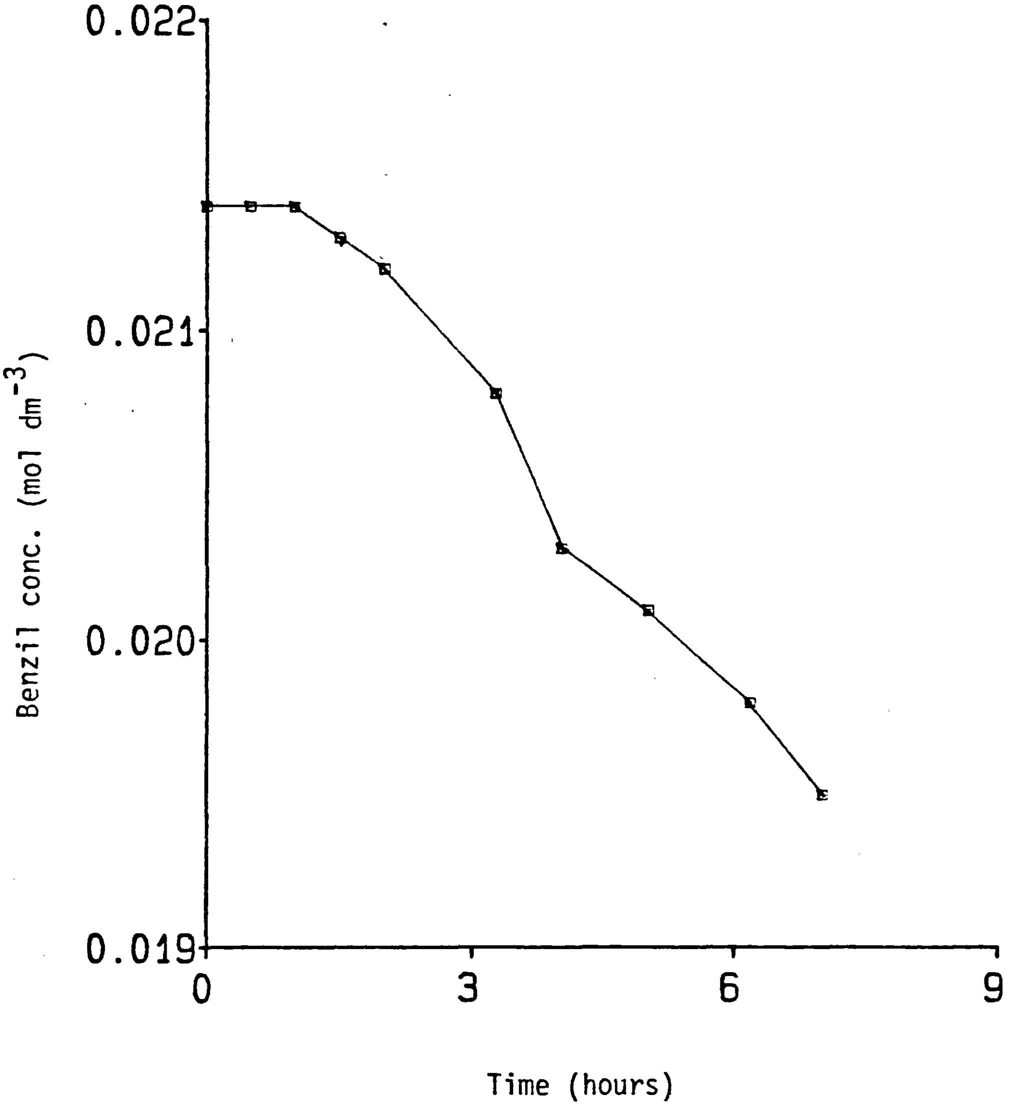
Volatile carbonyl compounds, formed by successive heat reversion and deodorisation ofsoyabean oil, were identified by Daubert.[237,238,239] These compounds included ethanal, propanal,

Table 33

Time (hours)	Benzil (mol dm^{-3})
0.00	0.0214
0.50	0.0214
1.00	0.0214
1.50	0.0213
2.00	0.0212
3.25	0.0208
4.00	0.0203
5.00	0.0201
6.17	0.0198
7.00	0.0195
21.50	0.0165

Least mean squares analysis of the line using the points from 1 hour to 7 hours gave a gradient of -0.32784×10^{-3} with an error of $\pm 0.3 \times 10^{-4}$ (95% confidence).

Figure 2.2.3.3.1.
Benzil concentration versus time during the autoxidation of methyl linoleate



hexanal and 2-pentenal. Hexanal was also found in the volatile decomposition products from cotton seed oil autoxidised at 70°C.[240] Thus Chang[117] proposed hexanal to be a degradation product of linoleic acid. Chang also studied the volatile decomposition products of ethyl linoleate as their hydrazones revealing the presence of propanal, pentanal and hexanal. Badings[98], from the autoxidation of ammonium linoleate identified hexanal, 2,4-decadienal and 2-octenal as their 2,4-dinitrophenylhydrazones. These were not analysed as volatile components but extracted from the 'bulk' reaction mixture. Thus the proposal that carbonyl compounds are one of the 'primary' products from hydroperoxide decomposition was made. Hexanal was proposed to originate from the hydroperoxide formed at carbon 13 and 2,4-decadienal from that formed at carbon 9, in methyl linoleate. The existence of these hydroperoxides has been discussed in section 1.5. The origin of 2-octenal was proposed to be from the hydroperoxide formed at carbon 11. However, this hydroperoxide has not been identified, to date, from the autoxidation of linoleic acid or any of its derivatives.

Horvart[241] analysed the volatile products from the autoxidation of methyl linoleate at 22°C for 18 days using a U tube trap at-178°C the compounds were separated and identified by gc-ms. The compounds identified are listed in table 34. Although capillary glc was employed

Table 34

Methyl formate
n-Pentane
Propanal
Butanal
Pentanal
n-Butanol
Hexanal
Pentyl methanoate
2-Heptanone
Methyl hexanoate
n-Hexanol
2-Heptenal
1-Octene-3-one
Methyl heptanoate
Methyl octanoate

the separations were often not sufficient for identification to be based on mass spectra alone. The authors confirmed their assignments by comparison of retention times with that of standards, no quantitation of the components was carried out.

Horvart[242] in a later publication also identified several carboxylic acids as their methyl esters from the autoxidation of methyl linoleate. The acids were extracted from an ether solution using a saturated sodium bicarbonate solution, then the extracted acids converted to their methyl esters using diazomethane. (This extraction was important as it removed the chance of confusion with the methyl esters previously identified[241]). The methyl esters were separated and identified by capillary gc-ms. Their corresponding acids are given in table 35.

Table 35

Methanoic acid
Pentanoic acid
Hexanoic acid
Heptanoic acid
2-Heptenoic acid
2-Octenoic acid
Octanoic acid
Nonanoic acid
2,3-Epoxyoctanoic acid
Octanedioic acid
Nonanedioic acid

Again Frankel[214] has provided the most complete study of the thermal degradation products from methyl linoleate hydroperoxides. (Experimental details given in section 2.1.4). The degradation products from both uncatalysed and photosensitized oxidation are shown in table 36.

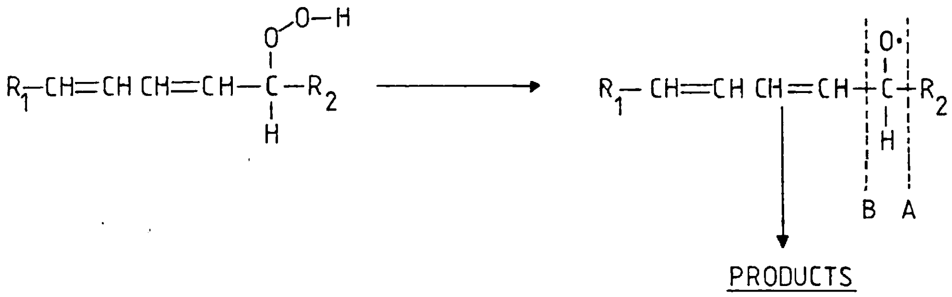
Table 36

Gc-ms analysis of products from thermally decomposed methyl linoleate hydroperoxides

	Autoxidation (rel.%)	Photosensitized oxidation (rel. %)
Ethanal	0.3	0.4
Pentane	9.9	4.3
Pentanal	0.8	0.3
1-Pentanol	1.3	0.3
Hexanal	15.0	17.0
2-Heptenal	Trace	9.9
1-Octen-3-ol	Trace	1.9
2-Pentylfuran	2.4	0.6
Methyl heptanoate	1.0	0.3
2-Octenal	2.7	1.5
Methyl octanoate	15.0	7.6
2-Nonenal	1.4	1.6
2,4-Nonadienal	0.3	0.3
2,4-Decadienal	14.0	4.3
Methyl 8-oxooctanoate	1.3	0.9
Methyl 9-oxononanoate	19.0	22.0
Methyl 10-oxodecanoate	0.7	0.7
Methyl 10-oxo-8-decenoate	4.9	14.0

Both reaction conditions produced similar compounds, but with significant differences in amounts. The autoxidised linoleate hydroperoxides produced much more pentane, 2-pentylfuran, 2,4-decadienal and methyl octanoate and much less methyl 10-oxo-8-decenoate and 2-heptenal than the photooxidised linoleate hydroperoxides.

Bell,[243] Frankel,[215] and Kimoto and Gaddis[244] have proposed that monohydroperoxides decompose to alkoxy radicals, and carbonyl compound formation results from the β-fragmentation of these radicals. See Scheme 2.2.4.1.



Scission A gives $R_1{-}CH{=}CH\,CH{=}CH\,CHO + {}^{\bullet}R_2$

Scission B gives $R_1{-}CH{=}CH\,CH{=}CH^{\bullet} + R_2CHO$

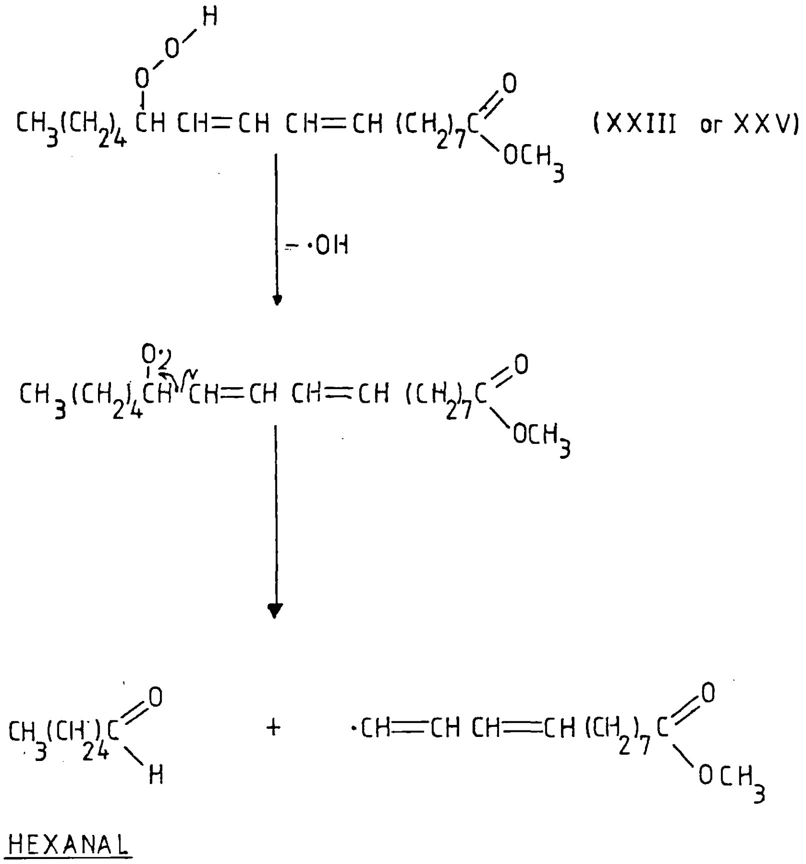
Scheme 2.2.4.1

(The fragmentation and chemistry of alkoxy radicals has been mentioned in sections 1.13 and 2.1.4). Scission of the C-C bond on the side of the oxygen-bearing carbon atom away from the olefinic linkages (Scission A), will result in the formation of 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 similarity between the thermal decomposition products (table 36) and those observed from the promoted autoxidation of methyl linoleate (tables 26, 29 and 31) indicate a common degradation pathway. There are however several compounds not detected in the ambient promoted autoxidations which are observed in the thermal decomposition of the methyl linoleate hydroperoxides. The absence of the higher molecular weight compounds i.e. 2-nonenal, 2,4-nonadienal, 2,4-decadienal, methyl 8-oxooctanoate, methyl 9-oxononanoate, methyl 10-oxodecanoate and methyl 10-oxo-8-decenoate is easily explained. The thermal degradation of the methyl linoleate hydroperoxides is carried out in the injection part of the gas-liquid chromatograph, and hence all the products are analysed. However, the degradation products from the promoted autoxidations at ambient temperature are transferred via a gas stream into a cold trap, thus only compounds which are sufficiently 'volatile' will be collected and analysed.

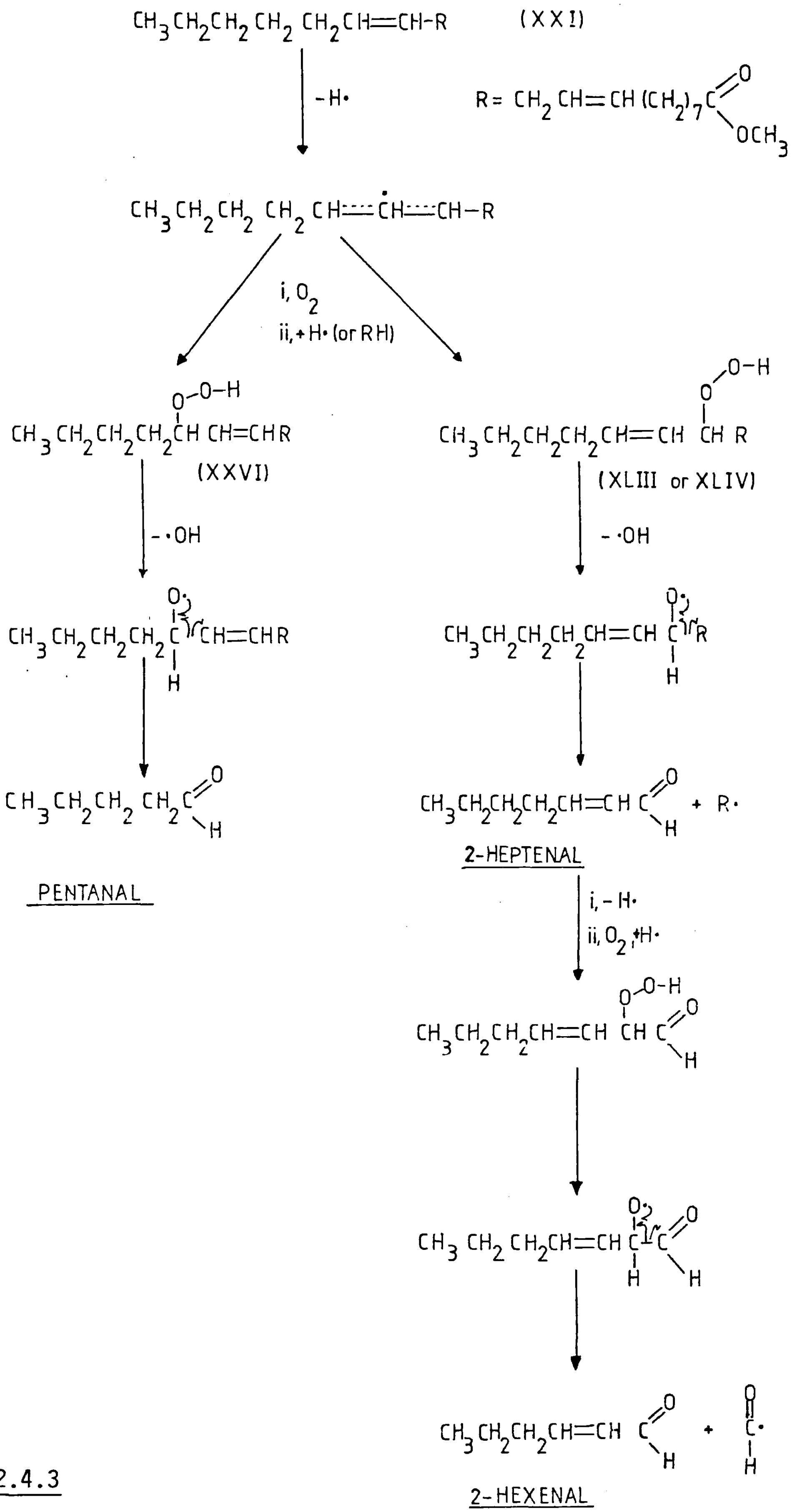
The major 'volatile' degradation product from all three promoted autoxidations of methyl linoleate is hexanal (~70%). This arises from the decomposition of the 13-hydroperoxides XXIII and XXV, see scheme 2.2.4.2, whose formation was discussed in section 1.5.

Other common products from the three promoted autoxidations are pentanal, 2-hexenal and 2-heptenal, see scheme 2.2.4.3. The formation of hydroperoxide XXVI has been discussed in section 1.5.



Scheme 2.2.4.2

The formation of hydroperoxides (XLIII or XLIV) is tentatively suggested but expected from the allylic radical proposed for the formation of XXII (methyl-9-hydroperoxy trans-10-cis-12-octadecadienoate). 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 36) also suggests that it results from secondary reactions.


(XXI)
-H•
R= CH2 CH=CH (CH2)7 C(=O)OCH3
i, O2
ii, + H• (or RH)
(XXVI)
(XLIII or XLIV)
- •OH
- •OH
+ R•
PENTANAL
2-HEPTENAL
i, - H•
ii, O2, +H•
2-HEXENAL

Scheme 2.2.4.3

The formation of the two other common products from the three promoted autoxidations i.e. methyl heptanoate and methyl octanoate are explained by Scheme 2.1.4.8 (Section 2.1.4).

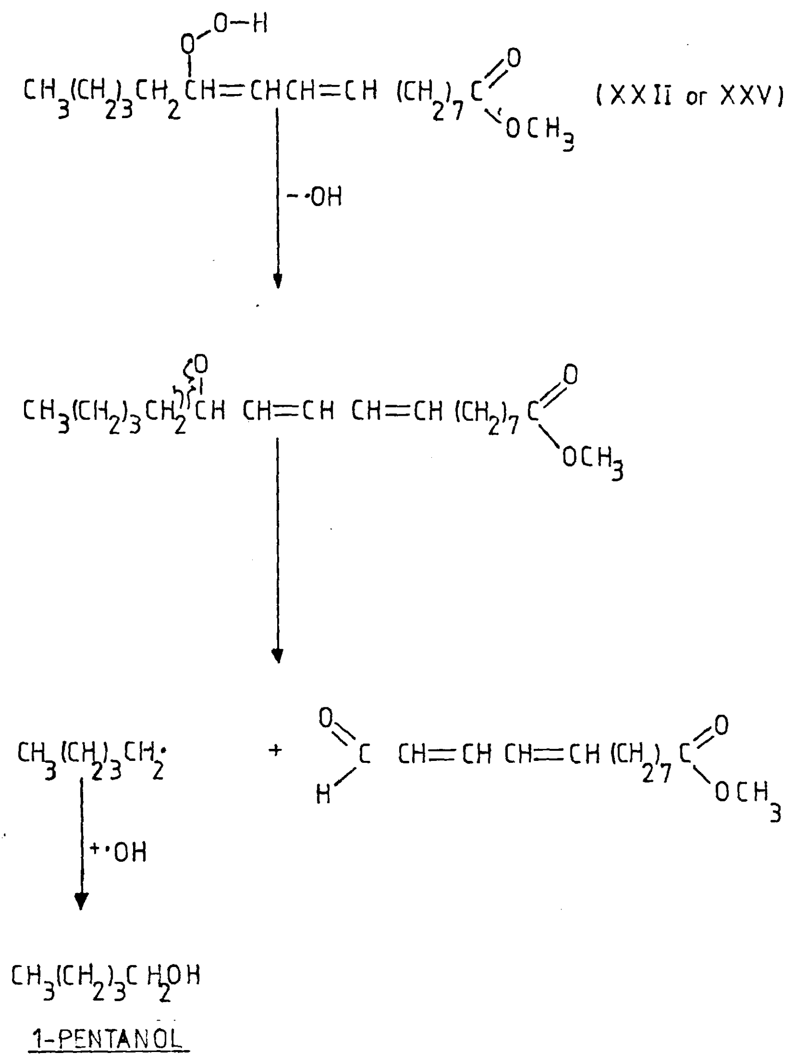
The 'volatile' products common to all three promoted autoxidations of methyl linoleate are summarised in table 37.

Table 37

1-Pentanol
Pentanal
Hexanal
2-Hexenal
2-Heptenal
Methyl heptanoate
Methyl octanoate

Some of the 'volatile' compounds detected arise directly from the promotors. The cobalt (II) and lead (II) bis(2-ethylhexanoate)s promotors gave 2-ethylhexanoic acid and methyl 2-ethylhexanoate benzil gave benzaldehyde, and the mixture of cobalt (II) bis(2-ethylhexanoate) and aluminium bis(2-butoxide) ethyl acetoacetate gave 2-butanol and ethyl acetoacetate.

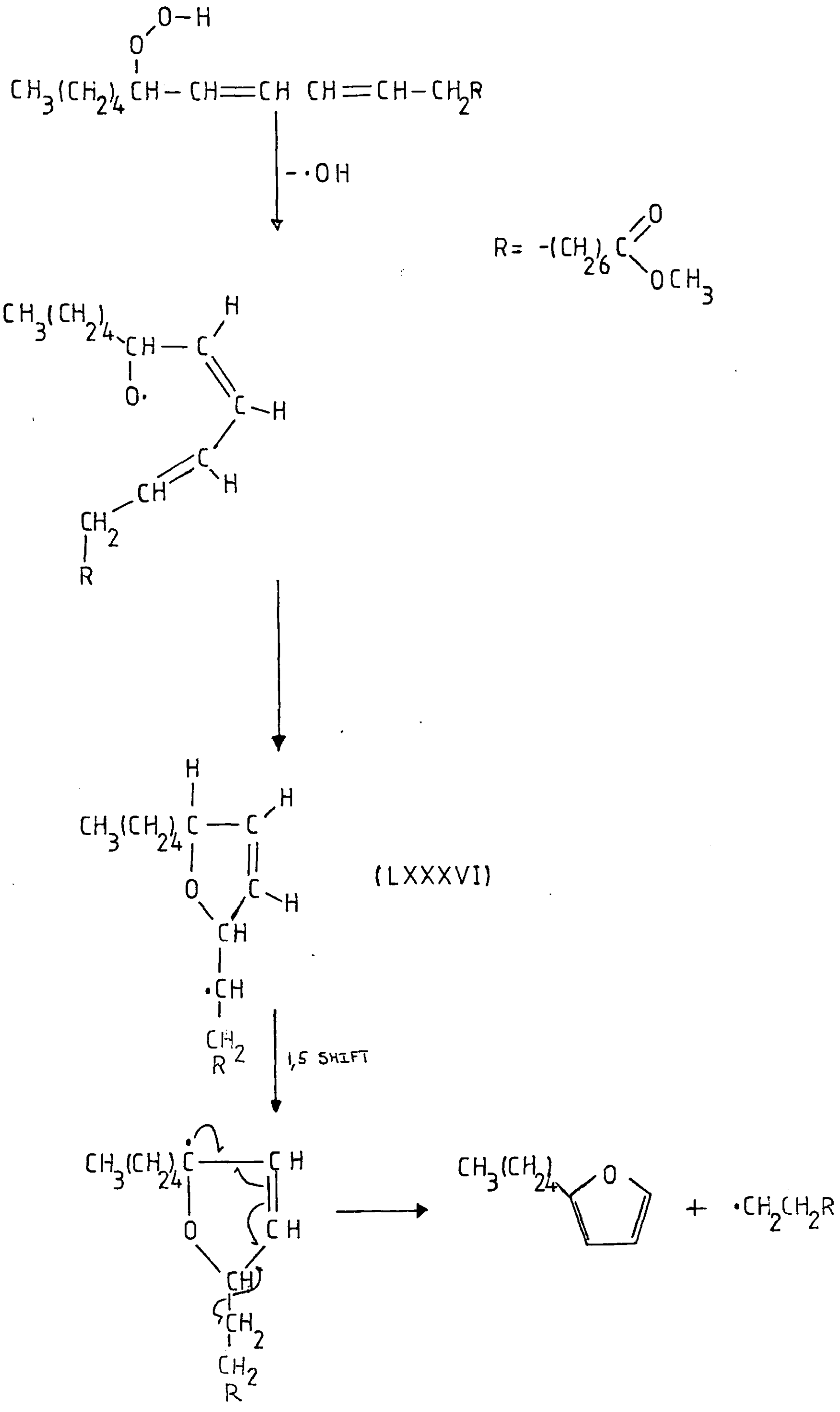
A common non-carbonyl product formed in all three promoted autoxidations is 1-pentanol. This probably arises from a pentyl radical combining with a hydroxyl radical (scheme 2.2.4.4), the pentyl radical arising from the decomposition of hydroperoxides XXIII or XXV. Hydroxyl radicals can be produced in the decomposition



Scheme 2.2.4.4

of hydroperoxides in the presence of the cobalt promotor, see section 1.12.

The identification of hexanoic acid from the Co/Pb promoted autoxidation provides evidence of further oxidation of hexanal. Pentyl furan, found in the thermal decomposition of methyl linoleate hydroperoxides, has only been identified in the cobalt/aluminium promoted autoxidations. Pentylfuran has been proposed to originate from the direct decomposition of C-10 hydroperoxides XLI or XLII (as yet unidentified), however the cyclisation of alkoxy radicals formed by the decomposition of the hydroperoxide seems more likely.

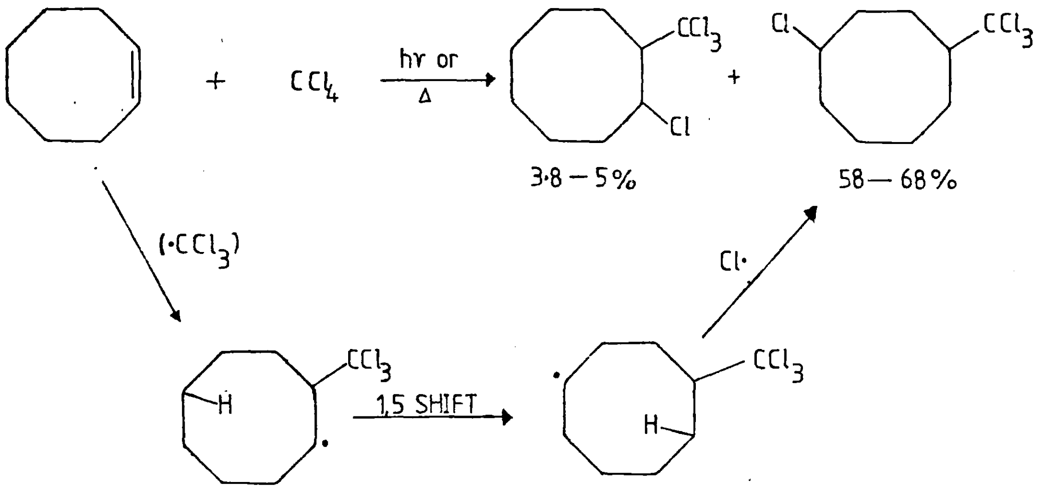


(LXXXVI)

Scheme 2.2.4.5

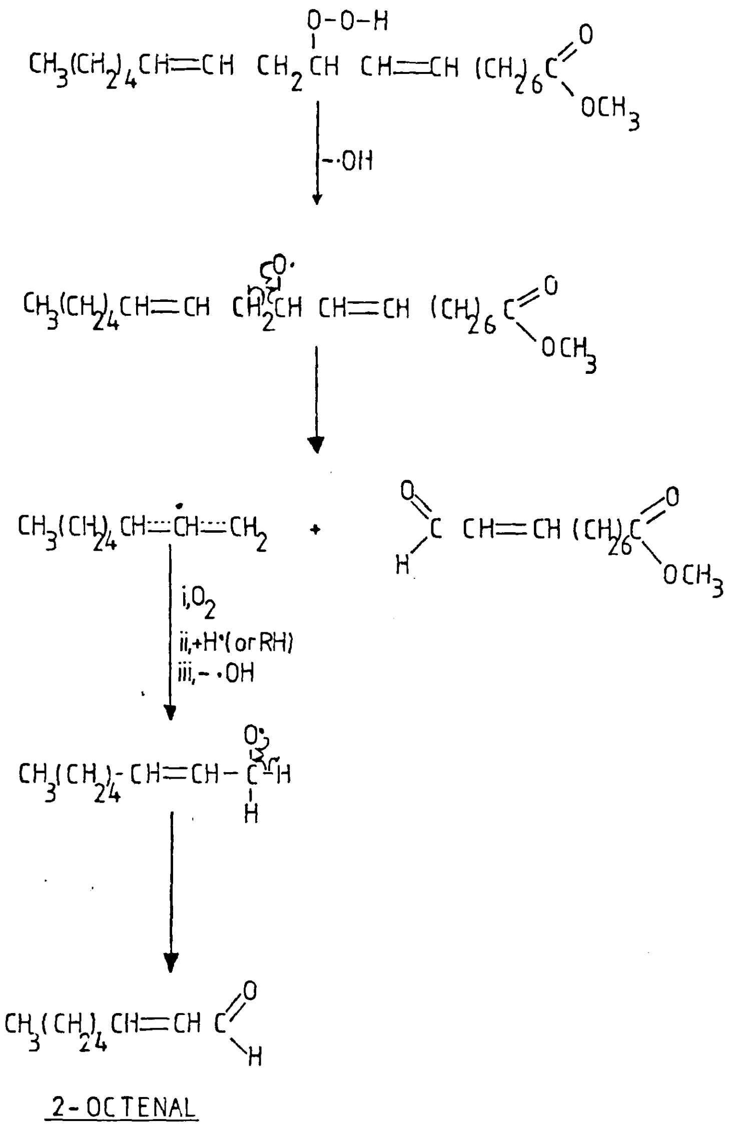
Cyclisation reactions of alkoxy radicals with alkenes have been studied by Surzur,[245] e.g. the reduction of pent-4-enyl hydroperoxide with titanium (III) chloride gives tetrahydrofurfuryl compounds. The formation of radicals similar to LXXXVI are proposed on the reaction pathways.

The 1,5 hydrogen shift, proposed in scheme 2.2.4.5, finds support in the literature,[231] e.g. the radical addition of carbon tetrachloride to cyclooctene,[253] scheme 2.2.4.6.



Scheme 2.2.4.6

A volatile product common to the Co/Pb and benzil promoted autoxidations is 2-octenal. It has been proposed that methyl-11-hydroperoxylinoleate LXXXVII exists[78] although this hydroperoxide has not so far been isolated despite the attempts of many research groups. The formation of 2-octenal could easily be explained by the decomposition of LXXXVII, but it could also result by a route such as scheme 2.2.4.7.

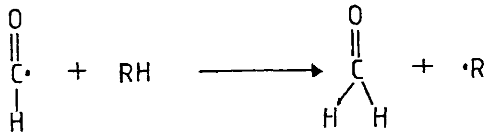


Scheme 2.2.4.7

The quantity of volatile products produced is dependent on the promotor used; the promotors containing cobalt (II) bis(2-ethylhexanoate) producing the greatest amount in the autoxidation of methyl linoleate. Unlike the autoxidation of methyl oleate promoted by a mixture of cobalt (II) bis(2-ethylhexanoate) and aluminium bis (2-butoxide) ethyl acetoacetate 'volatile' degradation products are found in the comparable autoxidation of methyl linoleate. When the quantity of 2-butanol and ethyl acetoacetate was subtracted from the total amount of 'volatiles' produced it was found to approximate to that produced from the Co/Pb promoted autoxidation. This suggests that the complexing promotor does not interfere with the autoxidative degradation by a competing Meerwein-Ponndorf-Verley reduction. However the absence of 2-ethylhexanoic acid and hexanoic acid from the 'volatiles' in the Co/Al system (but observed on the Co/Pb autoxidation) may suggest some complexing of these acids with the aluminium component.

The benzil autoxidation initiator, although producing the same volatiles, only forms about 9% of the quantity compared to the redox promotors.

Collection of the 'volatile' carbonyl compounds as their 2,4-dinitrophenyl hydrazones revealed via HPLC the formation of low molecular weight aldehydes, the Co/Pb promotor system producing the greatest range of compounds (table 28). The benzil promoted autoxidation also produced methanal. This compound may be formed by the methanyl radical (in scheme 2.2.4.3) abstracting a hydrogen atom from a suitable donor.



$$\mathrm{H{-}\dot{C}{=}O} + \mathrm{RH} \longrightarrow \mathrm{H_2C{=}O} + {}^{\bullet}\mathrm{R}$$

Equation 2.2.4.8

The low molecular weight aldehydes can be formed from methyl linoleate by hydrogen abstraction and hydroperoxide formation at carbons 14, 15, 16 and 17 followed by alkoxy radical formation and β-fragmentation. The formation of these non-allylic hydroperoxides is less favourable than those discussed in section 1.5. No explanation is offered for the absence of methanal using the Co/Al system.

Recent publications,[246,247,248] concerned with the formation of degradation products from autoxidation of methyl linoleate in the absence of promotors, also propose hydroperoxide decomposition to alkoxy radicals followed by β-scission.

2.3 Autoxidation of methyl cis-9- cis-12- cis-15- octadecatrienoate (methyl linolenate)

2.3.1 Autoxidation promoted by cobalt (II) bis(2-ethylhexanoate) and lead (II) bis(2-ethylhexanoate).

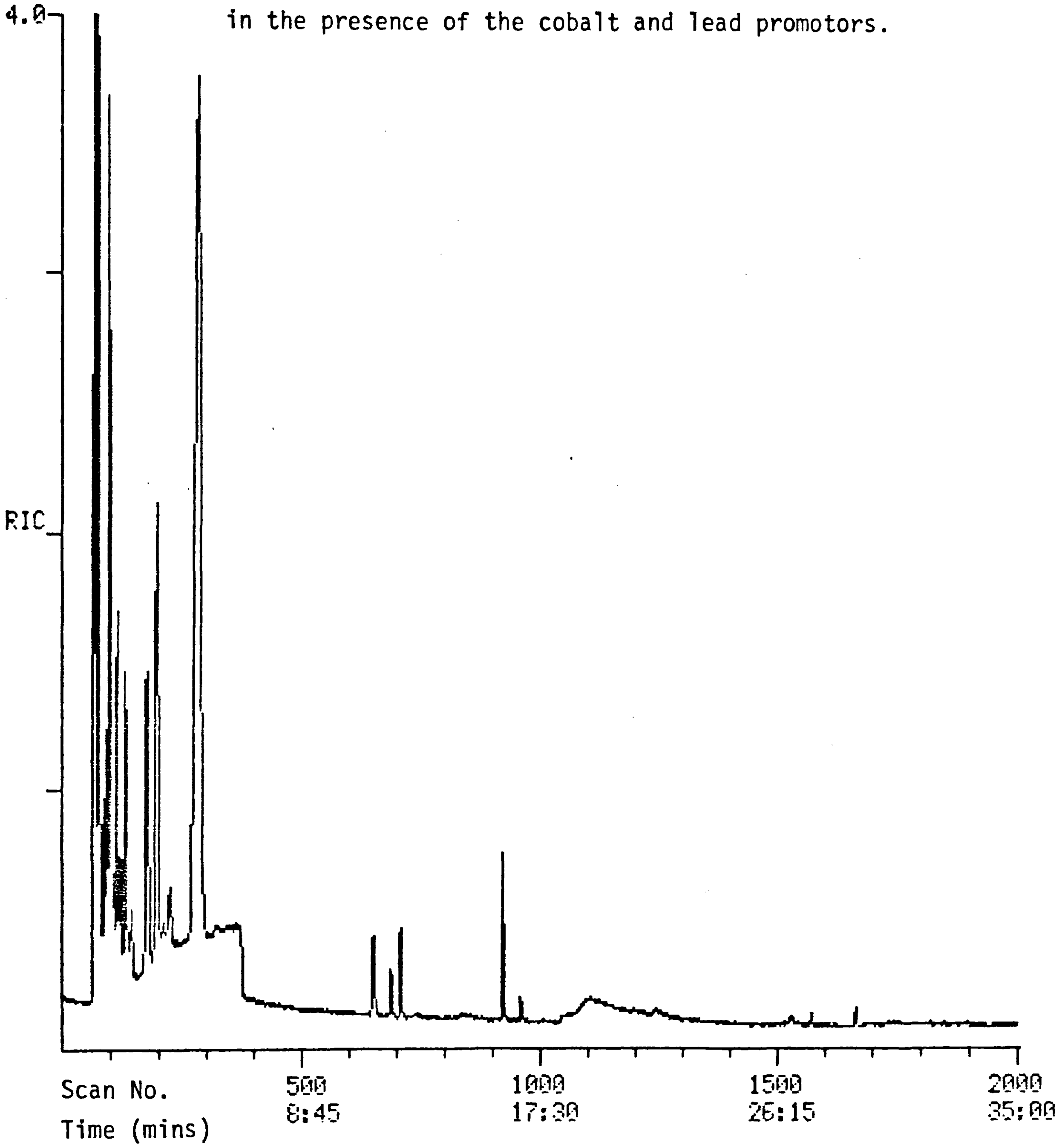
2.3.1.1 Determination of volatile products by gc-ms

The capillary gc-ms total ion current chromatogram of the volatile products collected in the cryogenic trap is illustrated in figure 2.3.1.1.1. The analysis of mass spectra obtained at the apex of each chromatographic peak is discussed below.

Scan No. 77

m/z	58	57	42	39	29	27
Rel. Ab. %	25.5	7.5	2.2	41	100	67.1

Figure 2.3.1.1.1
Total ion current chromatogram of the volatile products from the autoxidation of methyl linolenate in the presence of the cobalt and lead promotors.



The base peak ion at m/z 29 can have the compositions $CH_3CH_2^+$ or CHO^+. As this compound elutes after n-pentane it is concluded that this compound is oxygen containing. The molecular formula corresponding to a relative molecular mass of 58 being C_3H_6O. Thus it is proposed that this compound is propanal, confirmation was obtained by examination of the standard spectra.[206]

Scan No. 92

m/z	32	31	30	29
Rel. AB %	65.2	100	9.3	88.8

The relative molecular mass of 32 daltons and base peak ion at m/z 31 suggest that this compound is methanol. Confirmation was obtained by analysis of the standard spectrum.[206]

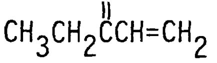
Scan No.109

m/z	46	45	43	42	31	30	29	27
Rel. AB %	9.9	25	7.5	3.7	100	6.8	35	30

The base peak ion at m/z 31 (CH_3O^+) suggests a primary alcohol. The relative molecular mass of 46 daltons permits C_2H_4O and CH_3O_2 as the molecular formula. Ethanol was confirmed by analysis of the standard spectrum.[206]

Scan No. 124

m/z	84	83	61	57	56	55	53	50	39	37	29	27	26
Rel. AB %	9.3	2.5	0.6	75	6.2	100	1.9	1.3	5	1.9	37	38	31

The loss of 29 daltons from the parent ion to form the base peak ion at m/z 55 indicates the presence of CH_3CH_2-. The molecular formula was determined to be C_5H_8O from the abundance of the M + 1 ion. With the base peak ion having the composition C_3H_3O, the suggested compound is  $CH_3CH_2\overset{O}{\overset{\|}{C}}CH{=}CH_2$ and this was confirmed by analysis of its standard spectrum.[206]

Scan No. 134

m/z	70	69	50	49	45	43	42	41	40	39	38	37	29
Rel. AB %	44.7	19.5	3.4	1.8	3.1	2.2	15.2	99	15.5	100	25	11.5	33

m/z	27	26
Rel. AB %	29.8	20

The molecular formula of this compound was established to be C_4H_6O from the abundance ratio $(M+1)/M$.. The principal ions in this spectrum are at m/z 41 (C_3H_5 or C_2HO) and m/z 39 (C_3H_3) thus this compound has olefinic unsaturation. The neutral fragment eliminated in the formation of the ion at m/z 39 is therefore CH_3O. The formyl ion m/z 29 is often indicative of a furan type structure. Comparison with some standard mass spectra[206] of furans identified this compound as 2,5-dihydrofuran.

Scan No. 146

m/z	100	85	57	56	53	44	43	42	29	27	26
Rel. AB %	7.5	0.6	23	0.9	1.3	5	100	8.7	70	37	13

This spectrum consists of five major ions at m/z 100, 57, 43, 29 and 27. The formation of the base peak ion at m/z 43 results from the elimination of 57 daltons but the presence of an ion at m/z 57 shows that during the molecular ion fragmentation the charge can remain on either fragment. These types of fragments are often observed from the α-cleavage in ketones. Examination of the standard spectra[206] provided no match for the hexanones, however the spectrum for 2,3-pentadione was in excellent agreement with that obtained from scan No. 146.

Scan Nos. 178 and 198

m/z	84	83	69	66	65	57	56	55	53	51	50	45	43
Rel AB %	175	29	5.3	3.7	3.7	6.2	14	70	16	10	12	2.2	7.1

m/z	42	41	40	39	38	37	36	29	27	26
Rel AB %	7.5	52	13	77	14	8	1.2	93	100	30.4

The abundant ions at m/z 29, 41 and 55 suggest an unsaturated compound, and the ion at m/z 45 indicates the possible presence of oxygen. The heavy isotope ratio (M+1)/M revealed the molecular formula as C_5H_8O.

The loss of water from the molecular ion (M-18) indicates a possible aldehyde structure. The abundant parent ion and M-1 is often observed in the lower α,β-unsaturated aldehydes. Comparison with the standard spectrum of 2-pentenal[206] gave a reasonable correlation but in the recorded spectrum the higher mass ions have lower abundances than expected. This may have arisen from the spectrum being recorded just past the apex of the chromatographic peak.

<u>Scan No. 283</u>

m/z	86	71	69	67	59	58	57	55	50	43	41	40
Rel. AB %	0.6	1.9	0.5	1.2	2.8	4.7	100	5.3	1.2	12.4	14.9	3.1

m/z	39	38	31	29	27
Rel. AB %	15.2	3.4	31.6	85	49

The presence of CH_3CH_2- in the molecule is shown by the loss of 15 and 29 daltons from the parent ion. The base peak ion at m/z 57 can have the following compositions, C_4H_9, C_3H_5O and C_2HO_2. C_4H_9 is doubted because the molecular formula would be C_6H_{14} and the retention time is too long for a hydrocarbon. The C_3H_5O composition appears the most probable as there is a loss of 17 daltons from the parent ion. An alcohol structure is suggested and comparison with the standard spectra of 1-penten-3-ol[206] and 3-pentanone[206] concluded that 1-penten-3-ol fitted the better.

Scan No. 654

m/z	116	98	97	70	69	59	57	55	53	45	43	41	39
Rel.AB %	0.2	1.9	21	43	70	100	17.4	7.5	2.5	13	33	86	30.5

m/z	31	29	27
Rel. AB %	78	78	85

This spectrum is very similar to that obtained in the autoxidation of methyl oleate promoted by cobalt (II) and lead (II) bis(2-ethylhexanoate) section 2.1.1.1 scan No. 936, and is therefore concluded to be 3-heptanol.

