University of Bradford eThesis

CATALYTIC EFFICIENCY OF ZEROVALENT IRON COMPOUNDS AS PAINT DRIERS COMPARED WITH CONVENTIONAL SUBSTANCES

The use of ferrocene and other iron compounds as driers in autoxidative paint systems at ambient and elevated temperatures.

by

Otokpa Christopher-Marius AGADA

A Thesis submitted for the
Degree of Doctor of Philosophy

Postgraduate School of Studies in
Colour Chemistry and Colour Technology,
University of Bradford.

July 1985

TO

My WIFE,

CHILDREN,

AND

PARENTS.

ACKNOWLEDGEMENTS

My utmost gratitude goes to Mr. T.W.J. Apperley for the supervision and most constructive advice throughout the period of my research work.

I wish to thank Dr. A.T. Peters, Chairman, Postgraduate School of Colour Chemistry and Colour Technology, for offering me the opportunity to undertake this research programme.

I also thank the following: Alan Hague and Ann Palliser for the photographs, Mr. W.A. Straw for his advice on some of the iron complexes, Valerie Hunter for undertaking to type this work and the entire staff and fellow students in the Department of Colour Chemistry for the most cordial relationship.

I am greatly indebted to my parents, who through all these years, have received no financial returns but have encouraged me to read to this level.

I thank my wife for her great patience and co-operation.

Above all, I thank The Almighty God for all His help.

ABSTRACT

Novel paint driers based on iron co-ordination complexes were investigated for use as stoving finishes in oil-based coatings. Cis 9, cis 12-octadecadienoic acid was employed as a model vehicle because of its high drying capacity. Iron compounds generally have low catalytic efficiency at low temperatures which however improve with rises in temperature.

The catalytic efficiency of some iron compounds was compared with those of some conventional driers at room temperature; 60°C, 80°C and 120°C. To make the results comparative, equal weights of drier (0.05%) metal were employed in one series of experiments. In another series, a much higher concentration (0.25%) metal based on the weight of 9, 12-octadecadienoic acid was employed.

Equal weights of drier combination(s) and variable drier weights were examined to determine synergism or antagonism in the autoxidative systems.

Maximum oxygen absorption, changes in iodine and peroxide values were monitored to determine a comparative catalytic performance of the driers at the reaction temperatures used.

The reactivity of iron co-ordination complexes was found to be influenced by the organic compound with which the iron is chelated.

Zerovalent iron complexes can be employed as high temperature driers.

For convenience some common names have been used for major chemicals of importance in this work, e.g.,

Linoleic acid; cis 9, cis 12-octadecadienoic acid.

Ferrocene; dicyclopentadienyl iron.

CONTENTS

CHAPTER 1

INTRODUCTION

CHAPTER 1

INTRODUCTION

A paint is a surface coating usually containing solids suspended in a liquid phase. When applied to a surface, it dries by various mechanisms to a more or less opaque adhering solid film. The solids are colour-or-opacity imparting finely ground pigments. The vehicle (liquid) consists of suitable oils, solvents, resins, aqueous colloidal solutions or dispersions containing other lesser ingredients.

Paints are applied for protective and/or decorative purposes. Usually, some time interval is needed for the paint film to dry after its application. Auto-oxidative drying processes can be accelerated by incorporating driers during the paint formulation.

1.1 HISTORICAL PREAMBLE

Petri(1) and Actius(2) have discussed the use of fats and oils as drying media as far back as the 6th century A.D. The use of oil in coatings was also mentioned by Ludius in 63 B.C. At about the same time, Vitruvius produced a varnish containing punic wax and oil(3). The sap of the "varnish tree" Rhus verniciflua was the earliest Japanese lacquer(4).

Galan 131-200 A.D. employed litharge, white lead, and umber to coagulate hempseed, nut and linseed oils. The Caveman 2000-3000 B.C., demonstrated his artistic abilities by daubing coloured mud on the walls of his cave or by the use of distemper. Milk and other cured paints were used for home decoration by the ancient Hebrews(5). The frescoes of the Romans and the Italians(6) were the applications of pigments to uncured plasters where the colours became fixed by the carbonation and drying of lime.

Drying oils were added to casein-containing paints to improve water resistance properties(7). The first U.S. paint patent (1865) had a composition of zinc oxide, potassium hydroxide, resin, milk and linseed oil.

The combined effects of heat and time on oil oxidation has a long recorded history. Specimens of the Eighteenth Dynasty period discovered by Bruyere in an ancient Egyptian town contained solid elastic fats made up of palmitic and stearic acids(2). It was suggested that these elastic materials were originally some kind of drying oils (linseed or safflower oils) which under the effects of heat and time, polymerized to a stiff elastic solid(2).

Metal-soap driers are among the most important additives used in the production of many coatings and of air-dried coatings in particular. The effects of driers were not generally known, although Galen, in the second century and Marcellus in the fourth century reported on their effects in paint drying(3). In 1644, Patiot suggested the use of driers as a practical approach to the drying of varnishes(3). Alberti of Magdeburg mentioned the use of turpentine as a thinner in 1736. Turpentine until recently has been a major varnish solvent, although petroleum distillates were used commercially as far back as 1880(3). In 1773, the first edition of Watin's book appeared. It contained many varnish formulations based on linseed oil and natural resins. The eighteenth century may be considered as the beginning of the modern varnish era.

As far back as the 19th century, J. Liebig(8) drew attention to the fact that considerable amounts of lead-oxide could be dissolved in linseed oil by heating thus increasing its drying rate. Little, if anything, was known about the action of driers in France until 1835-1850 when the French zinc oxide manufacturers undertook the substitution of zinc white for white lead in paints. In 1855, J.S. Stas summarized the work on driers at the International Exposition at Paris. By emphasizing the importance of the solubility of a drier, Stas opened the way for more understanding work, which finally produced the soluble drier. Previous to this, paints and varnish men had used as driers, metallic borates, chlorides, sulphates, and other salts insoluble in drying oils. Apparently, they did not realise that at the temperature of incorporation in the paint or varnish, some of these salts formed soaps and it was these soaps which were effective and not the inorganic salts themselves(9). Although the so-called soluble driers appeared in 1855, they received little attention because of their poor quality, which however, improved as time went on. Lead and manganese soaps of linseed oil or resin were the only driers known at this time.

Although research on the use of other metals was relatively fruitless, that concerned with the development of more satisfactory anions (acid radicals) produced very good results. The introduction of naphthenic acids whose soaps are vastly superior to those of the fatty or resin acids (in terms of solubility and stability in oils) was one of the most significant advances(9).

The discovery of the drying activity of cobalt salts of linseed fatty acids at the beginning of this century, opened a new chapter in the search for new paint driers. Eibner and Pallauf(10) in 1925 reported on the results of their studies of linseed oil drying performances achieved by 14 various drying catalysts(10).

1.2 RESEARCH OBJECTIVE

The aim of this research program was to investigate novel paint driers based on iron co-ordination complexes for use in stoving finishes. Iron compounds have low catalytic efficiencies at low temperatures, but their performances improve with rise in temperature. Recent work(11) showed that iron stearates at very low concentrations have catalytic efficiencies comparable with equal weights of cobalt and manganese stearates. While cobalt and manganese increased their rates of reaction with increase in concentration, iron behaved differently. These experiments were carried out at 26-27°C. The cobalt and manganese stearates performed better than iron as the temperature was increased. Iron is a relatively good catalyst at high temperatures. Based on the changes in the reactivity of iron stearates, iron co-ordination compounds were investigated as catalysts for stoving finishes.

The relative catalytic efficiencies of a range of driers were compared with those based on ferrocene compounds under varying experimental conditions. To make the results comparative, definite weights of driers based on the metal content were used in one series of experiments. In another series, definite weights of driers were used.

Where a combination of driers was used, the aim was to determine what effects such combination(s) would produce synergistically or antagonistically on the paint drying processes.

In some of the experiments, variable weights of driers were employed to determine whether such driers increased in performance as their concentrations were raised.

1.2.1 Fats and Oils

The common distinction between fats and oils is that fats are solid while oils are liquid at room temperatures.

Drying oils are liquid products of vegetable, animal, mineral and synthetic origins. They react with oxygen or under other conditions create free radicals and convert irreversibly from the liquid to a solid phase for example sea fish oils, linseed or tung oils, and asphaltic acids are derived from the animal, vegetable and mineral kingdoms respectively. Chemically, oils used for coating compositions contain a number of ethylene groups to which they owe their drying ability.

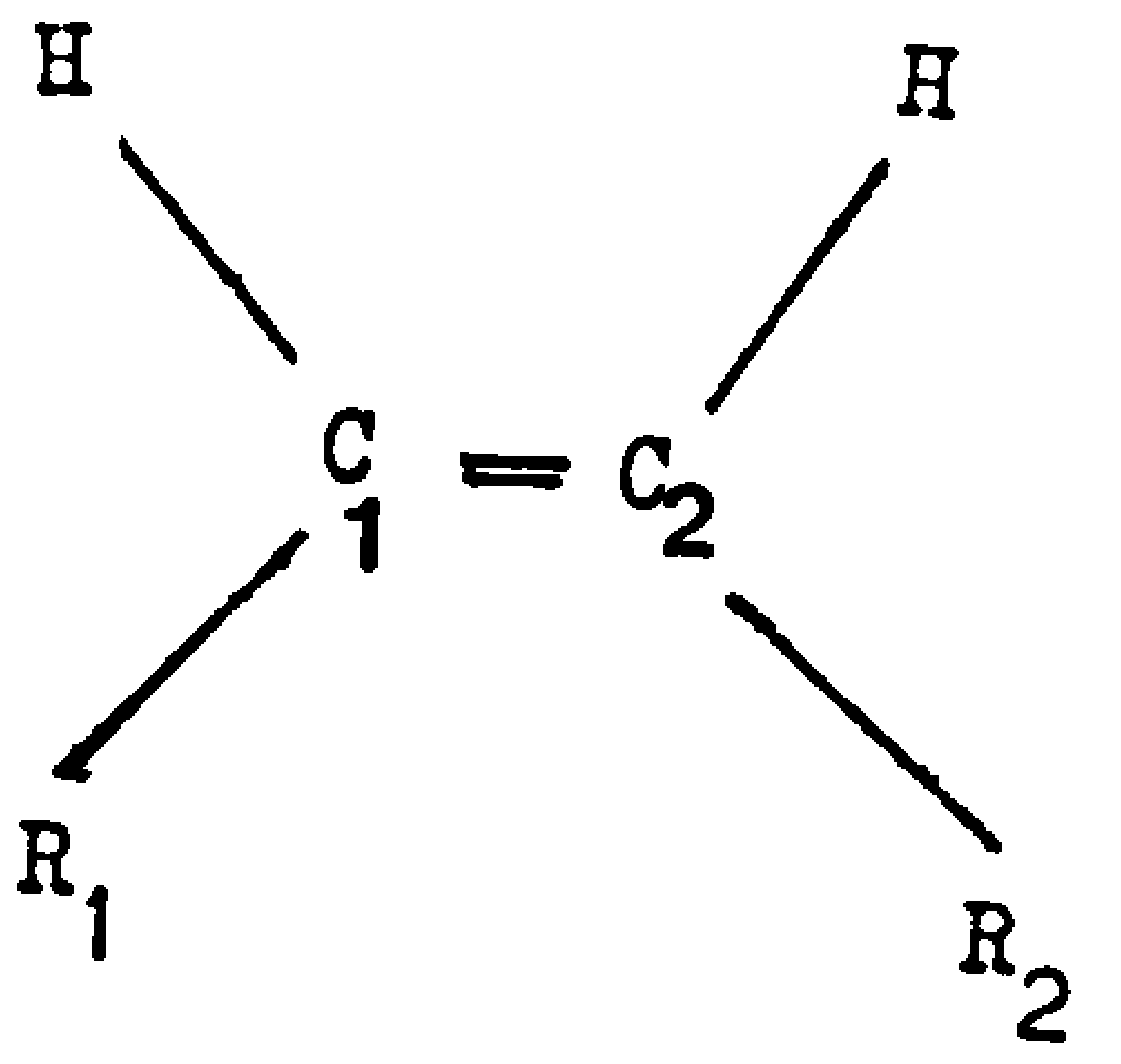
The ultimate quality of the drying film is a function of the degree of unsaturation. Linseed and tung oils are known as drying oils because they can dry to satisfactory films under normal conditions (i.e. 10-35^{0}C and 25-60% relative humidity). Non-drying oils such as castor or olive oils are unable to form films under the above conditions. Semi-drying oils give tacky and poor quality films under the same conditions, but convert to better films at higher temperatures or when used as modifiers for alkyd resins. A large porportion of all oils and fats is composed of a group of closely related compounds known as the triglycerides. These are substances which when hydrolysed give fatty acids and glycerol.

The predominant acids in natural fats occur as straight chains (containing 12-18 carbon atoms). A few shorter chain acids present in small proportions are characteristic of milk fats. Longer chains (20-22 carbon atoms) are found in certain types of materials especially in fish oils. Another significant feature of oils is the degree of unsaturation. A saturated fatty acid cannot add on any hydrogen atom because it is fully hydrogenated e.g. stearic and palmitic acids

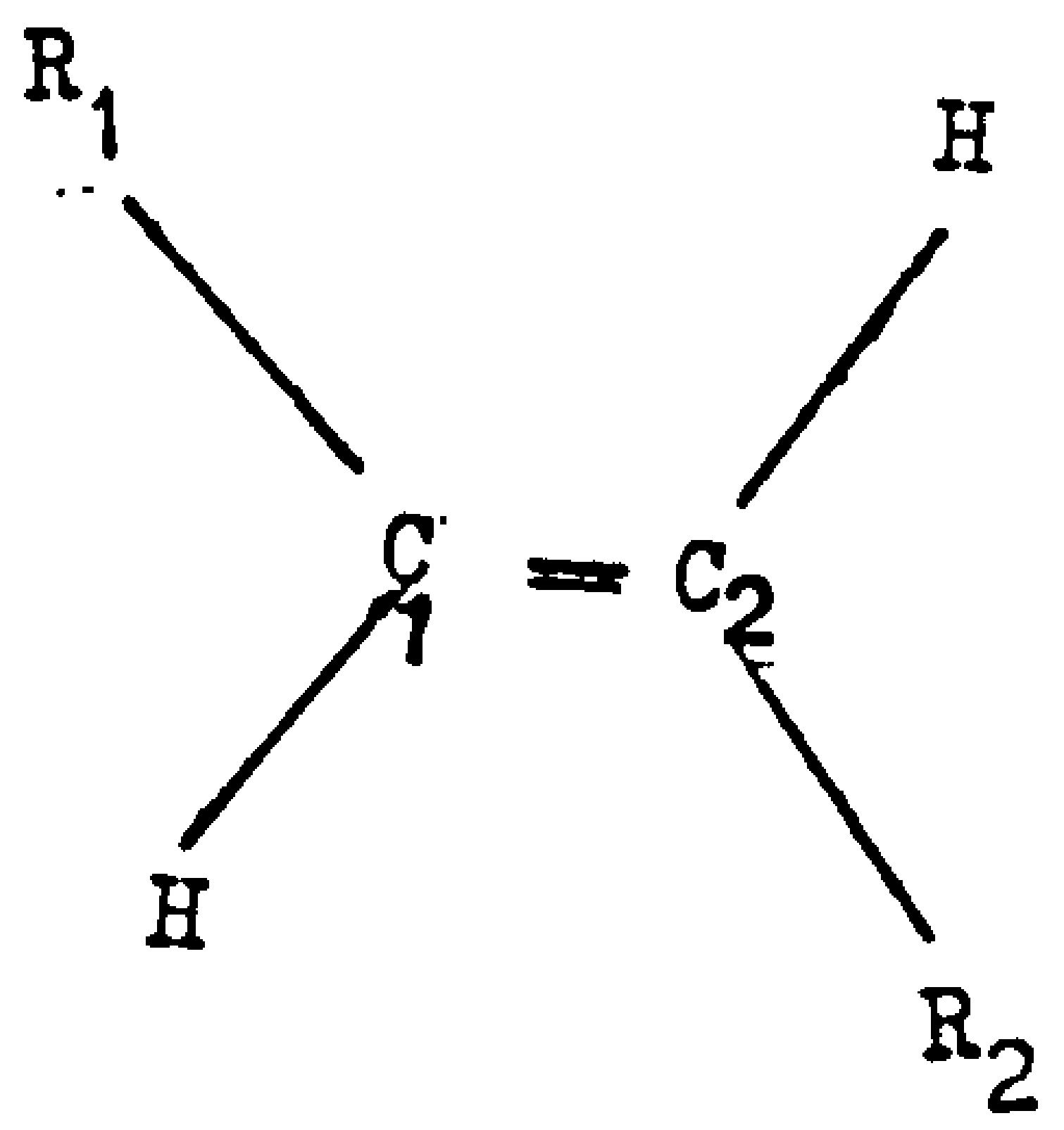
$CH_3(CH_2)_{16}COOH$ $CH_3(CH_2)_{14}COOH$.