Scan No. 691

m/z	89	86	68	67	58	57	55	53	51	50	45	43	41
Rel. AB %	1.9	6.8	6.8	5.9	5.6	100	17.4	13	6.2	7	30	36	55

m/z	39	31	29	27
Rel. AB %	61	47	95.6	86

The base peak ion at m/z 57 can have the following compositions; C_4H_9, C_3H_5O and C_2HO_2. However the parent ion could not be identified. The packed column EI gc-ms study did not reveal the presence of this compound and therefore the parent ion was not established by CI gc-ms.

Scan No. 711

m/z	133	86	83	71	69	68	67	58	57	55	53	51	50	44	43
Rel. AB %	1.6	1.9	1.9	6.2	3.4	19	17	5.6	92	17.4	17.	17.1	6.8	34	33

m/z	42	41	40	39	38	31	29	27
Rel. AB %	14	54	99	61.5	9.9	46.4	100	87

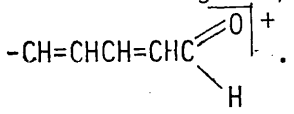
Again the parent ion in this spectrum could not be identified, thus making interpretation difficult as no similar spectrum could be found in the packed column EI gc-ms. CI gc-ms study did not provide any information regarding the relative molecular mass of this compound.

Scan No. 923

m/z	110	109	95	91	82	81	79	77	68	67	65	63
Rel. AB %	15	1.9	43	2.8	6.8	100	16	7.8	12	11.8	10.6	5.3

m/z	53	51	50	41	39	29	27
Rel. AB %	43	19.3	13	47	69	42	58

The loss of 15 and 29 daltons again shows the presence of CH_3CH_2-. The molecular formula of $C_7H_{10}O$ was established by the heavy isotope ratio (M+1/M). The base peak ion at m/z 81 must therefore have the following composition C_5H_5O, which may result from the structure



$$\left[-CH{=}CHCH{=}CHC\overset{\displaystyle O}{\underset{\displaystyle H}{\diagup\!\!\diagdown}}\right]^{+}$$

. Comparison with the standard spectrum of 2,4-heptadienal[206] confirmed its presence.

Scan No. 961

m/z	110	95	82	81	79	77	67	65	55	53	51	50
Rel. AB %	10.2	2.5	5.9	100	15.5	8	13.7	5.6	6.2	34.7	16	11.2

m/z	41	40	39	29	27
Rel. AB %	38	12.4	51	35	54

This spectrum is almost identical to that obtained in scan No. 923 and is concluded to be a cis-trans isomer of 2,4-heptadienal.

Scan No. 1530

m/z	101	88	87	73	69	58	57	42	41	39	27
Rel. AB %	15	69	21	53	12	12.5	21	22	68	37	100

This spectrum has some similarities to that of 2-ethylhexanoic acid. However neither the parent ion nor the Mclafferty rearrangement ion at m/z 102 is observed. The packed column EI gc-ms study did not yield a spectrum with similar fragmentation and hence the parent ion could not be deduced by packed column CI gc-ms.

Scan No. 1573

m/z	221	193	180	181	165	137	133	115	109	105	103	95
Rel. AB %	7.5	7.5	28	13	60	24	8	6.2	11.8	10.8	8	6.8

m/z	91	79	77	71	67	57	53	43	41	39	31	29
Rel. AB %	17	7.5	12.5	9.3	12.7	58	17	86	100	27	18.9	57

The molecular ion cannot be determined and thus interpretation was not possible.

Packed column gc-ms analysis identified the following compounds: methyl 2-ethylhexanoate, methyl octanoate and 2-ethylhexanoic acid. Analysis of the mass spectra of these compounds has been discussed earlier.

The volatile compounds identified by gc-ms are summarised in table 38.

Table 38

Volatile products formed during the autoxidation of methyl linolenate in the presence of cobalt and lead promotors

Compound	% Composition
1-Pentene-3-one	0.95
2,3-Pentadione	0.22
Propanal	27.8
2-Pentenal (both isomers)	9.42
2,4-Heptadienal	2.02
2,5-Dihydrofuran	4.03
Methanol	—
Ethanol	26.0
1-Pentene-3-ol	14.7
3-Heptanol	—
Methyl-2-ethylhexanoate	1.23
Methyl octanoate	7.42
2-Ethylhexanoic acid	0.07

The total amount of volatile material collected in the cold trap was 4.73 x 10^{-3}g based on dodecanal as the internal standard.

2.3.1.2 Determination of volatile products by HPLC

2,4-Dinitrophenylhydrazone derivatives of aldehydes, trapped by the coated silica gel, were identified by their retention times by HPLC using a C_{18} reversed phase column. The retention times and their assignments are given in table 39.

Table 39

Retention time (Mins)	Assignment
6.4	Methanal
9.5	Ethanal
12.3	Propanal
16.7	2-Butenal
17.4	Butanal

2.3.2 Autoxidation promoted by cobalt (II) bis (2-ethyl hexanoate) and aluminium bis(2-butoxide) ethyl acetoacetate

2.3.2.1 Determination of volatile products by gc-ms

The total ion current chromatogram obtained from the capillary gc-ms analysis of the volatiles collected in the cold trap is shown in figure 2.3.2.1.1. The volatile products are very similar to those found in the cobalt and lead promoted autoxidation. The exception being the absence of methyl-2-ethylhexanoate, 2-ethylhexanoic acid, 2,3-pentanedione and 2,5-dihydrofuran but with the added presence of 2-butanol and ethylacetoacetate. The compounds identified from this autoxidation are given in table **40** .

Figure 2.3.2.1.1.

Capillary total ion current chromatogram of the volatile products from the autoxidation of methyl linolenate in the presence of cobalt and aluminium promotors.

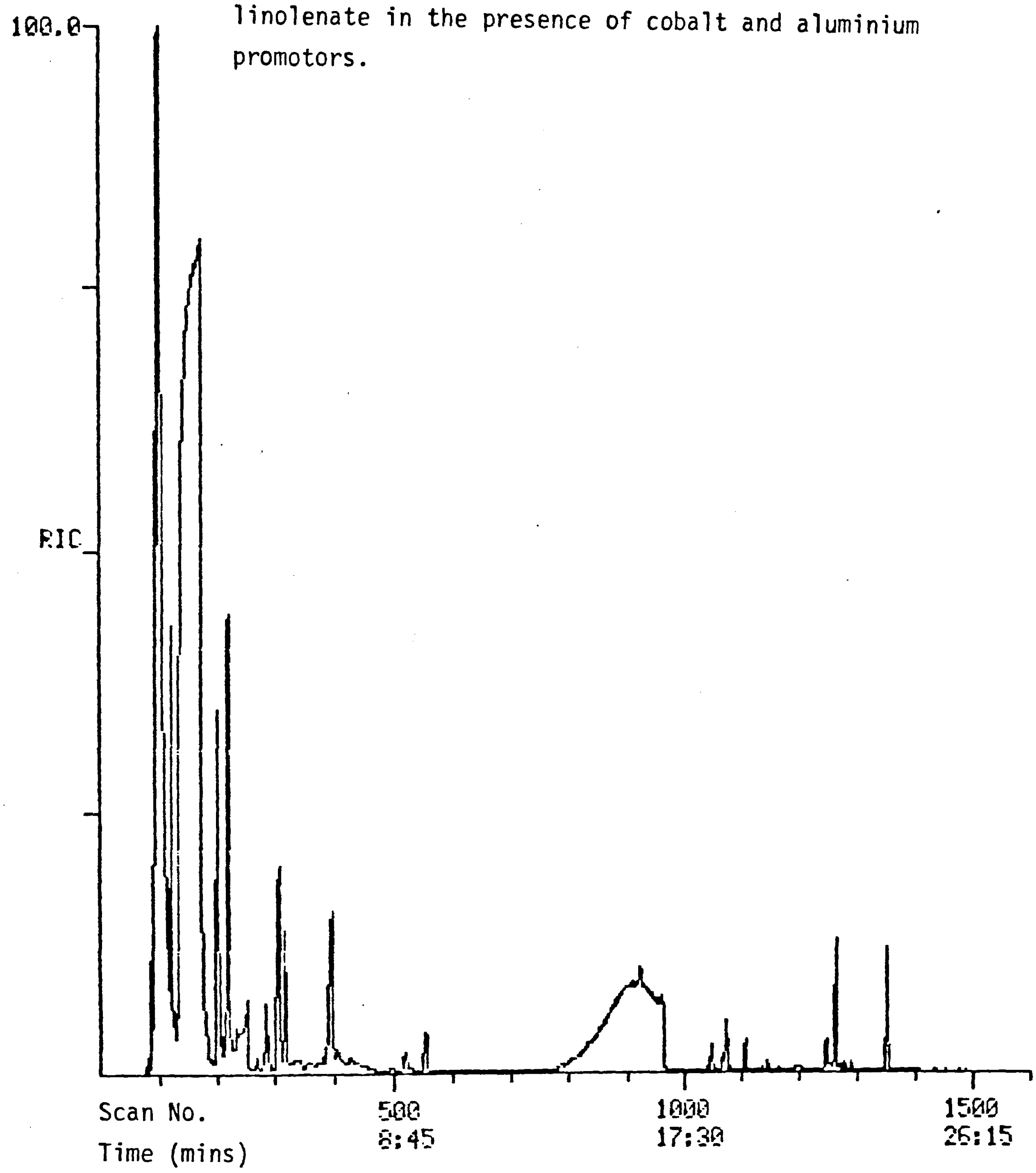


Table 40

Volatile compounds identified by gc-ms from the autoxidation of methyl linolenate in the presence of cobalt and aluminium promotors

Compound	% Composition
1-Pentene	
1-Pentene-3-one	1.3
3-Heptanone	
Propanal	29.7
2-Pentenal	10.6
2,4-Heptadienal	3.9
Ethanol	23.1
2-Butanol*	
1-Penten-3-ol	13.9
Methyl octanoate	8.2
Ethyl acetoacetate*	
Propanoic acid	1.1

* % Composition determined without the inclusion of 2-butanol and ethyl acetoacetate.

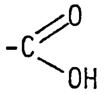
The total amount of volatile material collected in the cold trap was 4.18 x 10^{-2}g. The amount of volatile degradation products (i.e. excluding 2-butanol and ethyl acetoacetate) is 4.31 x 10^{-3}g.

The mass spectrum of one compound formed in the above reaction which could not be identified is now discussed.

Scan No. 1264

m/z	154	139	126	125	110	109	108	97	81	80	69
Rel. AB %	26.7	1.6	21.2	40.1	8.1	99.4	27	61	11.8	19.3	6.1

m/z	53	52	51	50	43	42	41	39	38	29	27
Rel. AB %	29.5	23.6	30	21	57	5.9	6.2	16.8	8.7	61.5	100

The heavy isotope ratio pointed to a molecular formula of $C_8H_{10}O_3$. The loss of 15, 29 and 45 daltons from the parent ion suggests the presence of the following groups: CH_3CH- and  $-C(=O)OH$ thus the abundant ion m/z 109 would be composed of $C_6H_5O_3$ or C_7H_9O. No assignment can be made from this spectrum.

2.3.2.2 Determination of volatile products by HPLC

The volatile compounds, collected in the chemical trap, were identified by HPLC as their 2,4 dinitrophenyl hydrazone derivatives. The retention times and assignments are given in table 41.

Table 41

Retention times (Mins)	Assignment
12.5	Propanal
17.3	Butanal

2.3.3 Autoxidation promoted by benzil

2.3.3.1 Determination of volatile products by gc-ms

In figure 2.3.3.1.1 the capillary gc-ms total ion chromatogram obtained from the volatiles trapped in the cold trap is depicted. The compounds identified from their mass spectra are very similar to those found in the cobalt and lead promoted autoxidation. Some differences occur, those being the absence of methyl-2 ethylhexanoate, 2-ethylhexanoic acid, 2,3-pentanedione and the presence of benzaldehyde. One compound of significant abundance could not be identified and its spectrum is reported below.

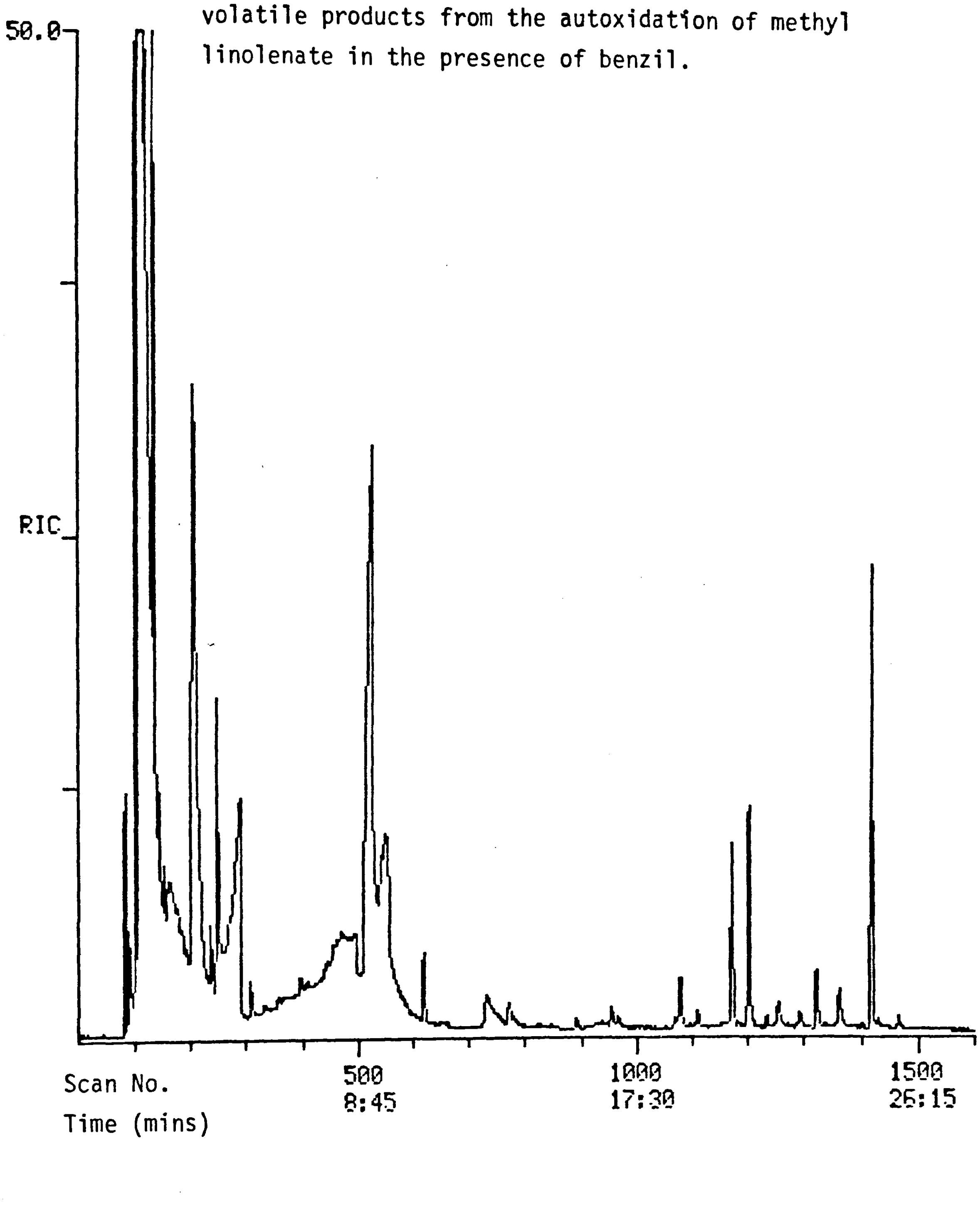
Scan No. 526

m/z	88	58	57	55	55	50	45	43	42	41	39	31	29	27	26
Rel. AB %	8.4	4.0	80.1	11.5	5.0	0.9	10.6	6.0	16.1	9.0	8.0	100	94.7	76.4	43

The molecular ion at m/z 88 could have the following compositions; C_7H_4, $C_5H_{12}O$, $C_4H_8O_2$ and $C_3H_4O_3$. There is a loss of 31 daltons from the parent ion and the base peak ion at m/z 31 thus suggesting the presence of OCH_3 in the molecule. The retention time of this compound rules out the hydrocarbon structure C_7H_4. Considering the formula $C_5H_{12}O$, the alcohols 1-pentanol, 2-pentanol and 3-pentanol are ruled out since their base peaks ions are m/z 42, m/z 45 and m/z 59 respectively. No aldehyde or ketone structures can be assigned, although ether structures may be possible. None of the possible ethers,however,has a fragmentation pattern similar to scan No. 526.

Figure 2.3.3.1.1.

Capillary total ion current chromatogram of the volatile products from the autoxidation of methyl linolenate in the presence of benzil.



The formula $C_4H_8O_2$ would allow butanoic acid or methyl propanoate. However butanoic acid would undergo a Mclafferty rearrangement under electron impact and have a base peak ion at m/z 60. The fragmentation of methyl propanoate is similar but has an ion at m/z 59 (~30% of base peak) and is thus ruled out.

It is possible that the ion at m/z 88 arises from fragmentation of an undetected parent ion and thus the true molecular formula is unknown.

The compounds which have been identified from the gc-ms studies are summarised in table 42.

Table 42

Volatile products formed during the autoxidation of methyl linolenate in the presence of benzil

Compound	% Composition
1-Penten-3-one	1.3
Propanal	25.1
2-Pentenal	10.4
2,4-Heptadienal	3.9
Benzaldehyde	1.67
Ethanol	13.2
1-Penten-3-ol	16.7
3-Heptanol	
Methyl octanoate	7.1
Unknown (scan 526)	4.7

The total amount of volatile material collected in the cold traps was 0.462×10^{-3}g based on dodecanal as the internal standard.

2.3.3.2 Determination of volatile products by HPLC

The volatile compounds trapped by the chemical trap were analysed by HPLC and identified by their retention times. The retention times and assignments are given in table 43.

Table 43

Retention time (Mins)	% Composition
9.4	Ethanal
12.5	Propanal
15.0	3-Buten-2-one
17.0	Butanal

2.3.4 Mechanistic Interpretation

Kawahara[249] studied the volatile components from the autoxidation of Soybean oil identifying hexanal, 2-pentenal, propanal and ethanal as their 2,4-dinitrophenylhydrazone (2,4-DNPH) derivatives. Dutton[250] showed that the linolenic acid component of glycerides is an unstable precursor of 'painty' and 'rancid' fractions.

Kawahara[251] studied the volatiles derived from methyl linolenate, by bubbling oxygen through the pure ester for 7 days at room temperature. The volatiles were collected in a cold trap immersed in an ethanol and solid carbon dioxide bath. In this study ethanal, propanal, 2-pentenal and hex-3-ene-1,6-dial were identified as their 2,4-DNPH derivatives. Thus the conclusion was drawn that ethanal, propanal and 2-pentenal obtained from Soybean oil must result from the linolenic acid component.

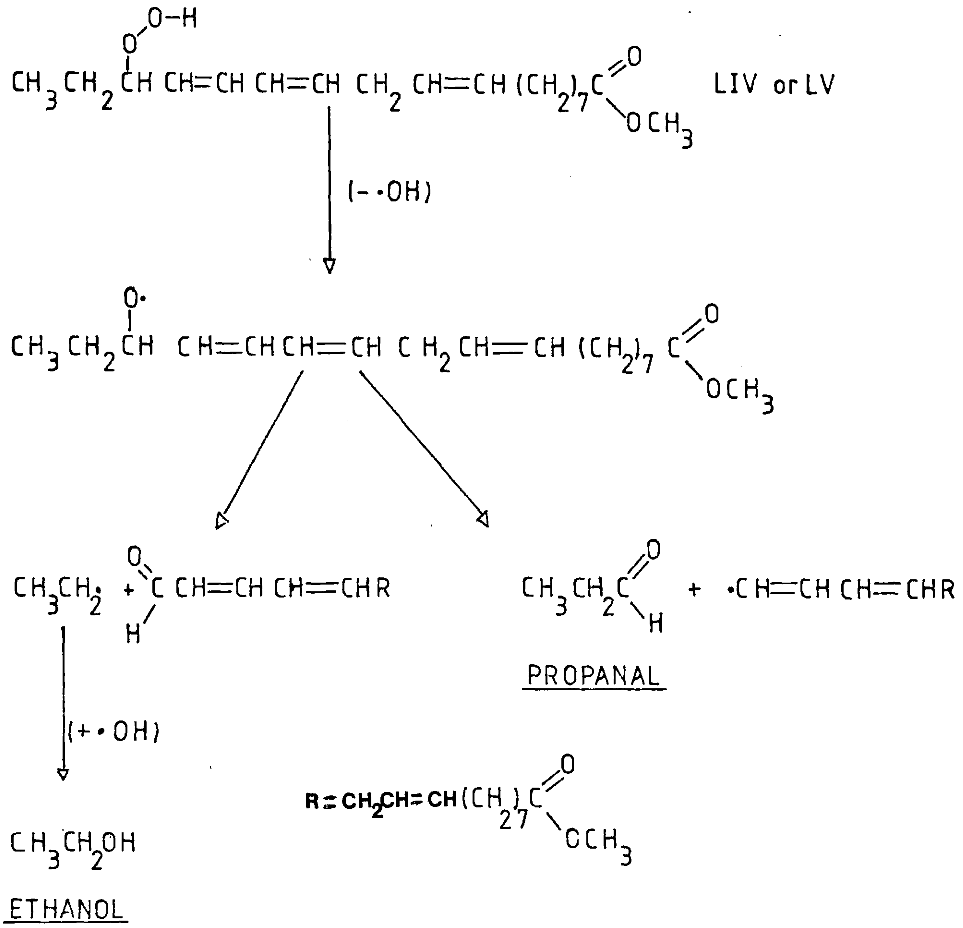
Johnson[252] using 'polymeric ethyl linolenate', again identified ethanal, propanal, 2-pentenal along with methyl ethyl ketone,but it has been Frankel[214] who has made the most complete study of the thermal decomposition products of methyl linolenate hydroperoxides. The hydroperoxides were decomposed in the injection port of the gas chromatograph. The compounds are summarised in table 44.

The 'volatiles' obtained from the promoted autoxidations of methyl linolenate (sections 2.3.1, 2.3.2 and 2.3.3) are similar to those in table 44., thus again suggesting similar degradation pathways from the hydroperoxide. Unlike the 'volatiles' obtained from methyl linoleate, which is characterised by ~70% hexanal, there is a greater spread of products from methyl linolenate. (See tables 38, 40 and 42.) The most abundant carbonyl product from all three promoted autoxidations is propanal and this is proposed to arise from the hydroperoxides LIV or LV. An abundant non-carbonyl product, ethanol, is also formed from the hydroperoxides LIV or LV, scheme 2.3.4.1. This illustrates the two carbon-carbon cleavages available to the alkoxy radical as shown in Scheme 2.2.4.1. (see section 2.2.4).

Table 44

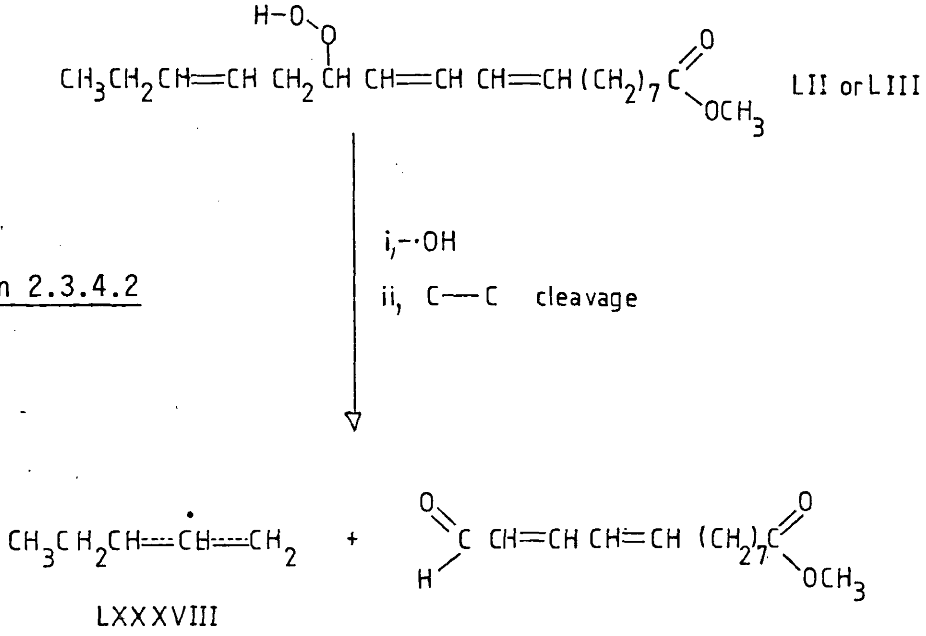
Gc-ms analysis of 'volatiles' from thermally decomposed methyl linolenate hydroperoxides

Compound	Autoxidation (rel %)	Photosensitised oxidation (rel %)
Ethane/Ethene	10	3.2
Ethanal	0.8	0.6
Propanal	7.7	9.0
Butanal	0.1	0.8
2-Butenal	0.5	11.0
2-Pentenal	1.6	1.2
2/3-Hexenal	1.4	3.4
2-Butylfuran	0.5	0.3
Methyl heptanoate	1.8	1.0
2,4-Heptadienal	9.3	8.8
Methyl octanoate	22.0	15.0
4,5-Epoxyhepta-2-enal	0.2	0.2
3,6-Nonadienal	0.5	1.1
Methyl nonanoate	0.7	0.3
Decatrienal	14.0	4.8
Methyl 8-oxo-octanoate	0.6	12.0
Methyl 9-oxo-nonanoate	13.0	12.0
Methyl 10-oxo-decanoate	1.0	1.5
Methyl 10-oxo-8-decenoate	4.2	13.0



Scheme 2.3.4.1

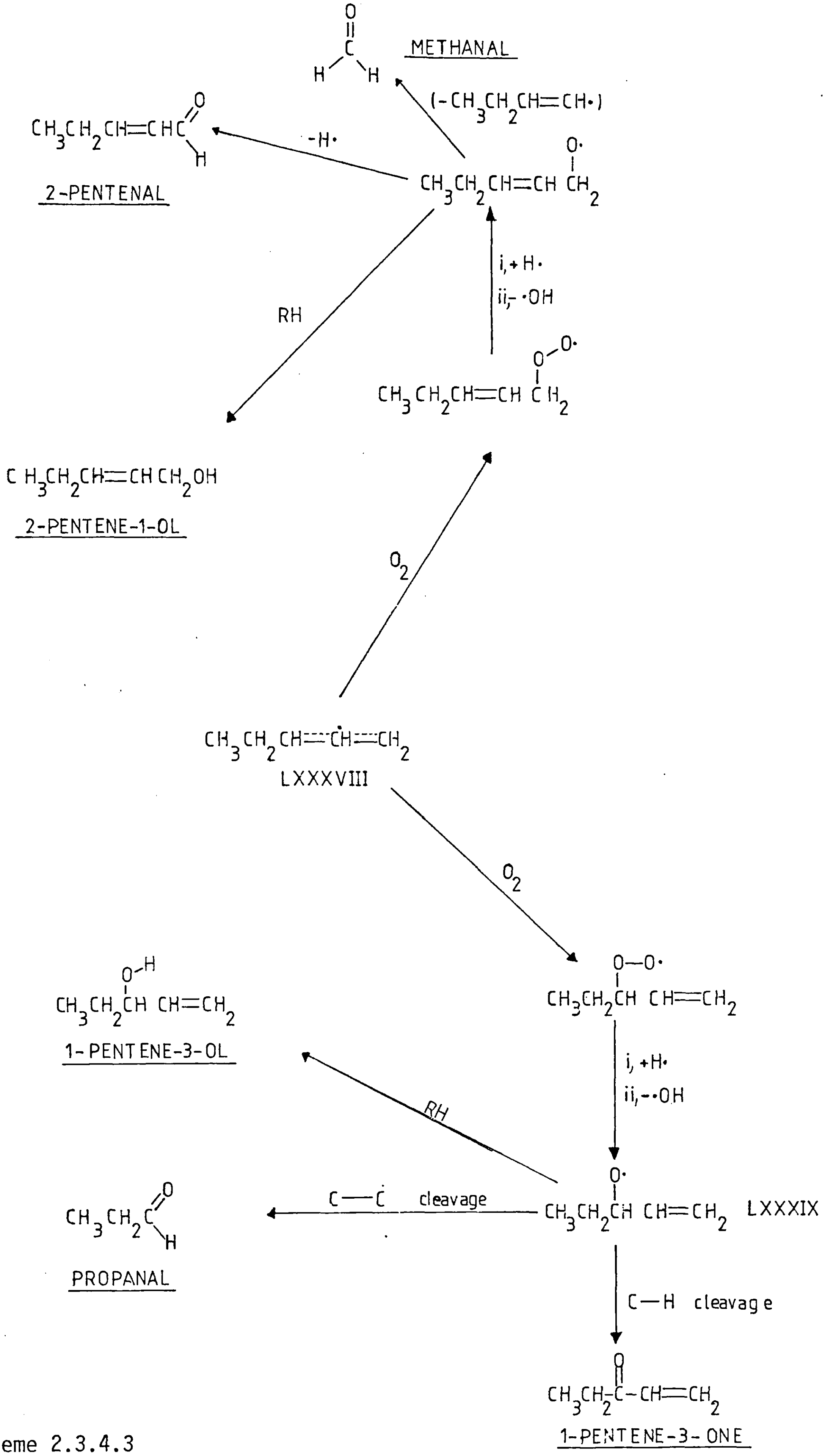
The formation of 1-pentene-3-one, 1-pentene-3-ol and 2-pentenal can be explained from the 13-hydroperoxides, LII or LIII. The mechanism involves the formation of a allyl radical LXXXVIII then the addition of either a hydroxy radical or oxygen to the system. The favoured formation of 1-pentene-3-ol is explained by the availability of two routes of formation, either directly from hydroxy radical addition to the allyl radical or from hydrogen abstraction by the alkoxy radical LXXXIX. The mode of cleavage of the alkoxy radical will either give propanal (C-C breakage) or 1-pentene-3-one (C-H cleavage). 2-Pentenal is formed via oxygen attack at the terminal carbon in the allyl radical LXXXVIII, then hydroperoxide formation and decomposition to form an alkoxy radical resulting ultimately in carbonyl formation. These reactions are given in equation 2.3.4.2 and scheme 2.3.4.3.



$$CH_3CH_2CH{=}CH\,CH_2\overset{O-OH}{CH}\,CH{=}CH\,CH{=}CH(CH_2)_7C(=O)OCH_3 \xrightarrow[\text{ii, C—C cleavage}]{\text{i, -·OH}} CH_3CH_2\dot{C}H{\cdots}CH{\cdots}CH_2 + OHC\,CH{=}CH\,CH{=}CH\,(CH_2)_7C(=O)OCH_3$$

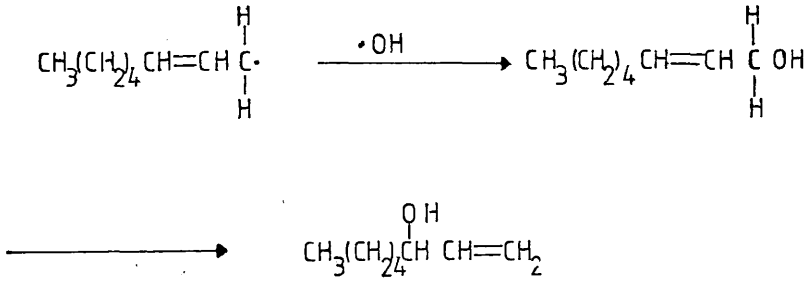
Equation 2.3.4.2

The formation of 1-pentene-3-one involves carbon-hydrogen bond fission. As the C-H bond is stronger than the C-C bond its fission is expected to play only a minor part in the decomposition of alkoxy radicals. However this mode has been observed in the decomposition of the ethoxy radical.[254] The minor role of C-H fission is perhaps reflected in the low yield of 1-pentene-3-one (~1.0%).


METHANAL
(-CH3CH2CH=CH·)
-H·
2-PENTENAL
RH
i, +H·
ii, -·OH
2-PENTENE-1-OL
O2
LXXXVIII
O2
1-PENTENE-3-OL
i, +H·
ii, -·OH
RH
C—C cleavage
LXXXIX
PROPANAL
C—H cleavage
1-PENTENE-3-ONE

Scheme 2.3.4.3

If radical LXXXVIII is an intermediate, then the formation of 2-pentene-1-ol should be expected. However this compound has not been observed in the volatile products. Frankel[214] explained the formation of 1-octen-3-ol from the rearrangement of 2-octen-1-ol. The primary alcohol originates from a 2-octene radical reacting with a hydroxy radical.

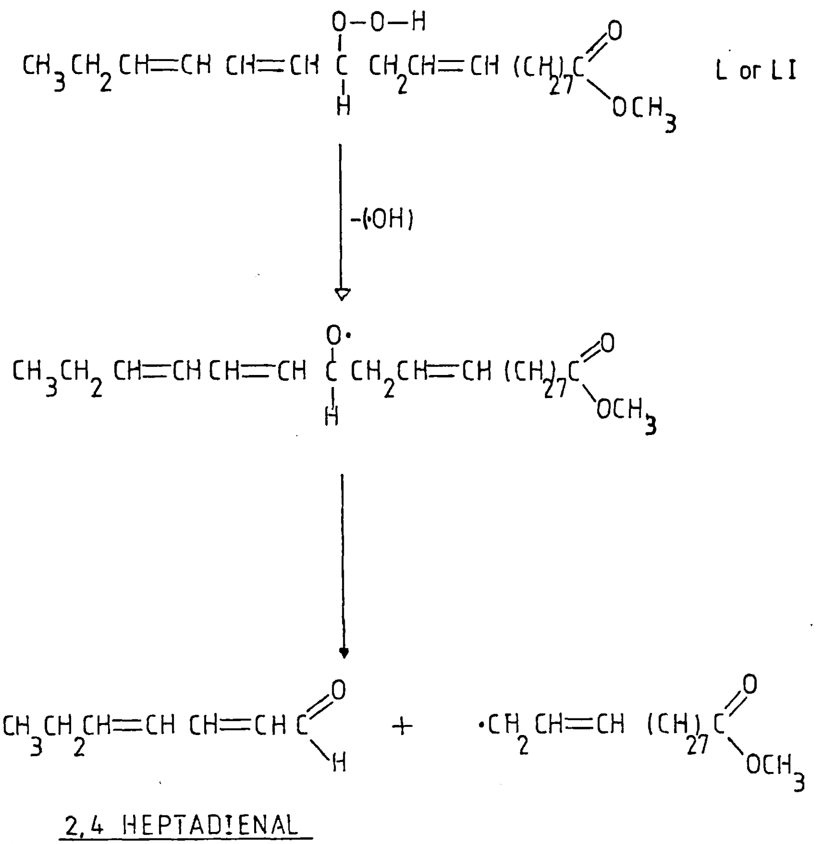


$$CH_3(CH_2)_4CH{=}CH\overset{H}{\underset{H}{C}}\cdot \xrightarrow{\cdot OH} CH_3(CH_2)_4CH{=}CH\overset{H}{\underset{H}{C}}OH \longrightarrow CH_3(CH_2)_4\overset{OH}{C}H\;CH{=}CH_2$$

Scheme 2.3.4.4

The formation of 1-octen-3-ol could be explained easily by the route proposed for 1-pentene-3-ol formation from methyl linolenate. The selective formation of the secondary alcohol, observed by Frankel[214] and in this work may possibly be explained by hyperconjugation by the ethyl group aiding stability of the secondary radical over the primary radical. Although the formation of 2-pentenal appears to contradict this theory.

2,4-Heptadienal is formed by the decomposition of the 12-hydroperoxides L or LI. This pathway, scheme 2.3.4.5, is similar to the other hydroperoxide decompositions discussed earlier. The stereochemistry of the double bonds in the 2,4-heptadienal are expected to be that in the parent hydroperoxides i.e. trans-2-, cis-4-heptadienal and trans-2-, trans-4-heptadienal. However, although



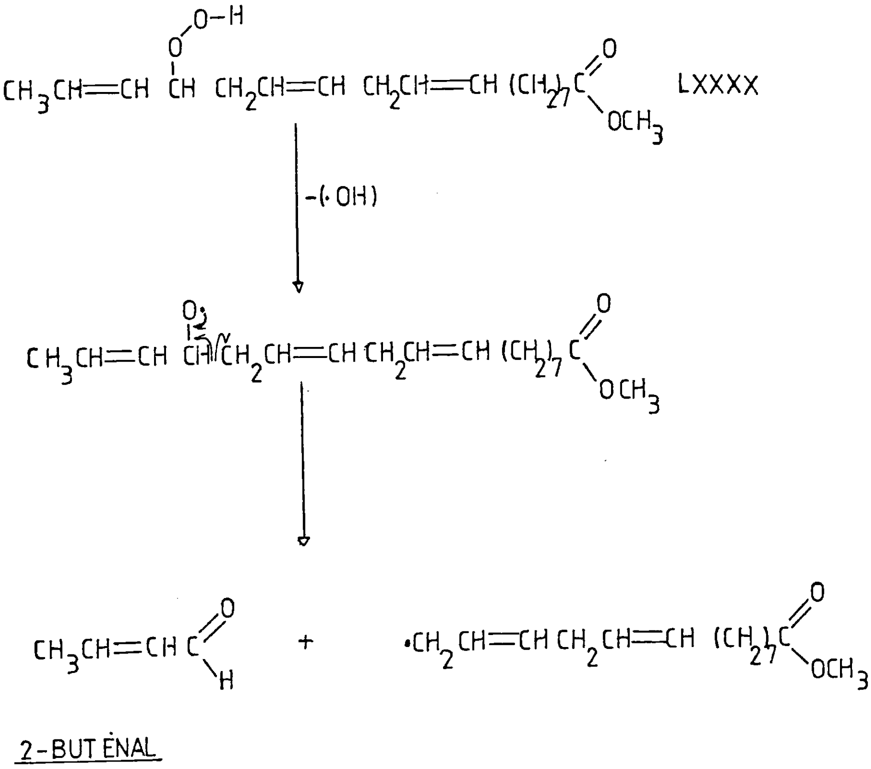
Scheme 2.3.4.5

two isomers were separated by capillary gc, electron impact mass spectrometry is not usually a suitable technique for identification of cis-trans isomers. It is expected that the second isomer to elute would be trans, trans. The last volatile compound common to all the promoted autoxidations is methyl octanoate. Its formation has been discussed earlier in section 2.1.4 (scheme 2.1.4.8).

As well as the above mentioned volatiles the autoxidation of methyl linolenate, promoted by cobalt (II) and lead (II) bis (2-ethylhexanoate), produced the following compounds: 2,3-pentadione, 2,5-dihydrofuran, methanol, 2-heptanol, methyl 2-ethylhexanoate and 2-ethyl hexanoic acid. The formation of the latter two compounds is discussed elsewhere (section 2.10.1).

Benzaldehyde was again found in the benzil promoted,and ethylacetoacetate and 2-butanol observed in the Co/Al promoted, autoxidation. A dependence of the quantity of volatile material produced upon the promotor was repeated, the benzil promoted autoxidation producing only 9.8% of that promoted by Co/Pb.

The short chain aldehydes identified as their 2,4-DNPH derivatives were again similar in each autoxidation, the cobalt (II) and lead (II) bis(2-ethylhexanoate) promoted autoxidation producing the greatest number ranging from methanal to butanal. The formation of the saturated aldehydes propanal and ethanal can be accounted for by hydroperoxide decomposition. Methanal is probably formed by the route suggested in scheme 2.3.4.3. 2-Butenal formation can be explained from the unconjugated hydroperoxide LXXXX. Scheme 2.3.4.6.



Scheme 2.3.4.6

However the existence of methyl 15-hydroperoxy-9-cis-12-cis-16-trans-octadecatrienoate LXXXX has not been reported to date.

2.4 Autoxidation of benzoyloxyethyl cis-9-cis-12-octadecadienoate

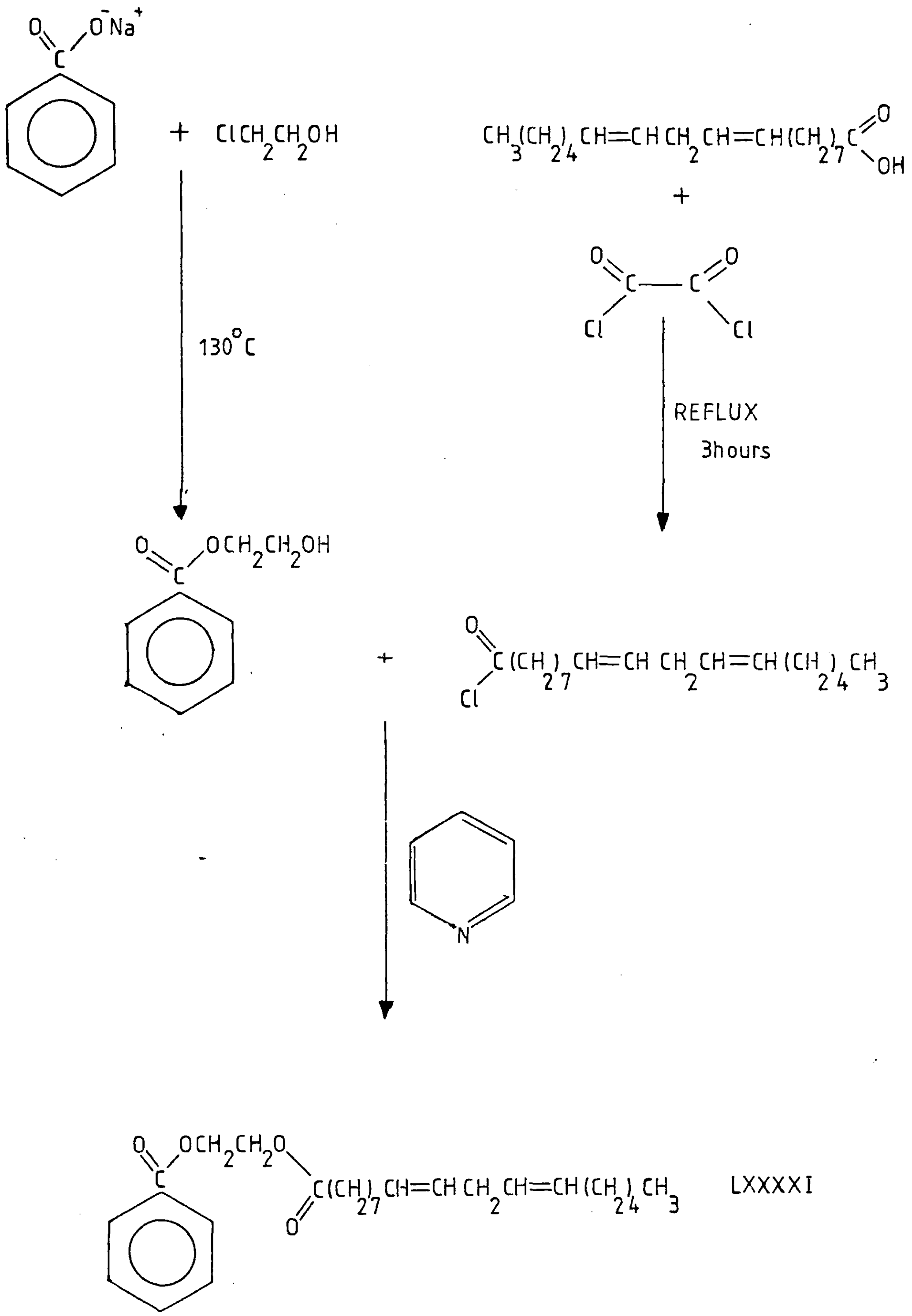
2.4.1 Synthesis

Benozyloxyethyl cis-9-cis-12-octadecadienoate (LXXXXI) was prepared in two steps. Firstly 2-hydroxyethylbenzoate was prepared using the method of Cretchner[255] by nucleophilic displacement of chlorine in chloroethanol. The product purified by distillation and used in the second step, a reaction with linoleyl chloride which was prepared using oxalyl chloride,[256] following several unsuccessful attempts using thionyl chloride. The esterification was carried out in the presence of pyridine to remove the HCl produced, scheme 2.4.1.1. The resultant ester was purified by column chormatography, then characterised by ^{1}H nmr (table 45) and infrared spectroscopy (table 46).