The unsaturated oil can add on hydrogen atoms, has a low melting point and is liquid at room temperature. The different acids present affect the melting point of the corresponding triglyceride. A triglyceride with three unsaturated acids is liquid whereas one with three saturated acids is a hard solid.

Unsaturated acids can exhibit stereoisomerism notably trans-cis isomerism.



cis



trans

Natural fatty acids are usually in the cis form but changes resulting in trans acid formation cause a subsequent shift in the melting point.

The properties of oils are generally the properties of the component glycerides. Oils have a lower density than water and are almost completely insoluble in it; although small amounts of water will dissolve in them. The solubility of fats in water increases with the rise in temperature and presence of free fatty acids. This property of oils can from a practical point of view affect experimental results in the determination of iodine, peroxide and acid values (see chapter 7)

Table 1·0

Characteristics of Common Fatty Acids

	Common name	chain length carbon atoms	Degree of unsaturation	Abbreviated structural formula	Melting point °C
1	Lauric acid	12	saturated	$CH_3 - (CH_2)_{10} - COOH$	44.2
2	Myristic acid	14	saturated	$CH_3(CH_2)_{12}COOH$	-
3	Palmitic acid	16	saturated	$CH_3(CH_2)_{14}COOH$	63.0
4	Palmitoleic acid	16	mono-unsaturated	$CH_3 - (CH_2)_5 - CH = CH - (CH_2)_7 - COOH$	-0.5
5	Stearic acid	18	saturated	$CH_3 - (CH_2)_{16} - COOH$	69.6
6	Oleic acid	18	mono-unsaturated	$CH_3 - (CH_2)_7 - CH = CH - (CH_2)_7 - COOH$	16.0
7	Linoleic acid	18	di-unsaturated	$CH_3 - (CH_2)_4CH = CH - (CH_2)_7 - COOH$	-0.5
8	Linolenic acid	18	tri-unsaturated	$CH_3 - (CH_2)_2 - CH = CH - CH_2 - CH = CH - CH_2 -$ $CH_2 - CH = CH - CH_2 - COOH$	-11.0
9	Arachidic acid	20	saturated	$CH_3 - (CH_2)_{18} - COOH$	75.4
10	Erucic acid	22	mono-unsaturated	$CH_3 - (CH_2)_7 - CH = CH - (CH_2)_{11}COOH$	34.0

1.2.2 Paint Drying Processes

Before considering the oxidative drying of oils, it is perhaps useful to examine the main mechanisms by which paints dry.

(i) Drying without chemical reaction

Paint films in this category are mainly produced by evaporation of liquids from solutions of the polymer. The paint hardens or dries when it is free of solvent. The polymer undergoes no chemical change. Nitrocellulose lacquers dry by this process which in this case is often called "lacquer dry".

Other drying processes involve chemical reactions after the paint application.

(ii) Chemical reaction between paint and air

Oxygen and water vapour in particular are reactive chemical ingredients of the air. Molecular oxygen reacts with drying oils and other unsaturated compounds to produce free-radicals which bring about polymerization. Water and isocyanates react to cause condensation polymerization. Both of these reactions produce cross-linked films, yet the principle remains the same.

Air is used as the chemical trigger for polymerization and must be kept away from the reactive ingredients in the paint during storage to avoid skinning. The skin if formed, may be either permeable or impermeable to air. In the latter, more reaction between the paint and air causes further cross-linking and swelling of the polymer. This is an irreversible gel and the paint at this point is useless. With complete exclusion of air, no reaction begins until the paint film is applied thus presenting a large surface area exposed to air. As solvents evaporate, cross-linking begins. The soft, sticky, low molecular weight, linear or branched polymers in the paint convert to hard, tough cross-linked insoluble film.

The reaction is slow at room temperatures, mainly because the reactive ingredients in the air must diffuse into the film before full hardening occurs. The paint hardens up more rapidly if the reactive molecules are large. Cross-linking rapidly causes gelation. This means that the paint film hardens much faster but this from application and economic point of view is undesirable. Low molecular weight polymers or large simple molecules give moderately high solids in the paint. However, high molecular weight materials require extensive use of expensive thickeners and a compromise may be required between drying rates and ease of application and economy.

Chemical reaction with the air continues long after the paint film is apparently dry to the touch. In fact, the paint film changes its chemical nature slowly all the time it is in use; detrimental aging is a feature of such paints.

(iii) Drying by chemical reaction between ingredients in the paint

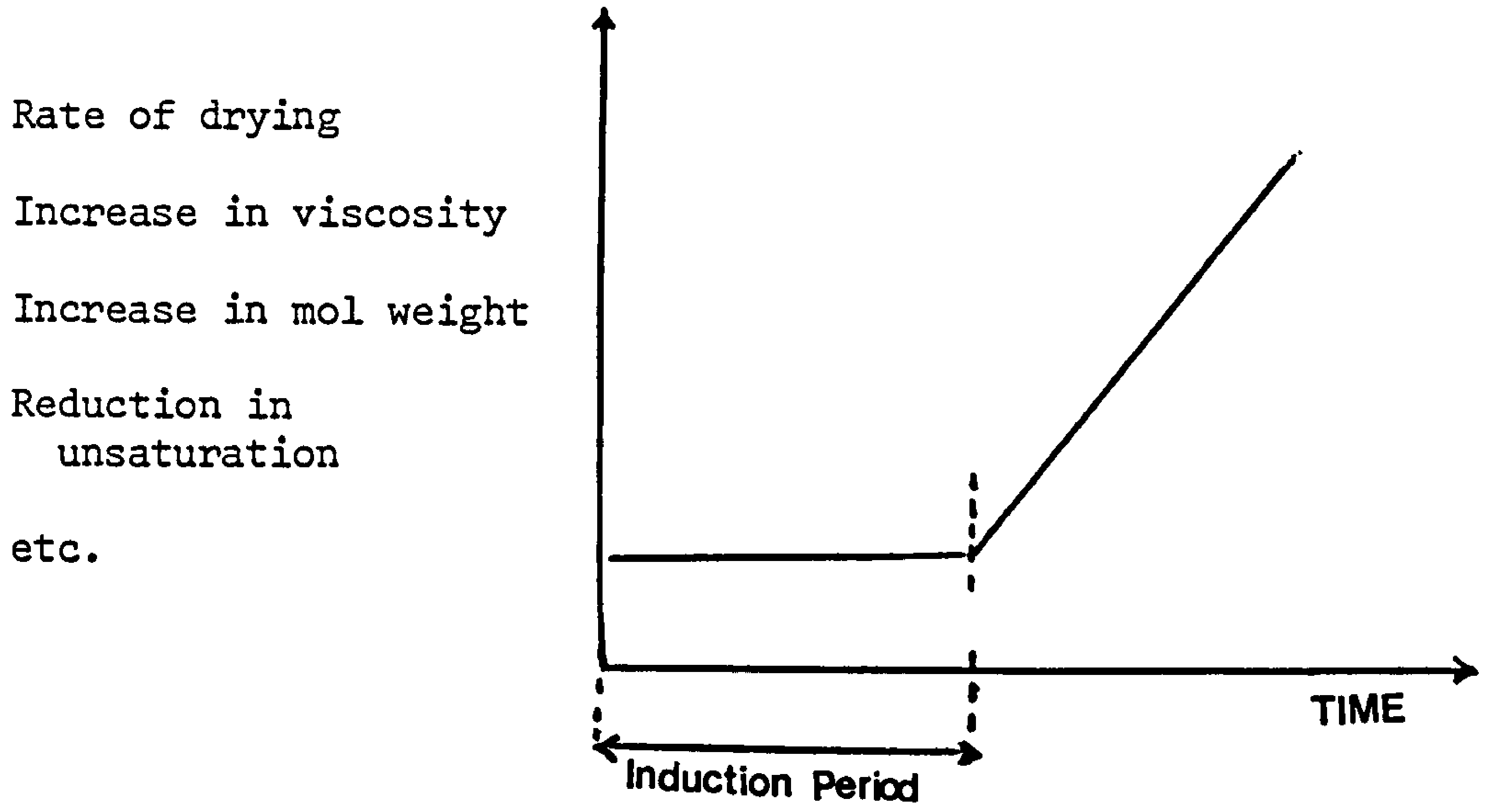
The reactants, though in the paint solution, must not react until the paint has been applied. This is achieved either by separating the reactive ingredients into two or more containers and mixing just before use, or by choosing ingredients which only react at higher temperatures or when exposed to radiation. The former technique produces what is known as a "two-pack paint". This is less popular than the ready-mixed equivalent. This is because measuring is required before mixing and there is a limited period after mixing during which the paint remains useable (the "pot life"). The use of "two-pack" paints can be avoided by diluting the reactants with solvents so that reaction is slow in the container but much faster on the surface after solvent evaporation. Even so, the paint cannot be said to be very stable but a tolerable "shelf-life" is achieved.

Figure below gives a summary of some of the properties associated with paint drying mechanisms.

1.3 AUTOXIDATION MECHANISM

1.3.1 The Induction Period

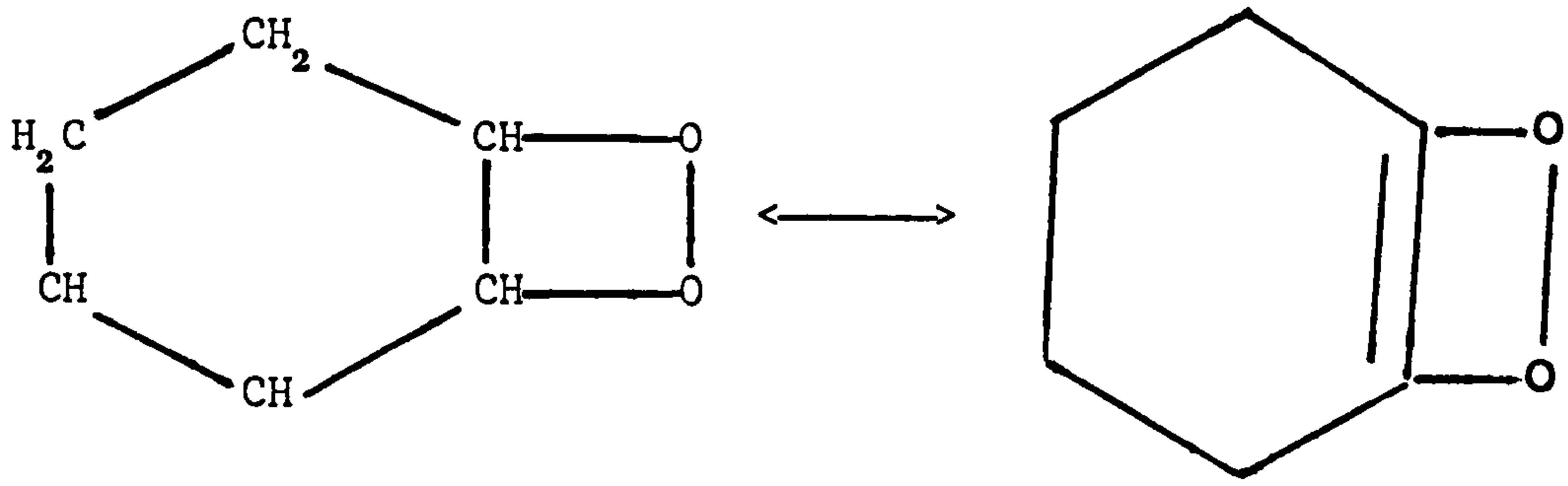
Before any obvious changes involving oxygen-uptake can occur in drying oils and alkyd paints, there is an indefinite preliminary stage called the induction period. It is not known what processes take place during the induction period. Once the period is over, several reaction rates can be used to describe the kinetics of the process e.g. increase in molecular weight; decrease in unsaturation and increase in viscosity.



Although drying oils have been studied for many years, our knowledge of the reaction mechanisms is still incomplete. The process is very complex, as are the type and number of end products. Most observers agree that the drying of thin films of vegetable oils is characterized by an induction period followed by rapid oxygen adsorption, peroxide formation and peroxide decomposition and polymerization. These stages are apparently not clearly defined, and one or more may be proceeding at the same time(12).

1.3.2 Oxidative Drying Processes

Molecular oxygen is capable of oxidizing drying oils. On exposure to air, these alkenes undergo cross-linking by polymerization to form a polymer as the principal product. Some earlier investigators believed that peroxidic compounds corresponding to the formula R_1-O-OR_2 were the primary products. Rawls(13) and Santen(14); Clement et al.(15) and Foote(16) have proved that Singlet Oxygen plays a role in initiating autoxidation in unsaturated fats. Singlet oxygen, superoxide and other species of activated oxygen have also been known to be implicated in paint drying processes, biological oxidation processes(17)-(22), in ageing of oils as well as in environmental pollution(23)-(25). For these reasons, there are renewed interests in the problems of fat autoxidation, so that oxidation chemistry has become an intensively active area of research(26)-(31). Because of the variety of products formed and the complexity of the reactions involved in the oxidation of oils, early investigators such as De Saussore (1820) and Schonbein (1838) employed a simple model unsaturated compound for their study. It was believed that molecular oxygen attacked the unsaturated compound at the double bond and for a compound such as cyclohexene, the product was a peroxide and cyclic in configuration(32).

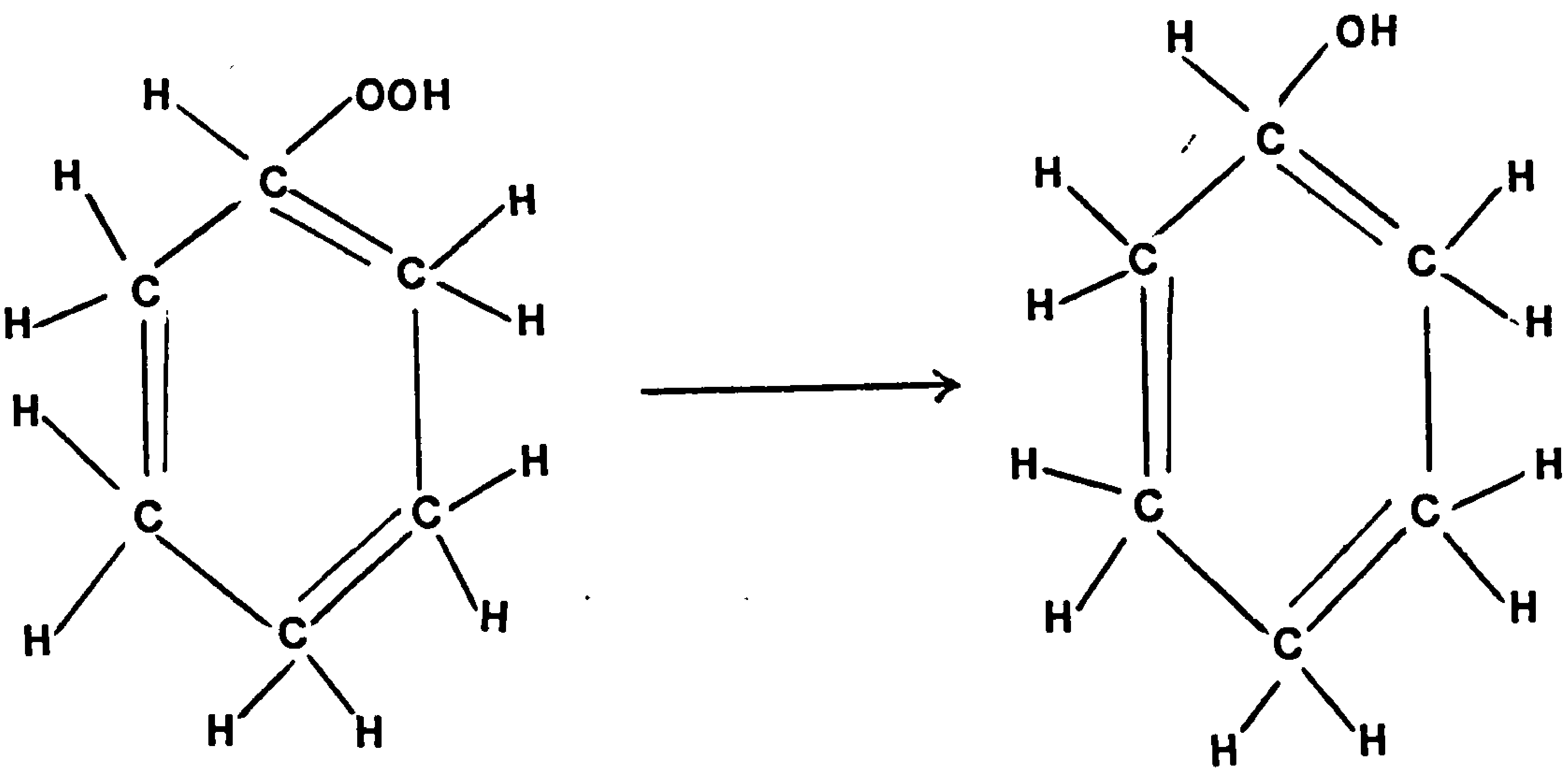


Later work by Criegree et al.(33),(34) and Farmer and Sundralingam(36) showed that the product was not a saturated cyclic peroxide but an unsaturated cyclic hydroperoxide. Three main reaction mechanisms motivated the investigators to suggest a new formula for the product:-

(i) The product can be reduced to cyclehexene-3-ol with sodium sulphite.