2.4.2 Autoxidation promoted by cobalt (II) bis(2-ethylhexanoate) and lead (II) bis(2-ethylhexanoate)

2.4.2.1 Determination of volatile products by gc-ms

The volatile products accumulated in the cold trap were analysed by packed column glc and gc-ms. The gc-ms experiments revealed the presence of the compounds listed in table 47. No quantitative determination of the volatile products was carried out, however the percentage composition (by area) of the products was determined.

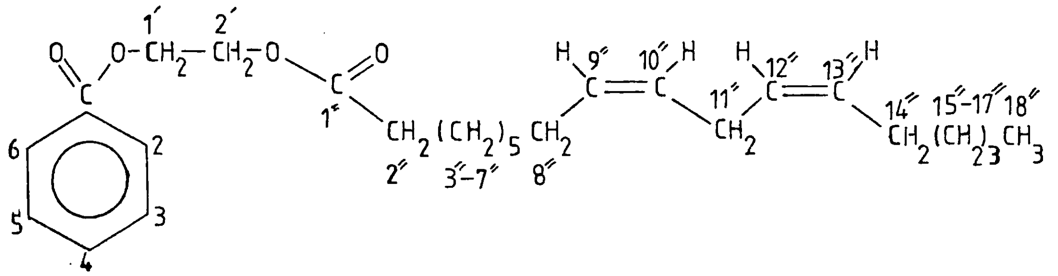


LXXXXI

Scheme 2.4.1.1

Table 45

Assignment of ^1H n.m.r. spectrum of benzoyloxyethyl linoleate



Type of signal	Chemical shift (PPM)	Coupling constants (Hz)	Integration
t	0.9 CH_3 (18")	$J_{17''\,18''} = 5.0$	3
s (br)	1.32 8CH_2 (3"-7",15"-17")		16
m/t	1.9-2.5 3CH_2(2",8",14")		6
t	2.80 CH_2 (11")	$J_{10''\,11''} = J_{11''\,12''}$ $= 5.0$	2
s	4.55 2CH_2 (1', 2')		4
t	5.44 4CH (9",10", 12", 13")	$J_{8''9''} = J_{10''11''} =$ $J_{11''12''} = J_{13''14''}$ $= 5{\cdot}0$	4
m/t	7.4 - 7.8 3H (3,4,5)		3
m/t	8.1 - 8.4 2H (2,6)		2

Table 46

Assignment of IR spectrum of benzoyloxyethyl linoleate

cm^{-1}	Assignment
3050	C-H aromatic stretch
3010	C-H olefinic stretch
2940	C-H,CH_3 asymmetric stretch
2928	C-H, $-CH_2-$ asymmetric stretch
2858	Symmetric stretch CH_3,$R-CH_2-R$
1740	C=O stretch higher aliphatic ester
1730	C=O aryl acid ester
1610	$\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretch
1450	Aliphatic C-H def.
1380	Aliphatic C-H def.
1275	C-O stretch aryl acid ester
1180	C-O stretch aliphatic ester
1110	C-O stretch aryl acid ester
720	out of plane C-H def. cis -CH=CH-
710	out of plane aromatic C-H def.

Table 47

Compound	% composition
Pentanal	8.1%
Hexanal	70.4%
2-Hexenal	1.0%
2-Heptenal	5.7%
2-Octenal	1.6%

The mass spectra of these compounds were discussed in sections 2.2.1.1, 2.2.2.1 and 2.2.3.1.

2.4.2.2 Determination of volatile products by HPLC

The volatile compounds trapped by the silica gel coated with 2,4-dinitrophenylhydrazine were analysed by HPLC and identified by comparison with the retention times of standard 2,4-dinitrophenylhydrazone derivatives (see table 15).
The retention times of the derivatives formed in the trap and their assignments are given in table 48.

Table 48

Retention time (mins)	Assignment
9.5	Ethanal
12.4	Propanal
17.5	Butanal

2.4.3 Autoxidation promoted by benzil

2.4.3.1 Determination of volatile products by gc-ms

The volatile products identified from the autoxidation of benzoyloxyethyl linoleate in the presence of benzil by packed column gc-ms were very similar to those observed in the presence of the cobalt and lead promotors, section 2.4.2.1, with the exception that benzaldehyde was observed in the former autoxidation The volatile compounds identified are summarised in table 49.

Table 49

Compound	% composition
Propanal	8.2
Hexanal	68.4
2-Hexenal	0.8
2-Heptenal	10.7
2-Octenal	0.6
Benzaldehyde	2.3

2.4.3.2 Determination of volatile products by HPLC

The volatile products converted to their appropriate 2,4-dinitrophenylhydrazone derivatives were identified by their retention times using HPLC. The retention times and analyses are given in table 50.

Table 50

Retention time (mins)	Assignment
9.3	Ethanal
12.5	Propanal
17.2	Butanal

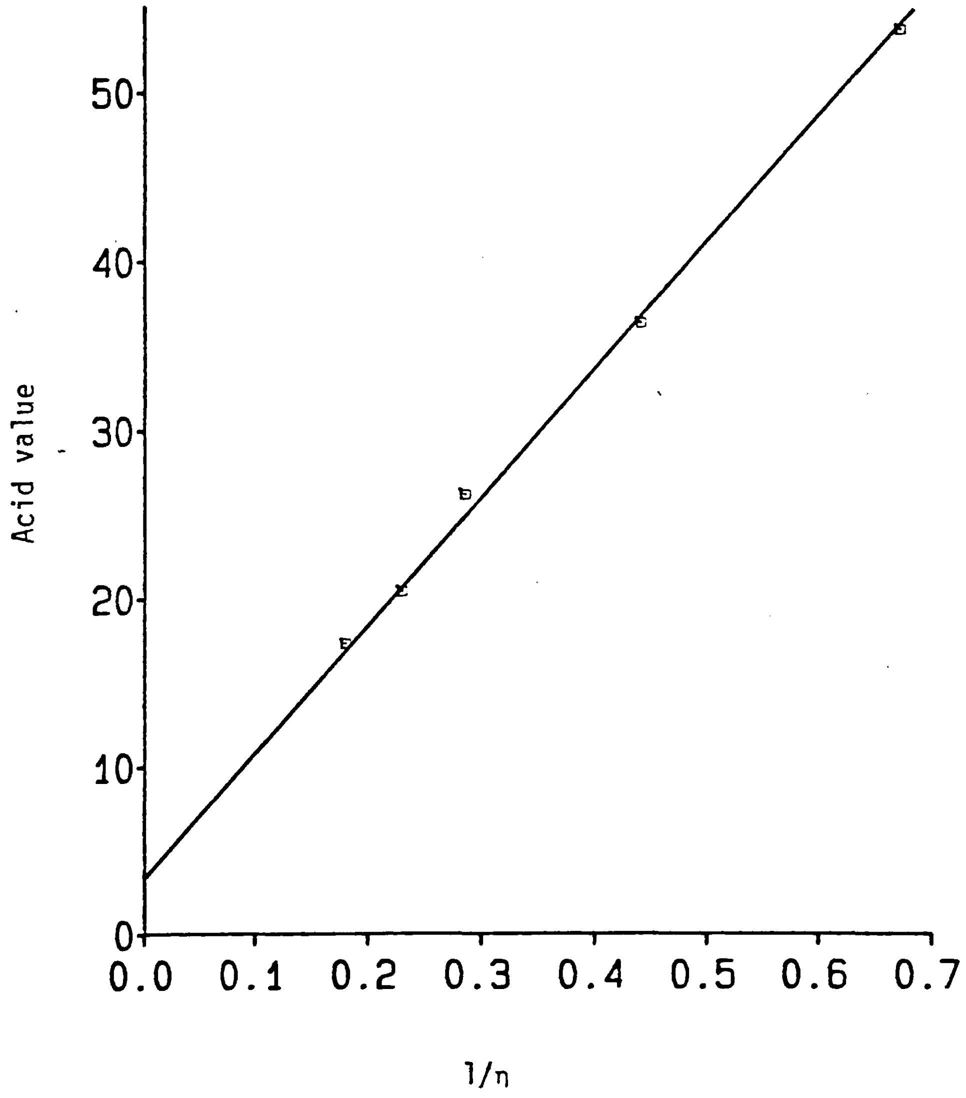
2.5 Autoxidation of Alkyd Resins - Series 1 and the'Low acid value' Alkyd

2.5.1 Synthesis

The alkyd resins were prepared by the fatty acid route described in section 1.1. The final acid value of the resins prepared were approximately 10 mg KOH/g non-volatile resin. The acid value of one resin was reduced to approximately 1 mg KOH/g non-volatile resin by further reaction with Cardurea E and this was used as the low acid value alkyd in the study of the aluminium drier.

During the condensation process for making the alkyd resins the acid value and viscosity were continuously monitored. Acid values should decrease as the esterification reaction proceeds and be accompanied by an increase on viscosity (η). There is a degree of reaction when the resin becomes solid, this is known as 'gelling'. Plots of acid value (AV) against $1/\eta$ are used to determine the acid value at which the resin will gel. Careful formulation will provide a resin which will not gel even at zero acid value. A plot of AV against $1/\eta$ is given for the preparation of alkyd $PE_2/PA_2/DCOFA_3$ in Figure 2.5.1.1.

Figure 2.5.1.1.
'Acid value' versus 1/η



The theoretical gel point of this alkyd is about 1.5 mg KOH/g non-volatile resin. Therefore there is no gelling problems in the preparation of this type of resin, provided the reaction is terminated at an acid value of 10 mg KOH/g non-volatile resin. The final parameters, determined for these resins, are summarised in table 51. It is to be noted that 'AnalaR' toluene was used as the solvent in all preparations.

2.5.2 Volatile product identification from the autoxidation promoted by cobalt (II) bis(2-ethylhexanoate) and lead (II) bis(2-ethylhexanoate)

2.5.2.1 Analysis by glc

The resins were not sufficiently mobile for the bubbling apparatus (diagram 3.5.1.1) to be used. The resins were therefore autoxidised as films, spread on glass panels. To first remove the toluene solvent the films were kept in a stream of dry nitrogen for 4 days. The volatile autoxidation products were collected by both the cryogenic and chemical traps. The products from the cryogenic trap were generally analysed by glc; however those from the alkyds D' and G' were analysed by packed column gc-ms. Thus the identification of the products relies mainly on their retention times. The retention times of some compounds on the carbowax 20 M column are given in table 52.

The results from the autoxidation of the various alkyds are given in table 53. Compounds having short elution times are masked by the large amount of toluene necessarily always present as a solvent used in the preparation of the alkyds.

Table 51

Series 1 and 'low AV' alkyds

General formula PE/PA/FA
2 2 3

Fatty acids	Acid value/ mg KOH	Viscosity/units	Solids (%)		Remarks
Soya bean oil	9.30	6.0	77.2	A'	
Linseed oil	8.01	6.5	77.1	B'	
DCO fatty acids	9.20	12.0	77.1	C'	
Tall oil	9.40	9.4	77.0	D'	
Isomerginic acid	13.0	30.0	79.4	E'	
Linoleic acid	13.1	16	75.1	F'	Synthesised with pure linoleic acid
Tall oil	1.22	32	83.8	G'	Low acid value alkyd

Table 52

Retention times of some volatile compounds on the Carbowax 20 M packed glc column

Compound	Retention time (Minutes)
Propanal	6
Butanal	10
Ethanol	12
2-Pentenal	17
Toluene	21
3-Penten-1-ol	25.5
Pentanal	30.5
Hexanal	39.0
2-Hexenal	48.0
3-Heptanone	55.5
Heptanal	61.5
Methyl heptanoate	66.0
Methyl-2-ethylhexanoate	77.0
Octanal	81.0
2-Heptenal	88.0
2-Octenal	91.5
Methyl octanoate	93.0
2,4-Heptadienal	109.5
Benzaldehyde	121.4
Hexanoic acid	136.0
2-Ethyl hexanoic acid	162.0

Table 53

Volatile compounds from the autoxidation of various alkyd resin films in the presence of cobalt (II) and lead (II) bis (2-ethylhexanoate)s

Resin	Retention time (Minutes)	Assignment	Remarks
A'	41.4 47.0 62.6 84.0 86.5 110.0	Hexanal 2-Hexenal Heptanal Octanal 2-Heptenal 2,4-Heptadienal	
B'	40.3 47.5 60.5 108.0	Hexanal 2-Hexenal Heptanal 2,4-Heptadienal	
C'	41.0 47.5 61.0 87.5 91.0 136.5	Hexanal 2-Hexenal Heptanal 2-Heptenal 2-Octenal Hexanoic acid	
D'	39.5 61.0 81.2 88.5	Hexanal Heptanal Octanal 2-Heptenal	Packed column gc-ms analysis carried out
E'	41.0 47.5 88.5 91.0	Hexanal 2-Hexenal 2-Heptenal 2-Octenal	
F'	38.5 47.6 86.0 90.0	Hexanal 2-Hexenal 2-Heptenal 2-Octenal	Packed column gc-ms analysis carried out

The volatile products from the autoxidation of the resins D' and F' were analysed by packed column gc-ms. In these later studies the films were placed under vacuum ($\sim$6 mm Hg) for about 1 minute to assist in the removal of more of the toluene solvent. Better chromatography was then obtained in the subsequent gc-ms studies. The mass spectral analysis confirmed the identity of the compounds proposed on the basis of their retention times in table 53, but also revealed the identity of propanal amongst the volatile compounds.

2.5.2.2 Analysis by HPLC

The 2,4-dinitrophenylhydrazone derivatives collected in the chemical trap were analysed by HPLC on a C_{18} reversed phase column, the compounds being identified by the retention times of standard 2,4-dinitrophenylhydrazones, (see table 15). The analysis of the volatiles by this method are summarised in table 54.

2.5.3 Volatile product identification from the autoxidations promoted by benzil

2.5.3.1 Analysis by glc

The mixtures of volatiles were analysed by glc and their identity determined from the retention times given in table 52. The results are summarised in table 55.

Table 54

Volatile compounds identified by HPLC as their 2,4-dinitrophenylhydrazone derivatives

Resin	Retention time (Minutes)	Assignment
A'	9.3 12.2 16.6 17.4	Ethanal Propanal 2-Butenal Butanal
B'	6.5 9.3 12.5 16.7 17.3	Methanal Ethanal Propanal 2-Butenal Butanal
C'	6.6 9.4 12.6 17.5	Methanal Ethanal Propanal Butanal
D'	6.5 9.4 12.5 17.4	Methanal Ethanal Propanal Butanal
E'	6.6 9.2 12.3 17.1	Methanal Ethanal Propanal Butanal
F'	No analysis carried out.	

Table 55

Volatile compounds from the autoxidation of various alkyd resin films in the presence of benzil

Resin	Retention time (Minutes)	Assignment
A'	42.0	Hexanal
	63.0	Heptanal
	83.5	Octanal
	87.0	2-Heptenal
	109.5	2,4-Heptadienal
	120.5	Benzaldehyde
B'	41.0	Hexanal
	61.0	Heptanal
	83.5	Octanal
	108.5	2,4-Heptadienal
	121.0	Benzaldehyde
C'	41.5	Hexanal
	60.5	Heptanal
	87.5	2-Heptenal
	81.5	Octanal
		Benzaldehyde
D'	41.0	Hexanal
	61.5	Heptanal
	88.0	2-Heptenal
	82.0	Octanal
	122.0	Benzaldehyde
E'	41.5	Hexanal
	47.5	2-Hexenal
	88.5	2-Heptenal
	92.0	2-Octenal
	123.0	Benzaldehyde
F'	41.8	Hexanal
	48.0	2-Hexenal
	88.0	2-Heptenal
	91.5	2-Octenal
	121.5	Benzaldehyde

2.5.3.2 Analysis by HPLC

The volatile compounds collected as their 2,4-dinitrophenylhydrazone derivatives were identified by HPLC using retention times of standard derivatives. The compounds identified this way from the autoxidised resins are summarised in table 56.

Table 56

Volatile compounds identified by HPLC as their 2,4-dinitrophenyl hydrazone derivatives

Resin	Retention time (Minutes)	Assignment
A'	6.7 9.5 12.6 17.4	Methanal Ethanal Propanal Butanal
B'	9.4 12.6 17.5	Ethanal Propanal 2-Butenal
C'	9.3 12.6	Ethanal Propanal
D'	6.6 9.3 12.7 16.6 17.3	Methanal Ethanal Propanal 2-Butenal Butanal
E'	9.5 12.7 16.5	Ethanal Propanal 2-Butenal
F'	No analysis carried out	

2.5.4 Autoxidation of 'low acid value' alkyd in the presence of cobalt (II) bis (2-ethylhexanoate) and aluminium bis (2-butoxide) ethyl acetoacetate

2.5.4.1 Analysis by GLC and HPLC

The analysis of the volatiles from this autoxidation was studied in the same manner as in sections 2.5.2 and 2.5.3. The compounds identified from the autoxidation of alkyd resin G' are given in table 57.

Table 57

Volatiles identified from the autoxidation of alkyd resin G'

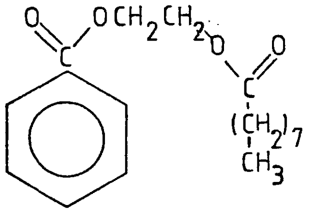
Separation technique	Retention time (Minutes)	Assignment
GLC	39.8 62.0 81.0 89.0 58.0 108.0	Hexanal Heptanal Octanal 2-Heptenal 2-Butanol Ethyl acetoacetate
HPLC	9.5 12.4 17.4	Ethanal Propanal Butanal

2.5.5. Mechanistic interpretation

The methyl esters of cis-9-octadecenoic, cis-9-cis-12-octadecadienoic and cis-9- cis-12- cis-15-octadecatrienoic acids were used as models of the alkyd resins employed by the paint industry. The hypothesis proposed was that the 'volatile' degradation products from autoxidation of the methyl esters would mimic those formed accompanying the autoxidative cross-linking of the alkyd resins.

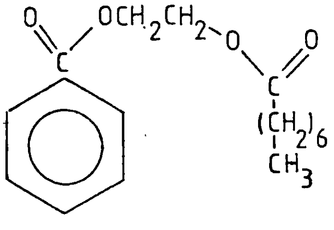
To test this hypothesis benxoyloxyethyl cis-9-cis-12-octadecadienoate (LXXXXI) was synthesised. LXXXXI provides a 'simple' molecule which contains the basic components of an alkyd resin, i.e. aromatic and aliphatic ester bonds to a polyol (ethane 1,2-diol).

The volatile products from the autoxidation of LXXXXI promoted by (i) cobalt (II) and lead (II) bis (2-ethylhexanoate)and (ii) benzil were very similar to those found in the autoxidation of methyl linoleate. Hexanal was again the major 'volatile' product and accounted for approximately 70% of the total volatiles. There was a total absence of methyl heptanoate and methyl octanoate. This was expected owing to the absence of the carboxymethyl groups, however the corresponding compounds from LXXXXI would be LXXXXII and LXXXXIII.



Benzoyloxyethyl nonanoate

LXXXXII



Benzoyloxyethyl octanoate

LXXXXIII

These compounds are presumed insufficiently volatile to be carried by the effluent oxygen stream to the cold trap.

The general nature of the volatile compounds indicates that the same autoxidative degradation process is occurring in this model of an alkyd resin. It is worth noting that no methyl-2-ethylhexanoate was found amongst the volatiles. The autoxidation of the alkyd resins in table 51 was carried out to determine whether the 'painty odour' resulted from the same autoxidative degradation observed in the methyl esters and the model alkyd.

The resins,apart from F',incorporated a mixture of fatty acid esters and thus made the product analysis more difficult. However the major complication was the large amount of toluene present (inherent as the resin solvent) obscuring the early eluting components. The volatile compounds formed nevertheless can be correlated with the unsaturated fatty acids present in the resin. The typical fatty acid composition of various oils used in the resin preparation are given in table 58.

It can be seen that resins containing oleic acid (i.e. resins A', B', D'), produce heptanal and octanal. Those resins which contain linoleic acid (i.e. resins A',B',D') produce hexanal, 2-hexenal,2-heptenal and 2-octenal. Those resins which contain linolenic acid (i.e. resins A',B') produce 2,4-heptadienal.

The linoleic acid alkyd resin F', when autoxidised, produced, with the exception of the methyl esters, those volatiles found in the autoxidation of methyl linoleate. The major product was again hexanal. This supports the theory that the alkyd resins autoxidatively degrade in the same manner as the methyl esters (VII, XXI and XLVII).

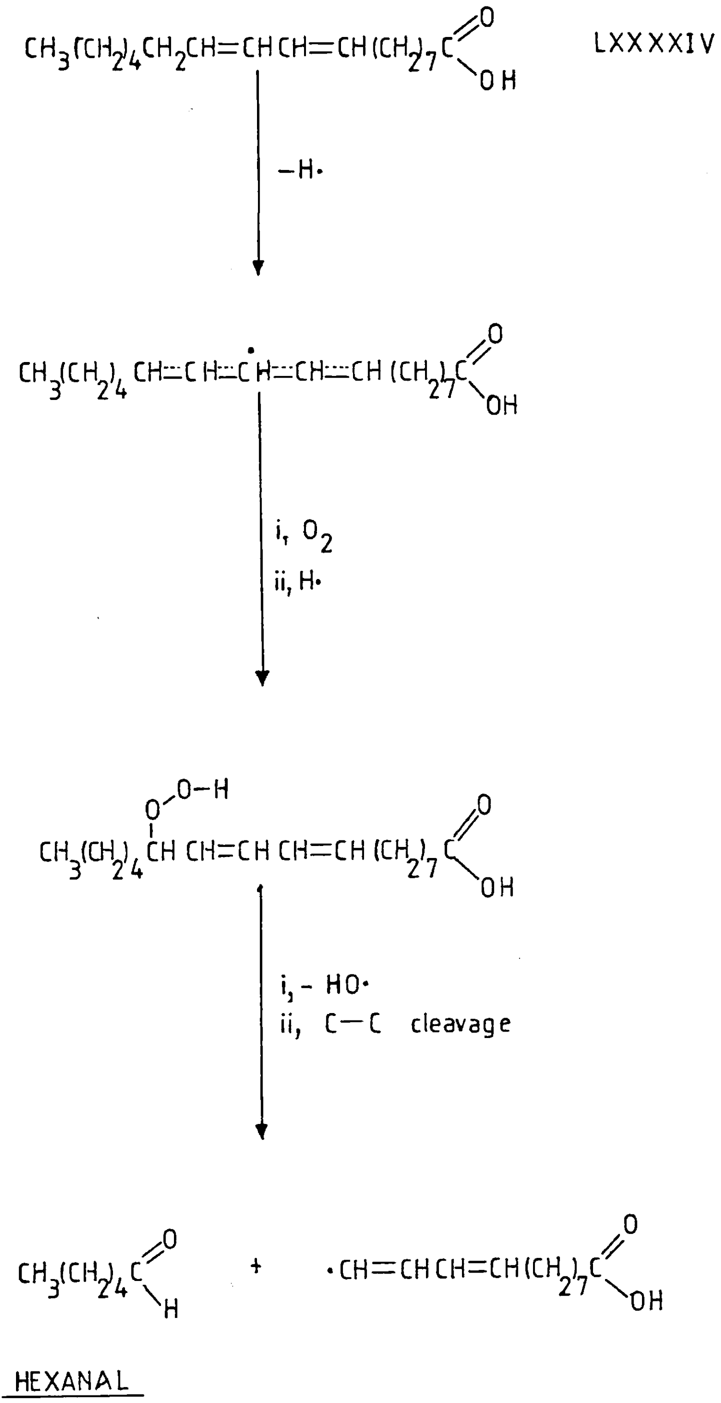
Table 58

Typical oil compositions

Oil (alkyd resins used in)	Unsaturated fatty acids		
	Oleic	Linoleic	Linolenic
Soya bean (A')	27.5	52.5	7
Linseed oil (B')	20	17.5	50
Tall oil (D' and G')	40	40	10
Dehydrated castor oil (C')	9	4	-

Resins C' and E' contain a high proportion of conjugated double bonds.[171] The main fatty acid in resin C' is 9,11-octadecadienoic acid (LXXXXIV) which would be expected to form 13-hydroperoxides similar to those in linoleic acid and this could explain the formation of hexanal as the volatile product. Resin E' is formulated using isomerised safflower oil. This isomerisation of mainly linoleic acid, would produce the conjugated acids LXXXXIV and 10,12-octadecadienoic acid. The hexanal observed during the autoxidation of this resin can again be explained from 13-hydroperoxide formation in LXXXXIV , see scheme 2.5.2.7.1.

In the redox promoted drying of the alkyd resins the 2,4-DNPH chemical trap revealed the presence of lower aldehydes. Each resin, except resin A', produced methanal as a volatile product. All the resins produced ethanal, propanal and butanal, again supporting the theory that autoxidative degradation occurs during alkyd resin crosslinking. Again no methyl 2-ethylhexanoate was found in the



Scheme 2.5.2.7.1

redox promoted autoxidation. Benzaldehyde was however produced in the benzil promoted crosslinking of the alkyd resins.

The autoxidation of resin G', promoted by cobalt (II) bis (2-ethylhexanoate) and aluminium bis(2-butoxide) ethyl acetoacetate, gave the expected degradation products showing that the aluminium promotor does not significantly influence the nature of the degradation products.

The author believes that the different odour characteristics reported[171] for this promotor system result mainly from the 'painty' odour being masked by the excessive amounts of 2-butanol and ethyl acetoacetate present.

2.6 Methane sulphonic acid promoted autoxidation

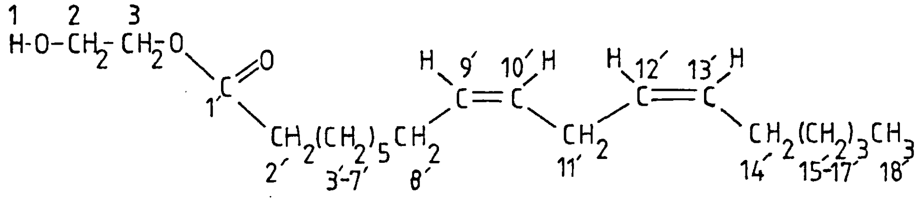
2.6.1 2-Hydroxyethyl cis-9-cis-12-octadecadienoate

2.6.1.1 Synthesis

The synthetic route was similar to that used in the preparation of benzoyloxyethyl linoleate (section 2.4.1). Linoleyl chloride was prepared and reacted with 1,2-ethanediol in the presence of pyridine. To reduce the formation of the diester a large excess of 1,2-ethanediol was employed. 2-Hydroxyethyl cis-9-cis-12-octadecadienoate LXXXXV was purified by column chromatography and analysed by ^{1}H nmr and IR; the assignments of absorptions are given in tables 59 and 60 respectively.

Table 59

Assignment of ^1H nmr spectrum of 2-hydroxyethyl linoleate



Type of Signal	Chemical shift ppm	Coupling constants (Hz)	Integration
t	0.91 CH_3 (18')	$J_{17'-18'} = 5.1$	3
s (br)	1.32 $8CH_2$ (3'-7', 15'-17')		16
m/t	1.9-2.5 $3CH_2$ (2',8',14')		6
t	2.8 CH_2 (11')	$J_{10'\,11'} = J_{11'}J_{12'}$ $\doteq 5{\cdot}0$	2
t	3.9 CH_2 (2)		2
s	4.1 HO (1)		1
t	4.6 CH_2 (3)		2
t	5.44 4CH (9',10',12',13')	$J_{8'9'} = J_{10'11'} = J_{11'12'}$ $= J_{13'}J_{14'} = 5.0$	4

Table 60

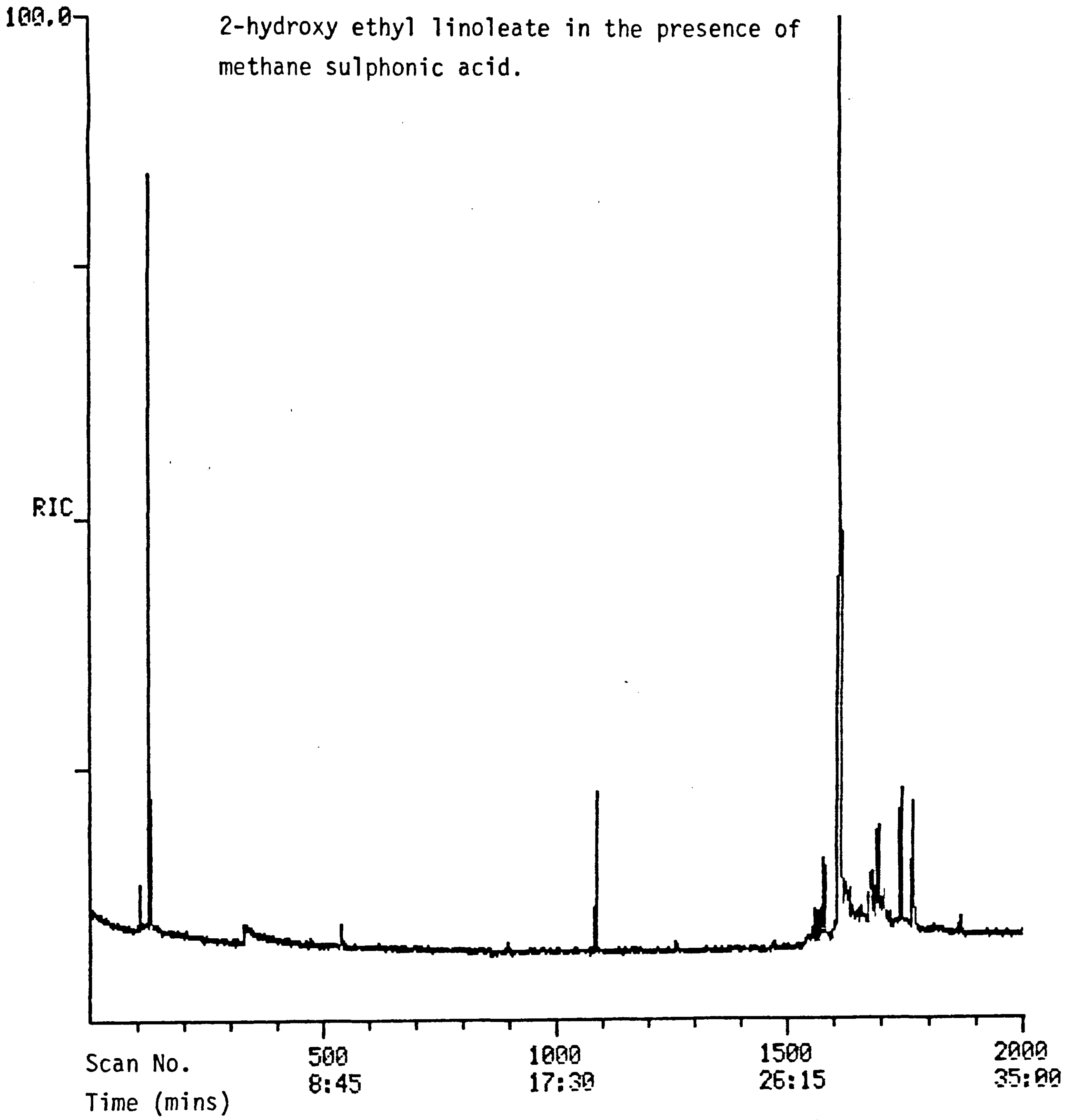
Assignment of IR Spectrum of 2-hydroxyethyl linoleate

cm^{-1}	Assignment
3400 (Broad)	-OH (H-bonded).
3010	-C-H olefinic stretch.
2940	-C-H CH_3 asymmetric stretch.
2930	-C-H $-CH_2-$ asymmetric stretch.
2860	Symmetric stretch, CH_3; $-CH_2-$.
1740	-C=O stretch higher aliphatic ester.
1650	-CH=CH-(-C=C-stretch).
1460	-CH deformation aliphatic.
1380	-CH deformation aliphatic.
1250	-C-O stretch alcohol.
1180	-C-O stretch aliphatic ester.
1080	-OH deformation primary alcohol.
720	-C-H out of plane deformation of cis olefin.

2.6.1.2 Identification of volatile products

The volatile products from the autoxidation of 2-hydroxyethyl linoleate promoted by methane sulphonic acid were collected in the cryogenic trap, then analysed by glc and gc-ms. The chromatogram obtained was different from any obtained in previous experiments, (figure 2.6.1.2.1). The analyses of the mass spectra are now discussed.

Figure 2.6.1.2.1.
Capillary total ion current chromatogram of the volatile products from the autoxidation of 2-hydroxy ethyl linoleate in the presence of methane sulphonic acid.



Scan No. 541

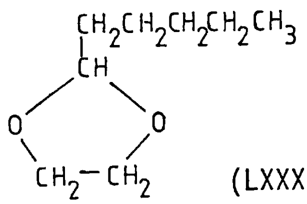
m/z	100	82	72	71	67	58	57	56	55	45	44	42	41	40	39	29	27
Rel. AB %	1.2	16.5	23	12	17	13	71	53	30.5	44	100	31.5	52	13	48	52	56

This spectrum, being similar to that obtained in section 2.2.1.1, Scan No. 536, corresponds to hexanal.

Scan No. 1088

m/z	143	83	74	73	71	67	57	55	45	43	41	39	36	29	27
Rel. AB %	.6	.6	3.3	100	3.6	.6	2.4	4.8	28.9	11.4	10.2	6.02	3.3	16	16.6

Packed column gc-CIMS analysis showed that this compound had a relative molecular mass of 144 ($[M+1]^+$ m/z = 145), thus the base peak ion resulting from the loss of 71 daltons could correspond to $CH_3(CH_2)_4$. The heavy isotope ratio indicated that the molecular formula was $C_8H_{16}O_2$, thus the ion corresponding to the base peak ion then has the composition $C_3H_5O_2$. Using the ratio of the abundances of m/z 74 and 73 the proposed composition of the m/z 73 ion was supported. Inspection of the mass spectra of 1,3-dioxolane and its alkyl derivatives[206] gave evidence that this compound probably is 2-pentyl-1,3-dioxolane LXXXXVI.



(LXXXXVI)

Scan No. 1613

m/z	198	169	155	141	127	113	99	85	71	57	43	41	39	29	27
Rel.AB%	0.6	0.3	0.6	0.6	0.9	2.1	4.8	23.5	45	89.8	100	50	8.4	37	18.7

The fragmentation pattern of this compound is characteristic of straight chain hydrocarbons. Comparison with the standard spectrum of tetradecane[206] confirmed this.

Scan No. 1696

m/z	141	113	99	97	85	84	79	71	57	55	43	41	39	29	27
Rel.AB%	3.4	5.6	8.1	3.0	23	7.5	3.4	57	88	15.5	100	41.6	5.6	22	13.9

The molecular ion could not be determined from packed column gc-CIMS making the analysis of this compound difficult. It appears to be a straight chain alkane from the general fragmentation pattern.

Scan No. 1744

m/z	141	126	119	113	99	97	85	71	69	67	57	55	44	43	42	41
Rel.AB %	1.5	1.5	1.5	1.9	4.5	4.4	23	46	11.6	5.2	87	26	12.7	100	13.4	58.7

m/z	36	29	27
Rel.AB %	11.2	39	21

This mass spectrum is very similar to that found in Scan No. 1696 but again the packed column gc-CIMS analysis did not reveal the presence of the parent ion. However it is concluded that this compound is a hydrocarbon similar to that corresponding to Scan No. 1696.

Scan No. 1769

m/z	220	206	205	189	163	161	147	145	135	133	131	129	121
Rel.AB %	18	11.8	90.7	2.5	1.8	4.3	4.3	18.6	3.1	5.9	6.8	5.9	7.5

m/z	119	115	105	95	93	9191	81	79	77	69	57	43	41	39	29	27
Rel.AB %	7.5	6.8	15.2	11.8	3.7	13.7	16	7.5	9.6	6.2	100	11.2	51.5	16.7	38	18

No conclusions were drawn from this spectrum.

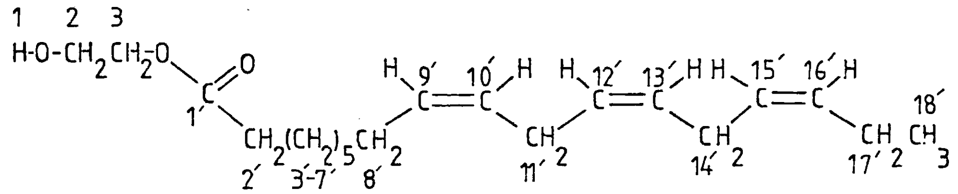
2.6.2 2-Hydroxyethyl cis-9-cis-12-cis-15-octadecatrienoate

2.6.2.1 Synthesis

The synthetic approach to this compound was identical to that used to prepare 2-hydroxyethyl cis-9-cis-12-octadecadienoate (section 2.6.1.1). 2-Hydroxyethyl cis-9-cis-12-cis-15-octadecatrienoate LXXXXVII, was purified by column chromatography, then analysed by ^{1}H nmr and infrared spectroscopy. The assignments are presented in tables 61 and 62 respectively.

Table 61

Assignment of ^1H nmr spectrum of 2-hydroxylinolenate



Type of signal	Chemical shift ppm	Coupling constants (Hz)	Integration
t	0.90 CH_3 (18')		3
s (br)	1.32 $5CH_2$ (3'-7')		10
m/t	1.9 - 2.5 $3CH_2$ (2',8',17')		6
t	2.9 $2CH_2$ (11',14')		4
t	3.85 CH_2 (2)		2
s	4.05 HO (1)		1
t	4.65 CH_2 (3)		2
t	5.50 6CH (9',10',12',13',15',16')	$J_{8'9'} = J_{10'11'} =$ $J_{11'12'} = J_{13'14'} =$ $J_{15'16'} = 50$	6

Table 62

Assignment of IR spectrum of 2-hydroxyethyllinolenate

cm^{-1}	Assignment
3410 (br)	-O-H (H-bonded)
3010	-C-H olefinic stretch
2941	-C-H $-CH_3$ asymmetric stretch
2930	-C-H $-CH_2$ asymmetric stretch
2855	symmetric stretch, CH_3; $-CH_2-$
1740	-C=O stretch higher aliphatic ester
1650	-CH=CH- (C=C stretch)
1465	-C-H deformation aliphatic
1380	-C-H deformation aliphatic
1250	-C-O stretch - alcohol
1180	-C-O stretch - aliphatic ester
1080	-O-H deformation primary alcohol
720	-C-H out-of-plane deformation cis-olefin

2.6.2.2 Identification of volatile products

The volatiles from this autoxidation were analysed by packed column gc-ms only. The chromatogram obtained consisted of three major components.

Component 1

m/z	84	83	69	68	67	56	55	43	42	41	29	27
Rel.AB %	100	4.0	22	1.6	2.4	87	26	8	16	36.8	4.0	8.1

The heavy isotope ratio (M+1)/M suggests that the molecular formula of this compound is C_6H_{12}. The abundant ion at m/z 56 rules out olefins therefore it is suggested that this compound must be a cyclic hydrocarbon. Comparison with the standard spectrum of cyclohexane[206] confirmed this assignment, the base peak ion of cyclohexane is m/z 56. The ions of high m/z were more abundant than in the standard spectrum. This could arise from the spectrum being recorded before the apex of the chromatographic peak.

Component 2

m/z	102	101	74	73	72	71	57	45	43	42	41	21	27
Rel.AB %	0.3	5	3.7	100	6.7	2.1	10.9	53	11.2	10.6	10.9	15	17

The base peak ion at m/z 73 was seen in section 2.6.1.2, Scan No. 1088 to result from an alkyl 1,3-dioxolane. The parent ion at m/z 102 would allow $C_5H_{10}O_2$ to be the molecular formula which corresponds to 2-ethyl-1,3-dioxolane. Comparison with the standard spectrum of 2-ethyl-1,3-dioxolane[206] confirmed this assignment.

Component 3

m/z	92	91	73	65	63	57	51	45	39	29	27
Rel.AB %	79	100	29	9.5	5.4	6.7	5.4	12	9.5	2.7	3.0

The parent ion at m/z 92 and base peak ion at m/z 91 indicate that this compound is toluene, and comparison with the standard spectrum[206] confirmed this analysis.

The other minor components had hydrocarbon type fragmentations, but no structural information could be concluded.

2.6.3 Variable hydroxyl content alkyds (Series 2)

2.6.3.1 Synthesis

These alkyds were prepared by the same general route as used in the synthesis of the series 1 alkyds. In these alkyds the amount of polyol was increased relative to the amount of dibasic and unsaturated fatty acids. Again the resin preparations were monitored by 'Acid Value' and viscosity and a typical 'Acid Value' versus time plot is given in figure 2.6.3.1.1. The reactions were halted when the resins reached an 'Acid Value' of approximately 10 mgKOH/g.n.v. resin. The final constants of the series 2 resins are given in table 63.

Table 63

Final constants for Series 2 resins

Resin	PE	PA	FA (Linseed oil)	Acid Value mgKOH/g v resin	Viscosity	Solids %
A''	0.93	1.0	1.33	12.9	12	76.9
B''	1.02	1.0	1.33	10.1	13	77.9
C''	1.11	1.0	1.33	9.94	21	79.4
D''	1.20	1.0	1.33	9.88	24	78.3
E''	1.24	1.0	1.33	9.1	18	79.0

A.R. Toluene used in all preparations.

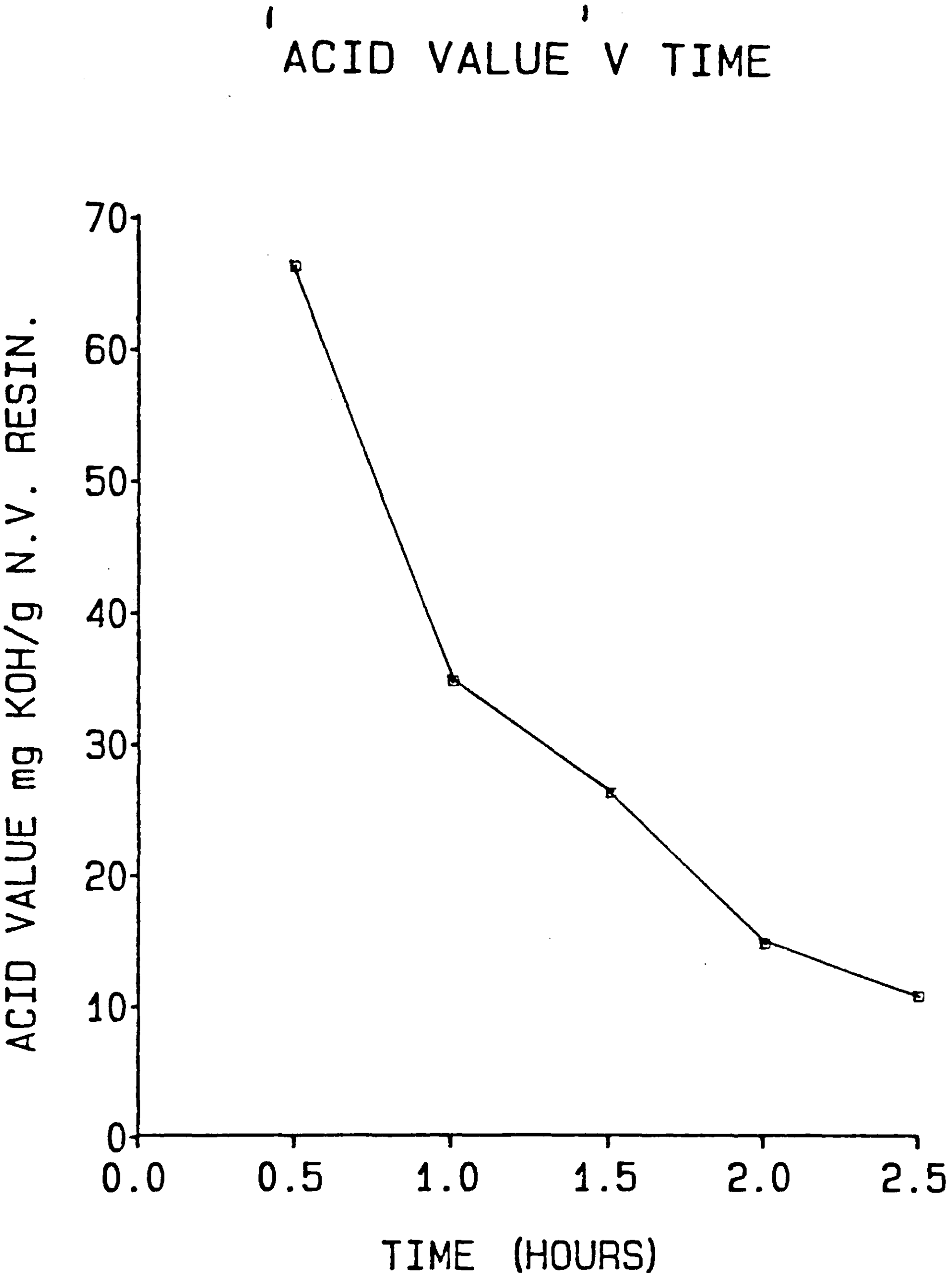


Figure 2.6.3.1.1.
'Acid value'v time for the preparation of an hydroxyl excess alkyd.

2.6.3.2 Identification of volatile products

The volatile products from the autoxidation of these alkyd films, using the apparatus shown in diagram 3.6.1.1, were collected using the cold trap then analysed by packed column glc. The volatile products did not vary with increasing hydroxyl content and the volatiles from alkyd resin D'' were chosen for packed column gc-ms analysis. The spectra obtained are now discussed.

Component 1

m/z	84	83	61	58	57	56	55	50	39	38	37	31	29	27	26
Rel.AB %	6.3	4.2	1.3	1.1	7.9	6.4	100	2.1	4	0.7	2.0	1.0	38	42	33

This spectrum is very similar to that obtained in section 2.3.1.1., Scan No. 124 and is therefore concluded to be 2-pentene-3-one.

Component 2

m/z	92	91	73	57	51	45	39	29	27
Rel.AB %	61	100	58	10.9	7.8	10	8.7	3.1	6.2

This spectrum is very similar to that obtained in section 2.6.2.2., component 3 and is therefore concluded to be toluene.

Component 3

m/z	100	82	72	71	70	67	58	57	56	55	45	44	42	41	40	39	29	27
Rel.AB %	1.1	19.3	21	11	20	16	13	70	53	31.2	27	100	27	56	13	47	53	40

This spectrum is very similar to the one obtained in section 2.2.1.1., Scan No. 536 and is therefore concluded to be hexanal.

Component 4

m/z	84	83	69	66	57	56	55	51	50	43	42	41	40	39	38	37	29
Rel.AB %	16	27	5	4	6	17	100	12	14	83	9	46	10	52	12	5.1	63

This spectrum is very similar to the one obtained in section 2.3.1.1 Scan No. 178 which was analysed to be 2-pentenal. Comparison with the standard spectrum of 2-pentenal[206] gave an excellent agreement and confirmed the assignment.

Component 5

m/z	86	71	67	58	57	55	43	41	40	39	31	29	27
Rel.AB %	1.0	3.0	1.5	4.9	100	6.0	14.0	16	4.1	15.6	3.7	73.4	37.6

This spectrum is very similar to that obtained from Scan No. 283 in section 2.3.1.1 and is concluded to be 1-pentene-3-ol.

Component 6

m/z	87	81	73	58	57	46	45	44	43	42	41	29
Rel.AB %	9.3	7.3	91	13	12	100	93	66	13	26	8	80

The abundant ion at m/z 73 could indicate a 1,3-dioxolane structure but no molecular ion could be identified therefore no assignment is possible.

Resin D'' was also autoxidised in the presence of cobalt (II) and lead (II) 2-ethylhexanoates and the compounds identified by gc-ms from this and the acid promoted autoxidation are summarised in table 64.

Table 64

Volatile products formed during the autoxidation of resin D'' in the presence of methane sulphonic acid compared to those formed in the presence of cobalt and lead promotors

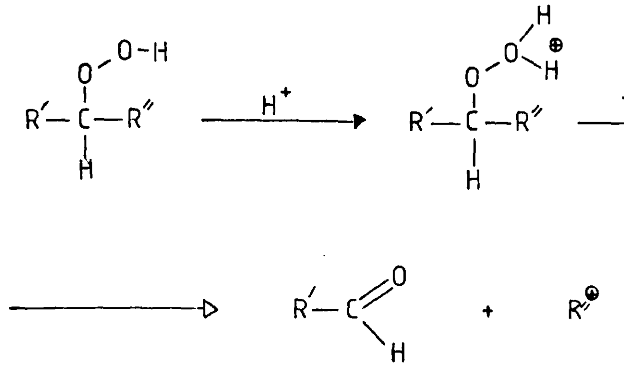
Methane sulphonic acid	Cobalt (II) and lead (II) bis (2-ethylhexanoate)s
2-Penten-3-one	Ethanal
Hexanal	Propanal
2-Pentenal	Butanal
1-Penten-3-ol	3-Pentene-2-one
	2,5-Dihydrofuran
	Hexanal
	2-Pentenal
	1-Pentene-3-ol
	Ethanoic acid
	Propanoic acid

2.6.4 Mechanistic interpretation

The autoxidation of methyl oleate (VII), methyl linoleate (XXI) and methy linolenate (XLVII) in the presence of methane sulphonic acid was attempted as a preliminary investigation. However no volatile products were detected in the 12 h collection period with oxygen as the reactive atmosphere. It has been shown[171] that for crosslinking to occur in an alkyd resin promoted by methane sulphonic acid there must be an excess of hydroxyl groups present (section 1.16.). Hence compounds LXXXXV and LXXXXVII were synthesised to provide simple model molecules containing the major functions of 'hydroxyl excess' alkyds.

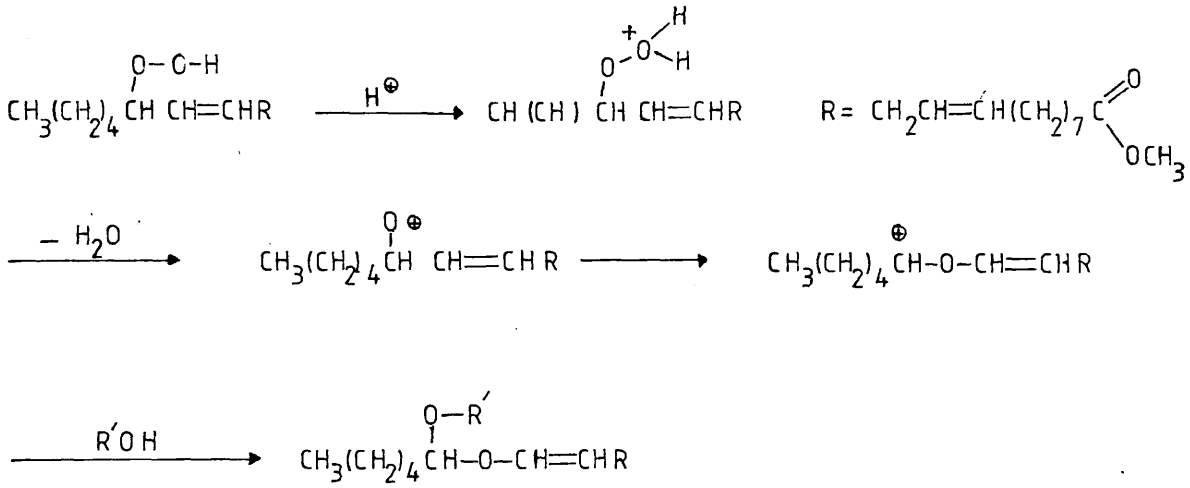
The autoxidation of LXXXXV and LXXXXVII in the presence of methane sulphonic acid did produce volatile products. The nature of the 'volatile compounds' differed from those found in previous redox and photochemical promoted autoxidative experiments, viz. the almost complete absence of aldehydes and the presence of hydrocarbons and 1,3-dioxolane derivatives. This suggests different mechanistic pathways for the production of the volatile components.

The autoxidation of the 'hydroxyl excess' alkyds A'' - E'' in the presence of methane sulphonic acid however did produce those aldehyde products which had been found in the redox and photochemical promoted autoxidations. Here similar degradation pathways to that proposed in sections 2.1.4, 2.2.4 and 2.3.4 may operate. Acid decomposition of hydroperoxides, previously discussed in section 1.16, can lead to the formation of aldehydes.[188] Scheme 2.6.4.1.



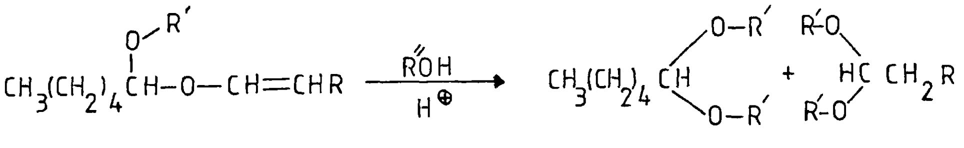
Scheme 2.6.4.1

However in the presence of alcohols, acetal formation occurs[257-259] as below in scheme 2.6.4.2.



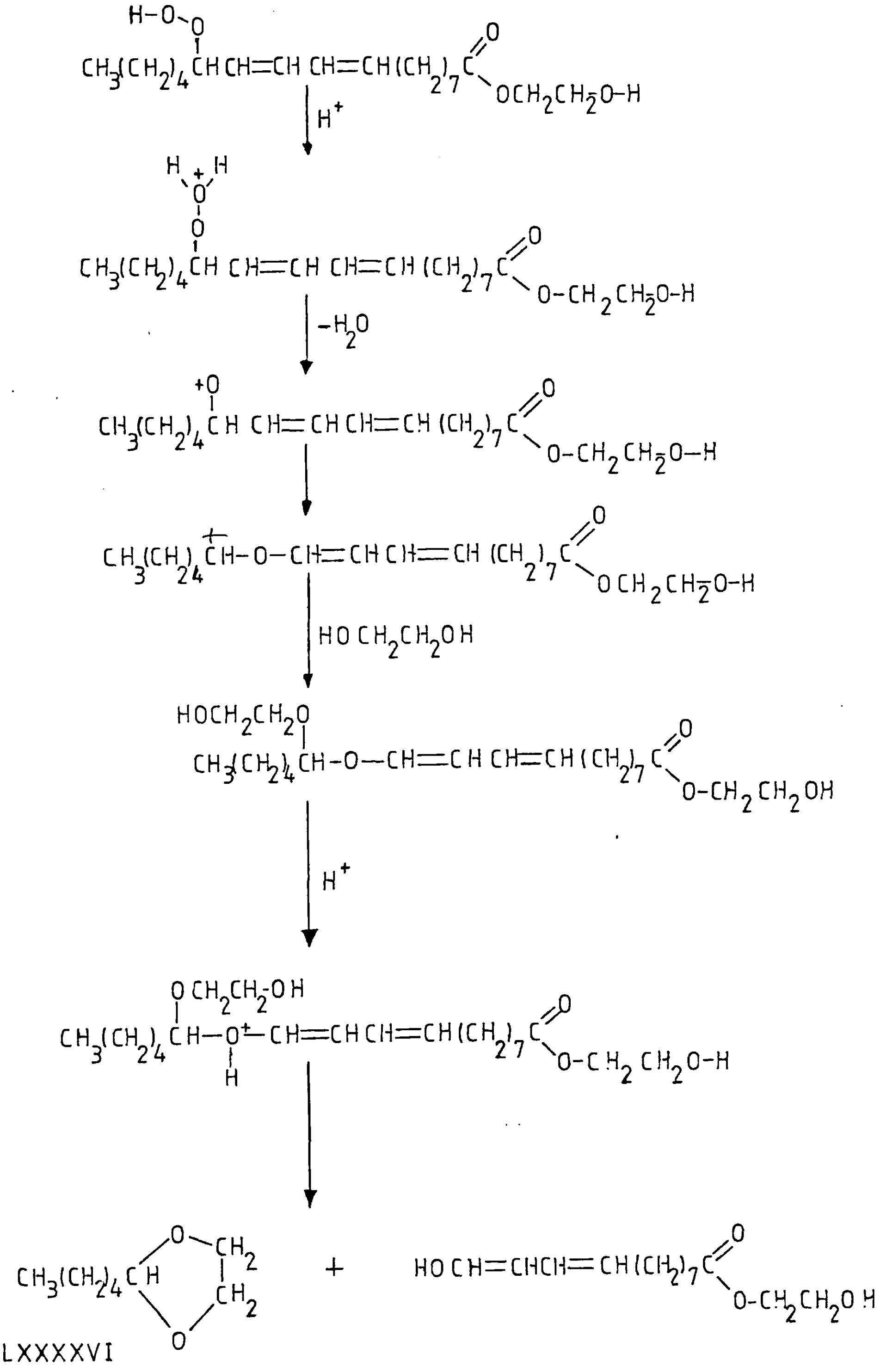
Scheme 2.6.4.2

Schoellner[192,193] has proposed that further acetal formation can occur to give structures such as represented in equation 2.6.4.3.



Equation 2.6.4.3

The formation of the alkyl-1,3-oxolane derivatives support Schoellner's proposal. The alkyl-1,3-oxolanes probably result from the addition of 1,2-ethanediol to the oxenium cation in the corresponding hydroperoxide decomposition. Thus pentyl-1,3-oxolane, LXXXXVI, formed during the autoxidation of 2-hydroxyethyl linoleate may result as in scheme 2.6.4.4.



Scheme 2.6.4.4

The presence of 2-ethyl 1,3-oxolane formed in the autoxidation of 2-hydroxyethyl linolenate could result from similar chemistry to that in scheme 2.6.4.4 but involving the 16-hydroperoxides rather than 13-hydroperoxides. The origin of 1,2-ethanediol is presumably from acid catalysed hydrolysis of the ester in the 2-hydroxyethyl esters.

The proposed mechanism of crosslinking in 'excess hydroxyl' alkyd resins promoted by methane sulphonic acid could be by the formation of acetals. Aldehyde formation would therefore be expected to be suppressed as found in the model compounds LXXXXIV and LXXXXVI. The initial hydroperoxide decompositions could lead to acetal and/or epoxide formation with accompanying alcoholysis (scheme 1.16.9, section 1.16) providing crosslinking. The mobility within the crosslinked resin becomes reduced and hydroperoxide decomposition probably proceeds as in scheme 2.6.4.1 with aldehyde formation.

The autoxidative nature of the acid promoted crosslinking of 'hydroxyl excess' alkyd resins will be discussed in sections 2.7.7 and 2.7.9.

2.7 Time lapse infrared studies of drying films in the presence of promotors

2.7.1 Introduction

The use of infrared spectroscopy to study the composition of alkyd resin films has been established for many years. The 'curing' reactions have also received attention,[260,261] making use of its potential to identify functional groups. The changes during these drying reactions however are difficult to interpret. The main reason for such studies has been to determine the yellowing of such alkyd resins during the ageing process.[262,263] Baer[264] studied the drying of linseed oil in the presence of several metal acetylacetonates (Zn^{2+}, Pb^{2+}, Cu^{2+}, V^{3+}, Vo^{2+}, Mn^{2+}) however complete interpetation was limited owing to the small changes occurring close to or at intense bands. Hartshorn[265] using a fourier transform infrared system studied the drying reactions of both a 60% soya oil-pentaerythritol-orthophthalic alkyd and linseed oil in the presence of cobalt (II) naphthenate at 0.05% cobalt metal. The spectra were analysed by use of a technique called time lapse infrared spectroscopy. This involves the spectra being stored on computer disc in a digital form and the use of point by point subtraction to give difference spectra. A much fuller analysis of the changes during the drying process could be undertaken. The changes observed were the increase in bands around 3400, 1750, 990 and 970 cm^{-1} along with decreases at 3010, 2930, 2860 and 720 cm^{-1}.. These were interpreted to correspond to the formation of hydroperoxides, carbonyl compounds and the formation of trans conjugated olefinic unsaturation along with the loss of cis unsaturation and hydrocarbon chain. Such changes are expected from the normal autoxidation reactions observed in the unsaturated methyl esters (sections 1.4, 1.6 and 1.8).

The time lapse studies carried out during this project did not use FTIR but an infrared spectrometer under computer control, which permitted the collection, storage and subtraction of spectral data over set time intervals. The time intervals used were every 15 minutes for the first 3 hours, then every hour up to 12 hours. Assistance in the interpretation of the difference infrared spectra were made with the help of two books.[266,267]

2.7.2 Cobalt (II) bis(2-ethylhexanoate)

The pure linoleic acid alkyd F' containing toluene was mixed with a n-pentane solution of the cobalt promotor and spread on a KBr disc. The solvents were removed under vacuum (~1 mm Hg) and the film thickness adjusted to give ~5% transmittance of the ester carbonyl band. This experiment was conducted to compare firstly the results obtainable using the available equipment, with those from the fourier transform experiments of Hartshorn.[265] The difference spectrum arising from the subtraction of the 'zero hour' spectrum from the 12 hour spectrum is given in figure 2.7.2.1, the analysis of this spectrum is given in table 65.

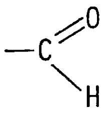
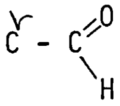
The changes in the infrared spectrum are uniform throughout the whole 12 hour period, with gradual increase or decrease in the appropriate bands with time.

2.7.3 Lead (II) bis(2-ethylhexanoate)

The pure linoleic acid alkyd F' was mixed with a n-pentane solution of the lead promotor and spread on a KBr disc. The spectra were collected and analysed as before (section 2.7.2). In this autoxidation experiment two types of changes occur, the first occurring in the initial hour and the second from 1 hour to 12 hours.

Table 65

Pure linoleic acid alkyd autoxidised in the presence of cobalt (II) octoate, analysis of 12 h - 0 h difference spectrum

Absorption		Assignment
Gain cm^{-1}	loss	
3440		(HO)-O
	3010	Unsaturation (olefinic)
	2955	$-CH_3$ asymmetric stretch
	2921	$R-CH_2-R$ asymmetric stretch
	2849	CH_3; $R-CH_2-R$ symmetric stretch
	1850	Phthalic anhydride
	1787	
	1774	
1712		 aldehyde formation
1630		α,β unsaturated ketone
	1464	CH_3-, CH_3CH_2-, $CH_3CH_2CH_2-$,
1406		
979		Trans unsaturation (trans,trans conjugated)
934		$CH=CH_2$
882		-O-O- in C-O-O-H
	715	Cis unsaturation

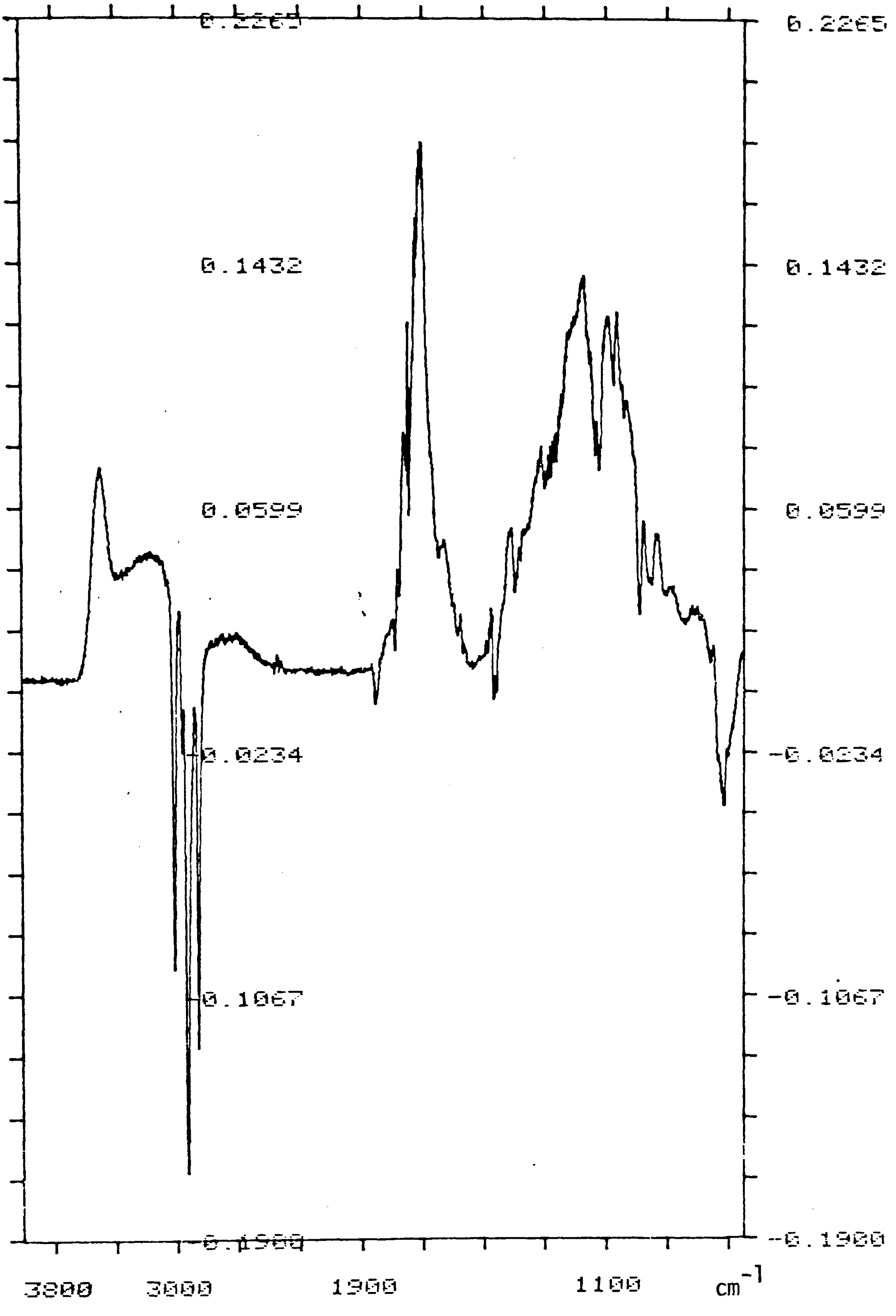


Figure 2.7.2.1.
Linoleic acid alkyd F' in the presence of cobalt promotor,
12 h - 0 h difference spectrum.

During the first period only one increase in absorbance was observed, all other changes being decreases in absorbance (table 66). During the second period the changes observed in the previous experiment (section 2.7.2, table 65) dominated the difference spectra. The differences between the 12 hour and initial spectra is given in figure 2.7.3.1.

Table 66

Pure linoleic acid alkyd autoxidised in the presence of lead octoate; analysis of 1 h - 0 h difference spectrum

Absorption		Assignment
Gain cm^{-1}	Loss	
	3010	Olefinic unsaturation
	2955	Hydrocarbon
	2921	
	2849	
	1850	Phthalic anhydride
	1787	
	1774	
	1740	Ester
	1460	CH_3CH_2; $CH_3CH_2CH_2$
	1271	Phthalate
	1170	Ester; propionate and higher carboxylates
	1133	Phthalate
	1125	
	1080	
981		Trans unsaturation (trans, trans conjugated)
	905	
	740	CH modes ortho disubstituted aromatic ring
	715	

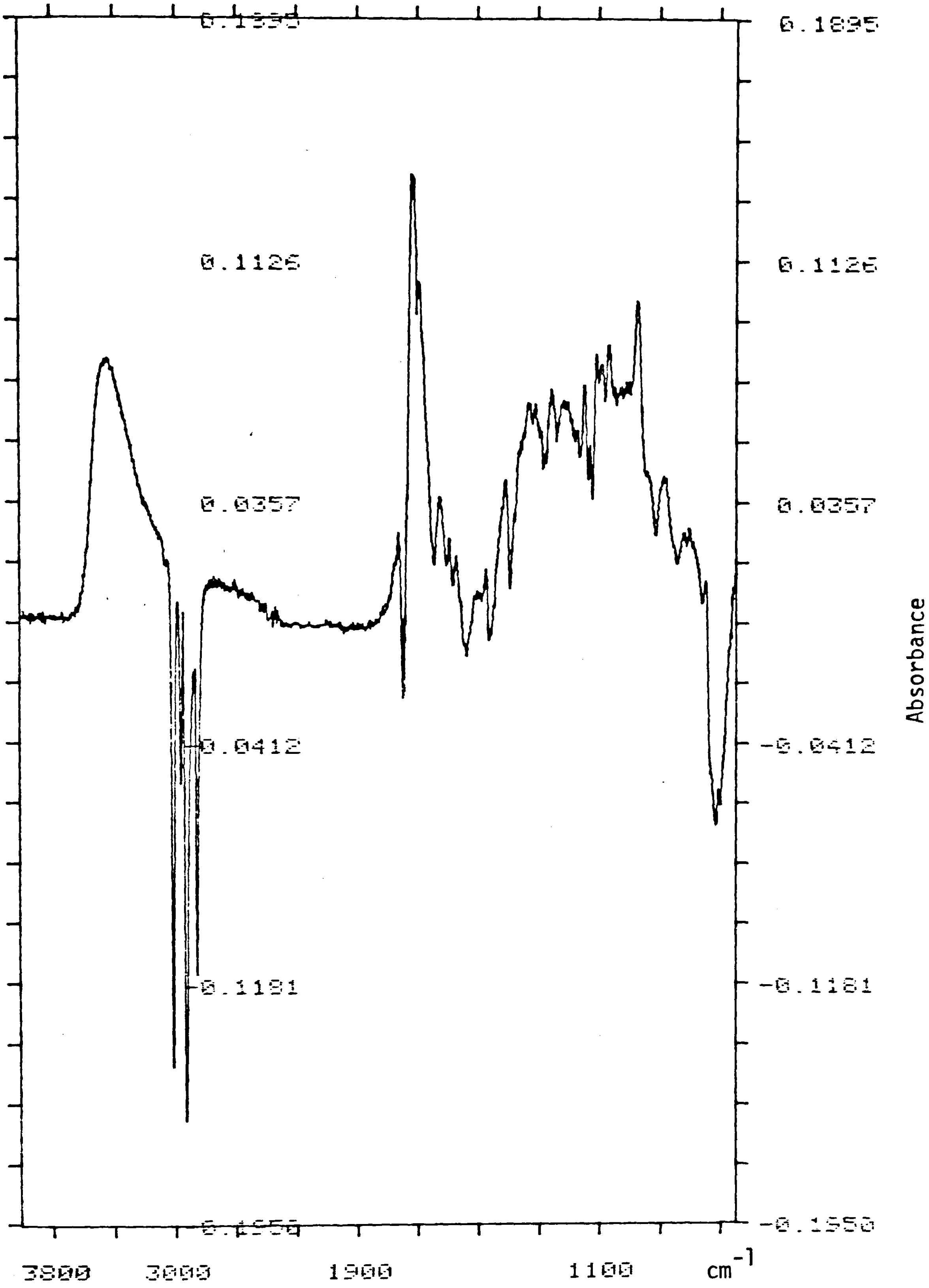


Figure 2.7.3.1.
Linoleic acid alkyd F' in the presence of lead promotor,
12 h - 0 h difference spectrum.

2.7.4 Aluminium bis(2-butoxide) ethylacetoacetate

The low acid value alkyd G' was mixed with the aluminium promotor and analysed as before. In this experiment only decreases in absorption were observed throughout the entire 12 hour drying period. This catalyst system is a mixture of aluminium bis(2-butoxide) ethylacetoacetate and 2-butanol, whose infrared spectrum will be discussed in section 2.10.5. The changes occurring in an alkyd in the presence of the aluminium promotor are similar throughout the full 12 hour period. The analysis of the 12 hour minus zero-hour difference spectrum is given in table 67. No increase in any bands was observed during this 12 hour reaction period.

2.7.5 Cobalt (II) bis(2-ethylhexanoate) in combination with the lead promotor or the aluminium promotor

The time lapse infrared study of the combined catalyst systems is dominated by the changes observed in alkyd films dried in the presence of cobalt promotor only. The changes observed when the secondary promotors were used on their own could also be observed. Figures2.7.5.1 and 2.7.5.2 show the changes occurring when cobalt (II) bis(2-ethylhexanoate) was combined with lead (II) bis(2-ethylhexanoate) or aluminium bis(2-butoxide) ethylacetoacetate respectively. The losses associated with the aluminium promotor are more dominant than those associated with the lead promotor.

2.7.6 Benzil

Analysis of the autoxidation of the pure linoleic acid alkyd F' promoted by benzil was carried out by time lapse infrared spectroscopy. The changes in the infrared spectrum occurring throughout a 12 hour period were similar, thus the analysis of the

Table 67

Low a.v. alkyd in the presence of aluminium bis(2-butoxide) ethylacetoacetate in 2-butanol solution. Analysis of 12 h - 0 h difference spectrum

Absorption (losses cm^{-1})	Assignment	
3529-3	Hydroxyl (OH)	
3006	Olefinic unsaturation	
2960 2928 2849	Hydrocarbon	
1740	Ester carbonyl C=0	
1627 1607	$C\overset{---}{-}O$	Ethyl acetoacetate complex with aluminium
1526	$C\overset{---}{-}C$	From complex of ethyl acetoacetate with aluminium
1418 1369	γ(C-0)	Metal alkoxide
1294	νC-0 Stretch β-keto (enolic)	
1173	γ(C-0) Metal alkoxide	
1140	γ(C-0) Metal alkoxide	
1124		
1061		
1023		
990	γ (C-0) Metal alkoxide	
918		
784		
738		

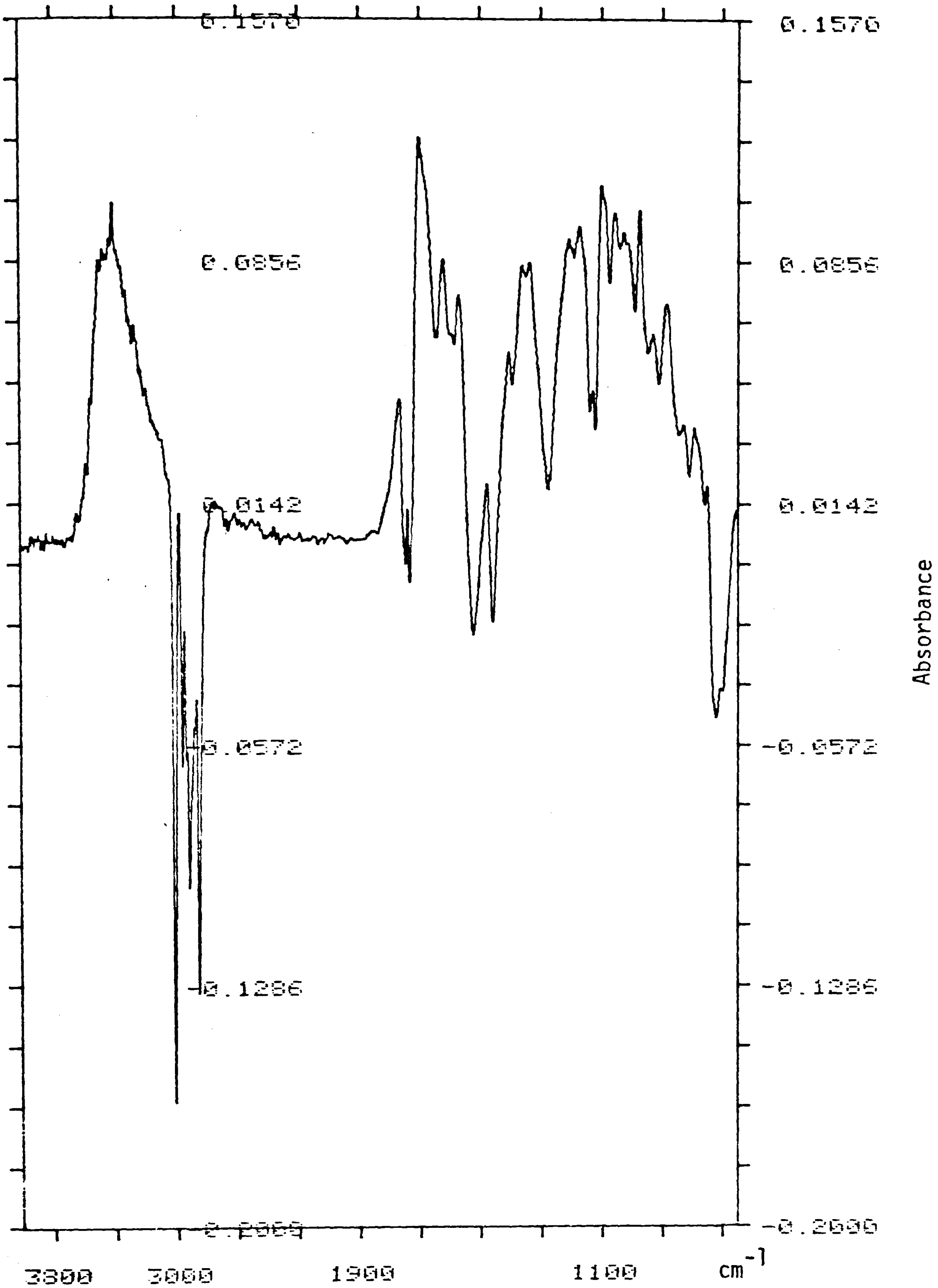


Figure 2.7.5.1.
Alkyd resin in the presence of cobalt and lead promotors, 12 h - 0 h difference spectrum.

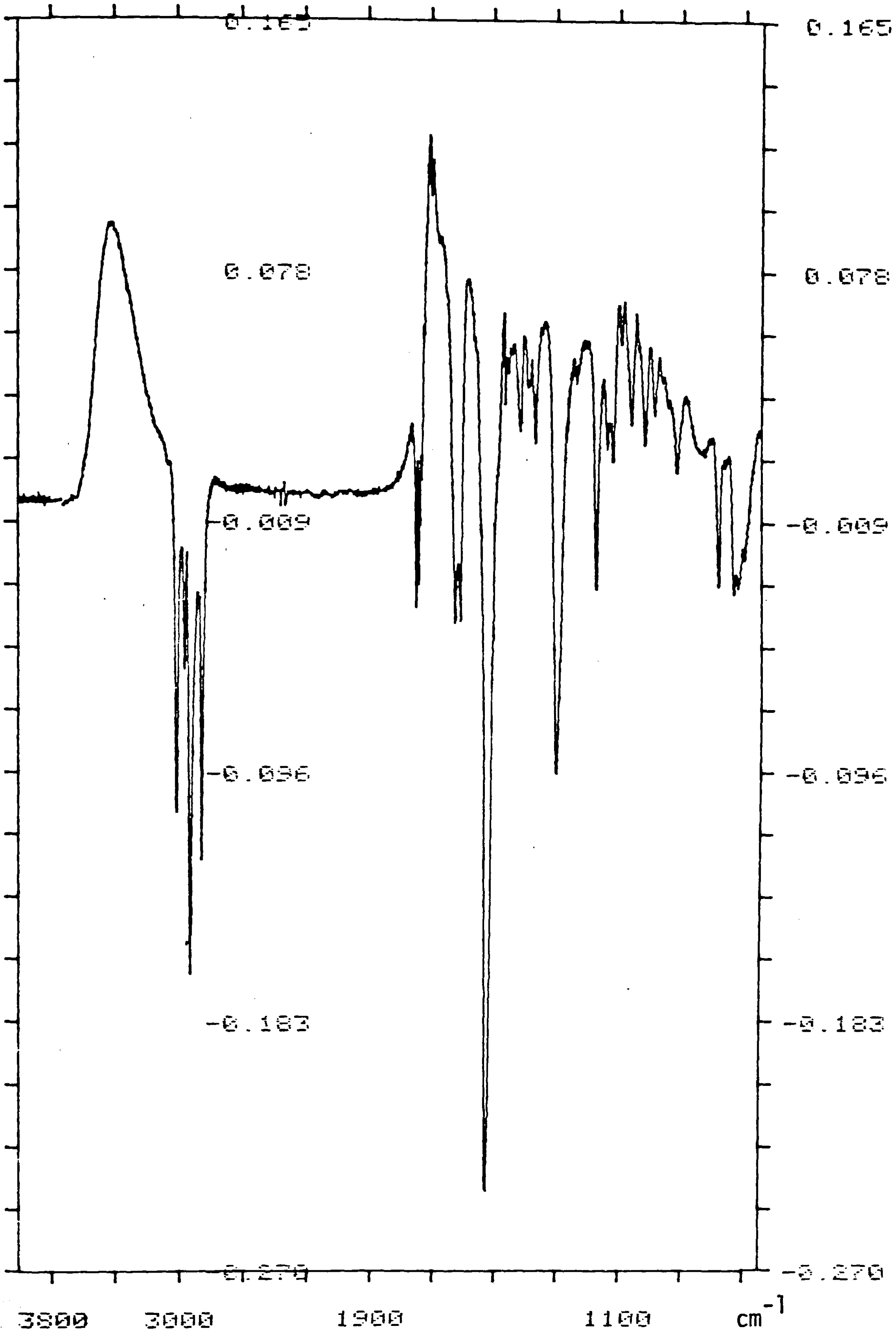
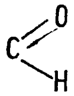
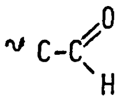


Figure 2.7.5.2.
Alkyd resin in the presence of cobalt and aluminium promotors,
12 h - 0 h difference spectrum.

12-hour minus the zero hour difference spectrum is representative of all the difference spectra obtained, see table 68. The difference spectrum is shown in figure 2.7.6.1.

Table 68

Drying of pure linoleic acid alkyd in the presence of benzil; analysis of the 12 h - 0 difference spectrum

Adsorption Gain	loss	Assignment
cm^{-1}		
3425		(HO)-0
	3006	Olefinic unsaturation
2944		C-H
	2921	R-CH_2-R asymmetric stretch
	2849	CH_3; R=CH_2-R symmetric stretch
	1849 1787 1774 1748	Phthalic anhydride
1718		 aldehyde
1630		α,β unsaturated ketone
1408		
1265		Phthalate $^{\nu}$C—0
1143		
1110		Phthalate $^{\nu}$C—0
1071		
980		trans unsaturation (trans trans conjugated)
882		-0-0- in C-0-0-H
	715	cis unsaturation.

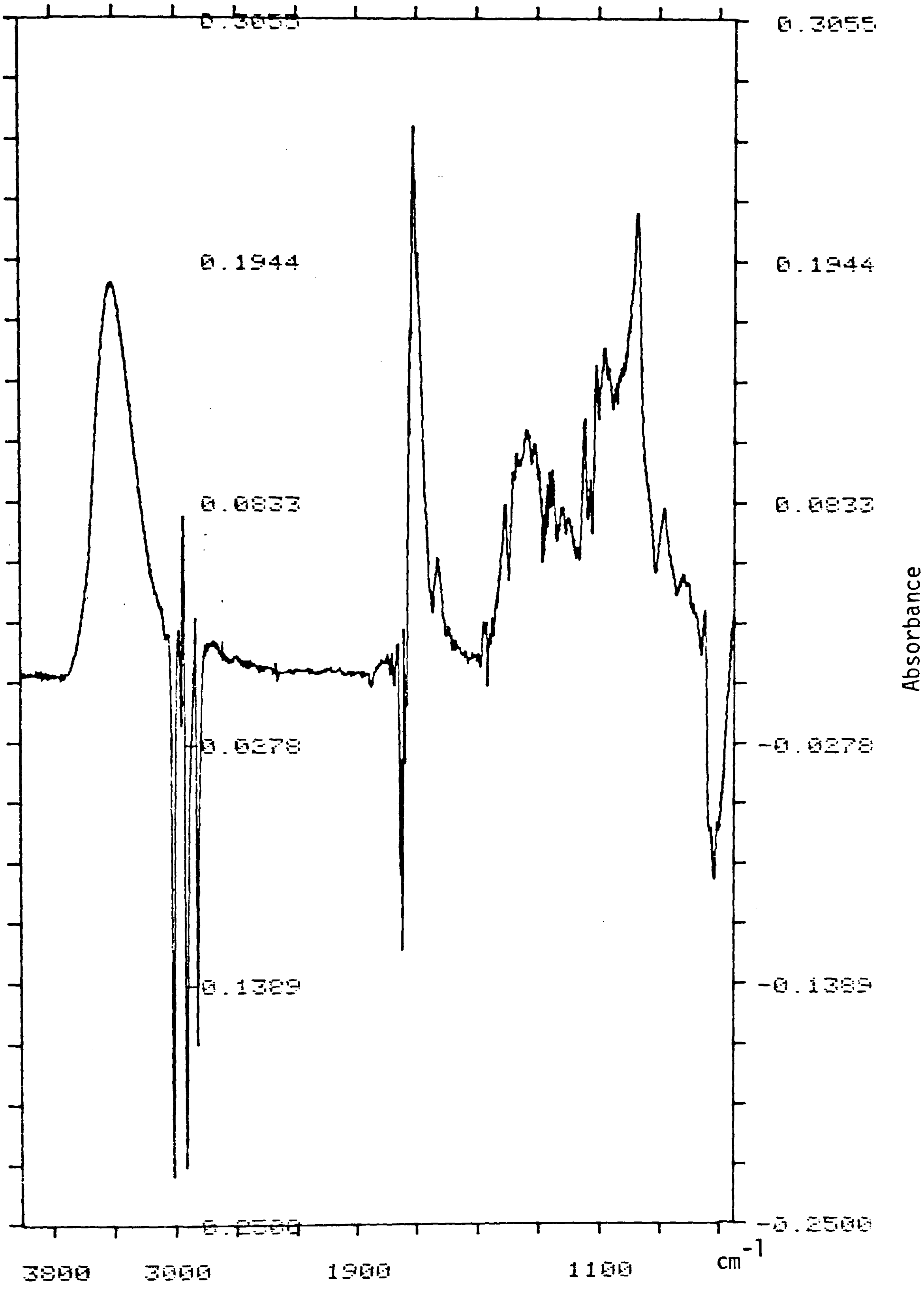


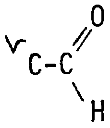
Figure 2.7.6.1.
Linoleic acid alkyd F' in the presence of benzil,
12 h - 0 h difference spectrum.

2.7.7 Methane sulphonic acid

The hydroxyl excess resin E'' was mixed with methane sulphonic acid then spread on a silver chloride IR disc (the sulphonic acid was found to react with the KBr discs) and the analysis conducted as before. The 12-hour minus zero hour difference spectrum is shown in figure 2.7.7.1 and analysed in table 69. Again the difference spectra recorded throughout a 12 hour period were qualitatively identical.