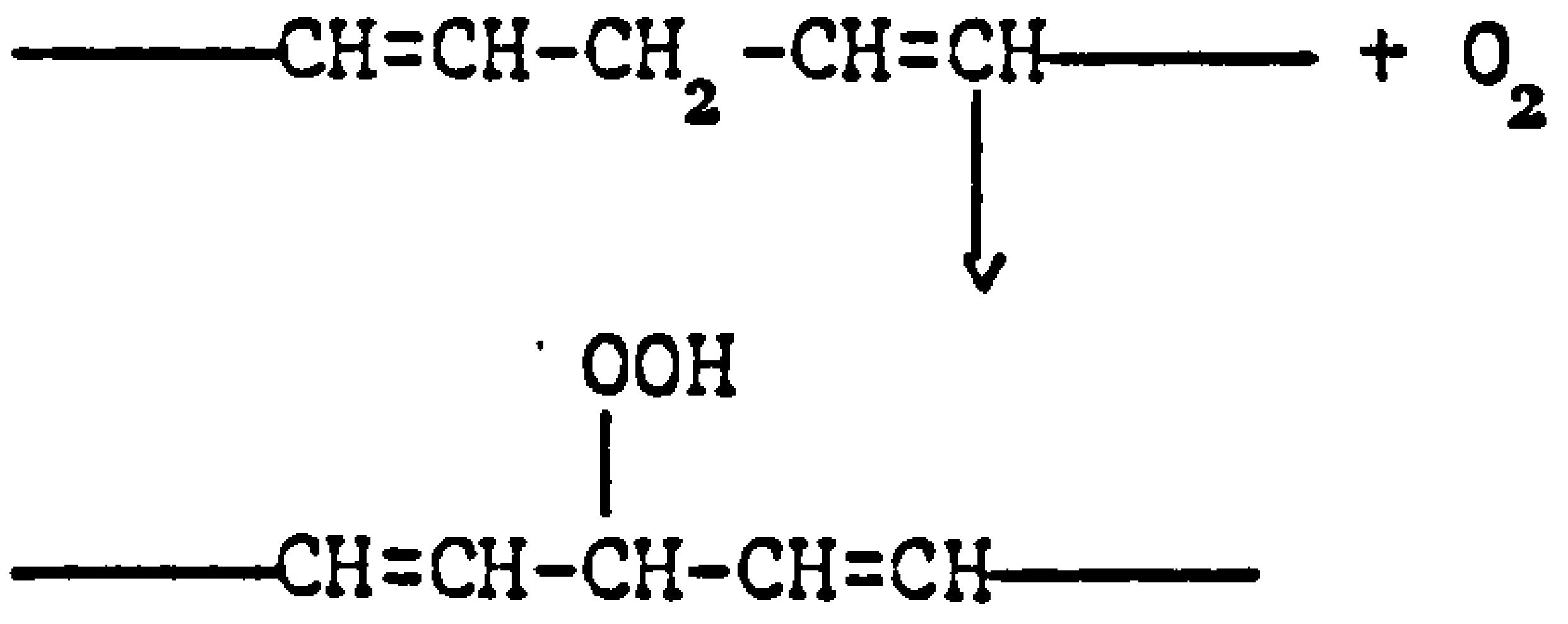
(ii) The product adsorbs one mole of bromine per mole and

(iii) The product contains one gramme atom of active hydrogen per mole.



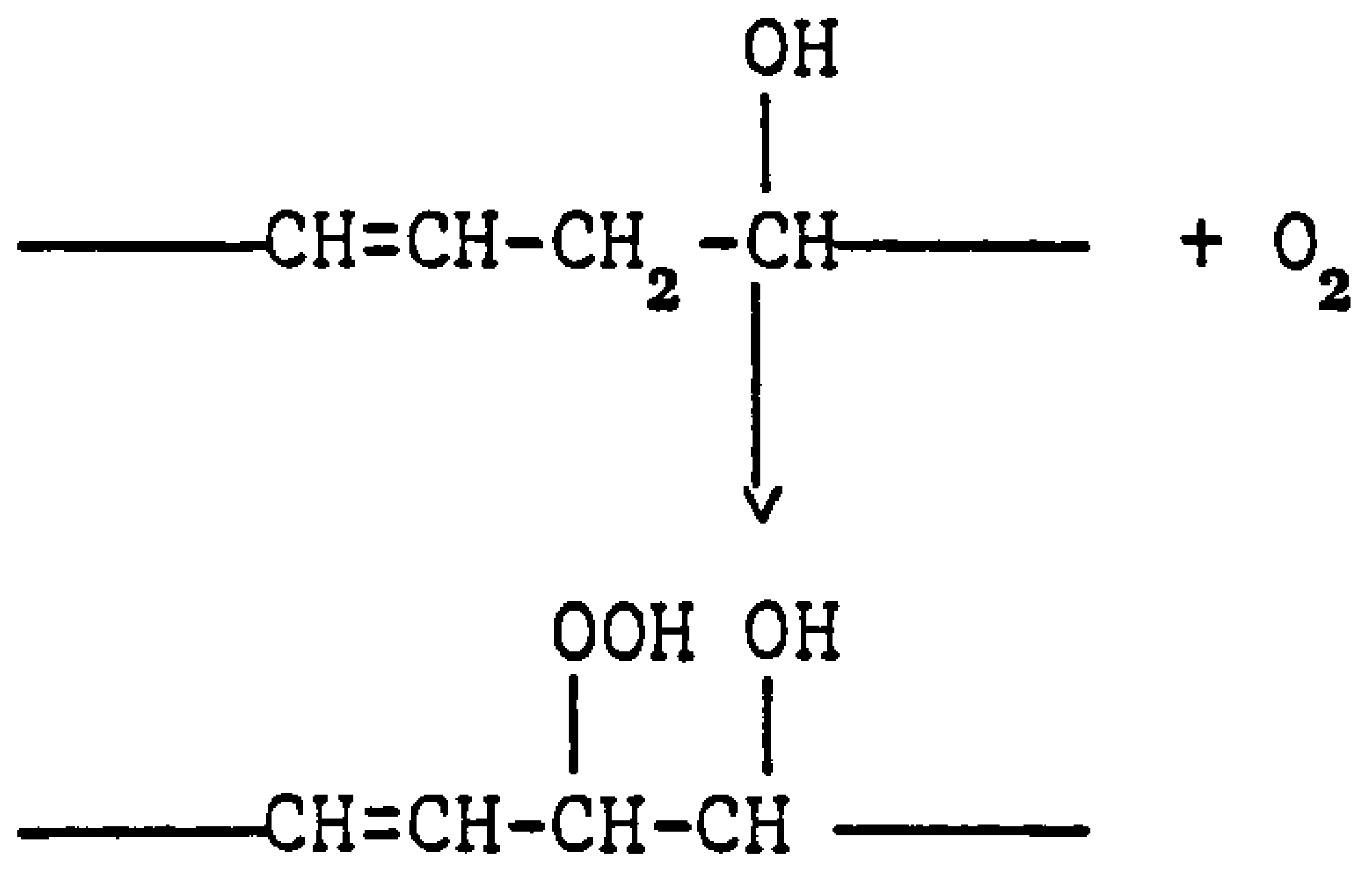
These reports portray the significance of the reactivity of α-methylenic carbon atoms in unsaturated compounds which has a possible resemblance of the reaction of oils and fats with oxygen.

Rieche⁽³⁵⁾ postulated that auto-oxidation of drying and semi-drying oils may be due to attack by molecular oxygen at activated methylene groups to form hydro-peroxides.



$$\text{——CH=CH-CH}_2\text{-CH=CH——} + O_2$$
$$\downarrow$$
$$\text{——CH=CH-}\overset{\displaystyle \text{OOH}}{\overset{|}{\text{CH}}}\text{-CH=CH——}$$

and



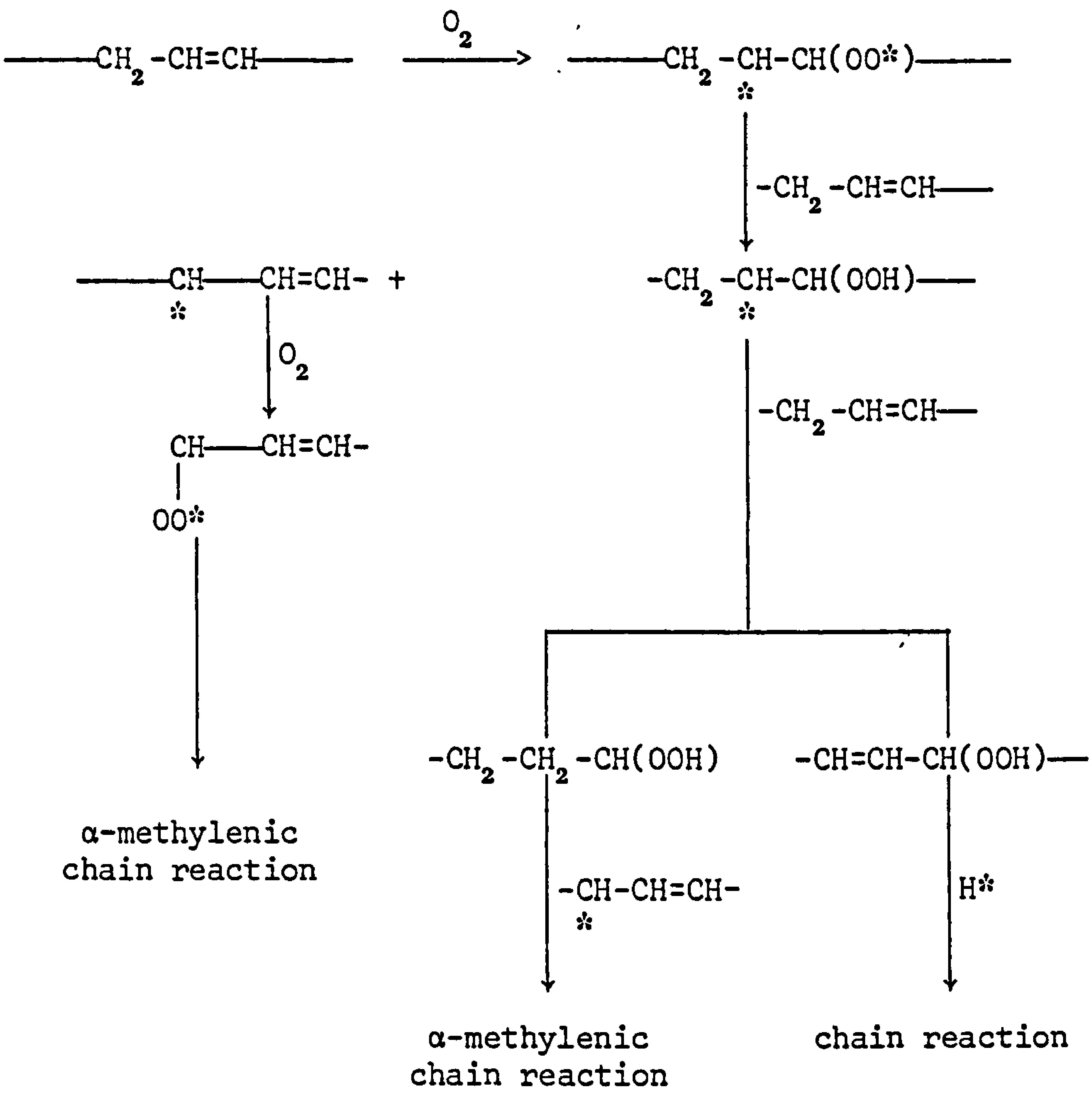
$$\text{—CH=CH–CH}_2\text{–}\overset{\text{OH}}{\overset{|}{\text{CH}}}\text{— + O}_2 \longrightarrow \text{—CH=CH–}\overset{\text{OOH}}{\overset{|}{\text{CH}}}\text{–}\overset{\text{OH}}{\overset{|}{\text{CH}}}\text{—}$$

Farmer et al.(36)-(39) have it that auto-oxidation processes of unconjugated olefinic compounds occur by a chain reaction. A molecule of oxygen is added to the carbon atom linked to the double bond to form a hydroperoxide with an intact double bond.

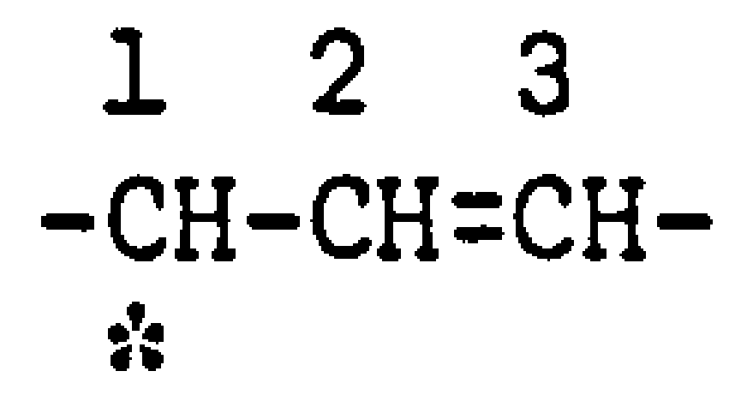
$$\text{—CH}_2\text{—CH=CH— + O}_2 \longrightarrow \text{—CH(OOH)—CH=CH—}$$

Although the presence of hydro- and dihydro-peroxides have been confirmed by workers like Farmer and Sutton(40), it is believed that other autoxidation products are also formed; a postulation which has been confirmed by the presence of other products during polarographic examination of methyl oleate(41)-(48) and by the accounts given by other early researchers as can be seen on pp.43-48.

The lack of a satisfactory source of energy required for the rupture of an α-methylenic carbon-hydrogen bond (80.3 k cal/mole) has led various workers to believe that the initial reaction between molecular oxygen and a mono-unsaturated fatty acid was an attack at the double bond. This addition reaction, while suggesting the formation of a free radical mechanism with subsequent rearrangement and further reaction, indicates that the initial point of oxidative attack is at the double bond and not at the α-methylenic group(47)-(51).