Table 69

'Hydroxyl excess' alkyd resin E'' autoxidised in the presence of methane sulphonic acid; analysis of 12 h - 0 h difference spectrum

Gain	loss	Assignment
cm^{-1}		
3424		(HO)-O-
	3010	Olefinic unsaturation
	2960	CH_3 asymmetric stretch
	2921	R-CH_2-R asymmetric stretch
	2850	CH_3; R-CH_2-R symmetric stretch
1722		Carbonyl formation
1627		α,β Unsaturated ketone
1470 1408 1378 1346		
1254		Aryl or vinyl ether νC-O stretch or
1097		possible acetal νC-O.
978		Trans unsaturation (trans,trans conjugated)
	715	Cis unsaturation

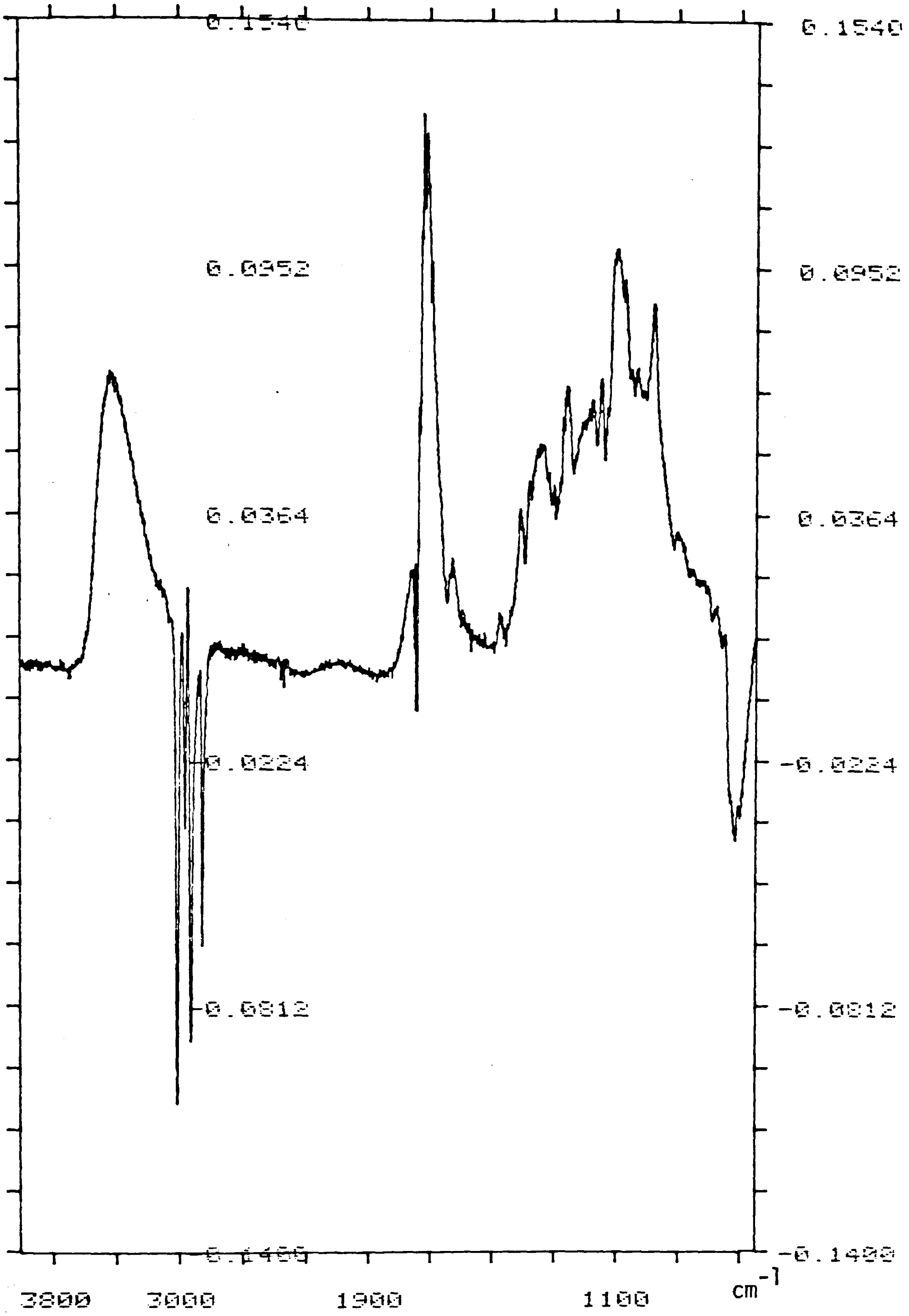


Figure 2.7.7.1.
Hydroxyl excess alkyd resin F' in the presence of methane sulphonic acid, 12 h - 0 h difference spectrum.

2.7.8 Near infrared studies of drying alkyd films

The increase of ν_{OH} at 3440 cm^{-1} absorption observed in figures 2.7.2.1, 2.7.3.1, 2.7.5.1, 2.7.5.2, 2.7.6.1 2.7.7.1, although assigned to the H-O stretch of a hydroperoxide, could also result from alcohols or carboxylic acids. The hydroperoxide harmonic band at 6850 cm^{-1} (1.46 μ) is however specific. The near infrared spectrum of drying alkyd films was recorded over the range 8330 cm^{-1} to 6667 cm^{-1} (1.2 - 1.5μ) in an attempt to give support to the assignment in the time lapse infrared studies. Increases were observed at 6850 cm^{-1} (1.46μ) in the resins autoxidised in the presence of the following promotors, (i) cobalt (II) and lead (II) bis(2-ethylhexanoate) (resin F'), (ii) cobalt (II) bis(2-ethylhexanoate) and aluminium bis(2-butoxide) ethylacetoacetate (resin G'), (iii) methane sulphonic acid (resin E") and (iv) benzil (resin F').

2.7.9 Discussion of time lapse infrared studies

The air drying mechanism of several alkyd resins in the presence of various promotors was investigated. All are initiated by oxygen via hydroperoxide formation as observed at 3440 cm^{-1}. This was confirmed by the near infrared studies with increases in intensity of the band at 6850 cm^{-1}.[268,269]

The spectral changes observed by Hartshorn[265] in the air drying of a soya alkyd promoted by cobalt (II) naphthenate, corresponded to that found in the study of pure linoleic acid alkyd (F') autoxidised in the presence of cobalt (II) bis (2-ethylhexanoate) (section 2.7.2).

The formation of hydroperoxides was accompanied by the loss of cis olefinic bonds and a corresponding increase in conjugated diene bands, the formation of carbonyl bonds was seen and a loss of aliphatic C-H bonds. These changes are expected from the mechanisms of hydroperoxide formation (see sections 1.4, 1.6 and 1.8) and their decomposition (sections 2.1.4, 2.2.4 and 2.3.4).

Investigation of the benzil promoted crosslinking of the alkyd resin F' revealed the same changes in the infrared spectrum as the redox promoted reactions. Thus the same hydroperoxide formation, double bond conjugation and carbonyl formation occurs. However it is suggested from the discussion in section 1.17 that benzil does not decompose hydroperoxides and crosslinking reactions occur from the combination of two pentadienyl radicals. Unfortunately no information can be gathered from the time lapse infrared spectroscopy to confirm this hypothesis.

The crosslinking reactions involved in the drying of hydroxyl excess alkyds, such as E'' , in the presence of methane sulphonic acids is somewhat unresolved. The evidence presented in section 1.16 suggests an autoxidative pathway and volatile studies in section 2.6 support this. The time lapse study of the drying of resin E'' in the presence of methane sulphonic acid,revealed the formation of hydroperoxides, loss of cis unsaturation and the formation of conjugated dienes thus confirming autoxidation. The formation of a carbonyl bond and loss of aliphatic C-H bondsendorses the observation of aldehydes among the volatile products from resin E'' . However the formation of acetal or ether linkages in the 'drying' resin is strengthened by the observation of a band increase at 1097 cm^{-1} (corresponding to γ_{C-O} in ethers, acetals and ketals).[267] Thus scheme 1.16.8 in section 1.16 appears to present a plausible mechanism forcrosslinking.

The changes associated when the secondary promotors alone are mixed with an alkyd resin proved interesting. The exact function of the lead (II) bis(2-ethylhexanoate) in autoxidation has not been solved. The time lapse study of alkyd resin F' in the presence of just the lead promotor reveals something of its mode of action. During the 1st hour after application there are losses in the ester and hydrocarbon bands but accompanied by only a slight increase in trans, trans conjugated diene. It is difficult to contemplate any chemical changes which involve only the loss of functionality. As there is no variation in the absorbance of the hydroxyl bands film creepage cannot provide any explanation. The changes in the infrared spectrum after the initial first hour show the normal autoxidative processes. The film, in this experiment was also found to crosslink and form a hard surface.

The time lapse study of the complexing agent, aluminium bis (2-butoxide) ethylacetoacetate, with the 'low Acid Value' alkyd G' showed only losses in the infrared spectrum. These corresponded to those of the ligands associated with the aluminium i.e. the loss of 2-butanol and ethylacetoacetate. The absence of any increase in functionality observed throughout the 12 hour period suggested no significant amount of autoxidation and was reflected in the inability of the film to dry.

When the secondary promotors were combined with cobalt (II) bis(2-ethylhexanoate), the combined effects of each promotor could be observed in the difference spectra (figures 2.7.5.1 and 2.7.5.2). However the changes associated with autoxidation tended to dominate the difference spectra.

2.8 Rate of hydroperoxide formation in the drying films in the presence of various promotors

2.8.1 Determination of rates

The rate of hydroperoxide formation was determined in a drying alkyd resin by time lapse infrared spectroscopy. The increase in hydroperoxides was monitored by determining the area under the band centred at 3440 cm^{-1} in the difference spectra. The plot of absorbance increase against time in all the experiments was found to be similar to figure 2.8.1.1. The data was treated as first order and the rate law $kt = \ln\left(\frac{A}{A - X}\right)$ used, where A is the absorbance after 'infinite' time and X the absorbance after time t. Plots of $\ln\left(\frac{A}{A - X}\right)$ against time are given in figures 2.8.1.2, 2.8.1.3, 2.8.1.4, 2.8.1.5, 2.8.1.6 and 2.8.1.7. The gradient of the lines was determined using least means square analysis and the rate coefficients are given in table 70.

The error in the gradients of the lines obtained is ~ 6% indicating first order behaviour for hydroperoxide formation. The observed rate coefficient is a composite one, as it is believed two basic processes are occurring during the autoxidation, i.e. hydroperoxide formation and hydroperoxide decomposition. Scheme 2.8.1.1.

$$\text{RH} + \text{O}_2 \xrightarrow{k_1} \text{ROOH} \xrightarrow{k_2} \text{decomposition products.}$$

Scheme 2.8.1.1

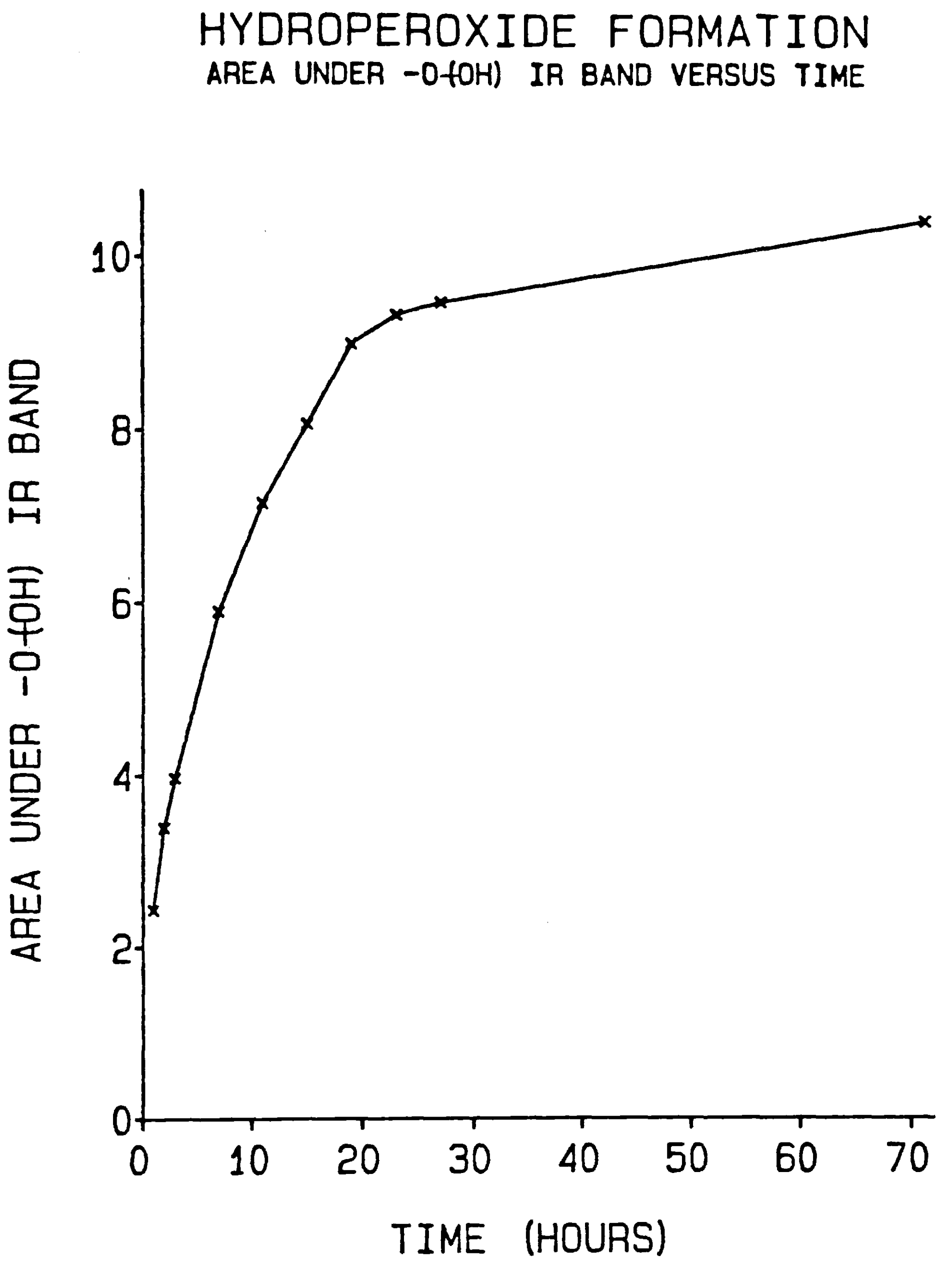


Figure 2.8.1.1

Linoleic acid alkyd autoxidised in the presence of cobalt (II) octoate

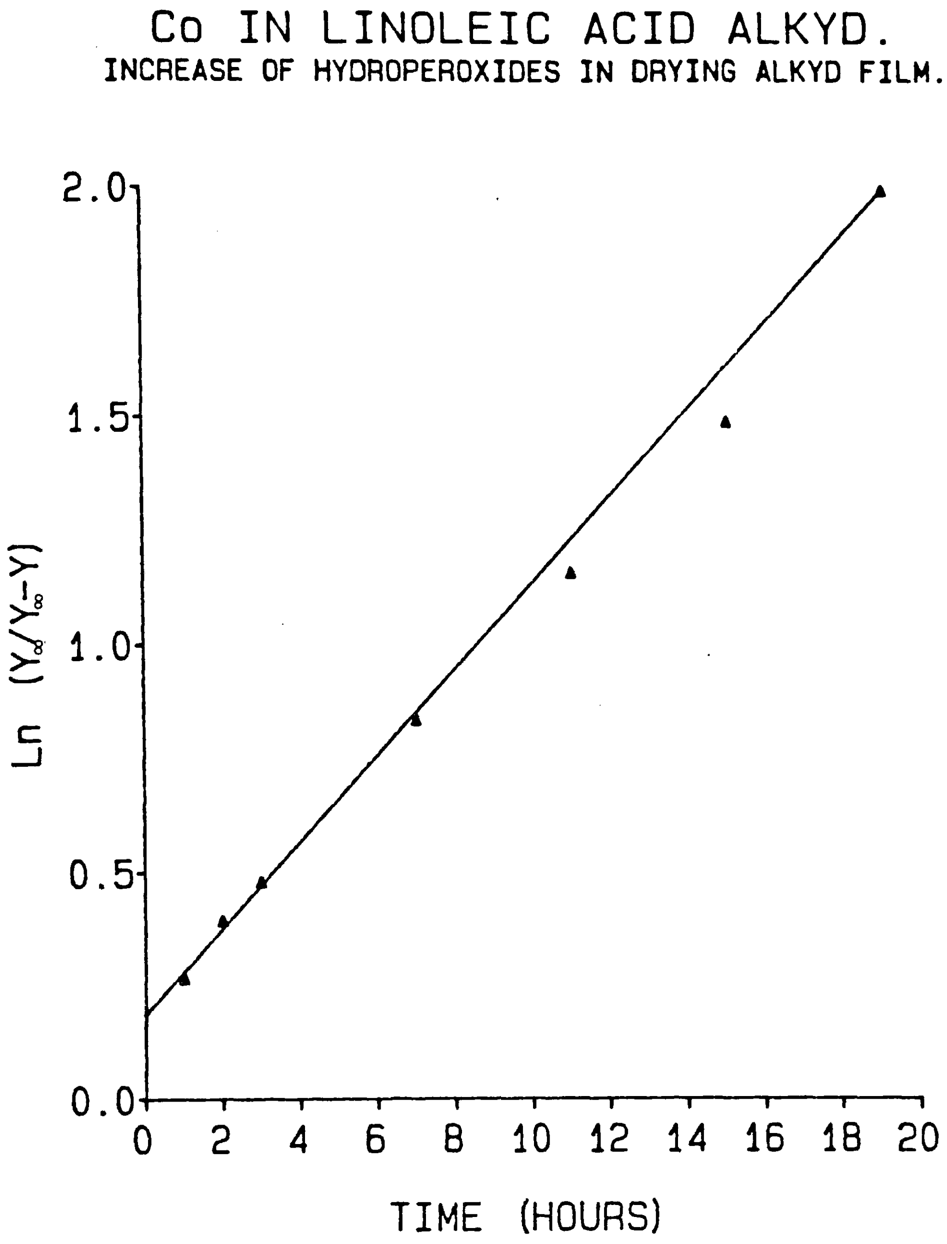

Co IN LINOLEIC ACID ALKYD.
INCREASE OF HYDROPEROXIDES IN DRYING ALKYD FILM.
2.0
1.5
1.0
0.5
0.0
Ln (Y∞/Y∞–Y)
0
2
4
6
8
10
12
14
16
18
20
TIME (HOURS)

Figure 2.8.1.2.

Pb IN LINOLEIC ACID ALKYD.

INCREASE OF HYROPEROXIDES IN A DRYING ALKYD FILM.

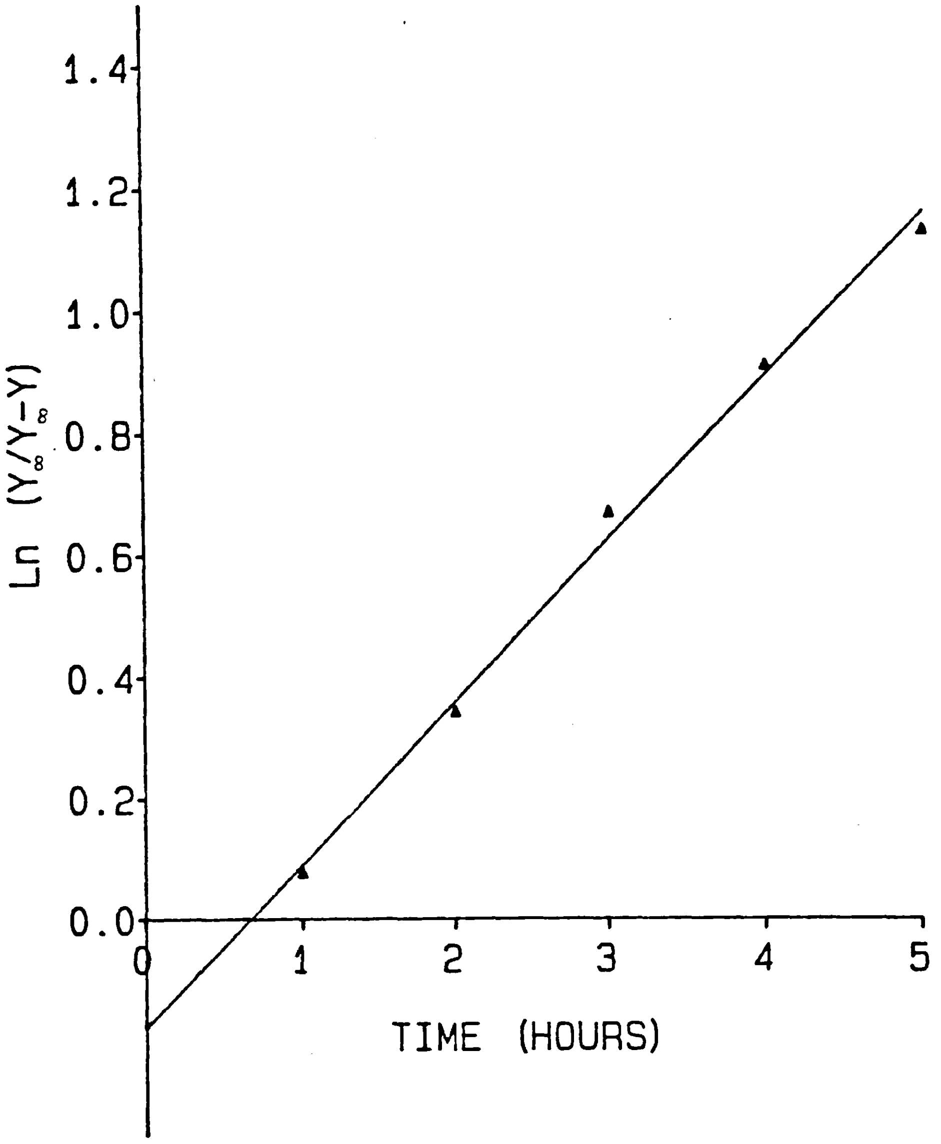


Figure 2.8.1.3.

Co/Pb IN LINOLEIC ACID ALKYD.
INCREASE OF HYDROPEROXIDES IN A DRYING ALKYD FILM.

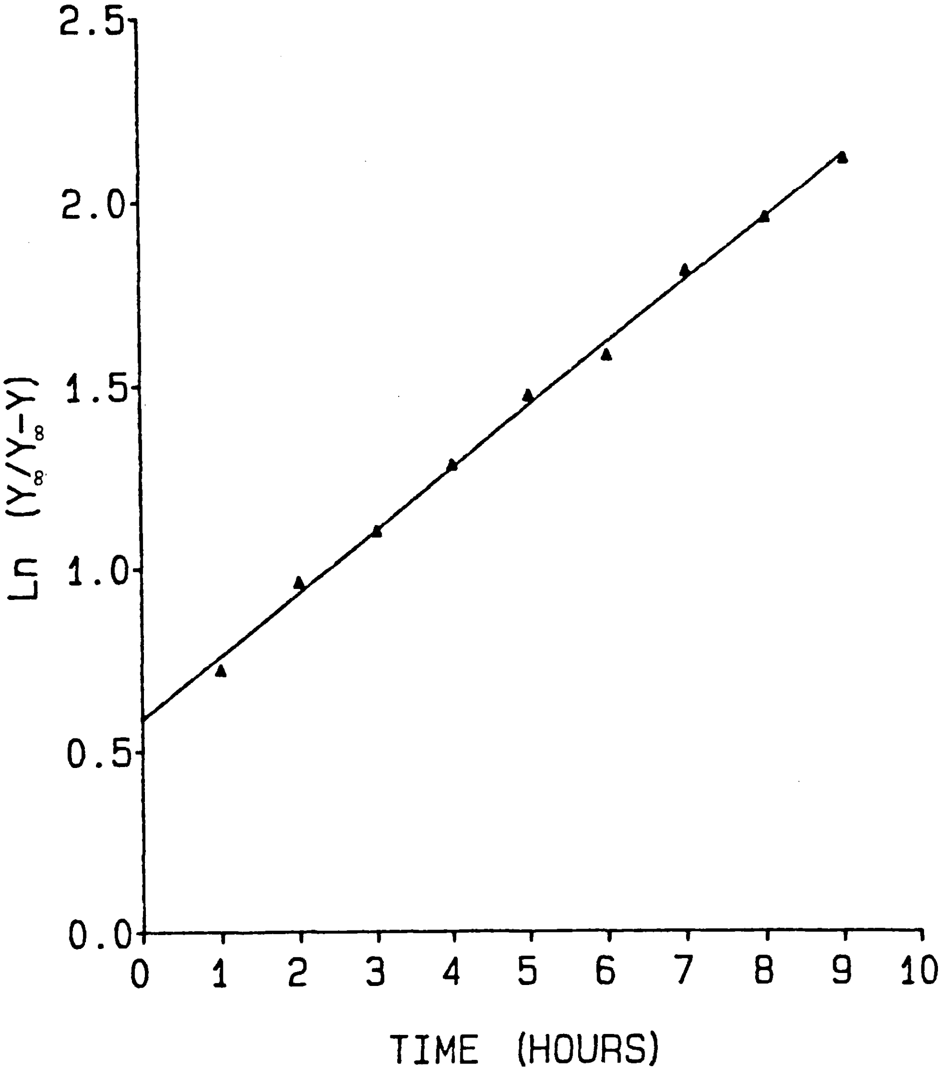
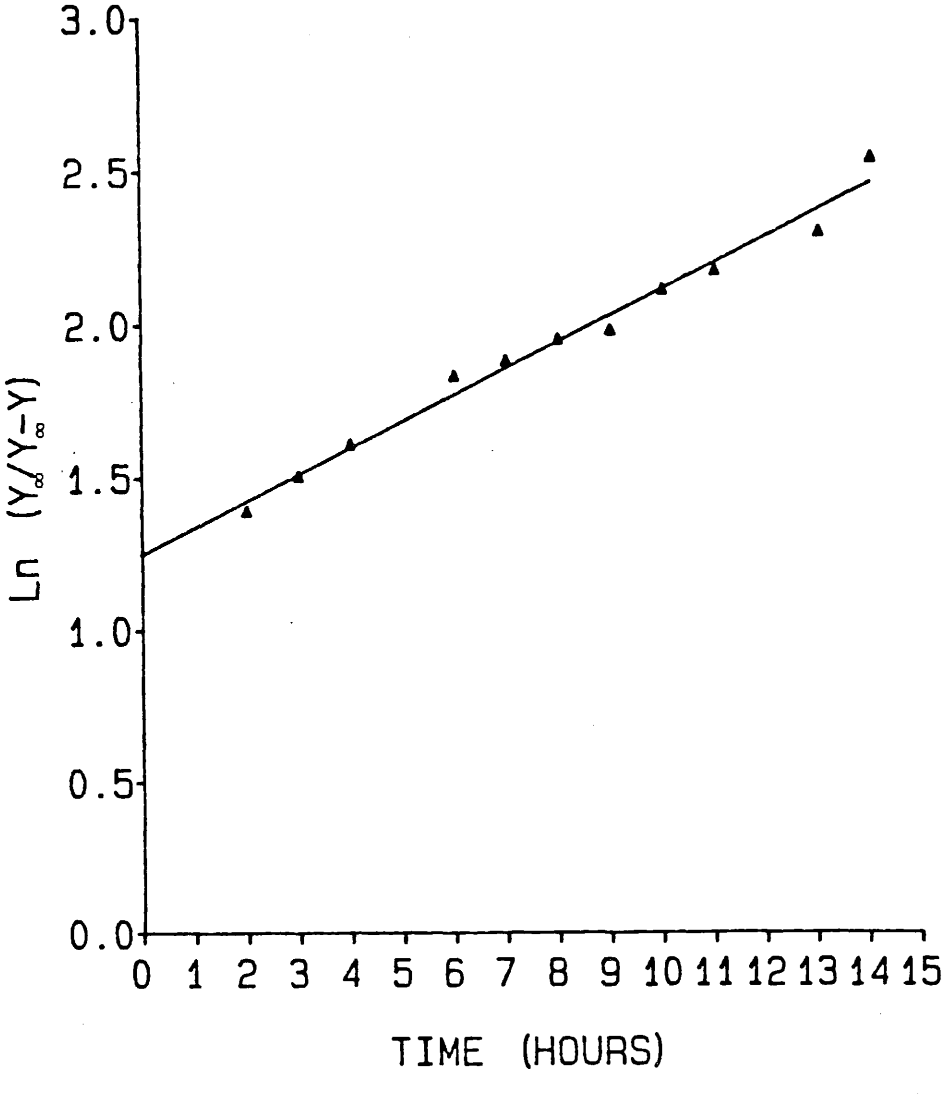


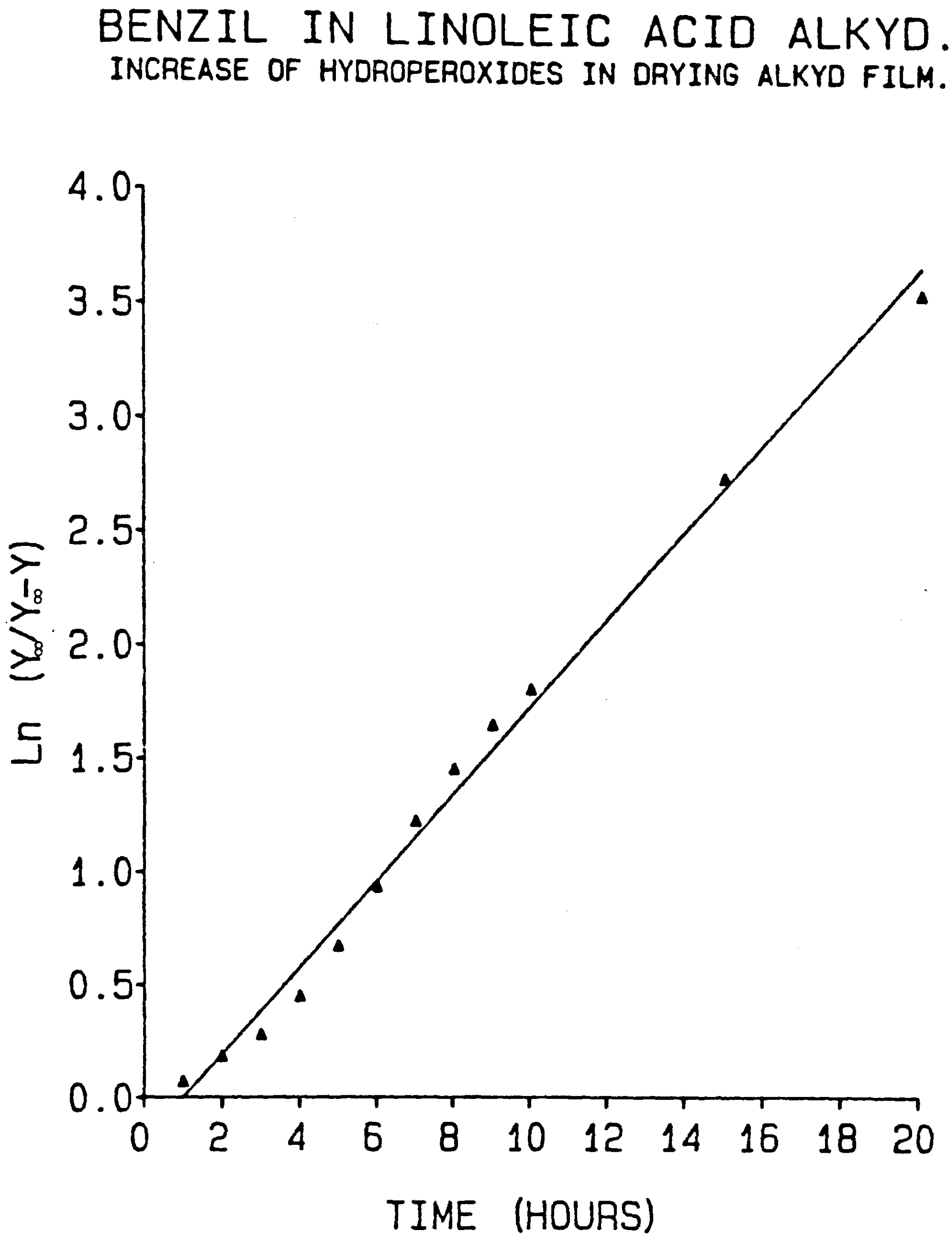
Figure 2.8.1.4.



Co/Al IN LOW ACID VALUE ALKYD.

INCREASE OF HYDROPEROXIDES IN DRYING ALKYD FILM.

Figure 2.8.1.5.



BENZIL IN LINOLEIC ACID ALKYD.
INCREASE OF HYDROPEROXIDES IN DRYING ALKYD FILM.

Figure 2.8.1.6.

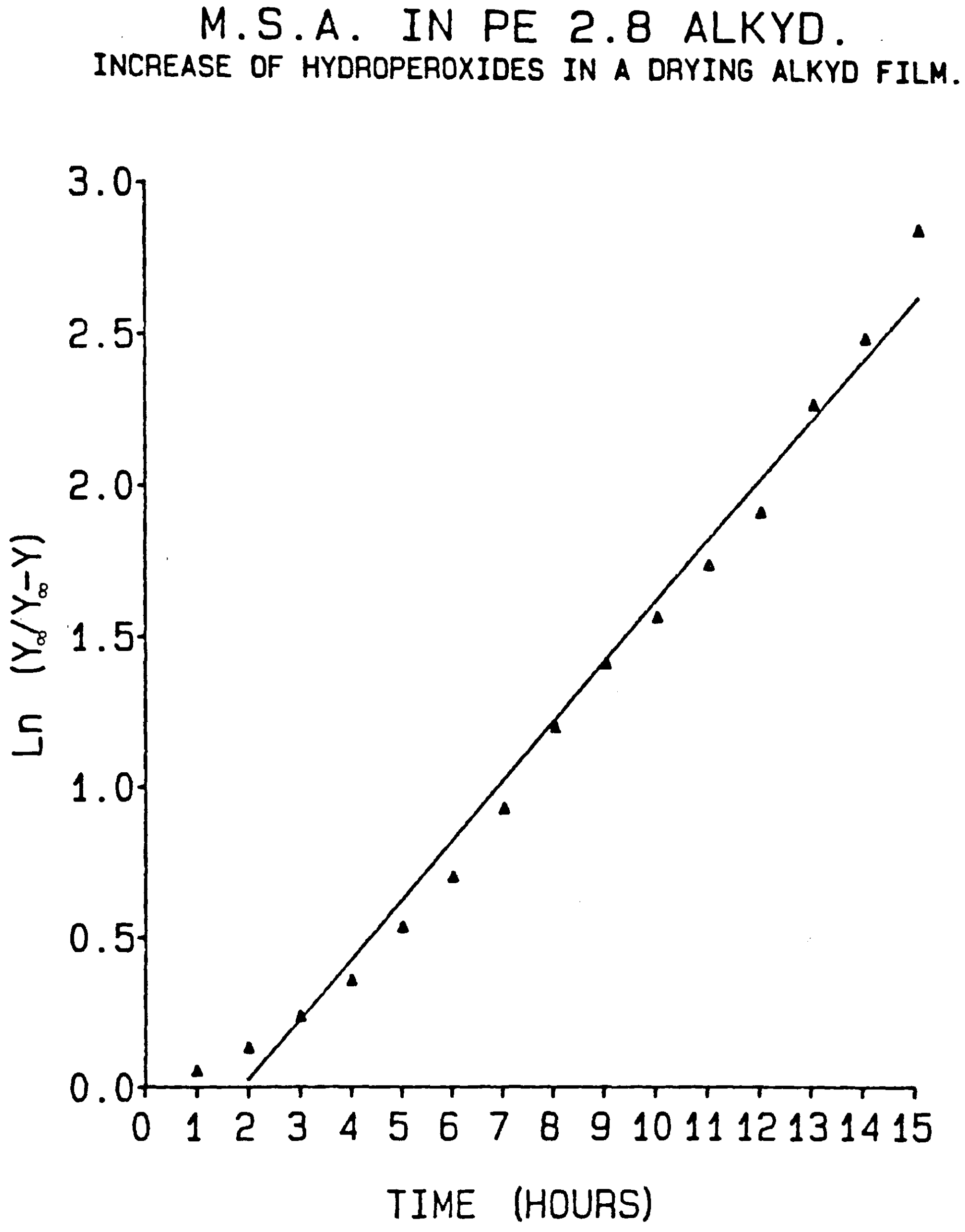

M.S.A. IN PE 2.8 ALKYD.
INCREASE OF HYDROPEROXIDES IN A DRYING ALKYD FILM.
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Ln $(Y_\infty/Y_\infty-Y)$
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
TIME (HOURS)

Figure 2.8.1.7.

Table 70

Kinetics of hydroperoxide formation as determined by infrared spectroscopy

Catalyst	Rate coefficient k/s^{-1} (10^5)	Error 95% confidence
Cobalt (II) bis (2-ethylhexanoate).	2.54	± 0.16 (6.3%)
Cobalt (II) bis(2-ethylhexanoate) and Aluminium bis(2-butoxide) ethylacetoacetate in 2-butanol solution.	2.44	± 0.21 (8.6%)
Lead (II) bis(2-ethylhexanoate).	3.13	± 0.12 (3.9%)
Cobalt (II) and lead (II) bis(2-ethylhexanoate).	4.80	± 0.29 (5.4%)
Benzil	5.36	± 0.29 (5.4%)
Methane sulphonic acid	5.56	± 0.39 (7.0%)

Thus if a promotor is efficient at decomposing hydroperoxides the observed rate would be smaller assuming k_1 is comparable for all the promotor systems. The rate coefficients and quantity of volatile material collected are compared in table 71.

Table 71

Comparison of rate coefficients with the quantity of volatile material

Promotor system	Rate coefficient k/sec^{-1} (10^5)	Volatile material collected $(\text{X } 10^{-3}\text{g})$*
Co/Al	2.44	2.37
Co/Pb	4.80	2.59
Co	2.54	2.34
Pb	3.13	0.78
Benzil	5.36	0.23

* based on volatile products from methyl linoleate.

The mechanism of volatile formation discussed in section 2.1.4, 2.2.4 and 2.3.4 all involved the homolytic cleavage of hydroperoxides. The redox promotor cobalt (II) bis(2-ethylhexanoate) will reduce hydroperoxides to alkoxy radicals thus aiding volatile formation and reducing the apparent rate of hydroperoxide formation. The benzil promotor, which probably does not induce hydroperoxide decomposition yet aids their formation by hydrogen abstraction, shows a greater observed rate of hydroperoxide formation with a lower yield of volatiles. The fact that benzil is regarded as a transient drier, i.e. not a true catalyst will also help to reduce the formation of volatiles. It has been demonstrated that approximately 25% of the benzil was lost in 21 hours of autoxidation (see section 2.2.3.3). The redox promotor, cobalt (II) bis (2-ethylhexanoate), however is considered to be truly catalytic.

The use of the complexing agent (aluminium bis(2-butoxide) ethyl acetoacetate) in combination with cobalt (II) bis(2-ethylhexanoate) did not significantly alter the observed rate of -OOH formation or the quantity of volatile compounds produced, compared to the cobalt (II) bis(2-ethylhexanoate) alone. This supports the assumption made in section 2.7.9 that the aluminium compound does not engage in any autoxidation reactions or hydroperoxide decompositions.

The combined use of lead (II) bis(2-ethylhexanoate) and cobalt (II) bis(2-ethylhexanoate) does however have an additive effect on the rate of -OOH formation but with only a slight increase in quantity of volatile material produced. This reinforces the theory that lead (II) bis(2-ethylhexanoate) aids hydroperoxide formation but only gives little decomposition.

Figure 2.8.1.8. compares the rate of hydroperoxide formation promoted by cobalt (II) bis(2-ethylhexanoate) benzil and methane sulphonic acid (M.S.A.), figure 2.8.1.9 compares the rate of hydroperoxide formation promoted by cobalt (II) bis (2-ethylhexanoate); cobalt (II) bis(2-ethylhexanoate) and lead (II) bis (2-ethylhexanoate) (Co/Pb), and cobalt (II) bis (2-ethylhexanoate) and aluminium bis (2-butoxide) ethylacetoacetate (Co/Al).

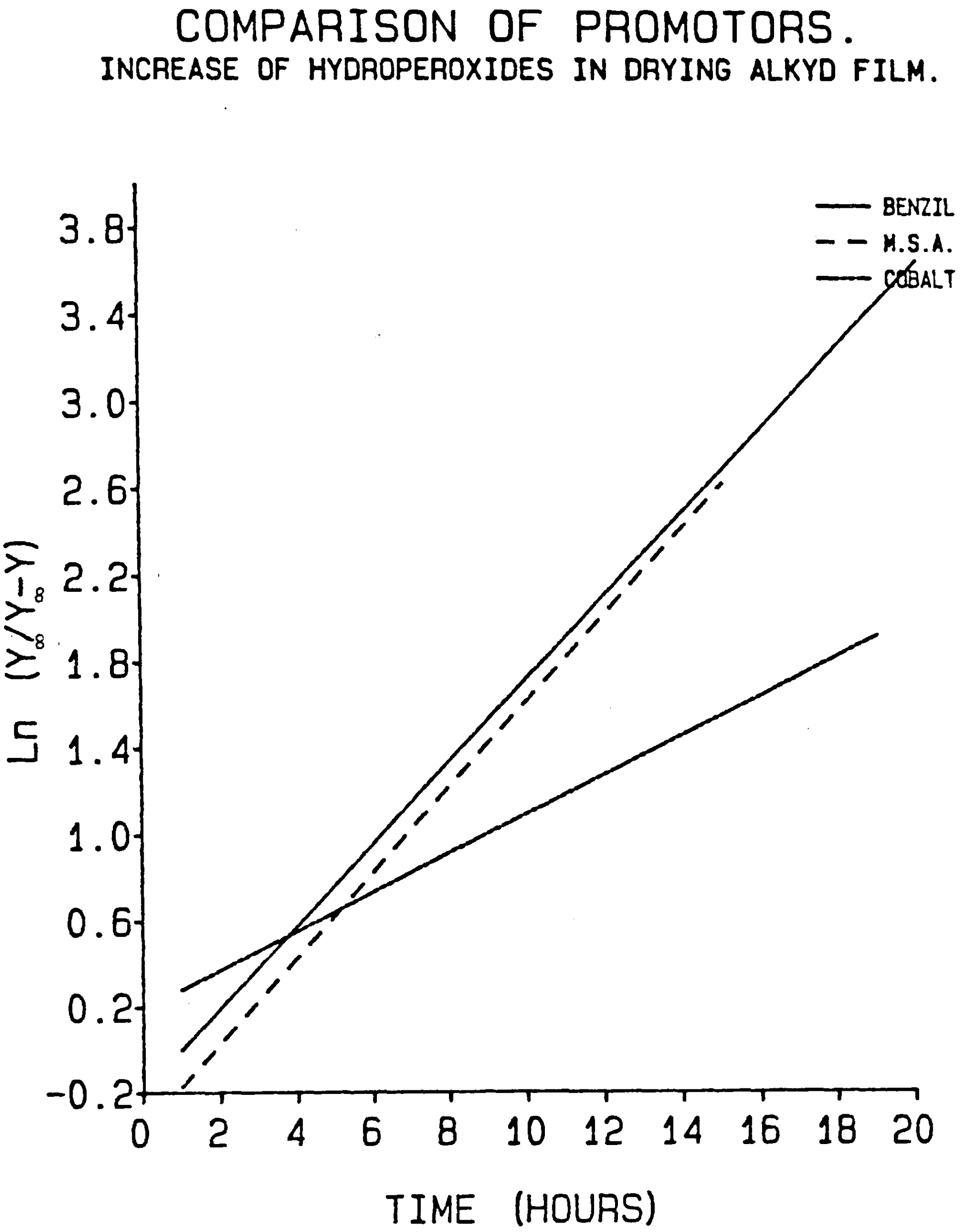

COMPARISON OF PROMOTORS.
INCREASE OF HYDROPEROXIDES IN DRYING ALKYD FILM.
BENZIL
M.S.A.
COBALT
Ln $(Y_\infty/Y_\infty - Y)$
3.8
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2
0
2
4
6
8
10
12
14
16
18
20
TIME (HOURS)

Figure 2.8.1.8.