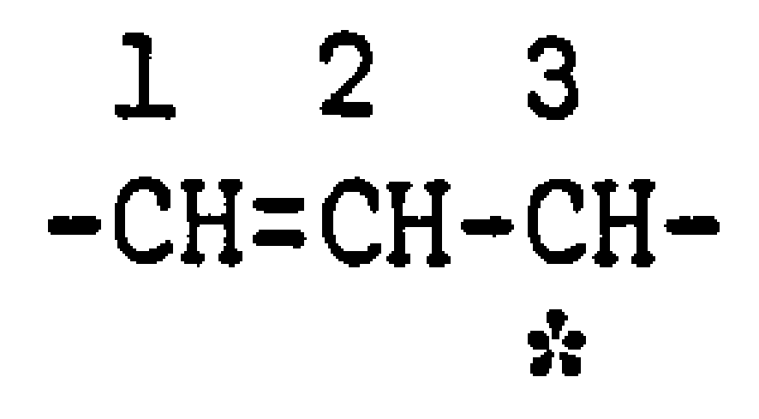


In the free radical three-carbon system, however, tautomerism could occur;



$\underset{*}{\overset{1}{-CH}}-\overset{2}{CH}=\overset{3}{CH}-$

and



$-\overset{1}{CH}=\overset{2}{CH}-\underset{*}{\overset{3}{CH}}-$

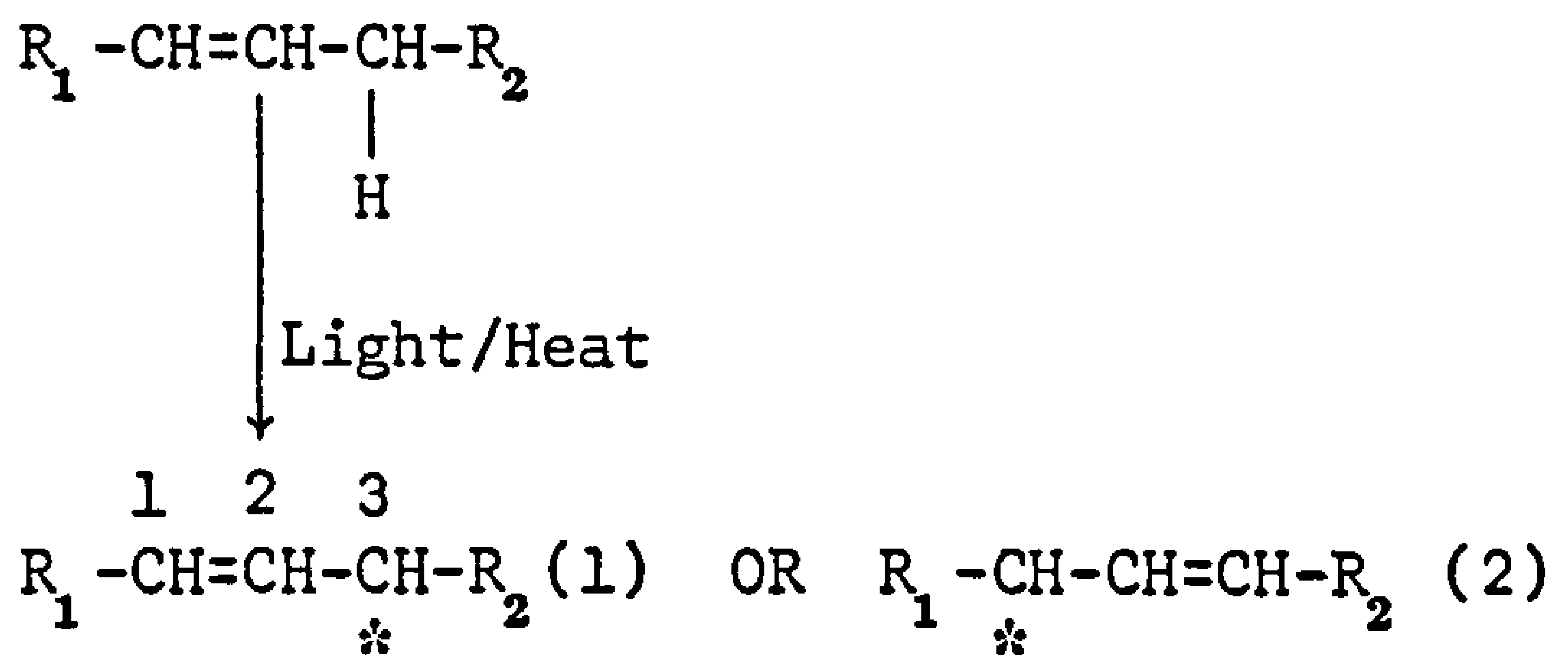
(A)

(B)

With the incorporation of a molecule of oxygen and an atom of hydrogen in the system, there arises an approximately equal tendency for the hydroperoxide group to appear at positions 1 or 3. Some of the double bonds are thus fixed in the 2 : 3-positions and the remainder at the adjacent pair of carbon atoms(40).

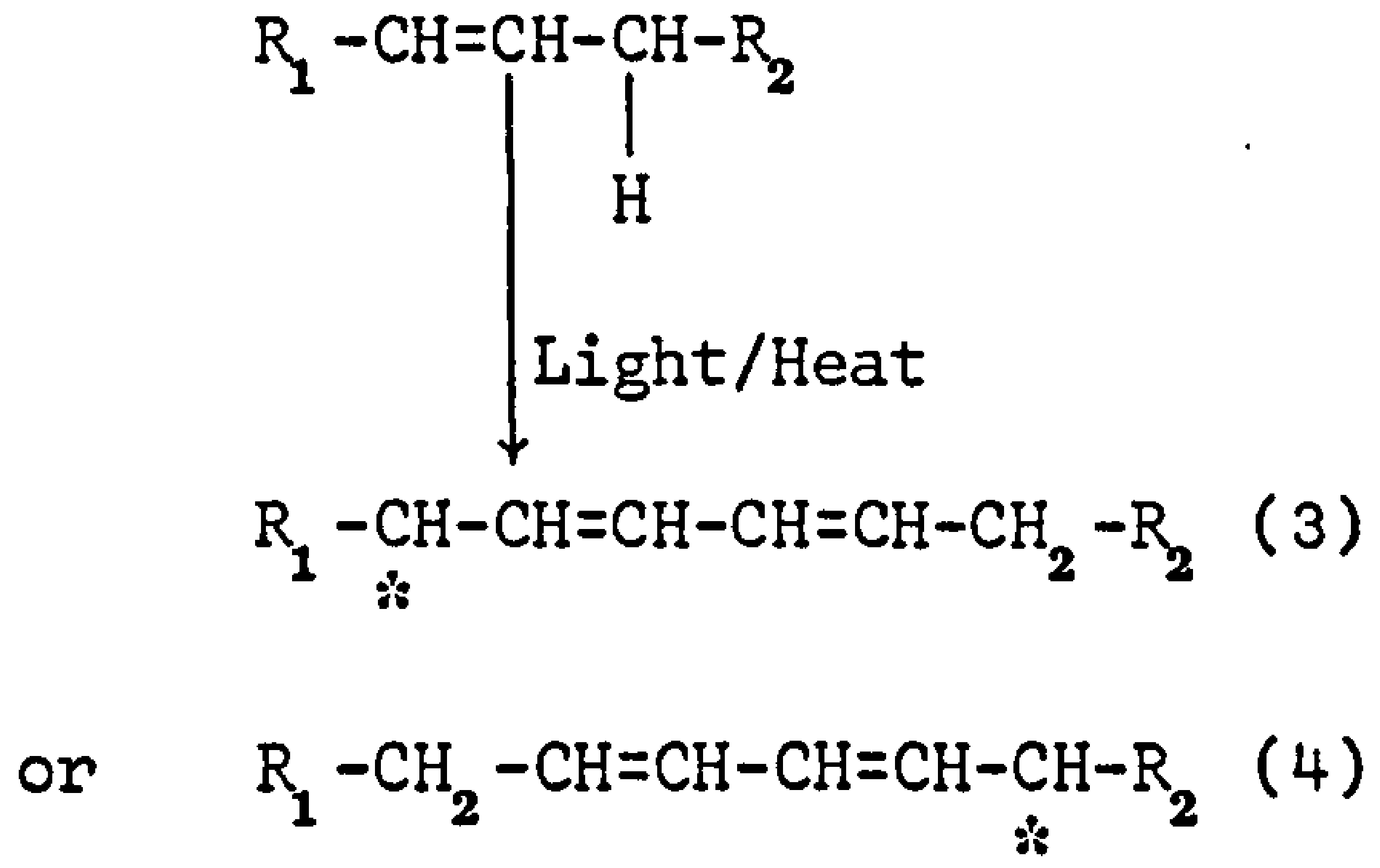
The two end carbon atoms are equally reactive. An explanation involves a knowledge of the relative strengths of the C-H bonds at the ethylene carbon atom (81 k cal/mole) and the methylene carbon

(99 k cal/mole). Dehydrogenation of the unsaturated system generates a resonance stabilised radical with the equivalent structures (A) and (B). The activation energy of the autoxidation reaction is reduced to 80.3 k cal (lower than the average strength of the ethylene C-H bond strength). Thus the C-H bond is more easily split at the α-methylene carbon than at the ethylenic C-H bond. This severance can be carried out thermally or photochemically.



$$R_1\text{-CH=CH-}\underset{\substack{|\\ H}}{\text{CH}}\text{-}R_2 \xrightarrow{\text{Light/Heat}} R_1\text{-}\overset{1}{\text{CH}}\text{=}\overset{2}{\text{CH}}\text{-}\overset{3}{\underset{*}{\text{CH}}}\text{-}R_2\ (1)\quad \text{OR}\quad R_1\text{-}\underset{*}{\text{CH}}\text{-CH=CH-}R_2\ (2)$$

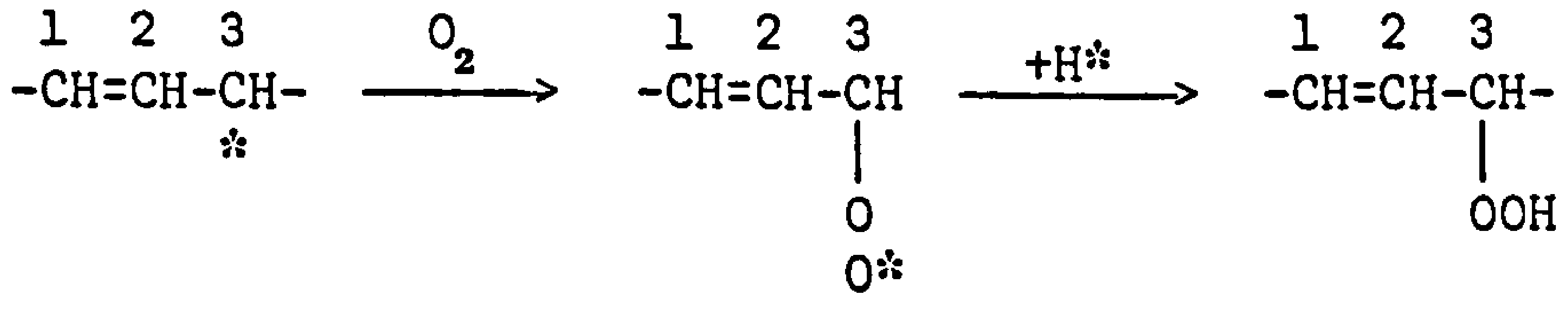
In polyunsaturated systems:



$$R_1\text{-CH=CH-}\underset{\substack{|\\ H}}{\text{CH}}\text{-}R_2 \xrightarrow{\text{Light/Heat}} R_1\text{-}\underset{*}{\text{CH}}\text{-CH=CH-CH=CH-}CH_2\text{-}R_2\ (3)$$

$$\text{or}\quad R_1\text{-}CH_2\text{-CH=CH-CH=CH-}\underset{*}{\text{CH}}\text{-}R_2\ (4)$$

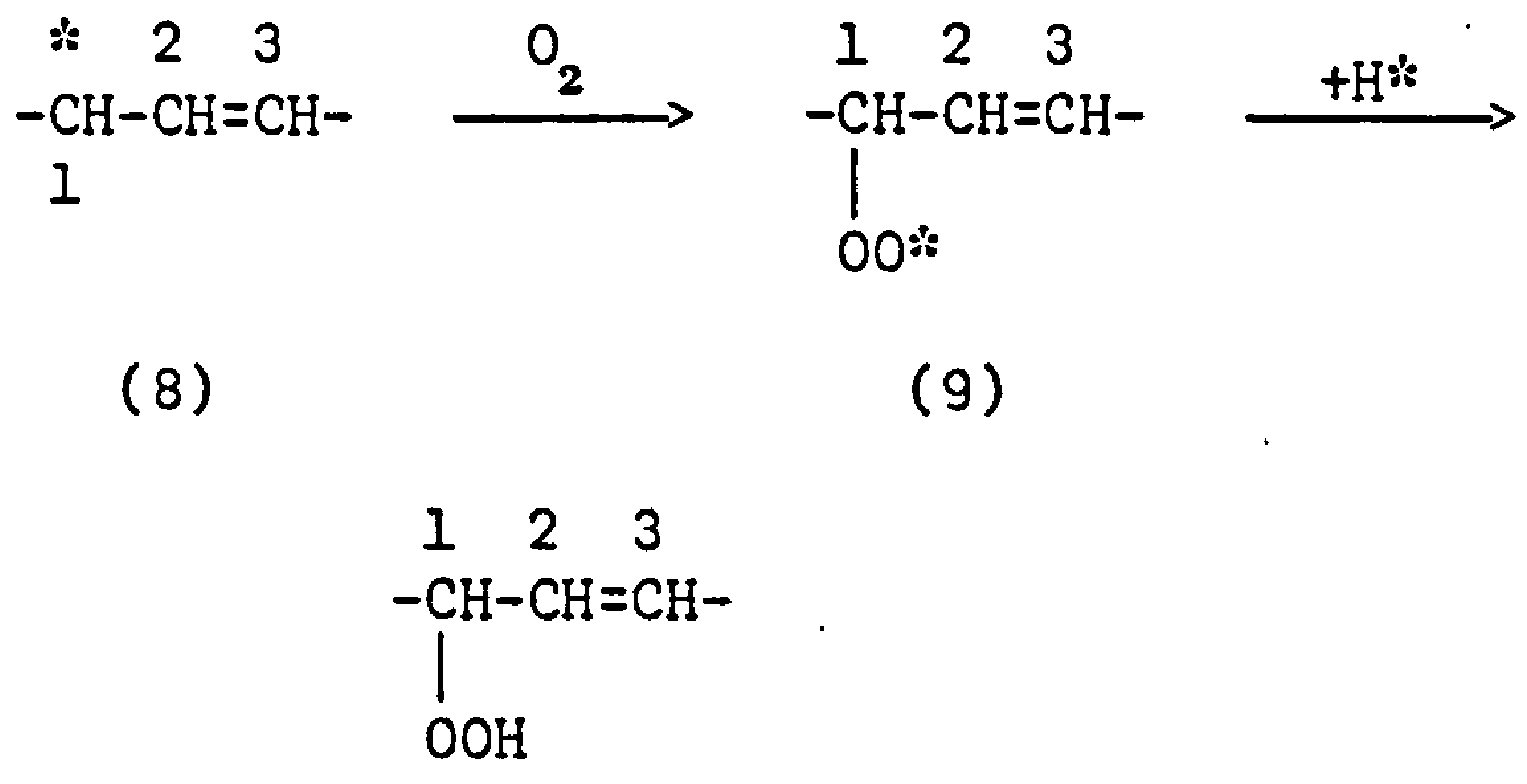
The products (1) - (4) occur in the presence of a molecule of oxygen and an atom of hydrogen (which later detaches from a nearby molecule) to cause the OOH group to appear at position 1 or 3 and the double bonds to appear in an adjacent position.



$$\text{-}\overset{1}{\text{CH}}\text{=}\overset{2}{\text{CH}}\text{-}\overset{3}{\underset{*}{\text{CH}}}\text{-} \xrightarrow{O_2} \text{-}\overset{1}{\text{CH}}\text{=}\overset{2}{\text{CH}}\text{-}\overset{3}{\underset{\substack{|\\ O\\ O^*}}{\text{CH}}} \xrightarrow{+H^*} \text{-}\overset{1}{\text{CH}}\text{=}\overset{2}{\text{CH}}\text{-}\overset{3}{\underset{\substack{|\\ OOH}}{\text{CH}}}\text{-}$$

(5) (6) (7)

or

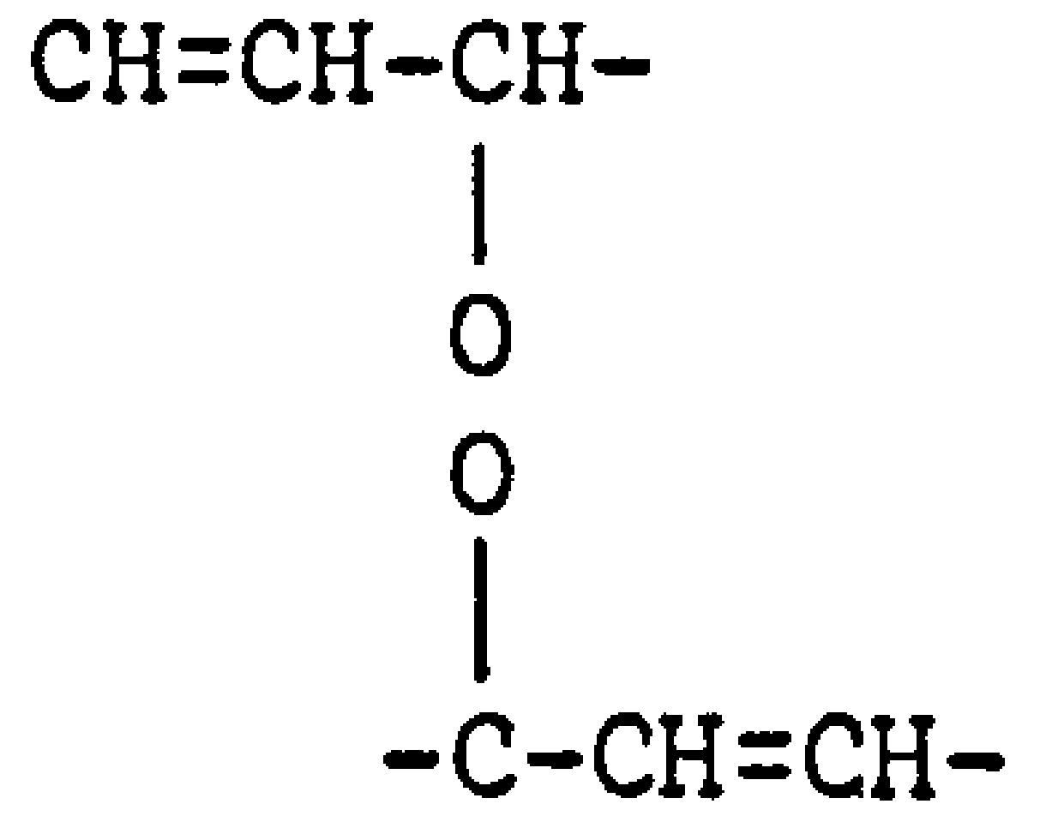


$$\underset{1}{\overset{*}{-CH}}-\overset{2}{C}H=\overset{3}{C}H- \xrightarrow{O_2} \underset{OO^{*}}{\overset{1}{-CH}}-\overset{2}{C}H=\overset{3}{C}H- \xrightarrow{+H^{*}} \underset{OOH}{\overset{1}{-CH}}-\overset{2}{C}H=\overset{3}{C}H-$$

(8) (9)

(10)

In some cases, cross-linking may occur between two radicals:



$$\begin{array}{l} CH=CH-CH- \\ \quad\quad\quad\;\; | \\ \quad\quad\quad\;\; O \\ \quad\quad\quad\;\; O \\ \quad\quad\quad\;\; | \\ \quad\quad\quad -C-CH=CH- \end{array}$$

(11)

It has also been shown that photosensitized oxidation initiates oxidative deterioration of vegetable oils(13),(15),(16). Chlorophyll-like pigments present in oils seem to act as sensitizers by absorbing visible light to produce hydroperoxides in unsaturated fatty acids. Photosensitized oxidations have been categorized into two classes:

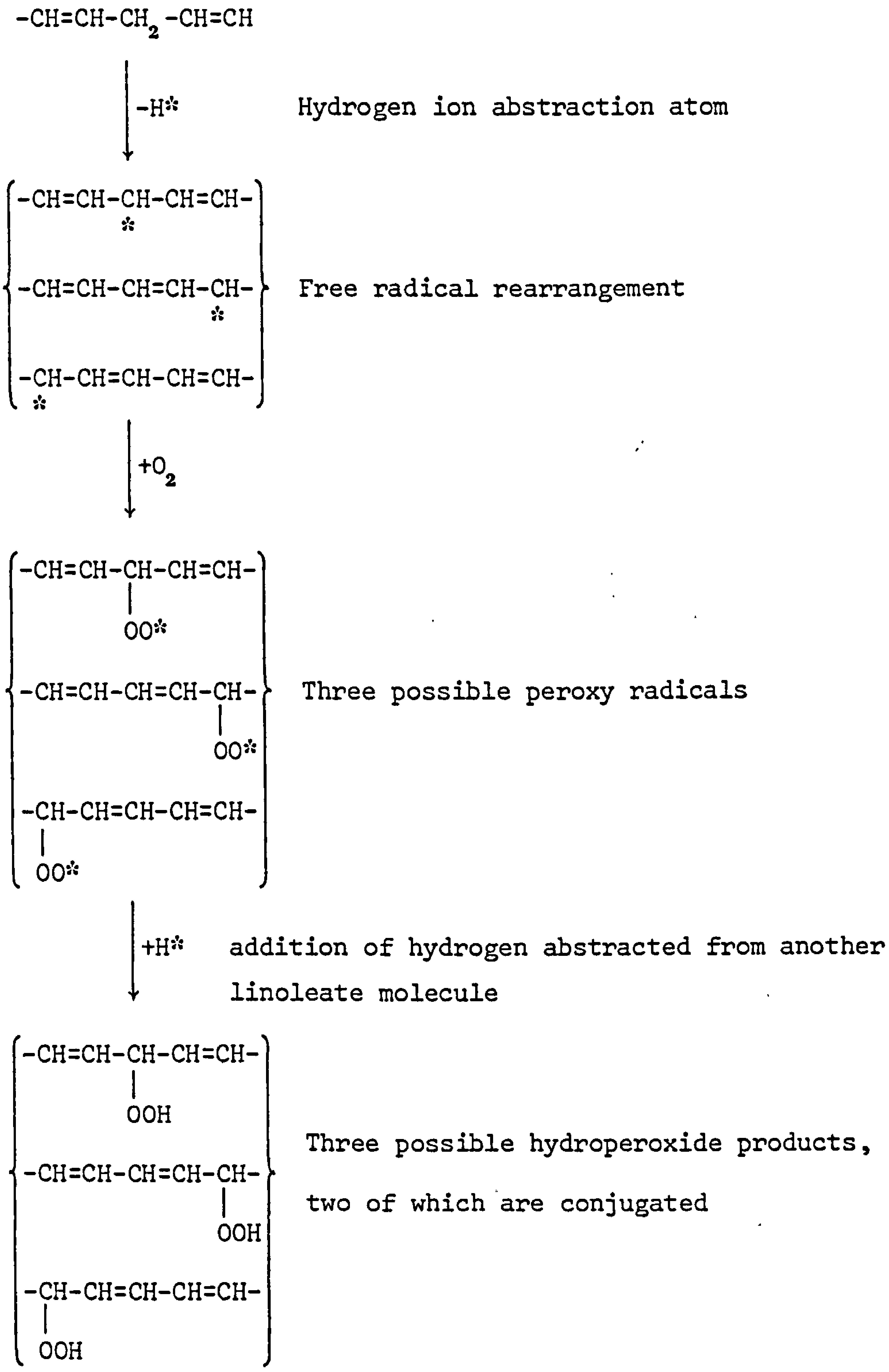
Type I, involves the production of free radicals by interaction of the excited sensitizer with a substrate.

In type II reactions, an excited sensitizer produces singlet oxygen by transferring excitation from the sensitizer to oxygen. This active oxygen molecule reacts with olefinic double bonds to produce hydro-peroxides (52).

There have been reports on the structures of isomeric hydroperoxides of several unsaturated fatty acids on their esters produced by chloropyll sensitized photoxidation(53)-(57).

1.3.3 Autoxidation of Poly-Unsaturated Compounds

Chan(58) studied the photosensitized oxidation of methyl linoleate and methyl oleates using erythrosine and riboflavin as sensitizers. It was demonstrated that both types of pathway could be distinguished by the analysis of hydroperoxide isomers. Terao and Matsushita(59) have clarified that the monohydroperoxide (MHP) of methyl oleate, methyl linoleate and methyl linolenate formed by the type II reaction of photosensitized oxidation, include positional isomers different from those formed by auto-oxidation. However, accurate isomeric compositions of MHP produced by singlet oxygen oxidation are still obscure because of the difficulties associated with the separating and quantification of these isomers. When oils containing linoleic acid or even more unsaturated systems are autooxidized, diene conjugation increases in parallel with the amount of oxygen uptake, and also with peroxide formation in the early stages of oxidation. This can be detected by U.V. light absorption at 2340A^{0}(60). Oxidized linoleate has a principal absorption at 2300-2360 A^{0} due to diene conjugation. A secondary absorption maximum at 2600-2800A^{0} may be due to the presence of small amounts of unsaturated ketones. The principal band is the same for linolenate. However, the greater the degree of unsaturation, the lower the diene conjugation absorption per mole of absorbed oxygen, compared with the absorption due to secondary reaction products. Thus, when methyl linoleate was oxidized, either by autoxidation in the dark at -10^{0}C, under visible or U.V. light or in the presence of a copper catalyst, the products consisted almost entirely of conjugated compounds. In cases where oxidation was stimulated by chlorophyll and irradiation a non-conjugated product was identified. The mechanism of reaction in the case of ethyl linoleate is shown below.



$-CH=CH-CH_2-CH=CH$

$\xrightarrow{-H^{*}}$ Hydrogen ion abstraction atom

$\left\{\begin{matrix} -CH=CH-\overset{}{\underset{*}{CH}}-CH=CH- \\ -CH=CH-CH=CH-\underset{*}{CH}- \\ -\underset{*}{CH}-CH=CH-CH=CH- \end{matrix}\right\}$ Free radical rearrangement

$\xrightarrow{+O_2}$

$\left\{\begin{matrix} -CH=CH-\underset{OO^{*}}{CH}-CH=CH- \\ -CH=CH-CH=CH-\underset{OO^{*}}{CH}- \\ -\underset{OO^{*}}{CH}-CH=CH-CH=CH- \end{matrix}\right\}$ Three possible peroxy radicals

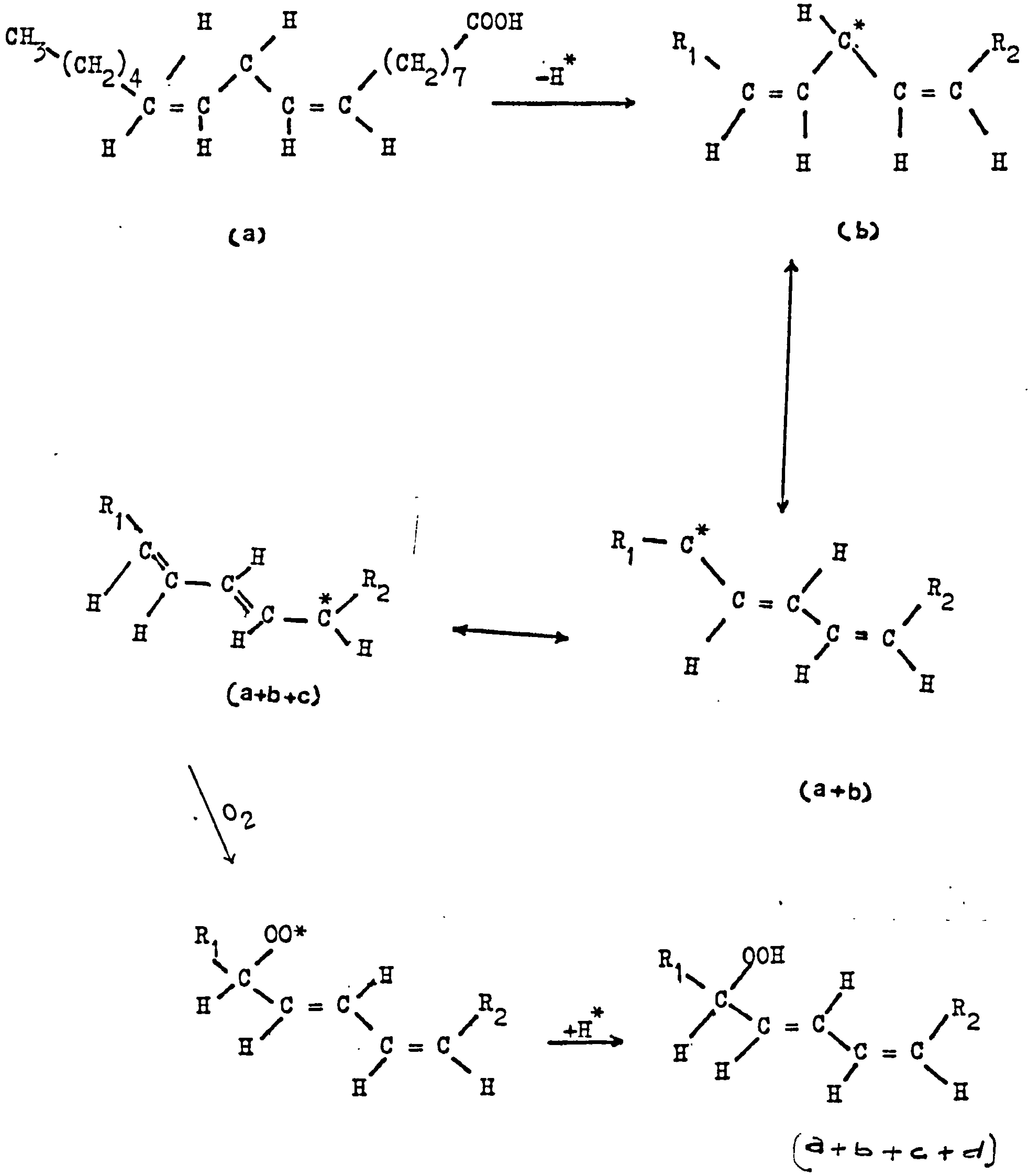
$\xrightarrow{+H^{*}}$ addition of hydrogen abstracted from another linoleate molecule

$\left\{\begin{matrix} -CH=CH-\underset{OOH}{CH}-CH=CH- \\ -CH=CH-CH=CH-\underset{OOH}{CH}- \\ -\underset{OOH}{CH}-CH=CH-CH=CH- \end{matrix}\right\}$ Three possible hydroperoxide products, two of which are conjugated

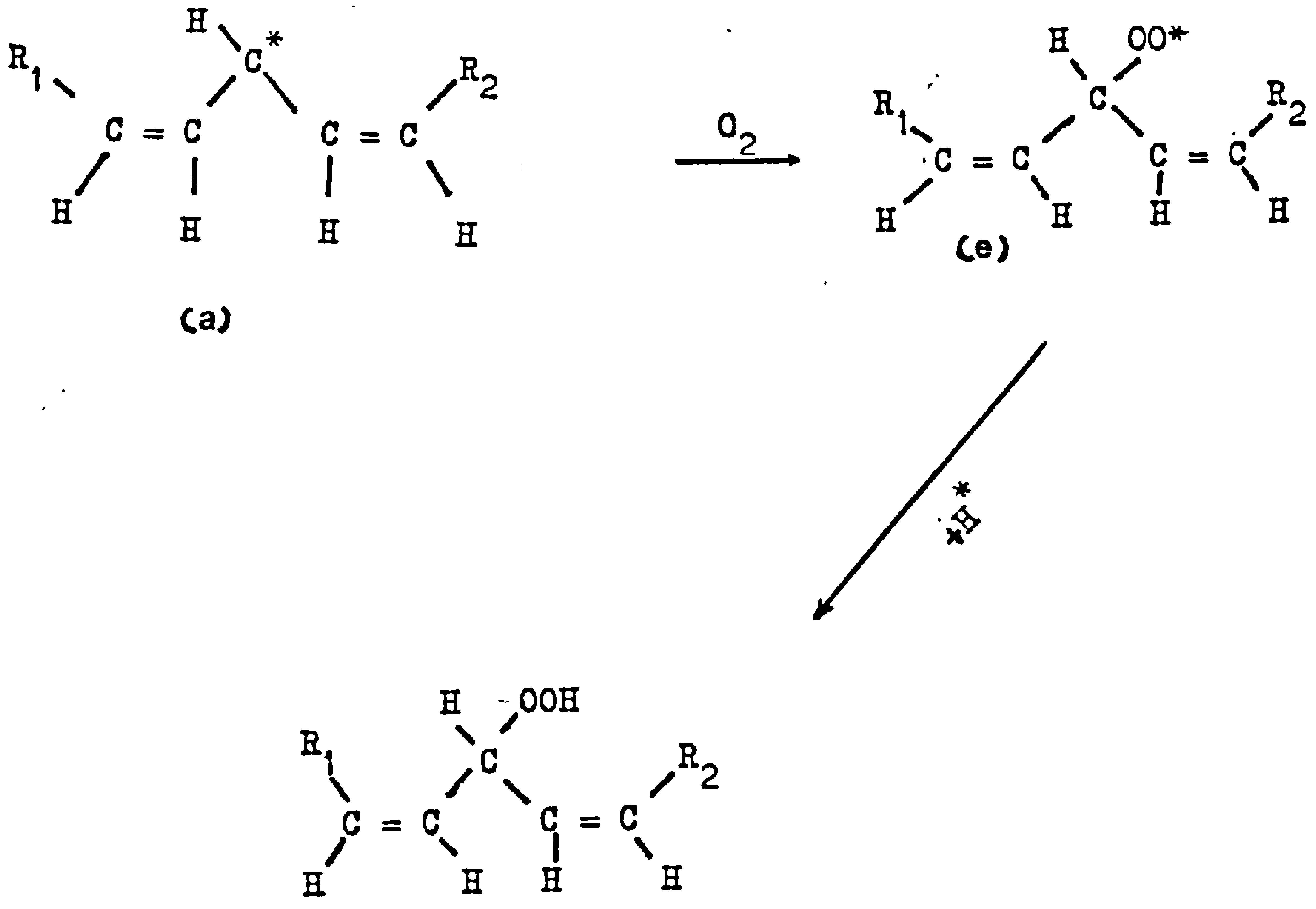
In this experiment, the monohydroperoxide which was formed was detected by U.V. absorption measurements to contain about 70% of conjugated diene isomers(40).