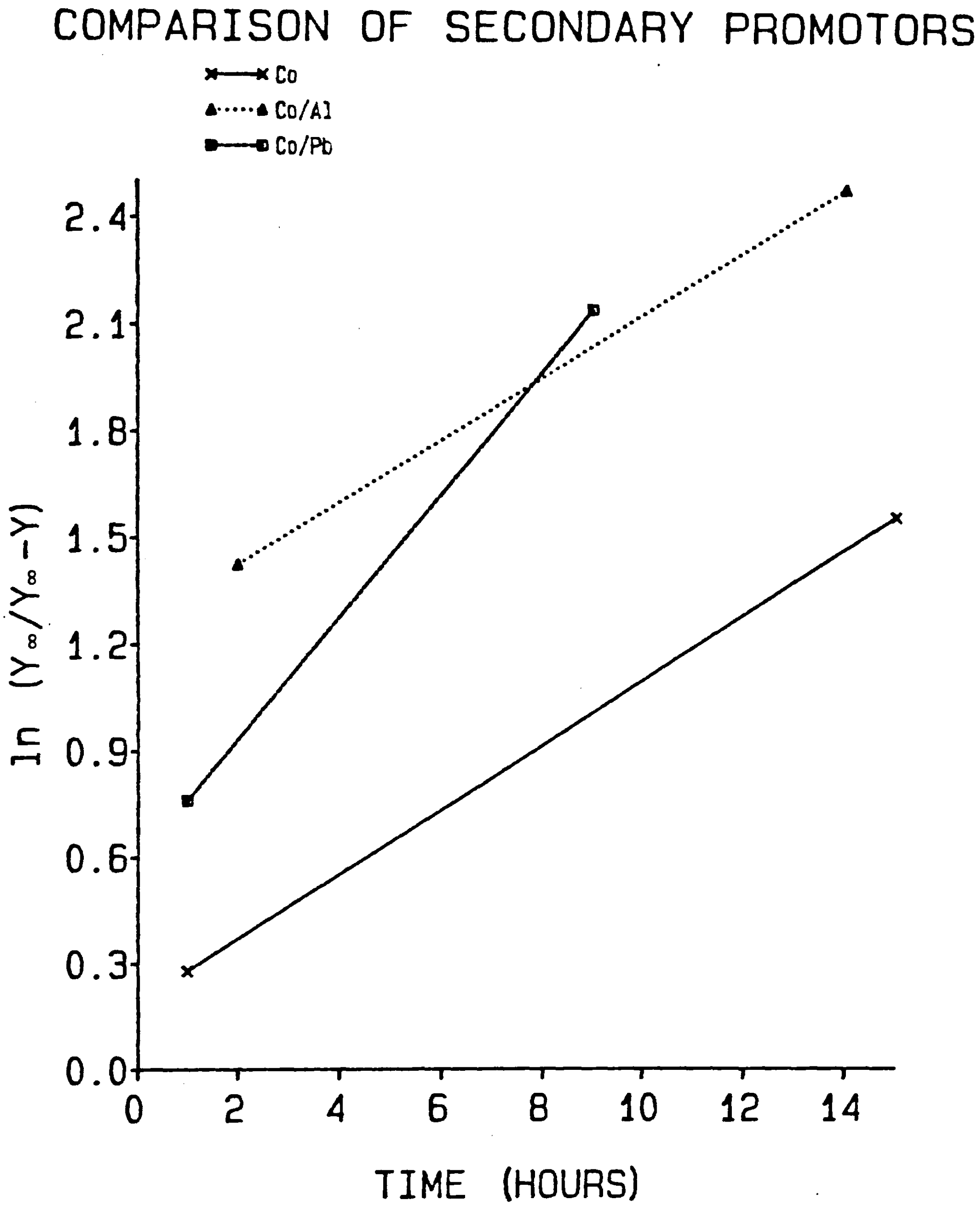

COMPARISON OF SECONDARY PROMOTORS
Co
Co/Al
Co/Pb
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
0.0
ln (Y∞/Y∞−Y)
0
2
4
6
8
10
12
14
TIME (HOURS)

Figure 2.8.1.9

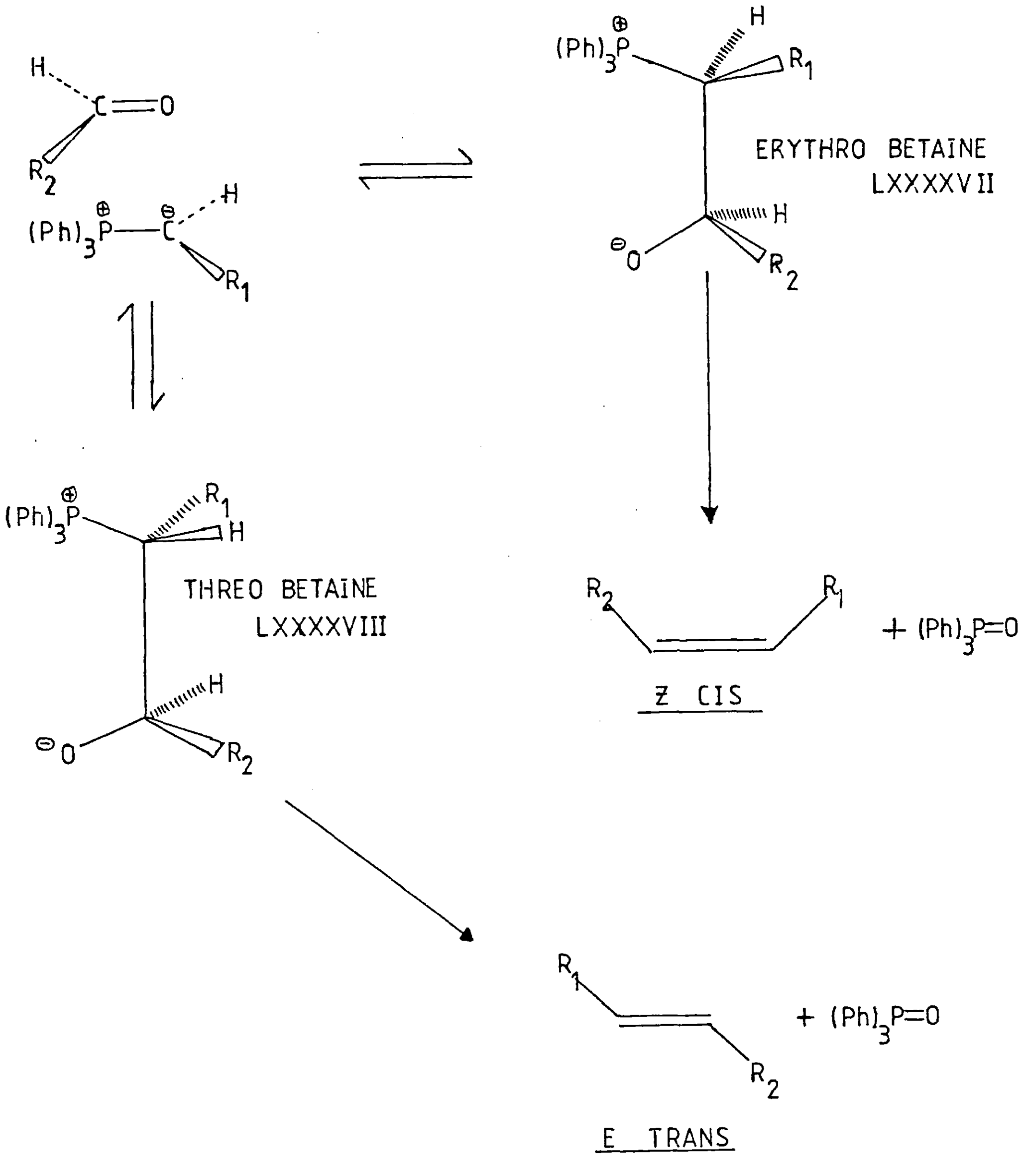
Unfortunately no quantitation of the volatiles produced by methane sulphonic acid promoted autoxidations was carried out, but the observed rate of hydroperoxide formation was similar to that found in the benzil promoted autoxidations.

2.9 Autoxidation of Model Olefinic Compounds

2.9.1 Introduction and synthesis

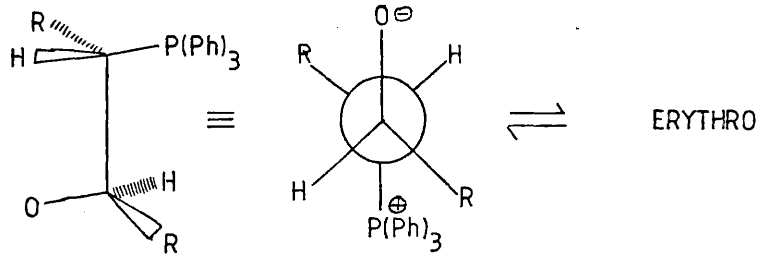
The autoxidation of methyl cis-9- cis-12-octadecadienoate is proposed to proceed by the preferential loss of a hydrogen from the doubly allylic methylene group (Section 1.6). The olefin 6,9-pentadecadiene should, on autoxidation, give similar volatile products to methyl cis-9- cis-12-octadecadienoate. However it was anticipated that if the central methylene hydrogens are replaced by methyl groups this could change the volatile products. Accordingly the synthesis of the following compounds was carried out; 6,9-pentadecadiene CI , 8-methyl-6,9-pentadecadiene CII and 8,8-dimethyl-6,9-pentadecadiene CIII .

The Wittig reaction was employed to prepare these compounds, (see Sections 3.3.4, 3.3.5 and 3.3.6). The synthesis of 6,9-pentadecadiene was relatively straightforward involving phosphonium salt formation (in ~90% yields) using triphenyl phosphine with 1,3-dibromopropane in refluxing dimethylformamide. The stereochemistry desired for the olefinic bond formation is cis and in an attempt to control this the solvent system tetrahydrofuran/hexamethylphosphoramide (2:1 v/v) as suggested by Sonnet[270] was used for the reaction of the ylid with the carbonyl compound. The mechanism of the Wittig reaction is believed to proceed via betaines LXXXXVII and LXXXXVIII , see Scheme 2.9.1.1.

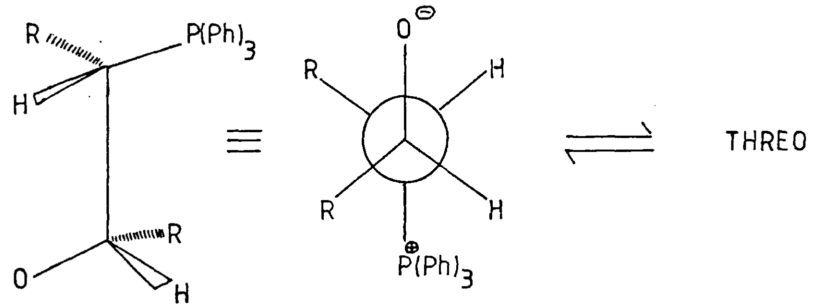


Scheme 2.9.1.1

There is a kinetic preference for the erythro betaine which presumably results from the relative energies of the two gauche adducts LXXXXIX and C formed by nuclephilic attack of the ylid on the carbonyl compound.



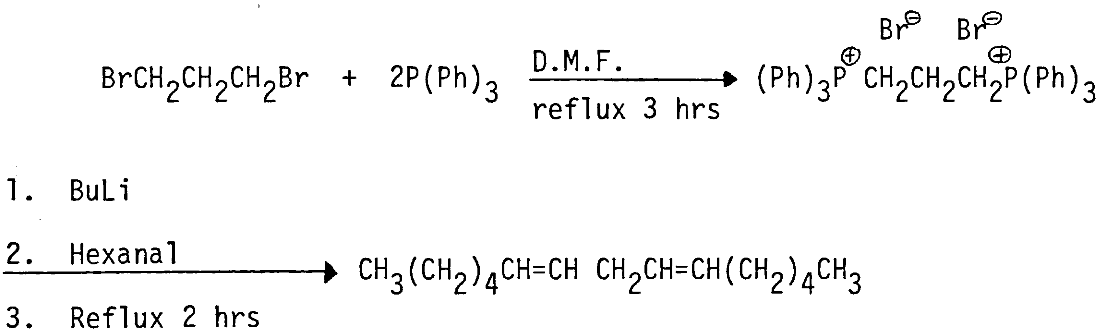
LXXXXIX



C

Adduct LXXXXIX has two interactions between two large groups compared to adduct C which has these with three thus adduct LXXXXIX has the lower energy. It is probable that torsional strain and charge dissipation involving ion-pair aggregation favours both these conformations LXXXXIX and C over those required for fragmentation and olefin formation. Provided the fragmentation of the betaines to olefins is faster than the dissocation there will be a preference for the cis configuration i.e. the kinetic product. However if the ylid is internally stabilised or there are metal cations (Li^+) present the rate of fragmentation is retarded and equilibration of the betaines occurs; leading to the trans olefin formation i.e. the thermodynamic product. The use of polar solvents e.g. HMPTA favours separation of ion-pairs and ion-aggregates; causing accelerated fragmentation of the betaines, to produce the kinetically favoured cis-olefins.

The Wittig reaction of the phosphonium salt with butyllithium to form the ylid followed by reaction with hexanal yielded 6,9-pentadecadiene (~30% theoretical), after purification by column chromatography. The synthetic route is given in scheme 2.9.1.2.



$$BrCH_2CH_2CH_2Br + 2P(Ph)_3 \xrightarrow[\text{reflux 3 hrs}]{\text{D.M.F.}} (Ph)_3\overset{\oplus}{P}CH_2CH_2CH_2\overset{\oplus}{P}(Ph)_3 \quad Br^{\ominus} \; Br^{\ominus}$$

$$\xrightarrow[\text{3. Reflux 2 hrs}]{\text{1. BuLi} \quad \text{2. Hexanal}} CH_3(CH_2)_4CH{=}CH\,CH_2CH{=}CH(CH_2)_4CH_3$$

Scheme 2.9.1.2

The olefin formed was identified by infrared; nuclear magnetic resonance (both ^1H and ^{13}C) and mass spectrometry. The data is given in tables 72, 73, 74 and 75, respectively. For elemental analysis see table 84.

The ratio of cis isomer to trans isomer was 2.9 : 1 (calculated by the intensities of the absorption bands at 720 cm^{-1} and 970 cm^{-1} respectively).

Table 72

Assignment of the infrared spectrum of 6,9-pentadecadiene

cm^{-1}	Assignment
3010	Olefinic unsaturation (C-H stretch)
2980	CH_3 Asymmetric stretch
2920	$R-CH_2-R$ Asymmetric stretch
2850	CH_3; $R-CH_2-R$ Symmetric stretch
1650	Olefinic unsaturation (C=C stretch)
1470	C-H Def) Saturated hydrocarbon
1380	C-H Def)
1275	
1110	
970	Trans unsaturation out-of-plane C-H def.
910	
720	Cis unsaturation out-of-plane C-H def.

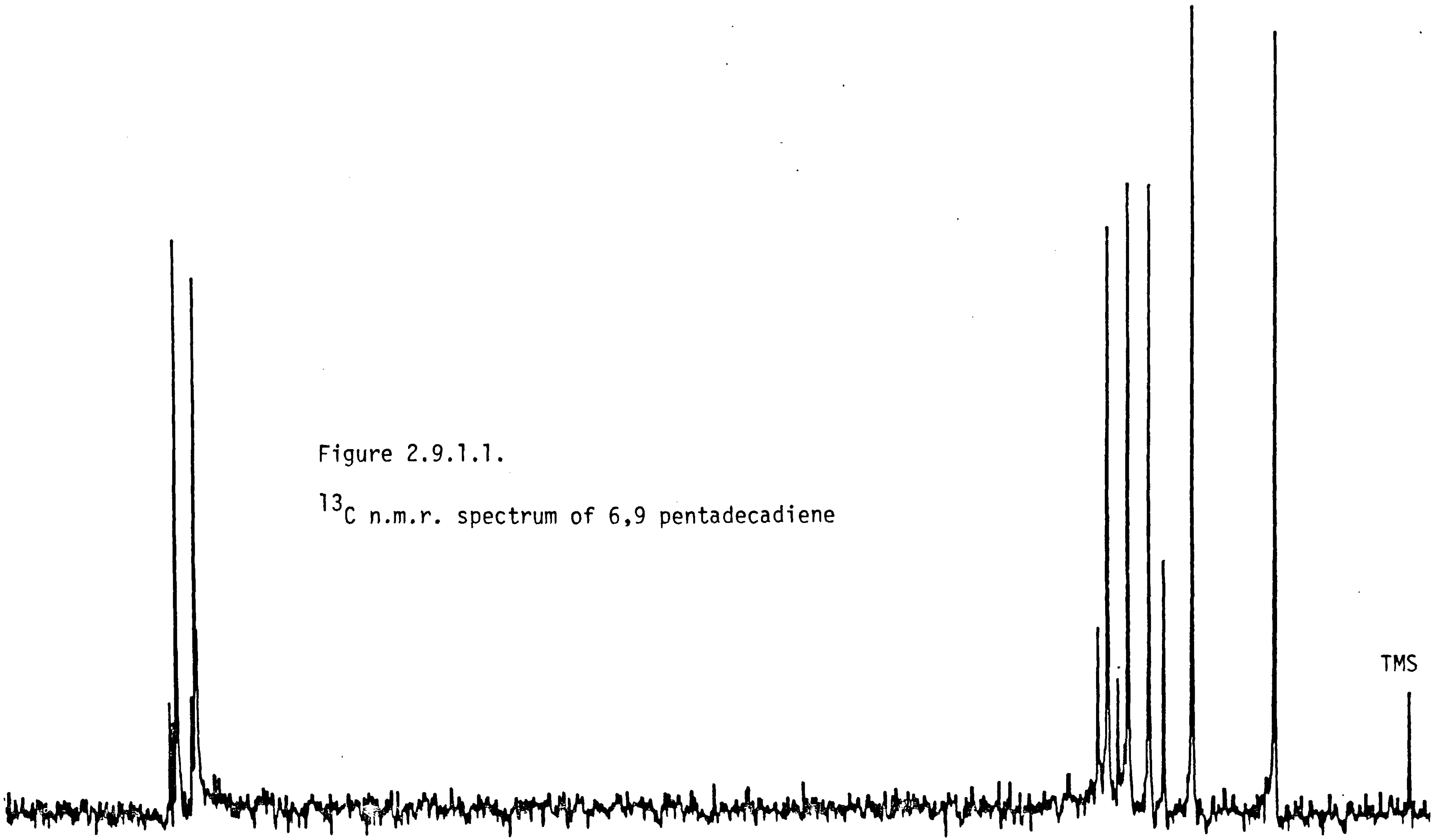


Figure 2.9.1.1.

^{13}C n.m.r. spectrum of 6,9 pentadecadiene

Table 73

Assignment of ^1H nmr spectrum of 6,9-pentadecadiene

$$(\overset{1}{CH_3}\ \overset{2-4}{(CH_2)_3}\ \overset{5}{CH_2}\ \overset{6}{CH} = \overset{7}{CH})_2\overset{8}{CH_2}$$

Type of signal	Chemical shift ppm	Coupling constants (Hz)	Integration
t	0.9 CH_3 (1)		6
s (br)	1.35 $6CH_2$ (2-4)		12
m/t	1.95-2.35 $2CH_2$ (5)		4
t	2.75 CH_2 (8)	$J_{7,8} = 5.0$	2
t/(m/t)*	5.5 4CH (6,7)	$J_{7,8} = J_{6,5} = 5.0$	4

* Prominent triplet (cis) with other peaks due to trans olefin.

Table 74

Assignment of ^{13}C nmr spectrum, figure 2.9.1.1, of 6,9-pentadecadiene

Carbon No.	Chemical shift[272] (ppm)
1	14.1
2	22.8
3	31.8
4	29.9
5	27.4
6	128.0
7	130.0
8	25.8

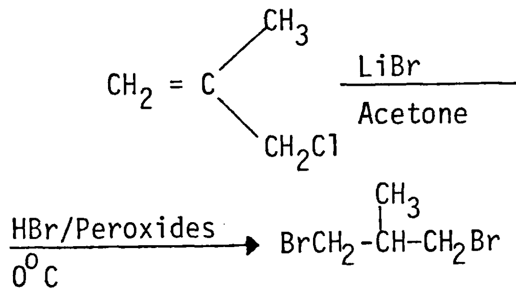
Table 75

EI Mass spectrum of 6,9-pentadecadiene

m/z	208	194	179	165	151	138	137	124	123	110	109	96	95	83	82	81	69	68	67	57	55	54	43	41	29	27
Rel. AB %	39.0	4.8	0.6	1.9	6.8	6.8	8.3	13.6	9.2	34.0	22.8	46.6	48.0	11.2	41.7	71.8	24.3	36.9	100	8.7	40.3	41.7	13.6	36.0	13.6	8.7

The mass spectrum, figure 2.1.9.2., confirmed the relative molecular mass of the compound as 208 daltons and the general fragmentation consistent with that of a hydrocarbon. The base peak ion at m/z 67 has the composition C_5H_7 which most likely is derived from the diene part of the molecule.

The synthesis of 8-methyl-6,9-pentadecadiene was complicated by the need for the preparation of 2-methyl-1,3-dibromopropane. The method of Brewster[271] was used, scheme 2.9.1.3, but the yields obtained were consistently lower than he reported. The triphenylphosphonium salt preparation proceeded with relative ease as did the Wittig reaction, the olefin was obtained in 29.6% yield,



$CH_2=C(CH_3)CH_2Cl \xrightarrow[\text{Acetone}]{\text{LiBr}} CH_2=C(CH_3)CH_2Br \xrightarrow[0^oC]{\text{HBr/Peroxides}} BrCH_2\text{-}CH(CH_3)\text{-}CH_2Br$

(yield: lit. 80%, obtained 32%)

Scheme 2.9.1.3

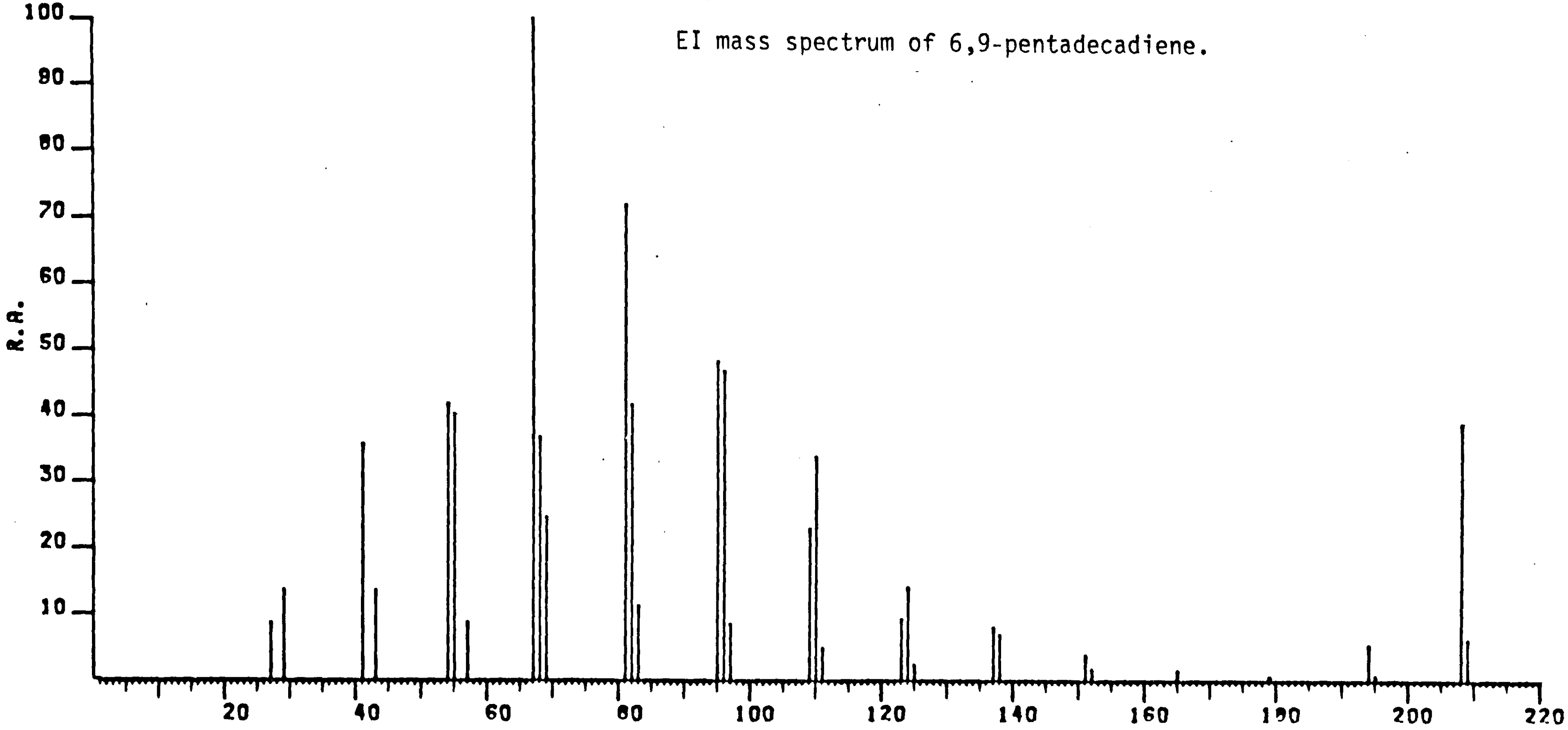


Figure 2.1.9.2.

EI mass spectrum of 6,9-pentadecadiene.

after purification by column chromatography. The product was identified by infrared, nmr (^1H and ^{13}C) and mass spectrometry. This analysis is given in tables 75, 77, 78 and 79 respectively. For elemental analysis see table 84.

Table 76

Assignment of infrared spectrum of 8-methyl-6,9-pentadecadiene

cm^{-1}	Assignment
3010	Olefinic unsaturation (C-H stretch)
2980	CH_3, Asymmetric stretch
2920	R-CH_2-R, Asymmetric stretch
2850	CH_3, R-CH_2-R Symmetric stretch
1650	Olefinic unsaturation (-C=C-stretch)
1470	C-H Def) Saturated hydrocarbon
1380	C-H Def)
1275	
970	Trans unsaturation out-of-plane C-H def.
923	
720	Cis unsaturation out-of-plane C-H def.

Table 77

Assignment of ^1H nmr spectrum of 8-methyl-6,9-pentadecadiene

$(\overset{1}{\mathrm{CH_3}}\overset{2\text{-}4}{(\mathrm{CH_2})_3}\overset{5}{\mathrm{CH_2}}\overset{6}{\mathrm{CH}}{=}\overset{7}{\mathrm{CH}})_2\overset{8}{\mathrm{CH}}\overset{9}{\mathrm{CH_3}}$		
Type of Signal	Chemical shift (ppm)	Integration
m/t	0.95 CH_3 (1,9)	9
s(br)	1.40 $6CH_2$ (2-4)	12
m/t	1.90 - 2.30 $2CH_2$ (5)	4
m/t (br)	2.65-CH (8)	1
d/t*	5.5 2CH (6,7)	4

* The peaks due to the olefinic protons are complex with a doublet overlying a triplet.

Table 78

Assignment of ^{13}C nmr spectrum of 8-methyl-6,9-pentadecadiene

Carbon No.	Chemical shift (ppm)[272]
1	14.0
2	22.6
3	31.7
4	29.4
5	27.6
6	128.5
7	134.8
8	27.4
9	30.6

Table 79

EI mass spectrum of 8-methyl-6,9-pentadecadiene - Figure 2.1.9.3

m/z	222	207	193	179	165	151	138	137	124	123	109	95	81
Rel.AB %	23.3	3.9	0.9	5.8	3.9	36.9	13.1	11.1	10.7	16.5	17.9	60.2	100.0

m/z	69	68	57	55	43	41
Rel.AB %	19.4	24.3	8.3	34.9	10.7	22.3

Its relative molecular mass of 222 daltons was confirmed by the mass spectrum, figure 2.1.9.3, and the general fragmentation was indicative of a hydrocarbon. The base peak ion in this compound at m/z is 14 daltons higher than in 6,9-pentadecadiene, and probably results from fragmentations, giving an ion derived from the central diene structure.

The preparation of 8,8-dimethyl-6,9-pentadecadiene again involved the synthesis of the parent dibromo compound, i.e. 2,2-dimethyl-1,3-dibromo propane. The alcohol 2,2-dimethyl-1,3-propanediol was brominated using the adduct $(C_6H_5)_3PBr_2$. Attempts were made to brominate the alcohol using phosphorous tribromide but rearrangement products were formed instead. The presence of two methyl groups hindered the phosphonium salt evidenced by the drastic reaction conditions required (Section 3.3.6). The Wittig reaction however proceeded as normal. The olefin was obtained in 46.4% yield after purification by column chromatography and identified by infrared, nmr (both ^1H and ^{13}C) and mass spectrometry, the data is given in tables 80, 81, 82 and 83 respectively. For elemental analysis see table 84.

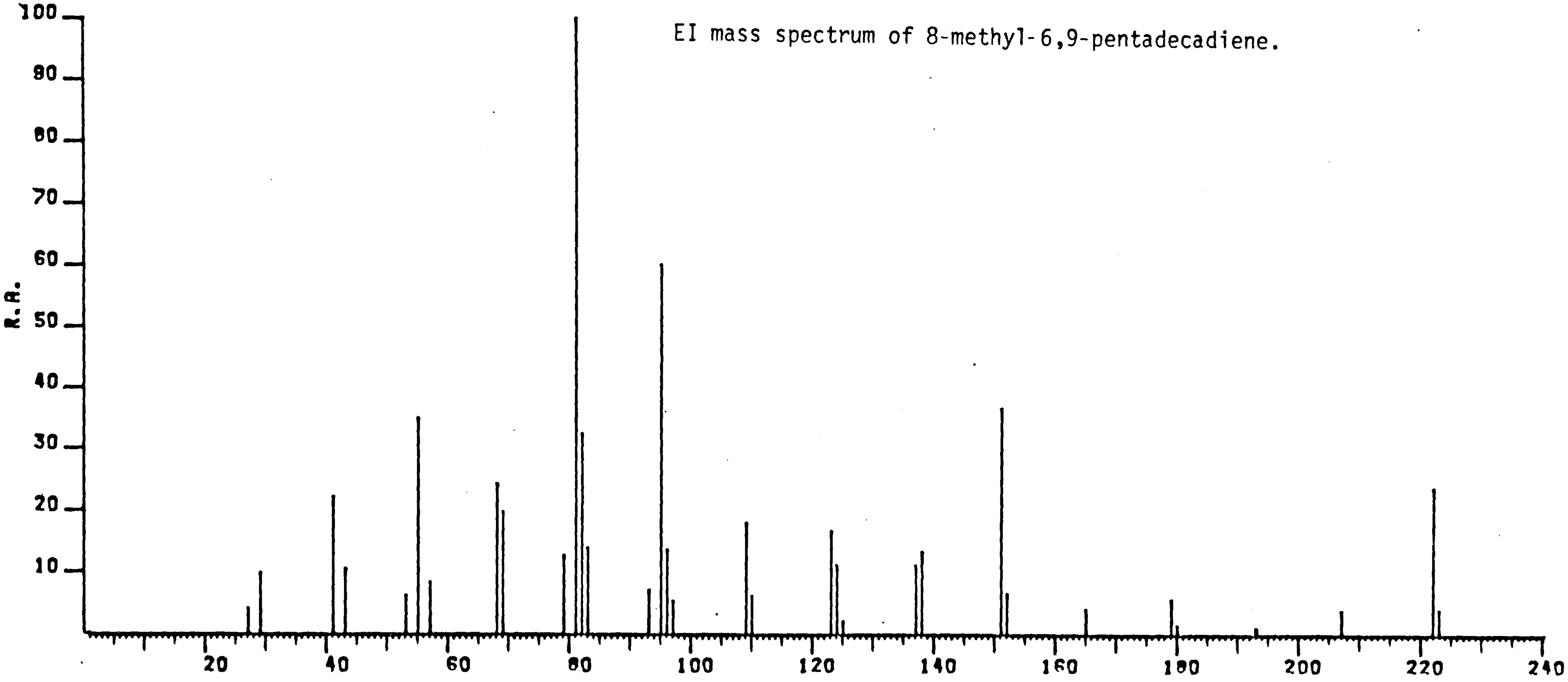


Figure 2.1.9.3.

EI mass spectrum of 8-methyl-6,9-pentadecadiene.

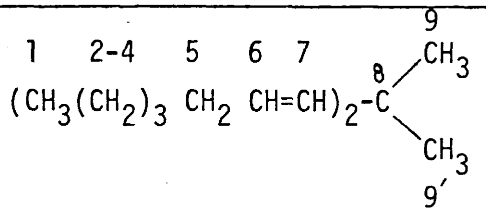
Table 80

Analysis of infrared spectrum of 8,8-dimethyl-6,9-pentadecadiene

cm^{-1}	Assignment
3010	Olefinic unsaturation (C-H)
2960	CH_3 Asymmetric stretch
2920	R-CH_2-R Asymmetric stretch
2850	CH_3, R-CH_2-R Symmetric stretch
1640	C=C Stretch
1460	C-H Def) Saturated hydrocarbon
1380	C-H Def)
1360	
1260	
1100	
1010	
970	Trans unsaturation
715	Cis unsaturation

Table 81

Analysis of ^{1}H nmr spectrum of 8,8-dimethyl-6,9-pentadecadiene



$$(CH_3(CH_2)_3\,CH_2\,CH{=}CH)_2{-}C\begin{matrix}\diagup CH_3 \\ \diagdown CH_3\end{matrix}$$

Type of Signal	Chemical shift (ppm)	Coupling constants Hz	Integration
t	0.85 CH_3 (1)	$J_{1,2}$ = 5.0	6
s	1.1 CH_3 (9,9')		6
s(br)	1.4 (2-4)		12
m/t	1.8-2.2 (5)		4
d/(m/t)	4.9 - 5.7 (6,7)		4

Table 82

Analysis of ^{13}C nmr spectrum of 8,8-dimethyl-6,9-pentadecadiene

Carbon No.	Chemical shift[272] (ppm)
1	14.1
2	22.8
3	31.9
4	31.4
5	28.4
6	129.8
7	139.3
8	36.7
9,9'	29.5

Table 83

EI mass spectrum of 8,8-dimethyl-6,9-pentadecadiene - figure 2.1.9.4

m/z	236	221	207	197	179	165	151	137	123	112	109	95	83	81	77	69	67	57	55	43	41
Rel.AB %	13.8	18.8	9.4	5.9	6.9	93.5	41.6	16.8	19.8	20.3	52.4	100.0	24.3	56.0	21.3	51.5	38.1	21.8	51.5	27.7	39.6

The parent ion of this spectrum, figure 2.1.9.4, confirms the relative molecular mass of the compound as 236 daltons. The base peak ion at m/z 95 is 14 daltons higher than that in 8-methyl-6,9-pentadecadiene. The general fragmentation again is that of a hydrocarbon. In this compound the expulsion of C_5H_{11} from the molecular ion is very pronounced (93.5%). In the other olefins 6,9-pentadecadiene and 8-methyl-6,9-pentadecadiene,this fragmentation gave ion abundances of 8.3% and 36.9% respectively. These relative abundances reflect the effect of stabilisation by the methyl groups. However, the reason for the lack of allylic cleavage (M-57) is not apparent.

Table 84

Elemental analysis of model compounds, CI, CII and CIII

Compound	Elemental analysis (%)			
	C_{calc}	H_{calc}	C_{found}	H_{found}
CI	86.54	13.46	86.49	13.68
CII	86.44	13.56	86.57	13.41
CIII	86.44	13.56	84.97	13.71

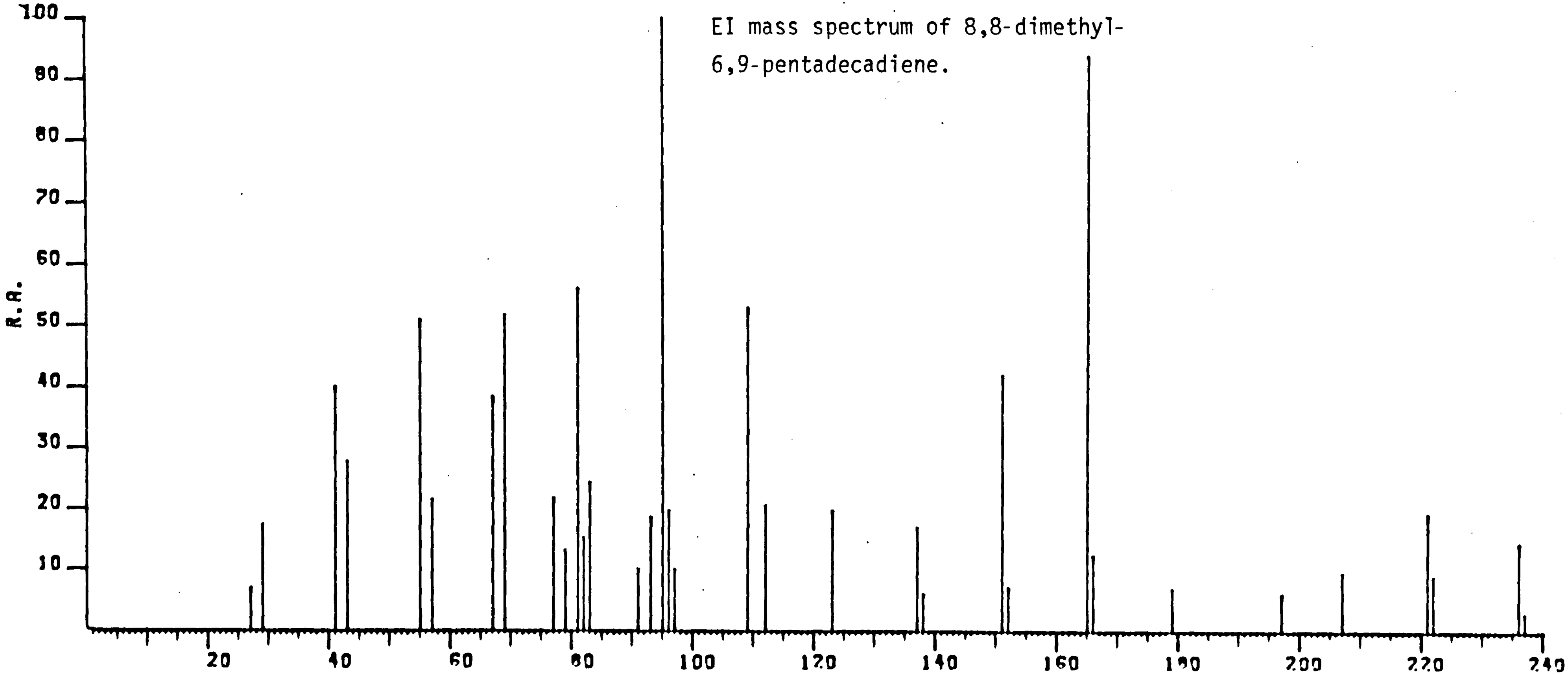


Figure 2.1.9.4.

EI mass spectrum of 8,8-dimethyl-6,9-pentadecadiene.

2.9.2 Autoxidation of 6,9-pentadecadiene, 8-methyl-6,9-pentadecadiene and 8,8-dimethyl-6,9-pentadecadiene in the presence of cobalt (II) bis(2-ethylhexanoate) and lead (II) bis (2-ethylhexanoate)or benzil promotors. Identification of volatile products by gc-ms.

The model olefinic compounds were autoxidised in the apparatus depicted in diagram 3.5.1.1. The volatile products collected in the cryogenic trap were identified by EI and CI packed column gc-ms and are summarised in tables 85 and 86.

Table 85

Volatile compounds identified from autoxidation of the model olefins CI, CII and CIII in the presence of cobalt and lead promotors

Olefin	Volatile compound	% Composition	Quantity produced
6,9-Pentadecadiene	Pentanal 2-Methyl-2-nonene Hexanal 2-Hexenal 2-Heptenal 2-Octenal	5.6 3.0 73.4 0.6 3.8 1.7	1.32×10^{-3}g
8-Methyl-6,9-pentadecadiene	Butanal Pentanal Hexanal 2-Heptenal 1-Pentanol Propanoic acid	0.4 3.2 71.0 5.1 0.5 1.0	1.44×10^{-3}g
8,8-Dimethyl-6,9-pentadecadiene	Pentanal 2-Methyl-2-nonene Hexanal 2-Hexenal 2-Heptenal	17.1 18.3 11.4 0.7 48.8	1.06×10^{-3}g

Table 86

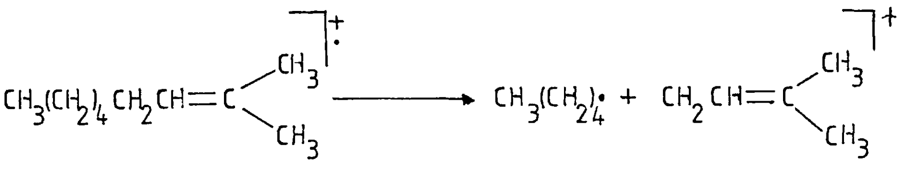
Volatile compounds identified from the autoxidation of model olefins CI, CII and CIII in the presence of benzil promotor

Olefin	Volatile compound	% Composition	Quantity produced
6,9-Pentadecadiene	1-Pentene Pentanal Hexanal 2-Heptenal	0.9 3.7 74.1 3.2	1.26×10^{-4}g
8-Methyl-6,9-Pentadecadiene	Butanal Propanal Hexanal 2-Heptenal	0.8 4.8 75.3 6.1	1.73×10^{-4}g
8,8-Dimethyl-6,9-pentadecadiene	Butanal Pentanal Hexanal 2-Heptenal	1.5 16.7 12.3 47.8	0.96×10^{-4}g

The identification of all these volatile compounds, except 2-methyl-2-nonene, has been discussed in previous sections. 2-Methyl-2-nonene was identified in the volatile products found during the autoxidation of 8,8-dimethyl-6,9-pentadecadiene, from the mass spectrum reported below:

m/z	140	125	111	97	84	83	70	69	57	56	55	43	42	41	39	29	27
Rel.AB %	29	2.2	12.8	27.6	34.0	44.7	38.2	100	31.9	40.4	53.2	40.4	27.6	89	21	19	17

The parent ion m/z 140 corresponds to the following molecular formulae, $C_{11}H_8$, $C_{10}H_{20}$, $C_{10}H_9O$, $C_9H_{16}O$, $C_8H_{12}O_2$ and $C_7H_8O_3$. The formulae containing 2 or 3 oxygens can be ignored as the retention time in the chromatogram suggests a less polar compound. The heavy isotope ratio indicates the molecular formula to be $C_{10}H_2O$, thus the base peak of m/z 69 results from the loss of 71 daltons (C_5H_{11}). As olefinic unsaturation is indicated by the molecular formula the base peak ion probably arises from an allylic cleavage, (equation 2.9.2.1).