The hydroperoxide theory as applied in the study of non-volatile and volatile compounds of oils, fatty acids and olefinic hydrocarbons has been confirmed by investigators such as Merit et al.(61), Horvat et al.(62),(63) and Forss et al.(64). Normal alkanes, branched or normal alkenes, alcohols, ketones and aldehydes were among the volatile compounds identified by them. A more detailed account will be given under Secondary Products of Autoxidation.

Holman et al. have proposed a simplified mechanism for the autoxidation of linoleic acids or methyl linoleates(65).

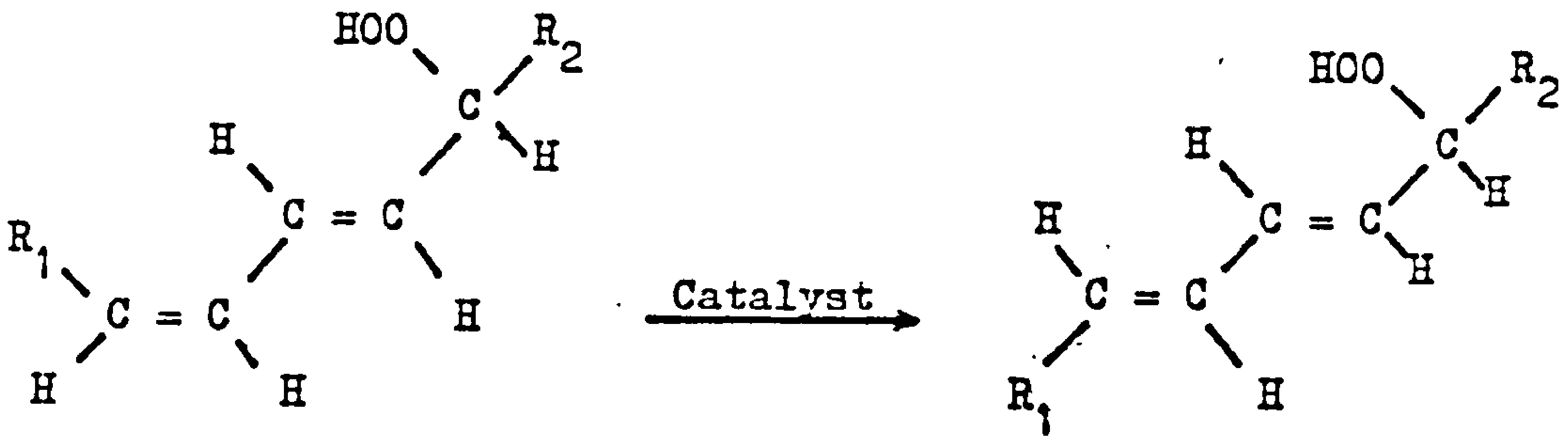


Linoleate (a) loses a hydrogen atom to a free radical and itself becomes a free radical (b) - a resonance hybrid with the structure (a + b). Oxygen adds to the resonating radical, predominantly at the ends of the resonating system to yield two types of hydroperoxy radicals (a + b + c). These radicals accept hydrogen atoms from other linoleate molecules to become isomeric conjugated cis, trans hydroperoxides (a + b + c + d) to complete the cycle.



An oxygen molecule could add to the intermediate form of the free radical (e) to yield non-conjugated peroxides.

The conjugated cis, trans linoleate peroxide may be isomerized to a trans, trans form.



(trans)

(cis)

Numerous possible structures for positional and geometrical isomers in compounds containing two or three double bonds exist. Bolland and Koch[66] have postulated 67% conjugation in the auto-oxidation of ethyl linoleate with the following isomeric forms:-

$R_1\underset{*}{CH}\text{-}CH{=}CH\text{-}CH{=}CH\text{-}R_2$ (1)

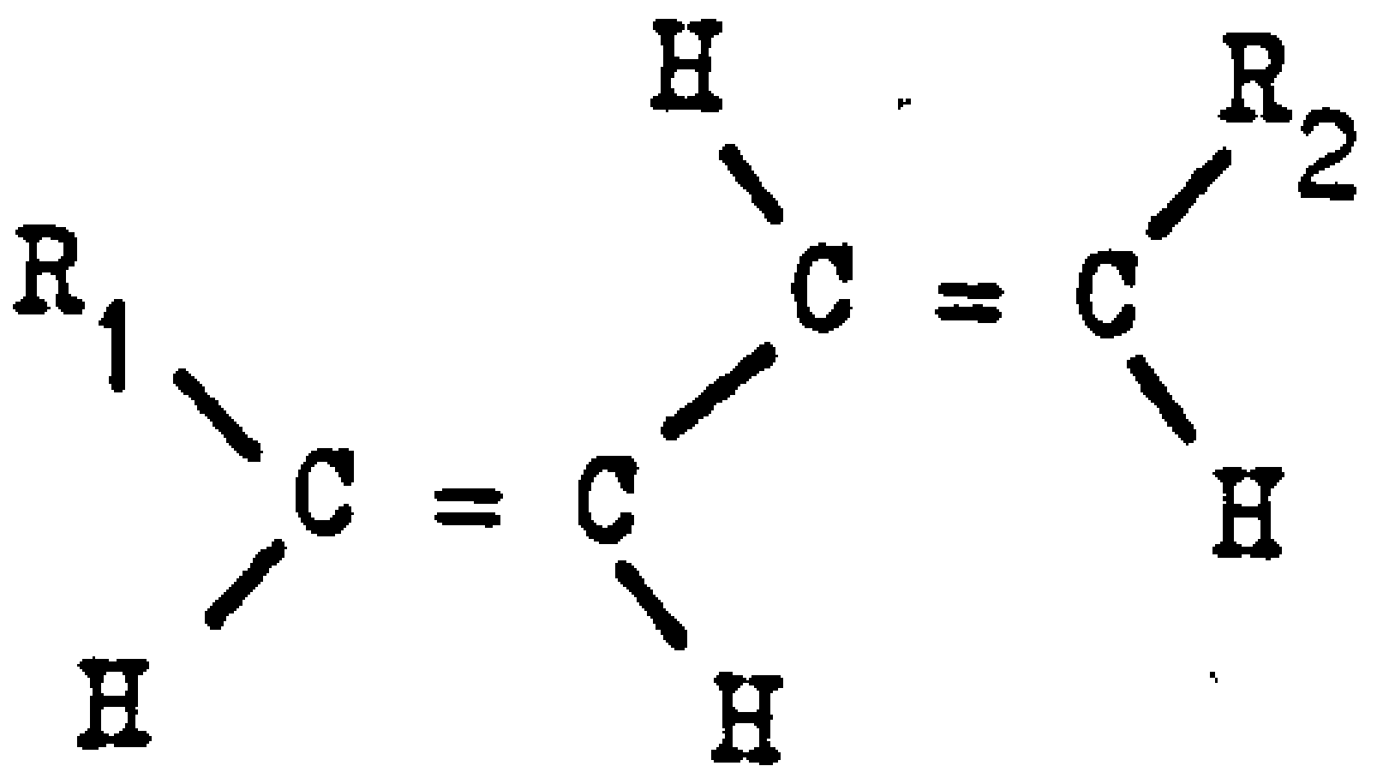
$R_1 CH{=}CH\text{-}\underset{*}{CH}\text{-}CH{=}CH\text{-}R_2$ (2)

$R_1 CH{=}CH\text{-}CH{=}CH\text{-}\underset{*}{CH}\text{-}R_2$ (3)

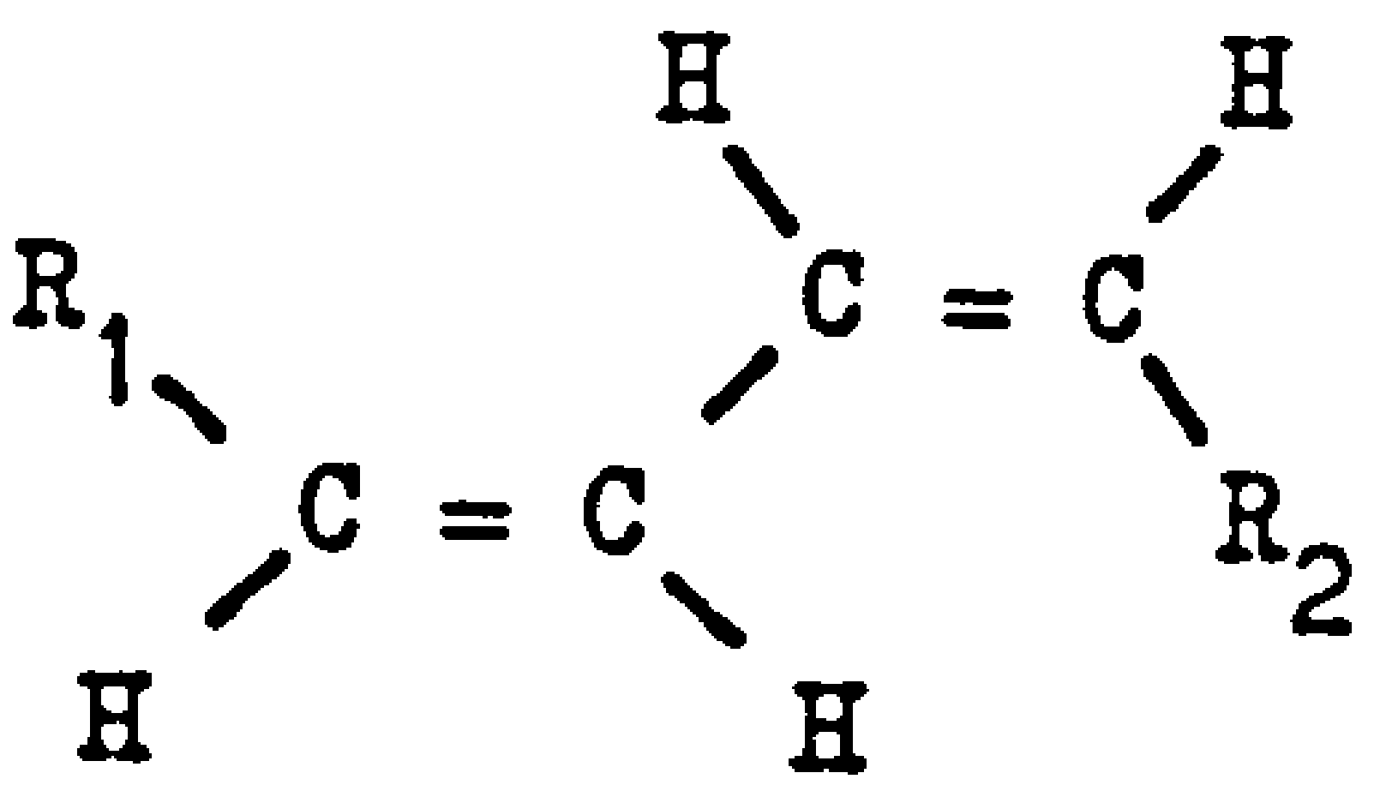
where $R_1 = [CH_3(CH_2)_4\text{-}]$

$R_2 = [\text{-}(CH_2)_7CO_2C_2H_5]$

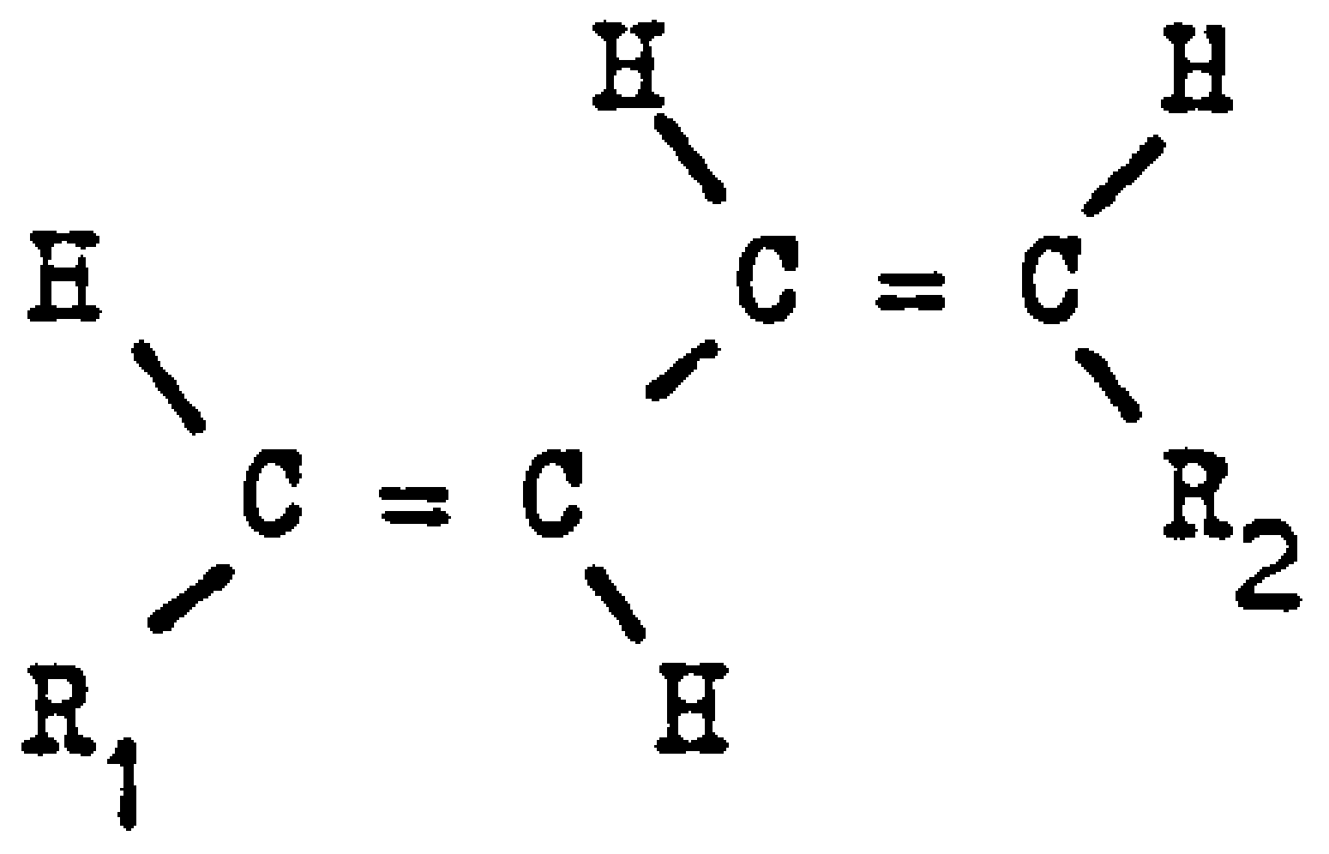
For conjugated systems (1) and (3); four possible arrangements of geometrical isomers exist:-