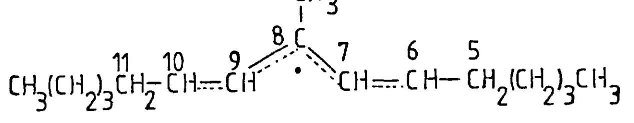
Equation 2.9.2.1

However, 3-methyl-2-nonene would also produce the same base peak ion. The rearrangement ion at m/z 70 may also be formed from both the 2- and 3-methyl compounds. No standard spectrum or commercial source of 2-methyl-2-nonene was available but the electron impact mass spectrum of 2-methyl-2-decene was available.[217] The fragmentation pattern of the unidentified compound is extremely similar to that of 2-methyl-2-decene suggesting that it is the 2-methyl rather than the 3-methyl derivative.

2.9.3 Mechanistic interpretation

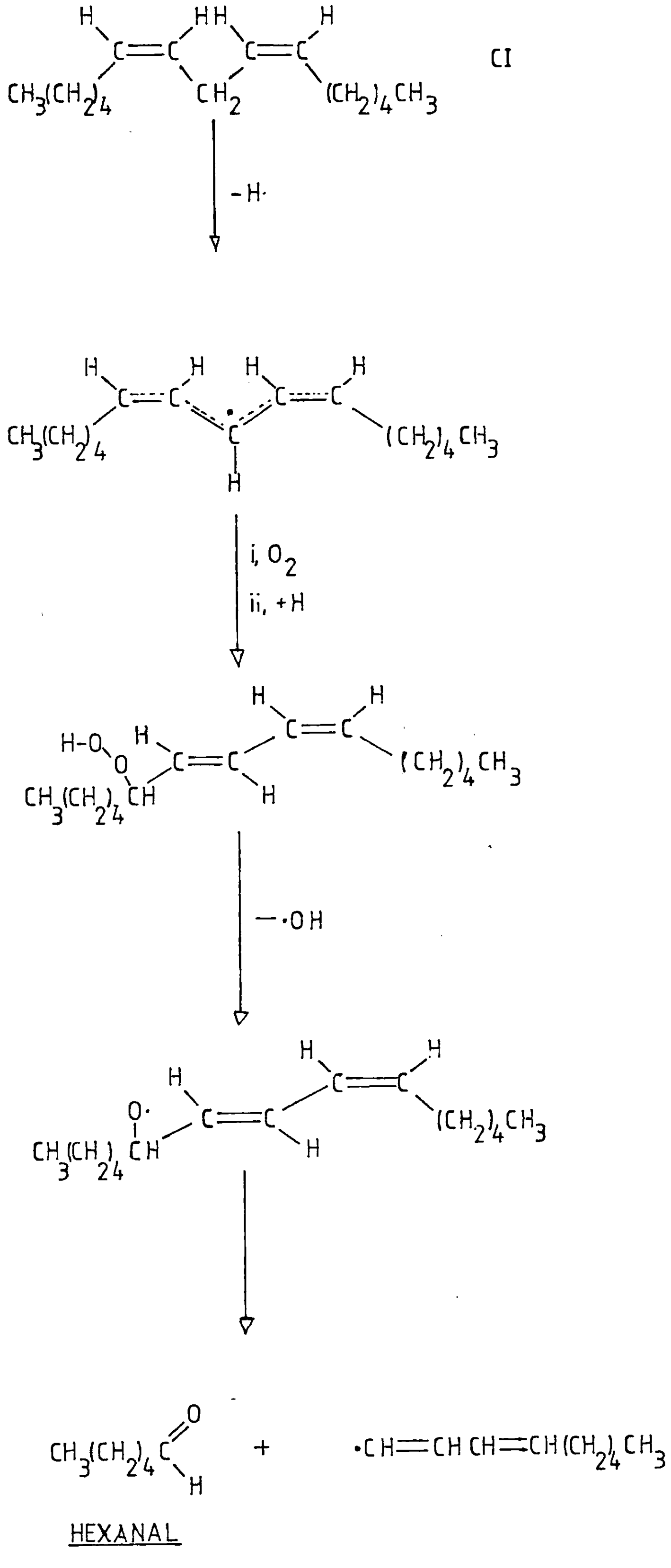
The autoxidation of 6,9-pentadecadiene (CI) produced the volatile compounds expected, viz: hexanal (70%), pentanal, 2-heptenal, 2-hexenal and 2-octenal. These compounds were found in the autoxidation of methyl linoleate (XXI) whose diene structure CI mimics. The yield of volatile material is however found to be greater than from the methyl ester, 0.066% w/w compared to 0.0518% w/w from the redox promoted autoxidation. This increase in yield could result from the symmetrical nature of the olefin. The benzil promoted autoxidation of 6,9-pentadecadiene produced only 9.5% of the material produced by the redox promoted autoxidation. This is in accord with previous results found for the methyl esters (see sections 2.1, 2.2 and 2.3). The volatiles are again proposed to arise from alkoxy radicals which result from hydroperoxide decomposition, scheme 2.9.3.1.

The volatile products from the autoxidation of 8-methyl-6,9-pentadecadiene are again those expected from the previous observations. Hexanal is the major product in both the redox promoted autoxidation and the benzil promoted autoxidation. The presence of the methyl group on the doubly allylic carbon appears to increase the yield of volatile material slightly. The methyl group may increase the rate of autoxidation by stabilising the pentadienyl radical CIV



$CH_3(CH_2)_3CH_2-CH=CH\overset{CH_3}{\dot{C}}CH=CH-CH_2(CH_2)_3CH_3$ CIV

although it is more probable that the rate is increased by the allylic

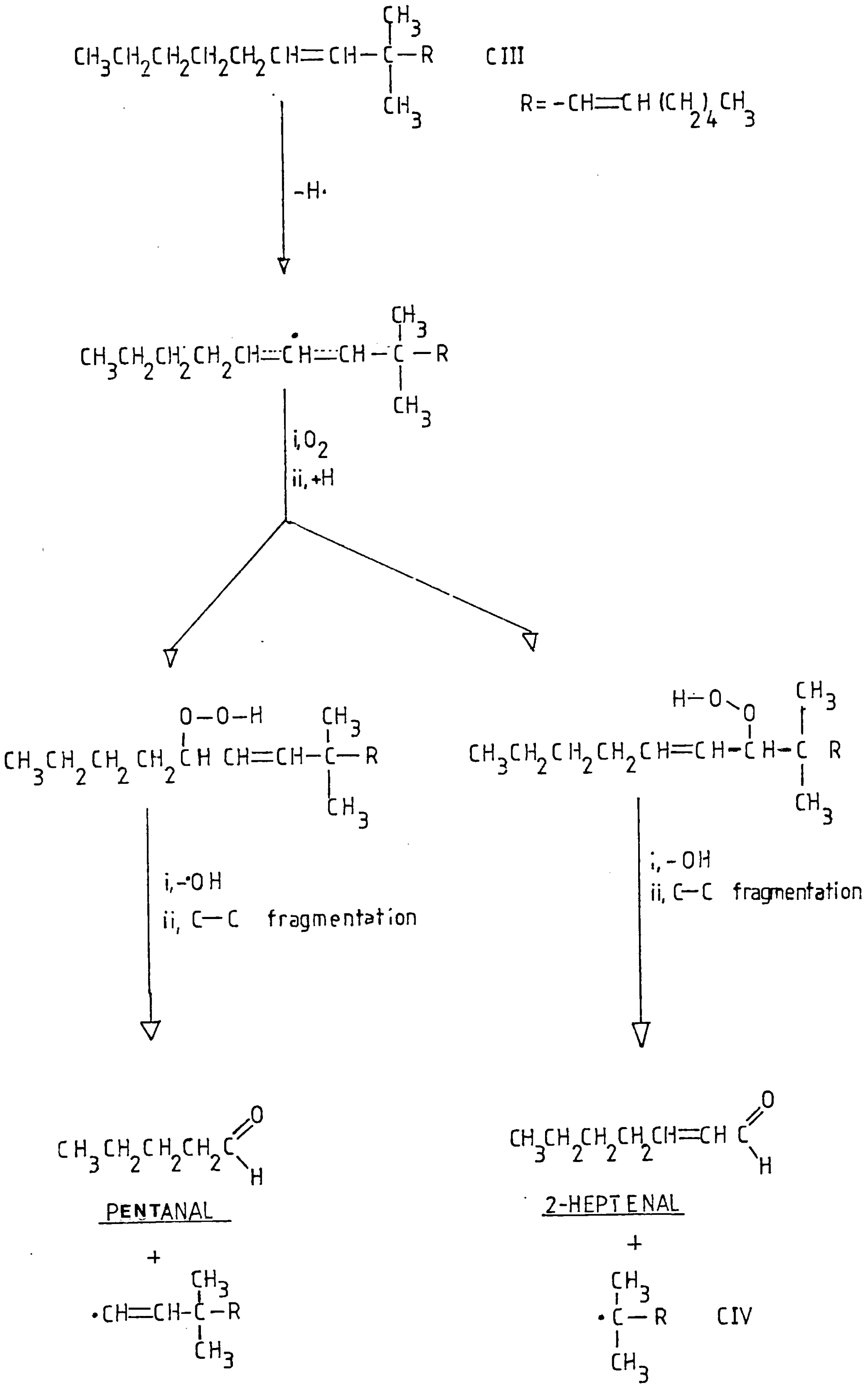


Scheme 2.9.3.1

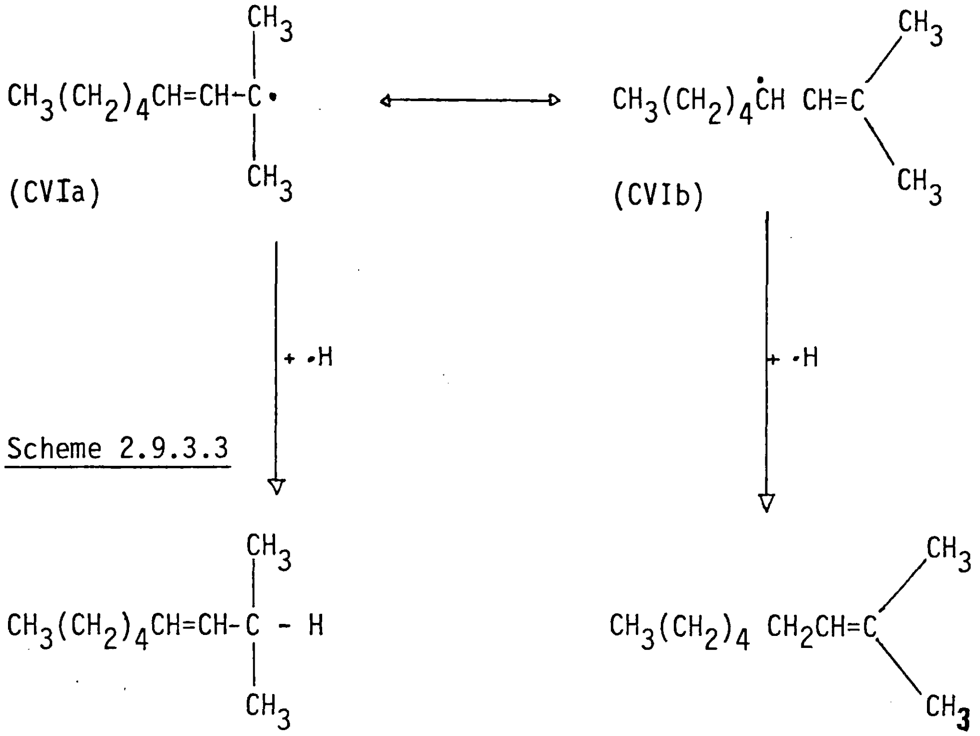
hydrogen being more susceptible to autoxidation by being on a tertiary carbon rather than secondary.[113,114,115] There is also an increase on the proportion of 2-heptenal formed. This is surprising in light of the above interpretation. With the apparent increased ease of breaking the C-H bond at position 8, a reduction in the relative proportion of C-H abstraction at positions -5 and -11 in CIV would be expected. The abstractions at -5 and -11 are necessary to form the hydroperoxides which are the precursors for 2-heptenal formation. The benzil promoted autoxidation produced only 12% of the volatiles found in the redox promoted autoxidation. This slightly higher percentage could again result from increased ease of cleaving the C-H bond at position 8.

The autoxidation of 8,8-dimethyl-6,9-pentadecadiene (CIII) produced a mixture of predicted and unpredicted volatile products. With the total absence of any doubly allylic hydrogens, the formation of a 5-centred alkyl radical is prevented thus the formation of hexanal would not be expected. The major products should result from hydroperoxide formation of the -5 and -11 positions and their subsequent decomposition i.e. the formation of pentanal and 2-heptenal, scheme 2.9.3.2.

2-Heptenal is found as the major product in both the redox and benzil promoted autoxidations but a significant volatile product found in the redox promoted autoxidation is 2-methyl-2-nonene. The formation of 2-heptenal involves the formation of the alkyl radical CIV, see scheme 2.9.3.2. From this radical a mechanism for the formation of 2 methyl-2-nonene can be postulated, see scheme 2.9.3.3.


CIII
R= -CH=CH(CH$_2$)$_4$CH$_3$
-H·
i, O$_2$
ii, +H
i, -·OH
ii, C—C fragmentation
i, -OH
ii, C—C fragmentation
PENTANAL
2-HEPTENAL
CIV

Scheme 2.9.3.2



Scheme 2.9.3.3

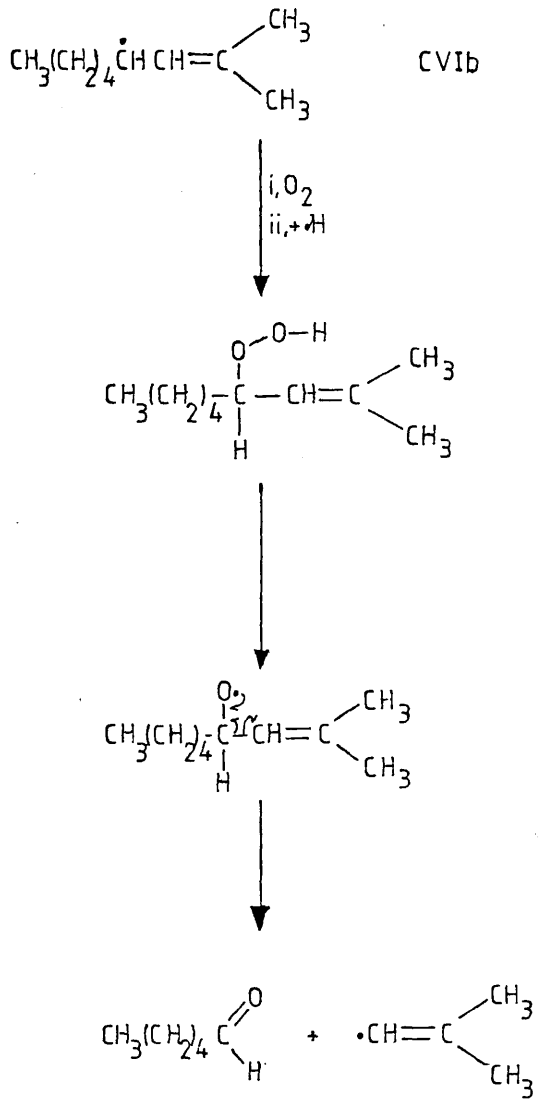
2-Methyl-3-nonene

2-Methyl-2-nonene

The formation of 2-methyl-3-nonene should accompany the formation of 2-methyl-2-nonene yet none could be identified amongst the volatiles.

? Radical CVIb may provide an explanation for the unexpected presence of hexanal in the volatile products via hydroperoxide formation and decomposition as in scheme 2.9.3.4.

The quantity of 'volatile' products from the autoxidation of 8,8-dimethyl-6,9-pentadecadiene is approximately 20% lower than that found in 6,9-pentadecadiene. This reflects the reduced ease of breaking the C-H bonds at positions 5 or 11 in 8,8-dimethyl-6,9-pentadecadiene compared to the abstraction of a hydrogen from the doubly allylic positions in 6,9-pentadecadiene. The benzil promotor again only forms 9% of the quantity of 'volatiles' produced by the redox promotor.



Scheme 2.9.3.4.

2.10 Miscellaneous experiments

2.10.1 Investigation into the formation of methyl 2-ethylhexanoate

To investigate the pathway by which methyl 2-ethyl-hexanoate is formed during the autoxidation of the methyl esters in the presence of cobalt (II) and lead (II) bis (2-ethylhexanoate) (sections 2.1.1.1, 2.2.1.1 and 2.3.1.1),ethyl linoleate and methyl(d_3) linoleate were similarly autoxidised.

Ethyl linoleate was obtained commercially but methyl (d_3) linoleate was prepared by the reaction of linoleyl chloride[256] with CD_3OH in the presence of pyridine, and analysed by infrared and nmr (both ^1H and ^{13}C) spectroscopy. Spectral details are given in tables 87, 88 and 89 respectively.

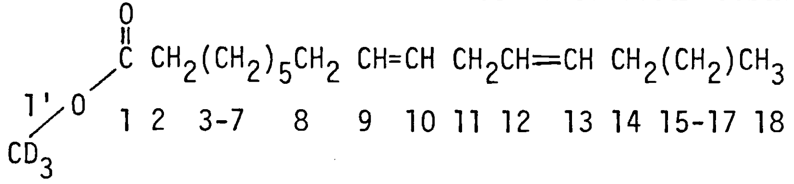
Table 87

Analysis of infrared spectrum of methyl (d_3) linoleate

cm^{-1}	Assignment
3010	Olefinic unsaturation
2980	CH_3, Asymmetric stretch
2920	$R-CH_2-R$ Asymmetric stretch
2850	CH_3,$R-CH_2-R$ Symmetric stretch
1740	Aliphatic Ester (C=O)
1460	C-H def.) Saturated hydrocarbon
1415	C-H def)
1200	Aliphatic ester C-O
720	Cis unsaturation

Table 88

Analysis of ^1H nmr spectrum of methyl (d_3) linoleate



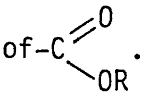
$CD_3OC(=O)CH_2(CH_2)_5CH_2\ CH{=}CH\ CH_2CH{=}CH\ CH_2(CH_2)CH_3$

Type of signal	Chemical shift (Carbon No. in brackets)	Coupling constant (Hz)	Integration
t	0.9 (18)	$J_{17,18}$ = 5.0	3
s(br)	1.3 (3-7, 15-17)		16
m/t	2.2 (2,8,14)		6
t	2.75 (11)		3
t	5.3 (9,10,12,13)	$J_{17,18}$ = 5.0	4

Table 89

Analysis of ^{13}C nmr spectrum of methyl (d_3) linoleate

Carbon No.	Chemical shift (ppm)
1	174.1
2	34.3
3	25.3
4	29.5
5	29.5
6	29.5
7	29.5
8,14	27.6
9,13	130.2
10,12	128.4
11	26.0
15	29.5
16	31.9
17	22.9
18	14.3

The presence of the ester carbonyl stretching in the infrared (1740 cm^{-1}) coupled with the presence of the ester carbonyl carbon (174.1 ppm) in the ^{13}C nmr spectrum show the presence of  $-C\begin{smallmatrix}\nearrow O \\ \searrow OR\end{smallmatrix}$. It was hoped the ^{13}C spectrum would show the seven peaks expected from the OCD_3 but the weaker signals of the deuterated carbons could not be detected. The absence of either methyl ester or carboxylic acid protons in the ^{1}H nmr spectrum provided evidence for the structure.

The volatile compounds identified from the autoxidation of the two esters by gc-ms are given in table 90.

Table 90

Volatile compounds identified by gc-ms from the autoxidation of ethyl linoleate and methyl (d_3) linoleate in the presence of cobalt and lead promotors

Ethyl linoleate	Methyl (d_3) linoleate
Pentanal	Pentanal
Hexanal	Hexanal
Pentanol	2-Hexenal
3-Heptanone	2-Heptenal
2-Pentyl furan	Pentanol
2-Heptenal	Methyl (d_3) 2-ethylhexanoate
Ethyl octanoate	Methyl (d_3) octanoate

The EI mass spectrum of the compound identified as ethyl octanoate is given below:

m/z	172	143	127	101	88	83	73	70	69	61	60	57
Rel.AB %	2.7	4.0	29.3	37.3	100	64	22.7	93.0	40	18.7	26.7	83.0

m/z	55	45	43	41	29	27
Rel.AB %	93.3	17.3	46.7	93	74.7	34.7

The base peak ion at m/z 88 arising from a McLafferty rearrangement similar to that described in section 2.1.1.1 is indicative of an ethyl ester or a carboxylic acid substituted with a β-ethyl group. The substituted acids have however been shown to fragment to an ion at m/z 73 which represents 87% of the base peak ion current. However, this compound forms m/z 70 readily, which could represent the loss of $CH_3CH_2CH_2CH_2$ from the $(M-OCH_2CH_3)$ ion at m/z 127.

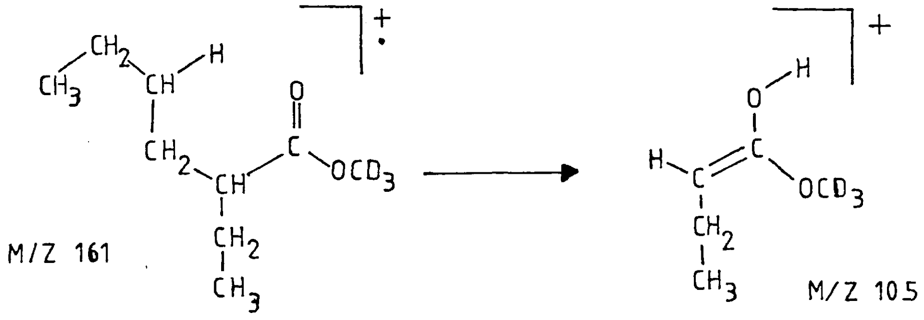
The detection of the deuterated esters from methyl (d_3) linoleate is evidenced by the following mass spectra.

Component A

m/z	161	146	143	127	118	105	90	69	59	57	56	43	41
Rel.AB %	1.5	2.3	1.0	6.9	23.4	100	92.1	7.1	7.9	49.1	12.7	16.3	13.7

m/z	29	27
Rel.AB %	6.6	4.5

The fragmentation of this compound is similar to that of methyl 2-ethylhexanoate except that ions containing OCD_3 are 3 daltons higher, e.g. the base peak ion at m/z 105 which arises from a McLafferty rearrangement, see scheme 2.10.1.1.



Scheme 2.10.1.1

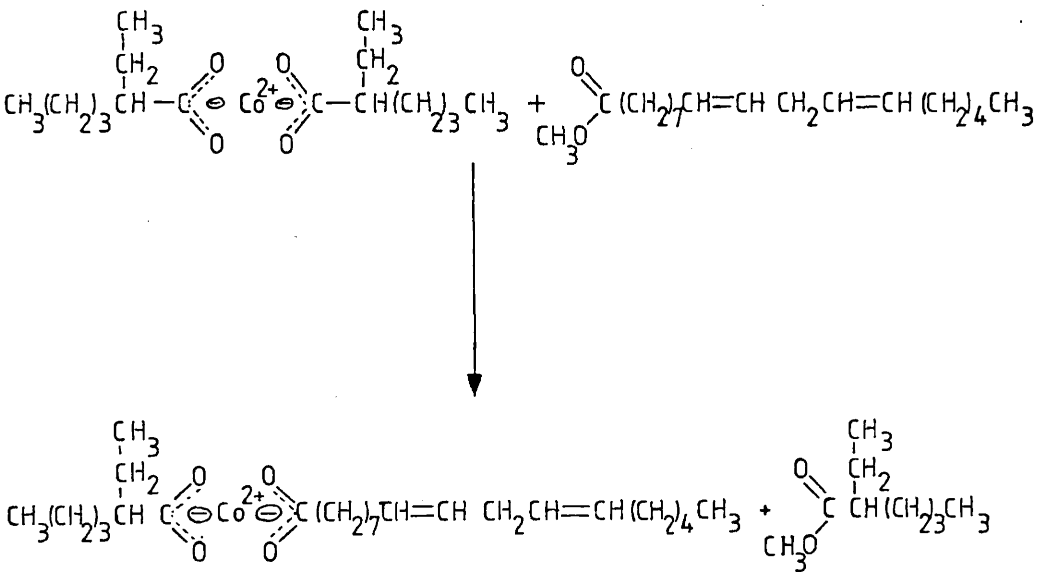
It was concluded that this compound is methyl (d_3) 2-ethylhexanoate.

Component B

m/z	161	146	143	132	130	118	104	91	77	69	57	43	41	29	27
Rel. AB %	1.0	2.4	0.6	3.5	14.7	8.0	7.5	31.1	100	4.7	10.8	10.7	6.7	4.7	2.1

The basic fragmentation here is similar to that of methyl octanoate except that some of the fragments are 3 daltons higher i.e. the base peak ion at m/z 77 which results from a McLafferty rearrangement of the parent ion. It was concluded that the compound is methyl (d_3) octanoate.

The observation that methyl (d_3) 2-ethylhexanoate is formed in the methyl (d_3) linoleate autoxidation provides evidence for catalyst anion exchange equation 2.10.1.2. However the absence of any



Equation 2.10.1.2

ethyl-2-ethylhexanoate from the autoxidation of ethyl linoleate appears to contradict this observation. If the methyl group exchanges, then the ethyl group would also be expected to exchange. The results from both experiments however confirm that methyl 2-ethylhexanoate does not result from a direct autoxidation reaction.

2.10.2 Studies on the expulsion of ethylacetoacetate from aluminium complexes during autoxidation

The volatile product and time lapse infrared studies both indicate that complexed ethyl acetoacetate is lost during the drying process. To confirm this a 2-butanol solution of cobalt (II) bis(2-ethylhexanoate) and aluminium bis(2-butoxide) ethyl acetoacetate was bubbled with dry nitrogen gas and the 'volatile products' collected. The glc analysis revealed only the presence of 2-butanol, the volatiles collected after addition of methyl linoleate, again only revealed the presence of 2-butanol. The bubbling of O_2 through the mixture for 12 hours produced ethyl acetoacetate. Thus the loss of ethyl acetoacetate appears to result from the interaction with autoxidation products, probably the carboxylic acids or alcohols formed. This collaborates the observation that the quantity of carboxylic acids detected is reduced in the autoxidations described in sections 2.1.2, 2.2.2 and 2.3.2. The observation that complexed ethyl acetoacetate may be lost is in contradiction to the work published by Love.[169]

2.10.3 Effect of oxygen partial pressure on the composition of volatile products

To study the effect of oxygen partial pressure on the nature of the volatile products, methyl linoleate in the presence of cobalt (II) and lead (II) bis(2-ethylhexanoate) was autoxidised using both an air and oxygen atmosphere. The products were collected in the cryogenic trap and analysed by packed column glc. The chromatograms showed that the products formed were identical and independent of the oxygen partial pressure. However, the quantity of the material produced was dependent on the partial pressure, the autoxidation using a pure oxygen atmosphere producing a greater amount of volatile material.

2.10.4 Control experiments

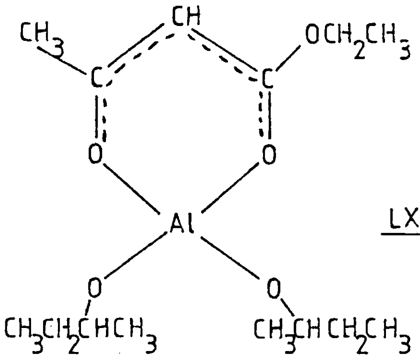
Experiments were conducted to ensure that the volatile compounds identified in the previous sections actually resulted from the combined action of oxygen and the promotor. The experiment in which nitrogen was passed through methyl linoleate, no volatile compounds were detected. Similarly when an oxygen atmosphere was used no volatile compounds could be detected. Methyl linoleate in the presence of cobalt (II) and lead (II) bis(2-ethylhexanoate) bubbled with nitrogen again produced no volatile products.

2.10.5 Synthesis of Promotors

The synthesis of the cobalt (II) bis (2-ethylhexanoate) catalyst gave a dark blue solid. The cobalt content was determined gravimetrically as the tetra-pyridine cobalt dithiocyanate and was found to be 17.0% (theoretical 17.07%). Evidence for the carboxylate was obtained from the infrared spectrum (recorded as a nujol mull), with two distinct bands seen at 1540 cm^{-1} and $143\underset{2}{0}$ cm^{-1} corresponding to assymetric $\nu\,\mathrm{C}\overset{\text{----}}{\text{====}}\mathrm{O}^{\ominus}$ and symmetric $\nu\,\mathrm{C}\overset{\text{----}}{\text{====}}\mathrm{O}^{\ominus}$ respectively.

Lead (II) bis(2-ethylhexanoate) proved more difficult to synthesise and was never isolated pure. The pale yellow viscous liquid obtained was found to contain 39.0% lead (theoretical 42.01) determined gravimetrically as lead chromate. The infrared spectrum (nujol mull) showed salt formation, bands at 1520 cm^{-1} and 1425 cm^{-1}, but also the presence of some free carboxylic acid (1690 cm^{-1}) with some anhydride (1810 cm^{-1} and 1740 cm^{-1}). The low band content is explained by the presence of free carboxylic acid and anhydride.

The complexing of ethyl acetoacetate with aluminium tris(2-butoxide) to form aluminium bis(2-butoxide) ethyl acetoacetate was observed by infrared spectroscopy. The absorption decreases at 1750 and 1720 cm^{-1}, corresponding to the carbonyl functionality in ethylacetoacetate, correlated with increases at 1610 and 1530 cm^{-1} assigned by Pinchas[273] as $\nu\,\mathrm{C}\overset{\text{----}}{\text{====}}\mathrm{O}$ and $\nu\,\mathrm{C}\overset{\text{----}}{\text{====}}\mathrm{C}$ respectively in the metal chelate. The infrared spectrum of the final reaction products showed no bands corresponding to a free carbonyl. These observations confirm the formation of the complex LXXVII in a 2-butanol solution.



LXXVII

3. Experimental

3.1 Materials, instrumentation and analysis

Methyl cis-9-octadecenoate, cis-9-cis-12-octadecadienoic acid, its methyl and ethyl esters and cis-9-cis-12-cis-15-octadecatrienoic acid, its methyl and ethyl esters, were supplied by Sigma Chemicals Ltd. at 99% purity and used without further purification. Methane sulphonic acid was supplied by Koch Light at 98% purity . Benzil was supplied by Fluka Chemicals at 98% purity and recrystallised from acetone before use. Other chemicals used were supplied by either British Drug House (BDH) or Aldrich Chemicals.

Packed column gc-ms analysis was carried out using a Pye 104 gas chromatograph and a V.G. 12F micromass mass spectrometer. Capillary column gc-ms analysis was carried out using a Finnigan 1020 quadrupole mass spectrometer and data base at P.C.M.U., Harwell by Dr C. Creaser.

GLC-FID analysis was carried out on either a Pye Unicam GCD instrument or a Varian model 3700 instrument. HPLC analysis was carried out on a Varian 5000 instrument with a UV detector at 254 nm.

Infrared spectra were recorded on either a Perkin Elmer 177 or 983 instruments. Time lapse infrared studies were carried out on the Perkin Elmer 983 instrument and associated data base. Near infrared studies were carried out on a Grubbs-Parsons spectrometer (modified) instrument. UV spectra were carried out on a Perkin Elmer 550S UV-visible spectrometer. 60 MHz ^{1}H n.m.r. were recorded using either a Hitachi Perkin Elmer R243 or a Varian EM360. 90 MHz ^{1}H and 22.6 MHz ^{13}C n.m.r. were recorded on a Joel FX90Q Fourier Transform instrument by Mr D Parkinson.

3.2 Synthesis of promotors

3.2.1 Cobalt (II) bis(2-ethylhexanoate)[274]

2-Ethyl hexanoic acid (25.5 g, 0.18 M) was dissolved in a 10% v/v mixture of 1-butanol in petroleum spirit (120°C) (0.5 dm^3). Cobalt (II) hydroxide (10 g, 0.11 M) was added, and the mixture heated to 120°C and refluxed for 6 h. On cooling, acetone was added to the brown slurry, shaken well and filtered off 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-ethyl hexanoic acid was partitioned between water and petroleum spirit and the salt obtained by evaporating the water off, then dried further by azeotropic distillation with toluene. It was a purple solid with a cobalt content of 17.0% (theoretical 17.07%) as determined by quantitative precipitation of tetrapyridine cobalt dithiocyanate.[275] The yield was 4.45 g (14.3%) and had ν = 1540 cm^{-1} ($C{=}O^{\ominus}$ asymmetric) and 1430 cm^{-1} ($C{=}O^{\ominus}$ symmetric). The infrared spectrum is discussed in section 2.10.5.

3.2.2 Lead (II) bis(2-ethylhexanoate)

2-Ethylhexanoic anhydride[276] (21.8 g, 0.08 M) was mixed with a stoichometric amount of dry lead (II) oxide (18 g, 0.08 M) and stirred at 80°C for 2 h.[277] On the addition of petroleum spirit (40° - 60°C) a white precipitate was observed and this was removed by filtration. The filtrate was collected and the petroleum spirit removed under reduced pressure. The product (11.31 g, 28.7%) was a pale yellow viscous liquid with a lead content of 39% (theoretical 42%) (determined by quantitative precipitation of the chromate[278]), and had ν = 1810, 1740, 1680, 1540, 1460 and 1420 cm^{-1}. The infrared spectrum is discussed in section 2.10.5.

3.2.3 Aluminium bis(2-butoxide) ethyl acetoacetate[171]

2-Butanol and ethylacetoacetate were redistilled, the fractions boiling at 78°C and 178°C respectively were collected. Aluminium tris(2-butoxide) (100 g, 0.41 M) was dissolved in 2-butanol (200 g) under nitrogen. The temperature was raised to 90°C and ethyl acetoacetate (53.3 g, 0.41 M) added over a period of 15 min. then the temperature maintained at 90°C for a further 30 min. The resultant solution had an aluminium content of 5.2% (theoretical 5.4%). The infrared spectrum of this promotor is discussed in section 2.10.5.

3.3 Synthesis of model compounds

3.3.1 Synthesis of benzoyloxyethyl cis-9-cis-12-octadecadienoate

Cis-9-cis-12-octadecadienoic acid (4 g, 0.015 M) was refluxed at 70°C with oxalyl chloride (5.4 g, 0.0435 M) for 4 h in all glass still.[279] The excess oxalyl chloride was removed under reduced pressure at 100°C, the cis-9-cis-12-octadecadienoyl chloride purified by vacuum distillation (150°C, 0.5 mm Hg) to yield 1.55 g (35.8%).

Sodium benzoate (14.41 g, 0.1 M) was reacted with 1-chloro-2-hydroxyethane (24.15 g, 0.3 M) at 130°C for 4 h.[280] The reaction was allowed to cool and the sodium chloride removed by filtration. 2-Hydroxyethylbenzoate was purified by distillation (b.p. 149° - 151°C at 11 mm Hg, Lit. value[280] 173°C at 21 mm Hg) giving 11.62 g (70% yield).

Cis-9-cis-12-octadecadienoyl chloride (1.55 g,0.005 M) was added to 2-hydroxyethyl benzoate (1 g, 0.006 M) at 0°C in the presence of pyridine (1 g, 0.0126 M) and left overnight. Diethyl ether (10 cm^3) was added to the reaction mixture and then this solution washed with water (3 x 25 cm^3). The ester was purified by column chromatography (Kieselgel 60, diethyl ether: Petroleum spirit (b.p. 40 - 60°), 40 : 60) to yield 1.39 g (62.5%) of the ester. Spectroscopic data is presented in section 2.4.1.

3.3.2 2-Hydroxyethyl cis-9-cis-12-octadecadienoate

Cis-9-cis-12-octadecadienoyl chloride (7.2 g,0.024 M) as prepared in section 3.3.1, was added to 1,2-ethanediol (11 g, 0.18 M) in the presence of pyridine (3 g, 0.038 M) at ice bath temperature and left overnight. The reaction mixture was washed with water (4 x 50 cm^3) and the hydroxy compound isolated by column chromatography (Kieselgel 60, diethyl ether: petroleum spirit (b.p. 40^o - 60^oC), 50:50) to yield 3.62 g (46.5%). The ^1H n.m.r. and IR of this compound are presented in section 2.6.2.1.

3.3.3 Methyl (d_3) cis-9-cis-12-octadecadienoate

Cis-9-cis-12-octadecadienoyl chloride (5.6 g,0.019 M) was added to C^2H_3OH (5 g, 0.14 M, 99% ^2H) in pyridine (3 g, 0.038 M) at ice-bath temperature. Diethyl ether (10 cm^3) was added to the reaction mixture and then this solution washed with water (3 x 25 cm^3). The ester was purified by column chromatography (Kieselgel 60, diethyl ether: petroleum spirit (b.p. 40^o - 60^oC), 50:50) to yield 2.27 g (40.2%) of the ester. Its ^1H n.m.r. and IR spectra are presented in section 3.3.3.

3.3.4 Synthesis of 6,9-pentadecadiene

1,3-Dibromopropane (10 g, 0.049 M) was added to triphenylphosphine (26 g,0.0992 M) in dimethylformamide (100 cm^3). This was refluxed for 3 h during which a white precipitate formed. The mixture was cooled and the solid collected by vacuum filtration. The bisphosphonium salt was washed with petroleum spirit (2 x 100 cm^3) and dried under vacuum to yield 34.62 g (96.3%).

1,3-Bis (triphenylphosphonium)propane dibromide (10 g, 0.014 M) (dried and pulverised) was suspended in dry tetrahydrofuran (28 cm^3) at 0^oC under an atmosphere of dry nitrogen. n-Butyl lithium

(20 cm^3,1.6 M soln. 0.032 M) was added over a period of 30 min. and left for a further 60 min. A dark red solution resulted, and to this hexamethylphosphoratriamide (15 cm^3) was added and stirred for 15 min. Hexanal (2.8 g, 0.028 M) was added and stirred at 0^{o}C for 60 min, then refluxed for 2 h. On cooling, water (150 cm^3) and petroleum spirit (40 - 60^{o}C) (100 cm^3) were added. The organic layer was concentrated and the diene purified by column chromatography (Kieselgel 60, petroleum spirit (boiling below 40^{o}C)) to yield 0.83 g (30.4%).

3.3.5 Synthesis of 8-Methyl-6,9-pentadecadiene

2-Methyl-1,3-dibromopropane (12.8 g, 0.06 M) prepared by the method of Brewster,[281] was reacted with triphenylphosphine (48 g, 0.18 M) for 144 h at 145^{o}C in the absence of solvent. To the white solid produced, dimethylformamide (30 cm^3) was added and the mixture refluxed for 3 h. The bis-phosphonium salt was collected by vacuum filtration and washed with diethyl ether (2 x 50 cm^3) then petroleum spirit (boiling below 40^{o}C) (2 x 50 cm^3). The salt was dried under vacuum to yield 12.10 g (27.7%).

2-Methyl-1,3-bis(triphenylphosphonium) propane dibromide (12.10 g, 0.16 M) was added to dry tetrahydrofuran under nitrogen. n-Butyl lithium (22 cm^3, 0.035 M) was added over 30 min. and left at ice bath temperature for 60 min. Then, to the dark red solution, hexanal (3.5 g, 0.035 M) was added and the mixture refluxed for 12 h. The diene was extracted and purified as in section 3.3.4 to yield 1.05 g (29.6%).

3.3.6 Synthesis of 8,8-dimethyl-6,9-pentadecadiene

Triphenyl phosphine (26.2 g, 0.1 M) was suspended in dry acetonitrile (100 cm^3) at 0^oC and bromine (16.0 g, 0.1 M) was added over 30 min. To the resultant triphenyl phosphonium dibromine suspension was introduced 2,3-dimethyl-1,3-dihydroxypropane (5.2 g 0.05 M), the suspension cleared, and the solution refluxed for 8 h. The acetonitrile was removed under reduced pressure and the 2,2-dimethyl-1,3-dibromopropane collected by distillation (bp 60 - 80^oC at 14 mm Hg) and then redistilled (bp 64^oC at 12 mm Hg, lit. 72^oC at 14 mm Hg) to yield 4.22 g (36.7%).

2,2-Dimethyl-1,3-dibromopropane (4.22 g, 0.018 M) was reacted with triphenyl phosphine (11 g, 0.0478 M) at 145^oC for 336 h. The 2,2-dimethyl-1,3-(triphenylphosphonium) propane dibromide salt was purified as in section 3.3.5 to yield 6.68 g (49.2%).

The Wittig reaction of the bisphosphonium salt with n-butyl lithium and hexanal was carried out with the appropriate amounts and the diene purified by the methods described in section 3.3.5 to yield 0.97 g (46.4%).

The n.m.r, IR and mass spectra of the dienes synthesised in sections 3.3.4, 3.3.5 and 3.3.6 are presented in section 2.9.1.

3.4 Synthesis of alkyd resins

The fatty acid route was employed for the synthesis of all the resins used in the autoxidation studies. This route was used as it is a one step synthesis and was therefore easier to perform.

3.4.1 Series 1 - Variable fatty acid composition

The following general method[171] was used to make all the resins in this series. Pentaerythritol (191 g, 1.4 M), phthalic anhydride (208 g, 1.4 M) and the fatty acids (600 g) were added to a five necked flanged lid glass reaction vessel together with Analar toluene (40 cm^3). The reaction was carried out with vigorous agitation and under a blanket of nitrogen. The temperature was raised to 240°C and the water produced azeotropically distilled off,and collected in a Dean and Stark apparatus. During the reaction a sample of the resin was removed every hour (or occasionally every 30 min.) and the 'acid value' determined by titration with 0.1 M ethanolic potassium hydroxide. The viscosity was determined by the method of measuring the time it takes an air bubble at 25°C to move through the resin in a glass tube. When the 'acid value' reached approximately 10 mg KOH/g non-volatile resin the reaction was stopped. Analar toluene (200 g) was then added and well mixed into the resin. The final 'acid value',viscosity and 'solids content' were then determined. The 'solids content' is calculated as the percentage of the non-volatile material in the final resin. The fatty acids used in the preparation were Soyabean oil fatty acids, Linseed oil fatty acids, dehydrated Castor oil fatty acids, Tall oil fatty acids and Isomerginic acid S.F. The final constants of the resins are presented in section 2.5.1.

3.4.2 Synthesis of alkyds-series 2- 'variable hydroxyl content'

The general method of preparation for this series of alkyds was the same as that in section 3.4.1. However the quantities of the reactants were different and are summarised in table 91.

Table 91

Linseed oil fatty acids g	(mole fraction)	Pentaerythritol g	(mole fraction)	Phthalic anhydride g	(mole fraction)
579	1.33	194	0.93	226	1.0
569	1.33	208	1.02	222	1.0
558	1.33	223	1.11	218	1.0
548	1.33	236	1.20	214	1.0
544	1.33	243	1.24	212	1.0

(Mole fraction based on phthalic anhydride)

The final constants are reported in section 2.6.3.1.

3.4.3 Synthesis of a low 'acid value' alkyd

The general method employed in section 3.4.1 was used in this alkyd preparation with Tall oil fatty acids (1800 g), pentaerythritol (574 g) and phthalic anhydride (625 g). The final acid value of this alkyd was found to be 8.8 mg KOH/g non volatile resin.

The alkyd (1290 g) was then reacted with Cardura E (51.16 g) at 170°C until the acid value was approximately 1.0 mg KOH/g non volatile resin. The physical properties are reported in section 2.5.1.

3.4.4 A linoleic acid alkyd

This alkyd was synthesised on a relatively small scale using linoleic acid (124 g), pentaerythritol (41.5 g) and phthalic anhydride (48.5 g). The general method was used as described in section 3.4.1. The physical properties are given in section 2.5.1.

3.5 Autoxidation of model compounds

3.5.1 Apparatus

Air or oxygen were dried by bubbling through concentrated sulphuric acid. A splash trap was employed to prevent acid contamination of the reaction mixture. The dried gas was then split into two streams, each going to an autoxidation vessel containing equal amounts of reactants,through which,the gas was bubbled. The gas streams were combined after leaving the reaction vessels. A schematic representation of the apparatus used is shown in diagram 3.5.1.1.

3.5.2 Volatile product collection techniques

Two methods were used; cryogenic trapping and chemical trapping.

Trapping method (i) Here the gas stream, containing the volatile products from the autoxidation was passed into a cold finger with the entrance tube extending almost the entire length and with the gas exit at the top of the apparatus as depicted in diagram 3.5.2.1. The cooling agent was a 'slush-bath' of liquid nitrogen and toluene which maintains a temperature of -95°C.[282] The trap may be sealed at points A and B with PVC tubing closed by Hoffman clips. The solid 'volatile' products so collected were removed by allowing them to liquefy, then dissolving in 100 μl (2 x 50 μl) of n-pentane, injected via point A and subsequently draining them to point C. The analysis discussed in sections 3.5.3.1 and 3.5.3.2 were carried out on such solutions.

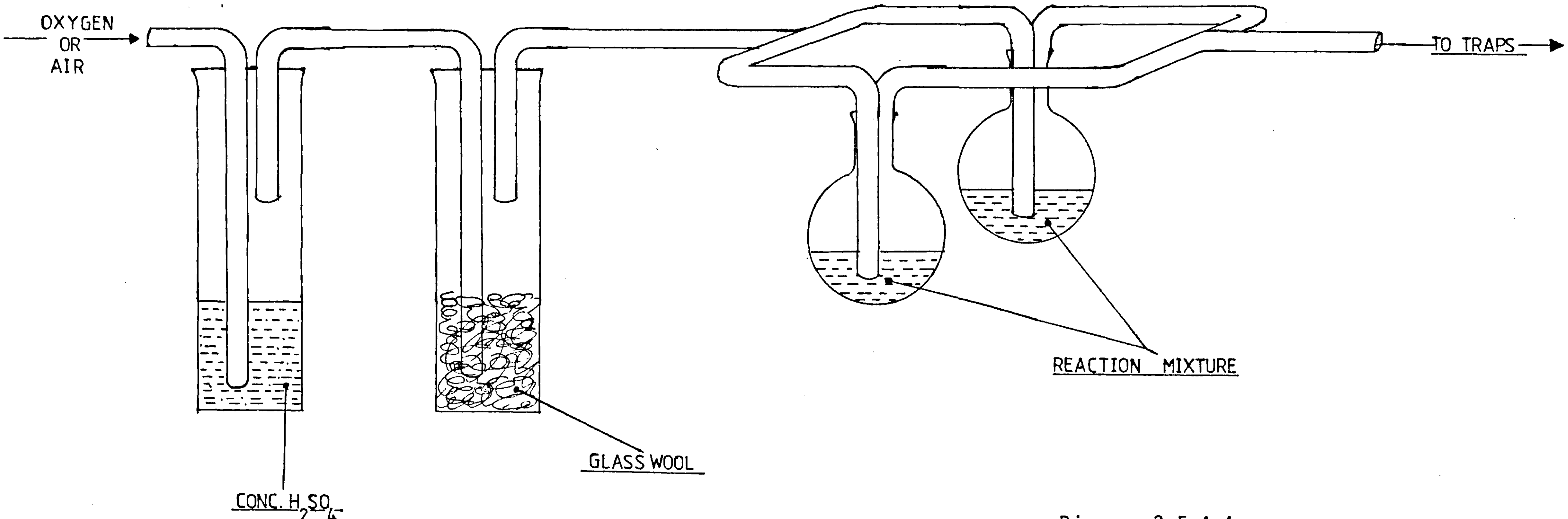


Diagram 3.5.1.1.
Schematic diagram of model compound autoxidation apparatus.

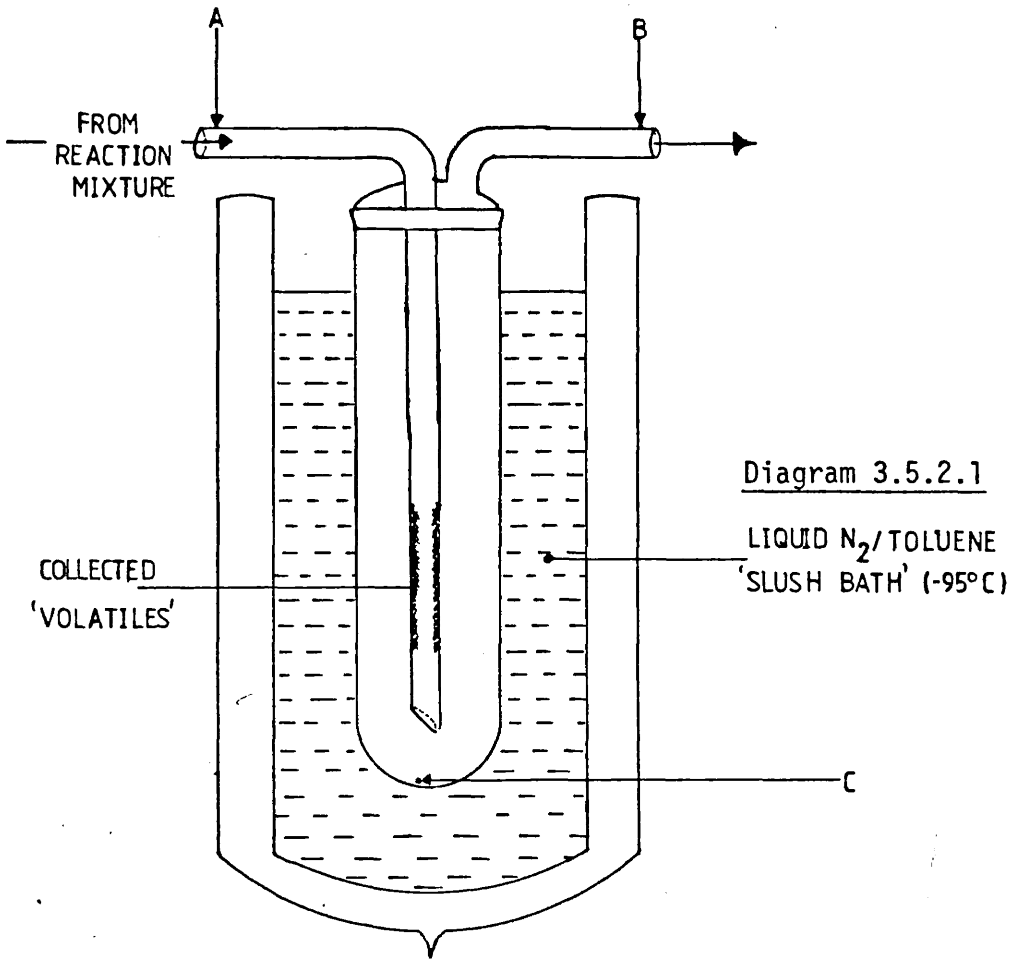


Diagram 3.5.2.1

Trapping procedure for carbonyl compounds (ii) Here the gas stream, containing the volatile products, was passed over silica gel (0.3 g) diagram 3.5.2.2, previously coated with 2,4-dinitrophenylhydrazine by the method of Beasley.[283] The resultant hydrazine derivatives were extracted from the silica gel with acetonitrile (1 cm^3) and this analysed as described in section 3.6.3.3.

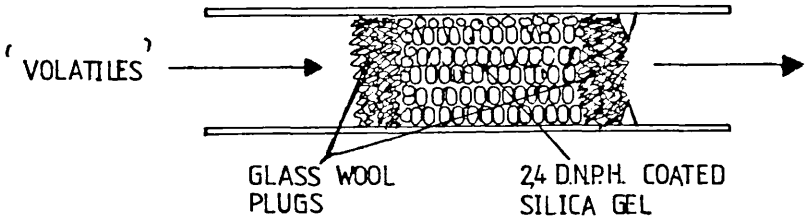


Diagram 3.5.2.2

It should be noted that only one trapping technique was used at any one time.

3.5.3 Chromatographic analysis

3.5.3.1. Gas liquid chromatography analysis

n-Pentane solutions of the volatile compounds were analysed by either packed column or capillary column glc, the conditions are summarised in tables 92 and 93 respectively.

Table 92

Packed column glc analysis

Stationary phase	10% carbowax 20 M terminated by TPA on chromosorb Q support
Column dimensions	2 metres x 3 mm (ID)
Carrier gas flow rate	40 cm^3 min^{-1}
Carrier gas	Nitrogen (oxygen free)
Oven temperature	60°C isothermal for 20 min. then rising at 1°C min^{-1} to 160°C.
Injection volume	5 μl
Detector	Flame ionisation detector
Injector temperature	120°C
Detector temperature	210°C

Table 93

Capillary column analysis

Stationary phase	SP 1000
Column length	25 metres
Carrier gas flow rate	$1 cm^3 min^{-1}$
Carrier gas	Helium
Splitter ratio	30:1
Oven temperature	50^oC isothermal 5 minutes then at 4^oC min^{-1} up to 140^oC
Injection volume	$0.5 \mu l$
Detector	Flame ionisation detector
Injector temperature	120^oC
Detector temperature	200^oC

In quantitative studies using glc, the internal standard was dodecanal. 50 μl of a solution of dodecanal (0.13 g) in n-pentane (50.0 cm^3) was accurately transferred to the 'volatile' solution collected at point C in the cold tap (diagram 3.5.2.1) and then this solution analysed by glc. The areas of the peaks were calculated by using either a Shannon 308 or a Varian CDS 111 computing integrator.

3.5.3.2 Gc-ms analysis of the volatile products

Electron impact (EI) and chemical ionisation (CI) mass spectrometry of the volatile products of autoxidation dissolved in n-pentane were carried out using a 6 mm packed column gc-ms.

The conditions for EI and CI analysis are given in tables 94 and 95 respectively.

Table 94

Mass spectrometer conditions for packed column EI gc-ms

Instrument	V.G. micromass 12F
Source temperature	~200°C
Emission current	10 μA
Repeller voltage	15V
Electron energy	70 eV
Main mass scan	10 s decade^{-1}, linear, up, 0 - 240 Dalton
Accelerating voltage	4 KV
Amplification setting	10^{-4}, 10^{-5} or 10^{-6} amp
Response time	0.003 s
Gain	1
Integration mass range	38 - 120 Dalton
Integration scan time	2 s decade, linear, up.
Carrier gas for glc	Helium at 30 cm^3 min^{-1}

The compounds, separated on the glc column passed into the ion-source via a glass lined tubing and jet separator. After ionisation the ions were accelerated, mass analysed and detected by a 17-stage dynode electron multiplier. The signal,from the electron multiplier after amplification,was integrated for each scan by the integrating ion monitor,and this displayed on a chart recorder giving a total ion chromatogram.

Table 95

Conditions for packed column CI gc-ms

Instrument	VG micromass 12F
Source temperature	$\sim 220^{o}$C
Emission current	1000 μ amp
Repeller voltage	2V
Electron energy	50 eV
Main mass scan	10 s decade^{-1}, linear, up,0 - 240 Dalton
Accelerating voltage	4 kV
Amplification setting	10^{-4}, 10^{-5} or 10^{-6} amp
Response time	0.003 s
Gain	1
Integration mass range	80 - 200 Dalton
Integration mass scan	2 s decade^{-1}, linear,up
Reagent gas	Isobutane
Source pressure	0.08 torr
Carrier gas for gc	Helium at 30 cm^{3} min^{-1}

The spectra were recorded manually onto Kodak linagraph direct print paper (type 1895) at the apex of each chromatographic peak.

The Finnigen 1020 quadrupole mass spectrometer was equipped to perform EI gc-ms only and operates under computer control. Spectra were acquired,digitised, centroids and areas stored on disc, for later retrieval and analysis. The instrument had an autotune capability so the precise operating conditions are unknown. However, the spectra were all recorded at 70 eV. One major difference with the capillary analysis was that the glc column terminated directly in the source.

3.5.3.3 High performance liquid chromatography (HPLC) analysis

The 2,4-dinitrophenylhydrazones in an acetonitrile solution, formed in the chemical trap (described in section 3.5.2) were analysed by HPLC. The conditions for the analysis are given in table 96.

Table 96

HPLC analysis of 2,4 DNPH derivatives

Instrument	Varian 5000
Column	C_{18} reversed phase (30 cm x 3.9 cm)
Column temperature	30^oC
Flow rate	2.0 cm^3 min^{-1}
Injection loop volume	10μℓ
Detector	UV at 254 nm
Biney solvent system	0 - 2 min 35% CH_3CN : 65% H_2O (v/v)
	2 - 15 min 35% CH_3CN: 65% H_2O to 45% CH_3CN : 55% H_2O (v/v)
	15 - 30 min 45% CH_3CN : 55% H_2O (v/v)

The aldehydes formed were identified by comparison of the retention times of their 2,4-dinitrophenylhydrazones with authentic derivatives. This technique provides an adequate method for the analysis of C_1 - C_4 aldehydes.

3.5.4 Autoxidation experiments

The apparatus, trapping and analytical techniques described in sections 3.5.1, 3.5.2 and 3.5.3 were employed in the autoxidations. The appropriate amount of promotors were used in the following forms:

(i) Cobalt(II) and lead (II) bis(2-ethylhexanoate) as n-pentane solutions.

(ii) Cobalt(II) bis (2-ethylhexanoate) and aluminium bis(2-butoxide) ethyl acetoacetate in 2-butanol solution.

(iii) Benzil as a diethyl ether solution.

(iv) Methane sulphonic acid.

for the experiments presented in table 97. The masses given are the amount of promotor contained in the 5 g of the methyl ester. The reactions were all bubbled with dry nitrogen for 12 h prior to autoxidation.

Table 97

Ester / Promotor	Methyl oleate (5 g)	Methyl linoleate (5 g)	Methyl linolenate (5 g)
Cobalt promotor Lead promotor	0.012 g 0.192 g	0.012 g 0.192 g	0.012 g 0.192 g
Cobalt promotor Aluminium promotor	0.012 g 0.0893 g	0.012 g 0.0893 g	0.012 g 0.0893 g
Benzil	0.05 g	0.05 g	0.05 g
Methane sulphonic acid	0.05 g	0.05 g	0.05 g

Experimental conditions

Oxygen flow rate	40 cm^3 min^{-1}
Reaction temperature	20^oC
Collection period	0 - 10 h (i.e. total of 10 h)
Trapping techniques and analytical methods	(i) cryogenic trap:- glc and gc-ms (ii) chemical trap:- HPLC

The experiments described in table 98 were not carried out under such rigorous conditions as those in table **97** .

Table 98

Ester Promotor	Benzoyloxyethyl linoleate 2 g	2-hydroxyethyl linoleate 3 g	2-hydroxyethyl linolenate 3 g
Cobalt promotor	0.005 g	——	——
Lead promotor	0.077 g		
Benzil	0.02 g	——	——
Methane sulphonic acid	——	0.03 g	0.03 g
Experimental conditions			
Oxygen flow rate	40 $cm^3 min^{-1}$		
Analysis carried out by glc and gc-ms			

The catalysts were in the form used for the methyl esters.

The autoxidation experiments carried out on the dienes are shown on table 99.

Table 99

Reactant Promotor	6,9-Pentadecadiene (1 g)	8-methyl-6,9-pentadecadiene (1 g)	8,8-dimethyl-6,9-pentadecadiene (1 g)
Cobalt promotor	0.002 g	0.002 g	0.002 g
Lead promotor	0.038 g	0.038 g	0.038 g
Benzil	0.002 g	0.002 g	0.002 g
Methane sulphonic acid in the presence of n-butanol (1 g)	0.002 g	——	——

All benzil promoted autoxidations were irradiated with light from a Shandon 2753 daylight lamp.

3.6 Autoxidation of alkyd resins

3.6.1 Autoxidation apparatus

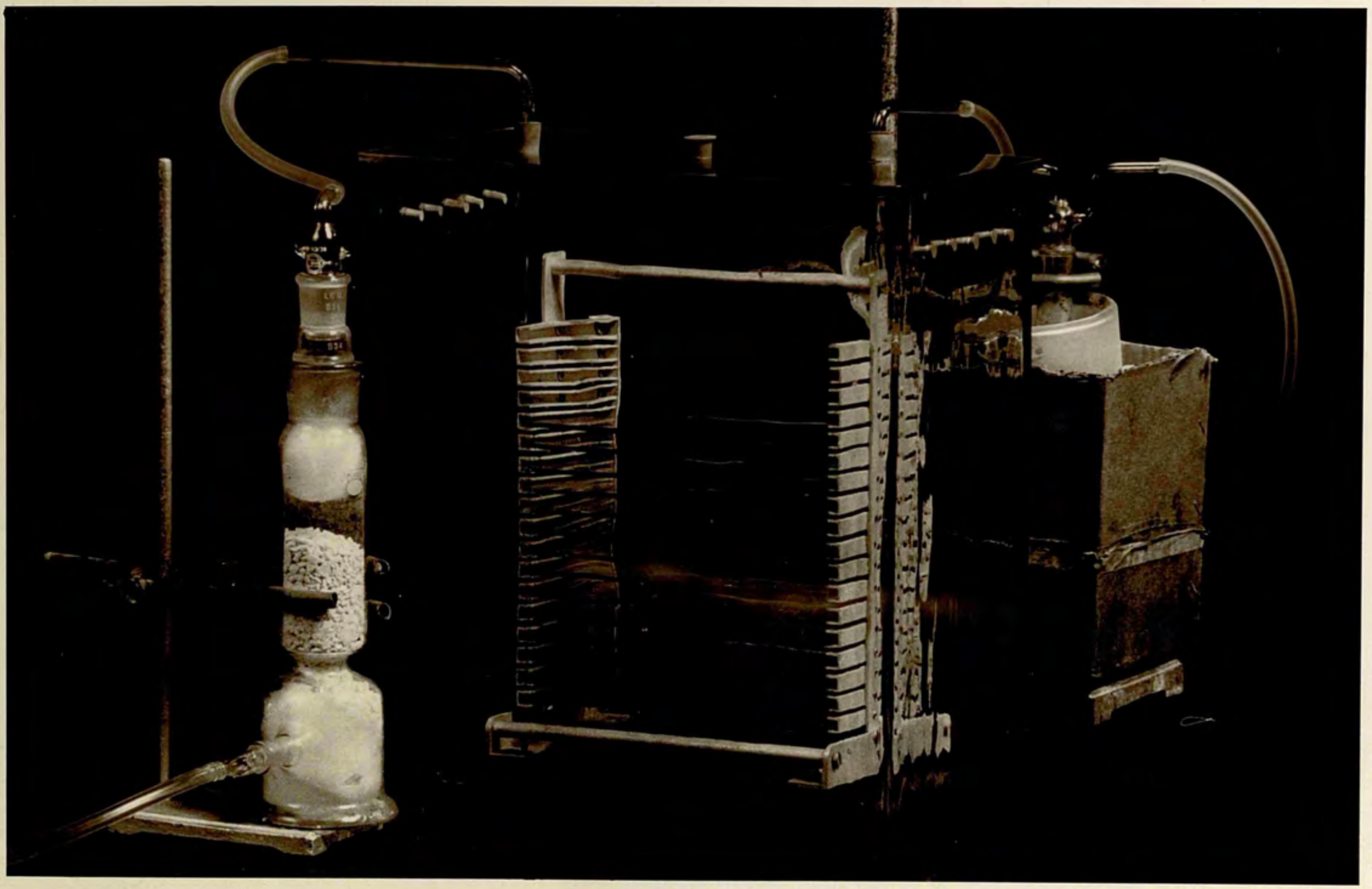
The alkyd resins do not permit the bubbling of gas through them as described in section 3.5.1. Thus the resins were spread on 15 glass plates (10 x 20 cm) at a thickness of approximately 0.004" using a block spreader. These plates were fitted into an aluminium rack and this placed into an air-tight 13" x 10" x 7" Shandon glass chromatography tank. Dry nitrogen was passed through this enclosure for 4 days to remove some of the toluene vapour formed through evaporation from the plates.

The apparatus was set up as shown in photograph 3.6.1.1 and diagram 3.6.1.1. The collection and analysis methods discussed in sections 3.5.2 and 3.5.3 were used in these autoxidation experiments. The dry gas enters the enclosure at point D and exits via E into the trapping apparatus. The benzil promoted autoxidations were irradiated with light from the daylight lamp above (diagram 3.6.1.1). The catalysts used were as in section 3.5.4.

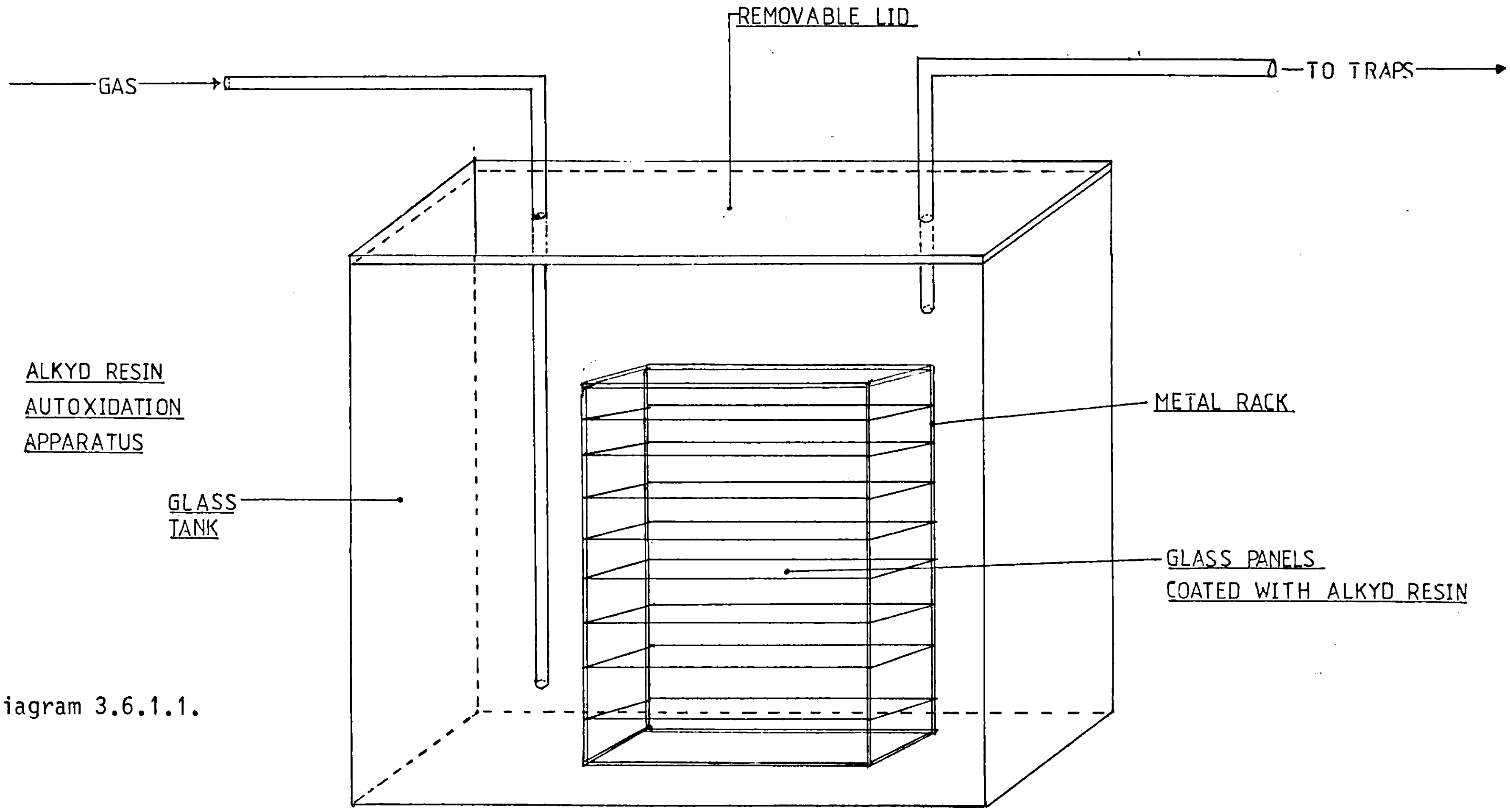
3.6.2 Alkyd autoxidation experiments

Alkyd autoxidations were carried out as tabulated in table 100.

The low acid value alkyd (40 g) was autoxidised using cobalt (II) bis(2-ethylhexanoate) (0.05 g) and aluminium bis(2-butoxide) ethyl acetoacetate in a 2 butanol solution (3.85 g). The autoxidation of series 2, the variable hydroxyl content,alkyds (40 g), was carried out in the presence of methane sulphonic acid (0.22 g).



Photograph 3.6.1.1. Alkyd resin autoxidation apparatus.



ALKYD RESIN
AUTOXIDATION
APPARATUS

Diagram 3.6.1.1.

Table **100**

Alkyd (all 40 g)	Wt. of promotor (g) cobalt	 lead	Benzil
Tall oil alkyd	0.05	0.85	0.19
Soya bean oil alkyd	0.05	0.84	0.18
Linseed oil alkyd	0.05	0.85	0.19
Isomerginic acid S.F. alkyd	0.05	0.87	0.21
Dehydrated castor oil alkyd	0.05	0.84	0.18
Pure linoleic acid alkyd	0.05	0.85	0.19
Linseed alkyd PE/PA/FA 1.24 1.0 1.33	0.04	0.68	-

3.6.3 Time lapse infrared spectroscopy studies

The autoxidation and drying reactions of several alkyd resins were studied by a computer controlled Perkin Elmer 983 infrared spectrometer, diagram 3.6.3.1. The alkyd resin and promotor mixture with the promotors used at the levels in section 3.6.2 was spread on either a potassium bromide or silver chloride disc and the excess solvent removed under vacuum (~6 mm Hg). The film thickness was adjusted to give approximately 5% transmittance at the ester carbonyl band (approximately 1740 cm^{-1}). The computer was programmed to record and store spectra in digitised form then to do so repeatedly after desired time intervals. The storage devices were floppy discs.
Point by point subtraction of two spectra could be performed to give a difference spectra and the area of peaks in a difference spectra could be calculated. The experiments carried out using time lapse infrared spectroscopy are summarised in table 101.

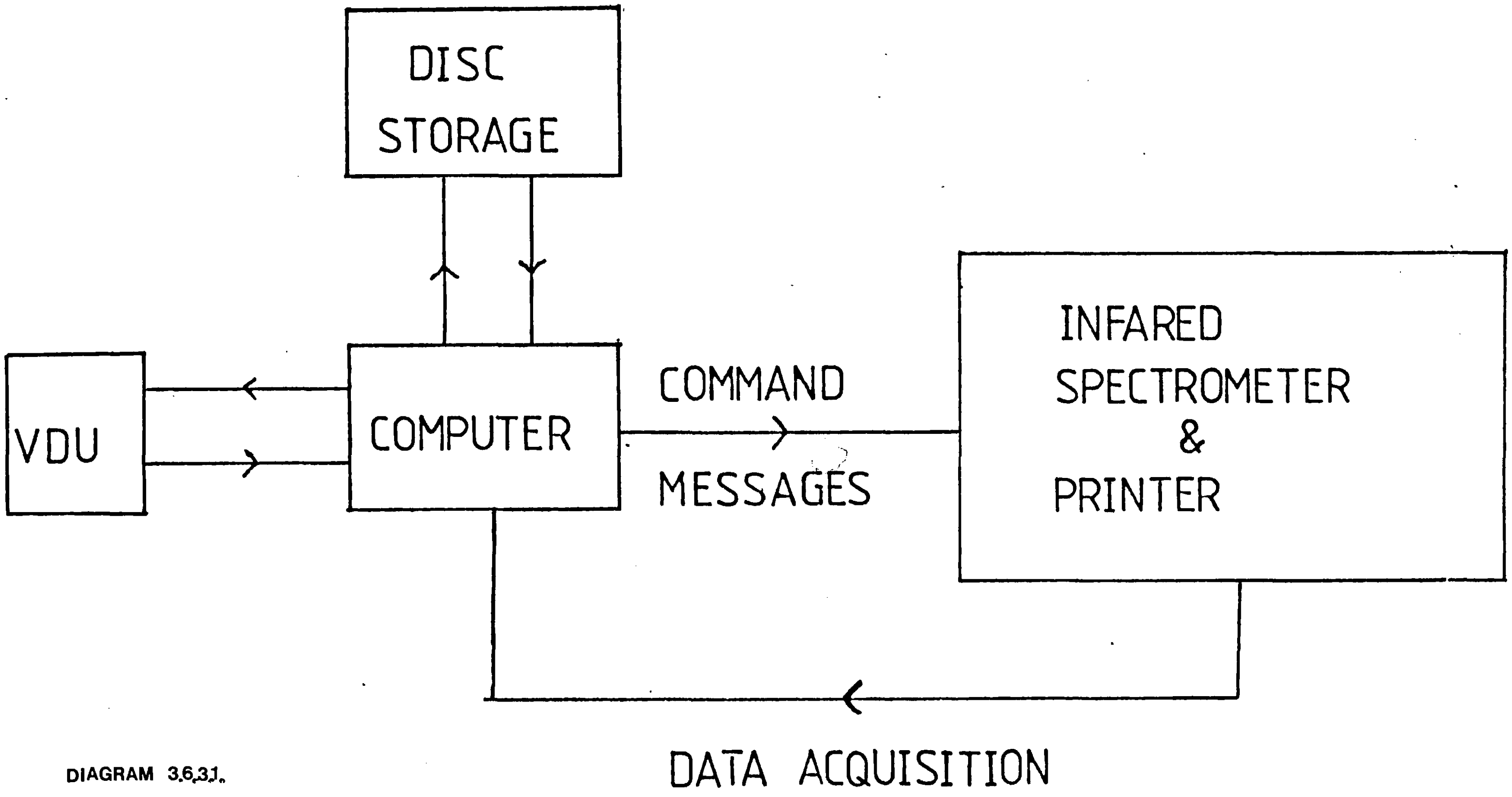


DIAGRAM 3.6.3.1.

TIME LAPSE INFARED SPECTROSCOPY

SCHEMATIC DIAGRAM OF INSTRUMENT

Table 101

Alkyd	Promotor	Plate used
Pure linoleic acid alkyd	Cobalt and lead promotor	KBr
Pure linoleic acid alkyd	Cobalt promotor	KBr
Pure linoleic acid alkyd	Lead promotor	KBr
Pure linoleic acid alkyd	Benzil promotor	KBr
Linseed oil alkyd PE/PA/FA 1.24 1.0 1.33	Methane sulphonic acid	AgCl
Low acid value alkyd	Cobalt and aluminium promotors	KBr
Low acid value	Aluminium bis (2-butoxide) ethyl acetoacetate	KBr

The reactions were analysed under two time conditions: (i) spectra recorded every 15 minutes for the first 3 hrs and then every hour until 12 hours reaction time; (ii) every 60 minutes for the first 15 hours and thereafter every 5 hours up to 45 hours reaction time. The results from these experiments are presented in sections 2.7 and 2.8 respectively.

Near infrared analysis of the hydroperoxide group (~ 6890 cm^{-1}) was conducted on films spread on either a potassium bromide or silver chloride disc. The solvent was removed as before but no adjustment was made to the film thickness. The spectra were manually recorded on a chart recorder, in the range 8330 - 6667 cm^{-1}, approximately every

15 minutes over a total period of 3 hours. The following autoxidation experiments were analysed by near infrared spectroscopy. Table 102.

Table 102

Alkyd	Promotor	IR Disc
Pure linoleic acid	Co/Pb	KBr
Low acid value alkyd	Co/Al	KBr
Linseed oil fatty acid Alkyd PE/PA/FA 1.24 1.0 1.33	M.S.A.	AgCl
Pure linoleic acid	Benzil	KBr

3.7 Collection of vapours accompanying autoxidation under reduced pressure

3.7.1 Collection method

The analysis of the less volatile components from the autoxidation of methyl cis-9- cis-12-octadecadienoate in the presence of cobalt and lead promotors was investigated by trapping the compounds at reduced pressure. The ester was first autoxidised under an oxygen atmosphere for at least 24 hours prior to the analysis. The apparatus, depicted in diagram 3.7.1 had two traps both at -95^{o}C (liquid nitrogen/ toluene slush bath). The compounds were collected by evacuating the apparatus to 10 mm Hg pressure and the flask F warmed gently; the material collected in trap H was analysed by gc-ms. No products were found at point G.

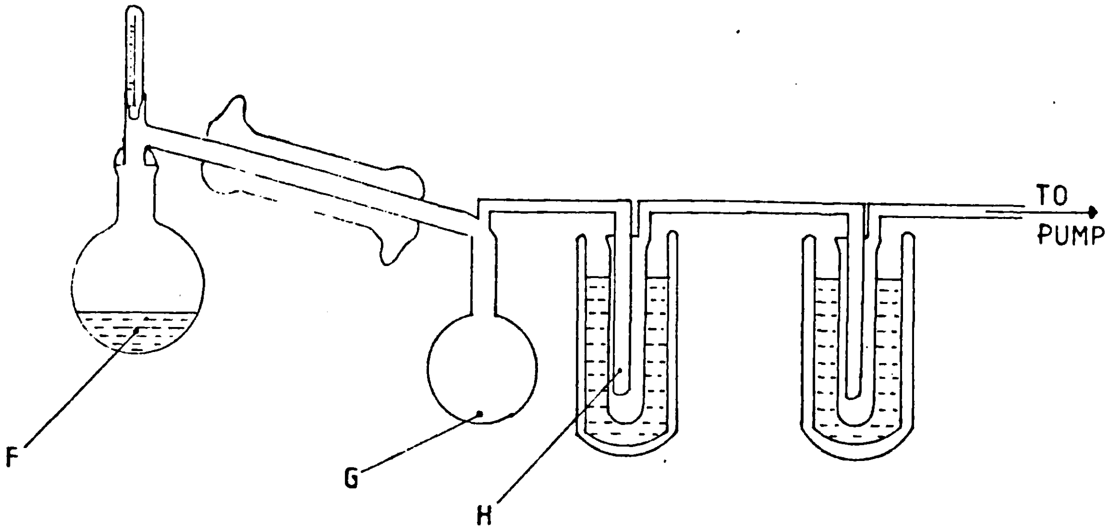


Diagram 3.7.1

3.7.2 Chromatography conditions

Packed column glc and gc-ms analysis were both performed on the material collected in trap H. The conditions for the glc separation are given in table 103.

Table 103

Stationary phase	SP1000
Column length	2 metres
Carrier gas flow rate	40 cm^3 min^{-1}
Carrier gas	Nitrogen (oxygen free), Helium used for gc-ms analysis.
Oven temperature	150°C isothermal 10 minutes then at 2°C min^{-1} up to 210°C.
Injector volume	2 μl
Detector	Flame ionisation detector
Injection temperature	200°C
Detector temperature	240°C

The gc-ms analysis was conducted under the conditions described in table 93.

3.8 Miscellaneous experiments

3.8.1 Autoxidation of methyl (CD_3) linoleate with cobalt (II) and lead (II) bis(2-ethylhexanoate).

Methyl (CD_3) cis-9-cis-12 octadecadienoate (2.2 g) was autoxidised in the presence of cobalt (II) bis(2-ethylhexanoate) (0.005 g) and lead (II) bis(2-ethylhexanoate) (0.085 g) for 10 h. The apparatus and trapping (cryogenic only) techniques were as described in sections 3.5.1 and 3.5.2. Packed column EI gc-ms analysis was carried out. The results and discussion are given in section 2.10.1.

3.8.2 Ethyl acetoacetate formation from aluminium bis(2-butoxide) ethylacetoacetate in 2-butanol solution

Nitrogen was passed through aluminium bis(2-butoxide) ethyl acetoacetate (0.1g) in 2-butanol solution (2 g) for 10 h using the apparatus described in section 3.5.1 and 3.5.2, and the condensed vapour analysed by packed column glc. To the remaining aluminium compound mixture was added methyl cis-9-cis-12-octadecadienoate (5 g) and this mixture had nitrogen passed through it for 10 h, again the collected material was analysed by packed column glc. These results are discussed in section 2.10.2.

3.8.3 Control experiments

The experiments given in table 104 were performed using the apparatus discussed in section 3.5.1 and 3.5.2 and the promotor amounts described in table 97.

Table 104

Ester	Promotor	Gas used in bubbling	Analysis techniques used
Methyl linoleate (5 g)	-	O_2	glc, HPLC
Methyl linoleate (5 g)	Co/Pb	N_2	glc, HPLC
Methyl stearate (5 g)	Co/Pb	O_2	glc
6,9-Pentadecadiene	-	N_2	glc

Chapter 4 Conclusion

The autoxidation of unsaturated fatty acids esters proceeds by radical reactions to give, as their primary products, hydroperoxides. The decomposition of hydroperoxides gives alkoxy radicals, which may either abstract hydrogen from a suitable substrate or else undergo β-scission reactions.

It is this chemistry which provides the air drying properties of alkyd resin based gloss paints. However, the drying process is usually accompanied by the formation of odourous compounds. These are believed to result from the unsaturated fatty acid components in the resin. Autoxidative crosslinking can be promoted by transition metal salts (e.g. cobalt (II) salts) or photoinitiators (e.g. benzil). In addition strong acids, such as sulphonic acids, promote crosslinking.

The redox and photochemical promotors are believed to increase the rate of drying by enhancing hydroperoxide formation; the redox promotors also catalytically decompose hydroperoxides. The strong acid promotors are believed to operate purely by decomposition of hydroperoxides and crosslink through acetal formation.

The 'volatile' products formed during the cobalt promoted autoxidation of methyl cis-9-octadecenoate, methyl cis-9- cis-12-octadecadienoate and methyl cis-9-cis-12-cis-15-octadecatrienoate were studied as simple autoxidation systems. The redox and photoinitiated autoxidations both gave similar volatile products (e.g. aldehydes, alcohols and methyl esters), but with benzil photochemically promoted autoxidations only ca. 10% of the quantity of 'volatile' material formed with the redox system was observed. By comparison this autoxidation of the methyl esters in the presence of strong acid (methane sulphonic acid) did not produce any detectable volatile products. However, the strong acid promoted drying of alkyd resins had been found to proceed only in the presence of a sufficient excess of hydroxyl groups.

The volatile products arise from hydroperoxide decomposition. The difference in quantity of products may result from the apparent inability of benzil to decompose hydroperoxides.

To mimic better the autoxidation conditions in an alkyd resin, three model alkyds were prepared namely: benzoyloxyethyl linoleate LXXXXI, 2-hydroxyethyl linoleate LXXXXV, and 2-hydroxyethyl linolenate LXXXXVII. The autoxidation of LXXXXI in the presence of either cobalt (II) bis(2-ethylhexanoate) or benzil produced similar volatile products to those from the simple methyl esters, with the notable exception of any methyl carboxylates owing to the absence of a carboxymethyl group in the substrate. The autoxidation of LXXXXV and LXXXXVII in the presence of methane sulphonic acid gave 2-pentyl-1,3-dioxirane and 2-ethyl-1,3-dioxirane respectively along with some unidentified hydrocarbons. No significant carbonyl formation was observed. These observations support the suggestion of acetal formation caused by acid decomposition of hydroperoxides in the presence of alcohols.

The effect of the secondary promotors i.e. lead (II) bis(2-ethylhexanoate) and aluminium bis(2-butoxide) ethyl acetoacetate was found to be minimal. The different odour characteristics found from cobalt (II) bis(2-ethylhexanoate) and aluminium bis(2-butoxide) ethylacetoacetate promoted autoxidation results purely from the preponderance of 2-butanol and ethylacetoacetate among the volatile products. Ethyl acetoacetate results from displacement reactions, from the metal complex, by some of the autoxidation products. The incorporation of the lead promotor with the cobalt promotor had no marked effect on the volatile products.

Some volatile compounds result from the promotors e.g. in autoxidation promoted by cobalt (II) bis(2-ethylhexanoate) or lead (II) bis(2-ethylhexanoate), methyl-2-ethylhexanoate and 2-ethylhexanoic acid are generally found. Further methyl-2-ethylhexanoate is not formed if the carboxymethyl group is absent from the autoxidation mixture. The autoxidation of methyl (d_3) linoleate in the presence of cobalt (II) bis(2-ethylhexanoate) formed methyl (d_3) 2-ethylhexanoate in the volatiles and appears to result from a transesterification process. No methyl 2-ethylhexanoate was observed in any alkyd resin autoxidation. All autoxidation reactions promoted by benzil were found to produce, _inter_ _alia_, benzaldehyde. This originates from radicals formed as the result of hydrogen abstraction by the benzil triplet state.

The redox and photoinitiated autoxidation of a series of alkyd resins with varying oil composition (alkyd series 1) produced the volatile compounds expected from the individual unsaturated fatty acids present, thus showing that the mechanism of volatile formation in alkyd resins is the same as that in the methyl esters.

The autoxidation of a series of 'variable hydroxyl excess' alkyds (alkyd series 2) in the presence of methane sulphonic acid, showed similar products to those found in the redox and photoinitiated autoxidations e.g. aldehydes. This may be explained by the immobility within the drying resin, i.e. the hydroxyl groups were too remote for reaction with the oxenium cations. Consequently the products associated with β-scisson of alkoxy radicals dominate.

Time lapse infrared studies of the drying alkyd films provided support for the above observations. The redox and photoinitiated autoxidations all showed hydroperoxide formation, increase of trans unsaturation, carbonyl formation coupled with the loss of cis unsaturation and hydrocarbon groups. The 'hydroxyl excess' alkyds in the presence of methane sulphonic acid showed the above changes but also the formation of acetals during the drying process and accords with the proposed mechanism of crosslinking.

The observed rate of hydroperoxide formation in the drying alkyd resins was determined and found to depend on the promotor present. There was a correlation between the quantity of volatile material produced in the promoted autoxidations and the rate of hydroperoxide formation. Those promotors which induced the formation of the largest amount of 'volatiles' showed a lower observed rate of hydroperoxide formation. Thus if a promotor does not induce the decomposition of hydroperoxides, leading to volatile formation, the concentration of hydroperoxides increases.

The effect of varying the autoxidation site by adding methyl groups to the central doubly allylic methylene group was observed. The 'volatile' autoxidation products from 8-methyl-6,9-pentadecadiene showed a greater quantity of both the total volatiles formed and the amount of 2-heptenal, hexanal being the major product, compared to those from 6,9-pentadecadiene (hexanal the major product). The autoxidation of 8,8-dimethyl-6,9-pentadecadiene however produced a greater proportion of 2-heptenal (now the major product) but overall a lower total quantity of volatile material.

In conclusion, the volatile compounds formed during the autoxidative crosslinking of alkyd resins include aldehydes, ketones and carboxylic acids. The use of secondary driers or complexing promotors does not significantly change these products. The methyl esters, methyl cis-9-octadecenoate, methyl cis-9-cis-12-octadecadienoate and methyl cis-9-cis.12-cis-15-octadecatrienoate, are good models for the study of alkyd resins and their autoxidation.

The strong acid promoted air drying of alkyd resins is an autoxidative process, with the acid decomposition of the hydroperoxides to oxenium cations and their reaction with alcohols providing the crosslinking. In the model 'hydroxyl excess' alkyds LXXXXV and LXXXXVII carbonyl volatile formation is suppressed. Whilst in an 'hydroxyl excess' alkyd resin carbonyl formation is dominant.

The quantity of volatile produced was seen to depend on (i) the promotor used, i.e. cobalt (II) bis(2-ethylhexanoate) promotes 10 times the quantity of that promoted by benzil, and (ii) the degree of unsaturation present. Yields of 'volatile' products was found to be in the order methyl linolenate>methyl linoleate>methyl oleate.

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