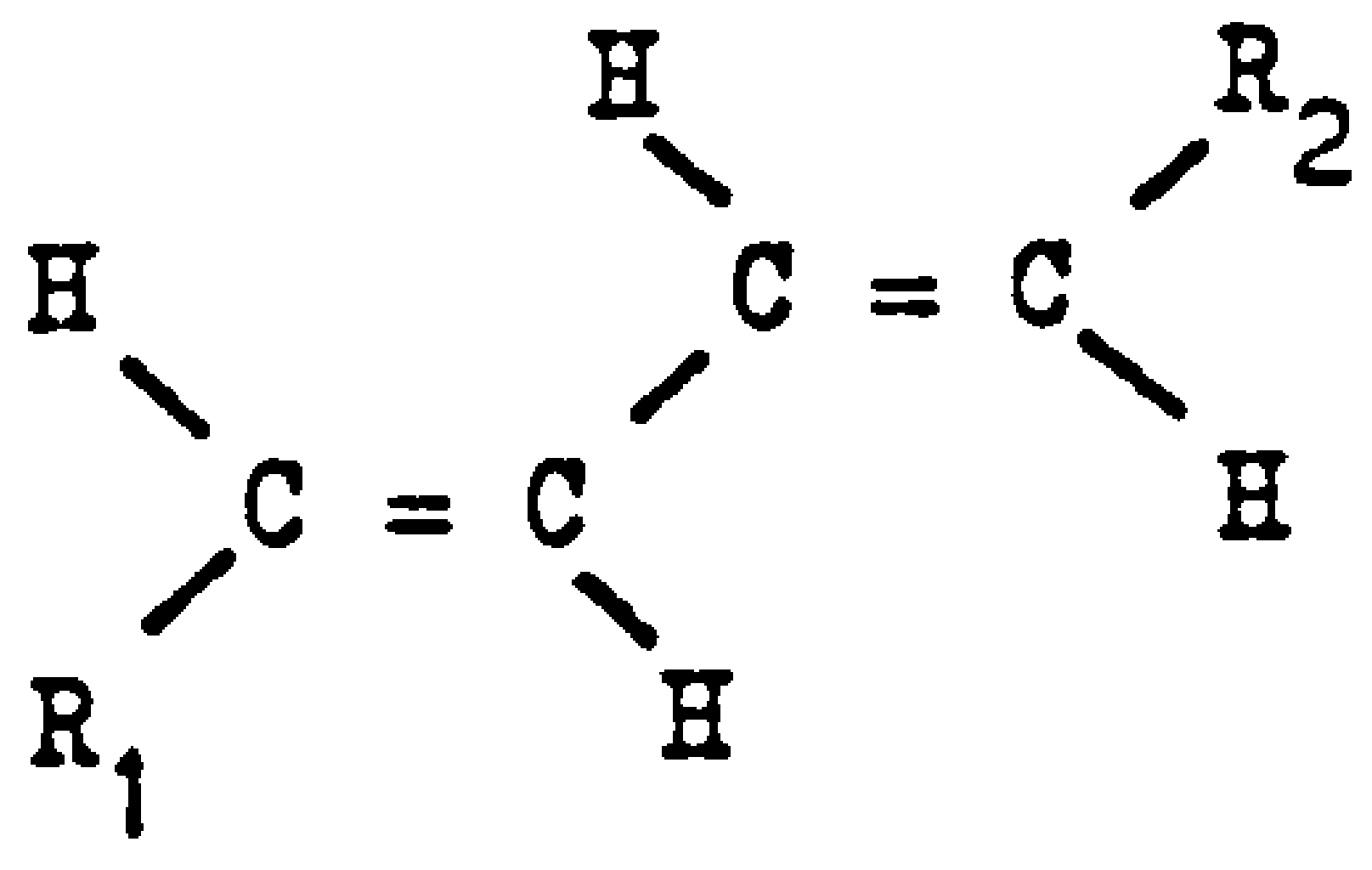
cis,trans



cis,cis



trans, cis



trans, trans

Linolenic acid for example can exist in eight geometrical isomers:

(1)	cis, cis, cis	(5)	cis, trans, trans
(2)	cis, cis, trans	(6)	trans, trans, trans
(3)	cis, trans, cis	(7)	trans, trans, cis
(4)	trans, cis, cis	(8)	trans, cis, trans

A considerable number of isomers are involved in the drying process of oils. A clear understanding of the chemistry of the drying oil phenomena is made even more complex by these isomers. Whether steric isomers can improve or reduce the reactivity in autoxidation processes cannot be said with confidence. However, one example does exist. Sbornik Khim(67) has it that cis bonds (in oleic acid) can be more easily oxidized than trans bonds (in elaidic acid).

Besides oxygen, other compounds such as sulphurous acid or a saturated solution of sodium bisulphite, phosphorous acid, sulphur, selenium, nitrous acid, iodine, nitrogen dioxide (and also U.V. light) are able to alter (isomerise) the unsaturated fatty acids or oils.

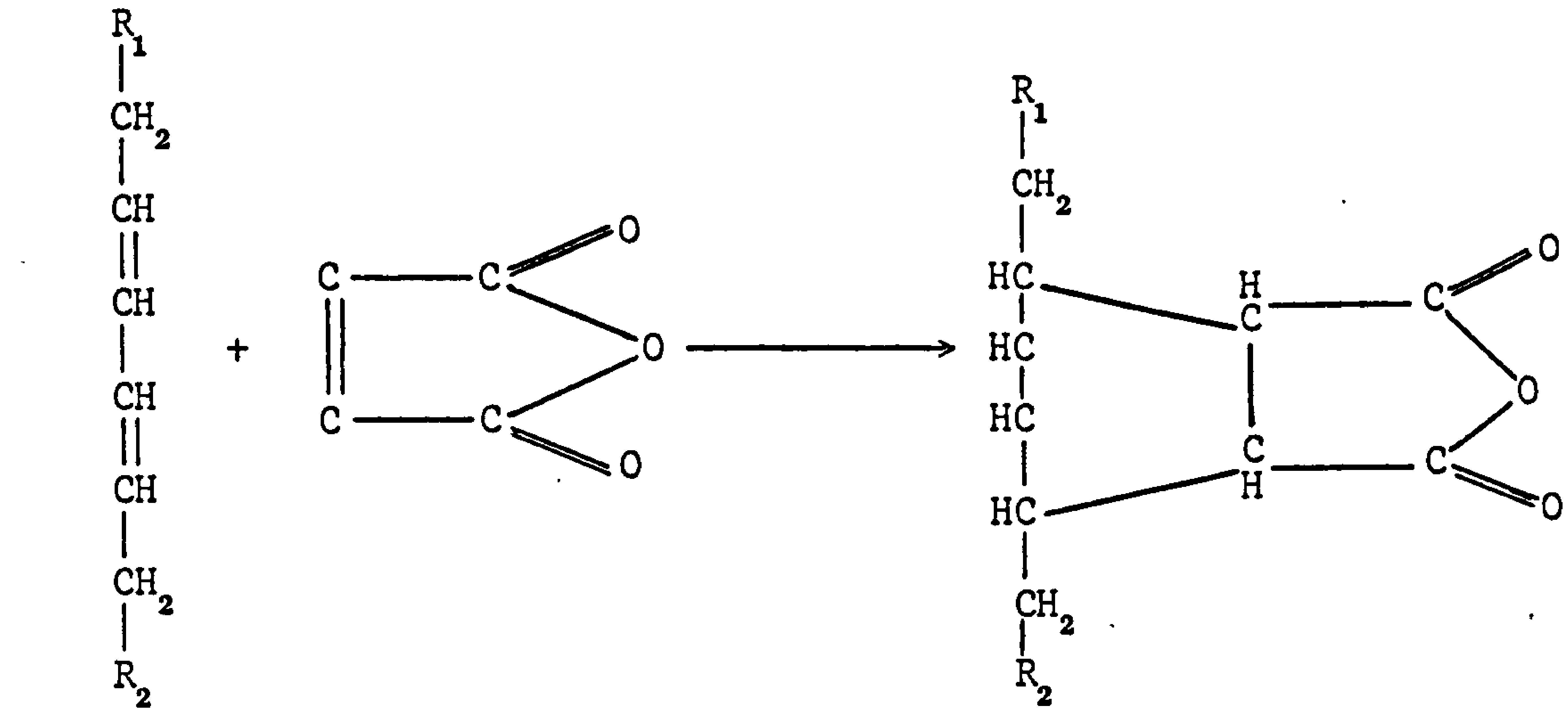
Crecelius(68) et al used alkaline compounds for catalysing the shift of the double bond. Wexler(69), in an attempt to explain the mechanism of the shift of the double bond in the presence of alkali has used an ionic intermediate involving the abstraction of a proton. This is shown schematically in the following equation:

$$\begin{array}{l}
R_1\,CH{=}CH{-}CH_2\,CH{=}CHR_2 \;+\; \bar{O}H \\[1ex]
R_1\,CH{=}CHC\bar{H}{-}CH{=}CH{-}R_2 \;+\; H_2O \\
\qquad\qquad \updownarrow \\
R_1\,CH{=}CHCH{=}CH{-}\bar{C}HR_2 \\
\qquad\qquad \updownarrow +H+ \\
R_1\,CH{=}CHCH{=}CH{-}CH_2\,R_2
\end{array}$$

Recently, Frankel et al.(70) demonstrated that mass chromatographic approach is a powerful method for the analysis of the isomeric composition of MHP of autoxidized fatty acid esters. The mass chromatographic technique has been applied in the determination of the isomeric composition of MHP from the photosensitized oxidation of methyl linoleate by artificial colourings(71). The reaction of the unsaturated acyl group of triglycerides with singlet oxygen to produce hydroperoxides has also been ascertained(72). The homolytic decomposition of hydroperoxides is considered to induce autocatalytic oxidation of oils resulting in polymerization.

1.3.4 Autoxidation of Conjugated Polyunsaturated Compounds

The conjugated polyunsaturated fatty acids such as those present in tung oil, oitica oil, and dehydrated castor oil undergo autoxidation mechanisms quite different from those of the non-conjugated systems and their reaction products are not the same. Morrel and Samuels(73) have described the reaction of maleic anhydride with conjugated oils to be a typical Diels-Alder 1, 4 addition reaction. It is exothermic and takes place at 80-90°C as follows:



R_1, R_2 represent the remaining portions of the oil molecule. A similar reaction has been suggested for the polyunsaturated non-conjugated oils. It is also believed that oxidation occurs by addition of oxygen to the double bond to yield mainly polymeric noncyclic peroxides(73). Methyl 9, 11-octadecadienoate adds oxygen both (9, 10) or (11, 12) and (9, 12) to form low molecular-weight oxygen co-polymers which autocatalyze the oxidation reaction and are stable. Apart from these oxygen-containing polymers, the presence of keto and enol compounds has also been reported to be among the products of autoxidation of these compounds(75).

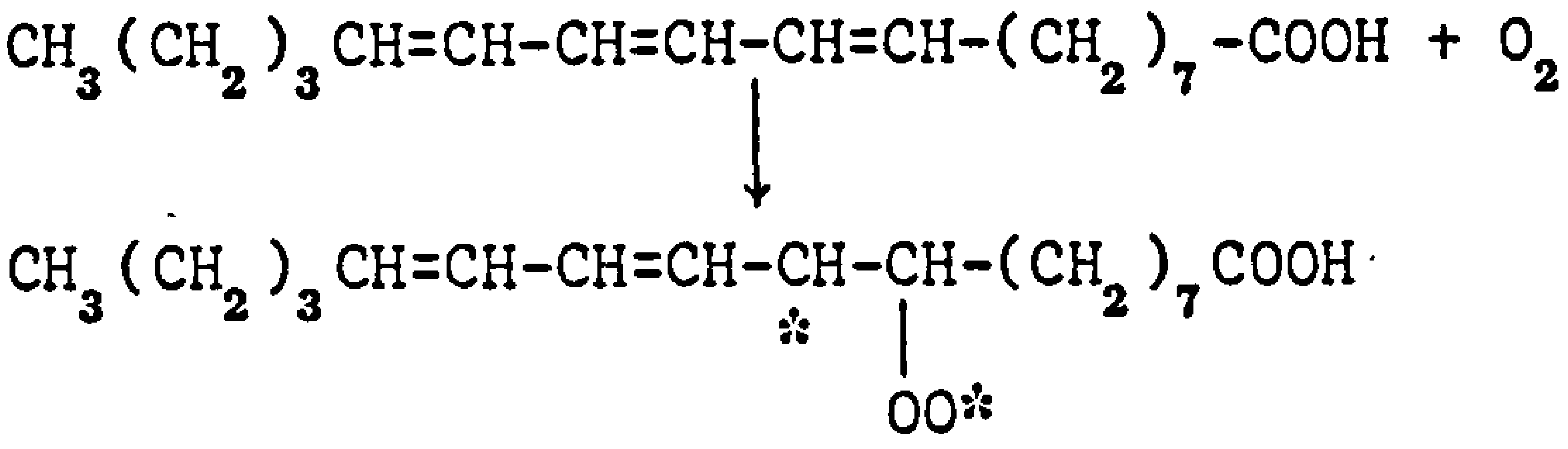
In general, the oxidation of conjugated unsaturated fatty compounds is accompanied with less breakdown and faster oxidation rates when compared with non-conjugated isomers(76),(77). The attack of oxygen on the conjugated system was postulated to be at (1, 2), (1, 4), or (1, 6), to give the following possible partial structures:

$$R-\overset{6}{CH}=\overset{5}{CH}-\overset{4}{CH}=\overset{3}{CH}-\underset{*}{\overset{2}{CH}}-\underset{*}{\overset{1}{CH}}-R$$

$$R-\underset{*}{CH}-CH=CH-\underset{*}{CH}-CH=CH-R$$

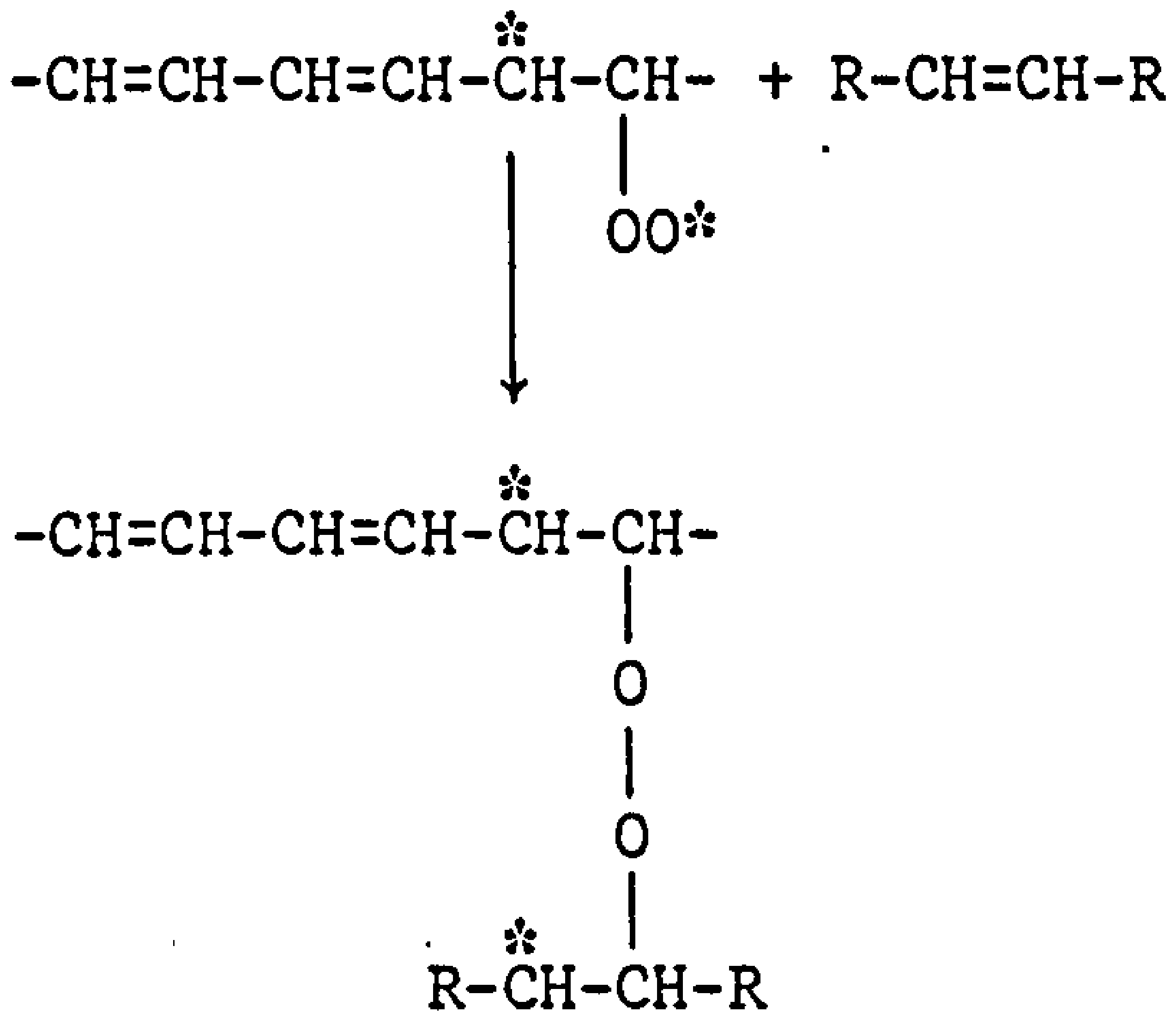
$$R-\underset{*}{CH}-CH=CH-CH=CH-\underset{*}{CH}-R$$

Another possible line of autoxidation of these compounds is as shown below:

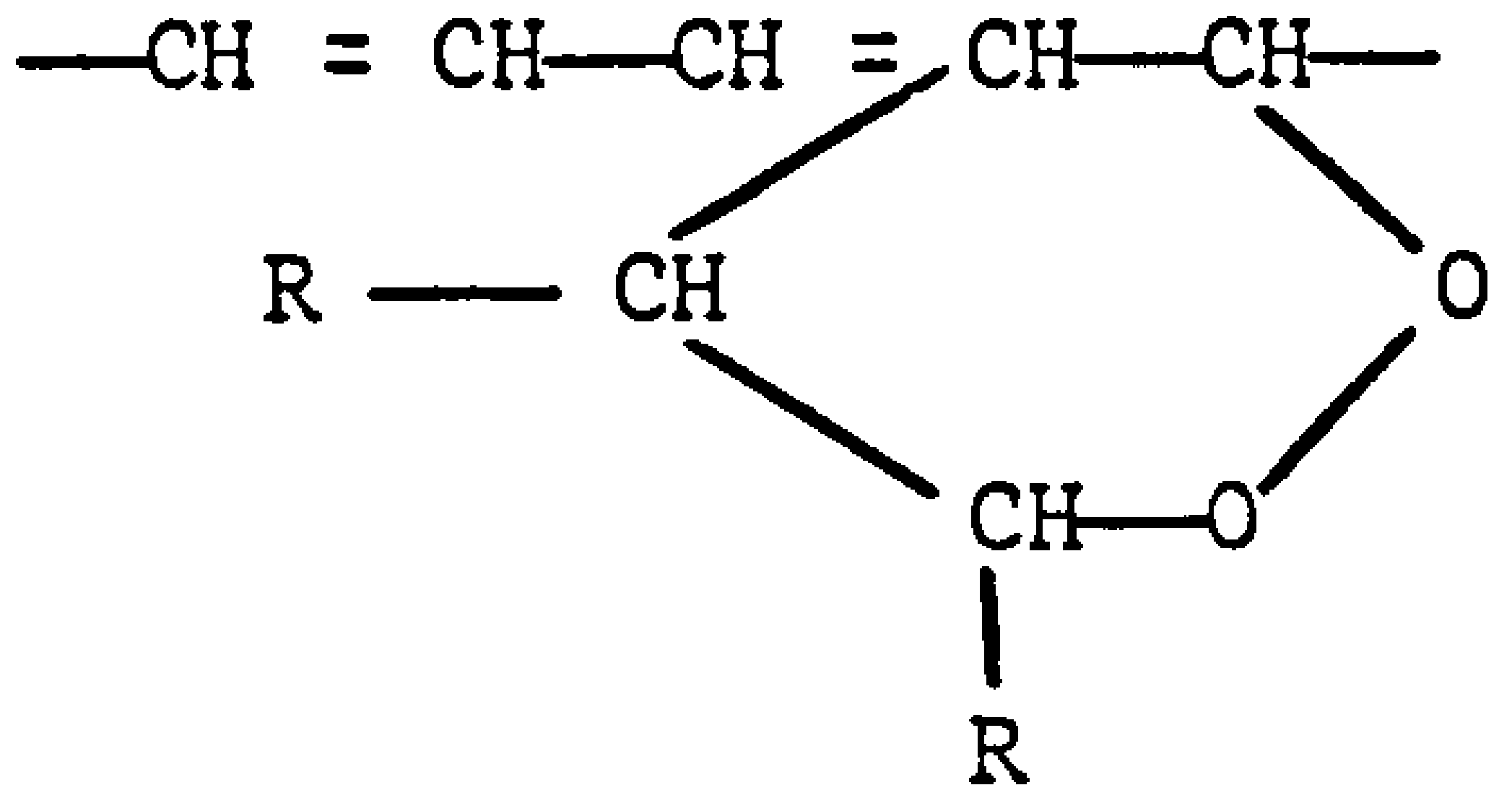


$$CH_3(CH_2)_3CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_7{-}COOH + O_2 \longrightarrow CH_3(CH_2)_3CH{=}CH{-}CH{=}CH{-}\underset{*}{C}H{-}\underset{OO^*}{\underset{|}{C}H}{-}(CH_2)_7COOH$$

This diradical is stable because of the resonance along the unsaturated system and allows further additions at any of the carbons of the triene system. Its reaction with another unsaturated molecule would produce a dimer still possessing free radical centres.



This dimeric diradical can undergo polymerization or stabilize itself internally to form a cyclic peroxide.

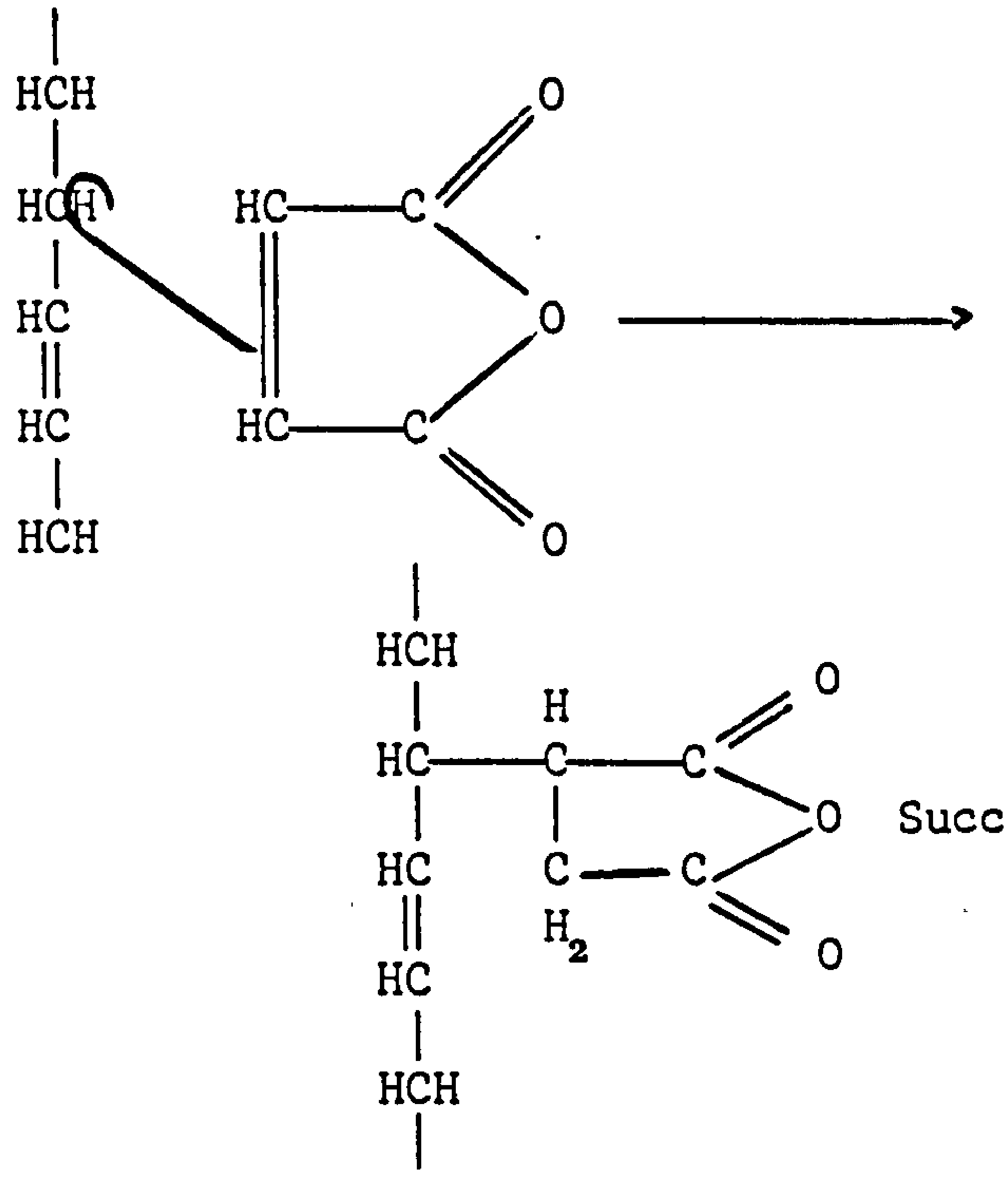


The above mechanism is not acceptable for oxidation of all conjugated polyunsaturated compounds because the formation of some low molecular-weight products identified⁽⁷⁸⁾ following the oxidation of oleostearates cannot be explained by the above reaction.

1.3.5 Other Free Radical Reactions of Non-Conjugated Polyunsaturated Compounds

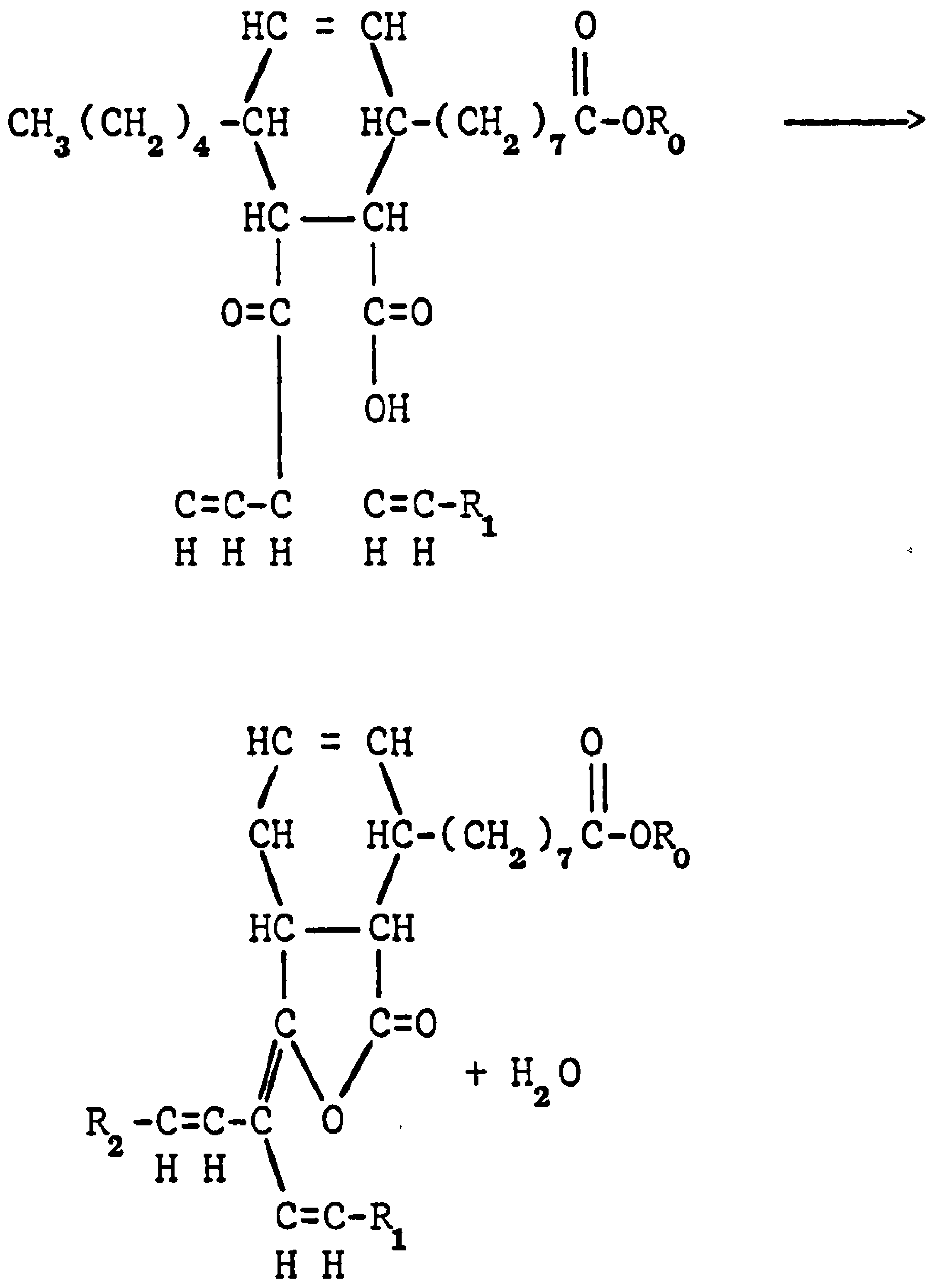
The reaction products of maleic anhydride and fumaric acid with non-conjugated oils are by far the most important to coating technology. This reaction appears to be one of addition-substitution at a methylene group adjacent to the ethylene group. This is the most widely accepted explanation but several other less likely reactions have been suggested. The reaction requires temperatures above 150°C and is not quantitative. The Diels-Alder type addition reaction is quantitative and can be used to determine conjugation as shown by Kaufman , Baltes

(79) techniques. The reaction with trans-ethylene groups is selective and quantitative and this is the basis for the Von Mikusch pandiene number(80). The reaction is as follows:



Succinyl derivative

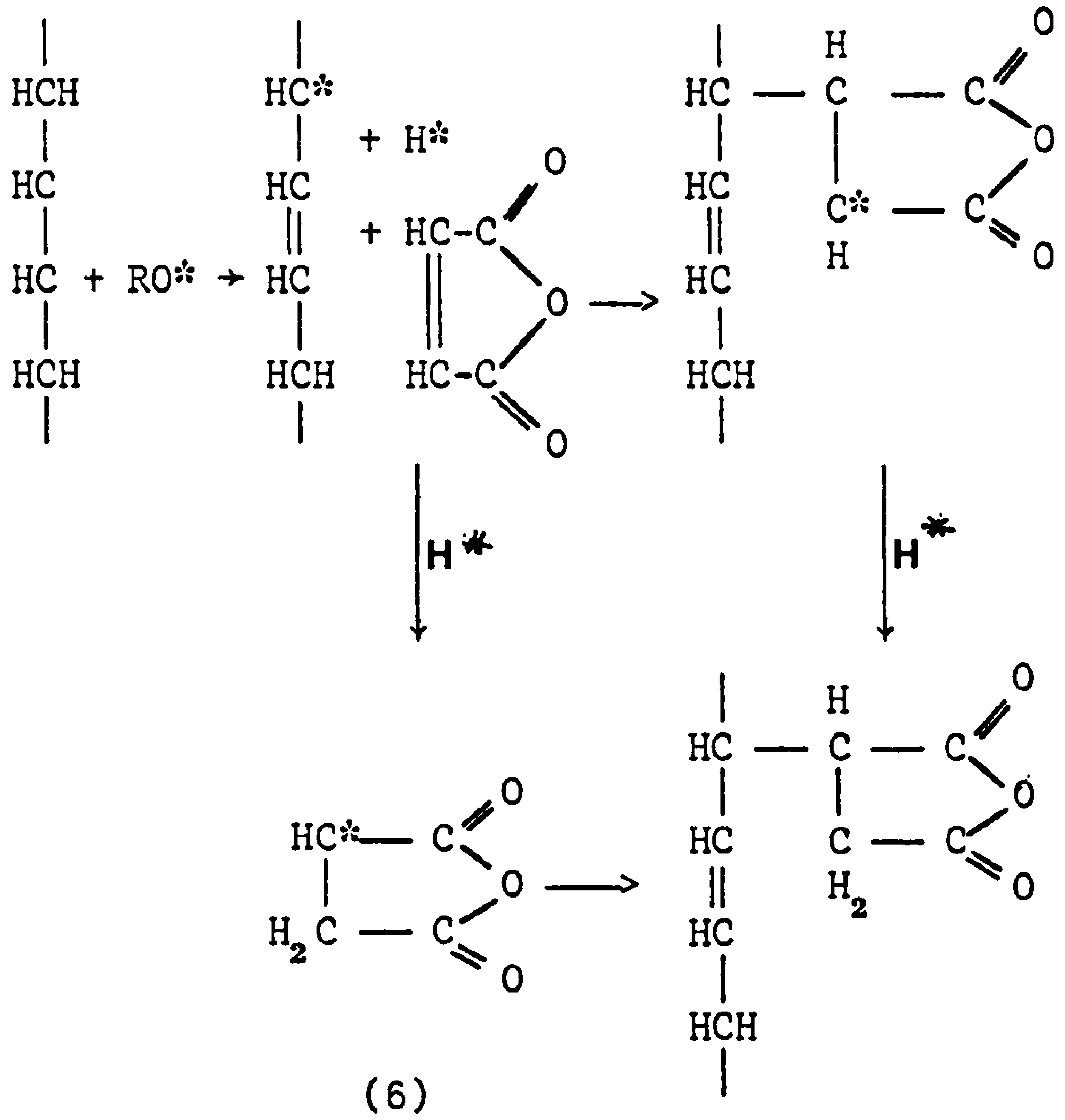
A number of structures for addition products have been proposed(79),(81) but the most generally accepted is that shown above. Plimmer(82) suggested that either the Diels-Alder or Succinyl derivative may react further to form a bridge between two oil molecules, shown in part as follows:



R_0, R_1 and R_2 are portions of the two cross-linked oil molecules. Plimmer's structures seem to be justified by his saponification values. In the case of maleic-containing compositions, good agreement with saponification values is not always obtained. Shaw and Formo(83) showed that butanol gives saponification values which agree with the theoretical estimate but this is not the case with ethanol.

Other reactions and product structures have also been suggested(84). The addition of maleic anhydride to non-conjugated oils may also be catalyzed with peroxides, strong acids, and blown oils(82),(85). The reaction takes place at between 80-90°C. This indicates the possibility of a free-radical mechanism in which the methylene group is activated as follows:

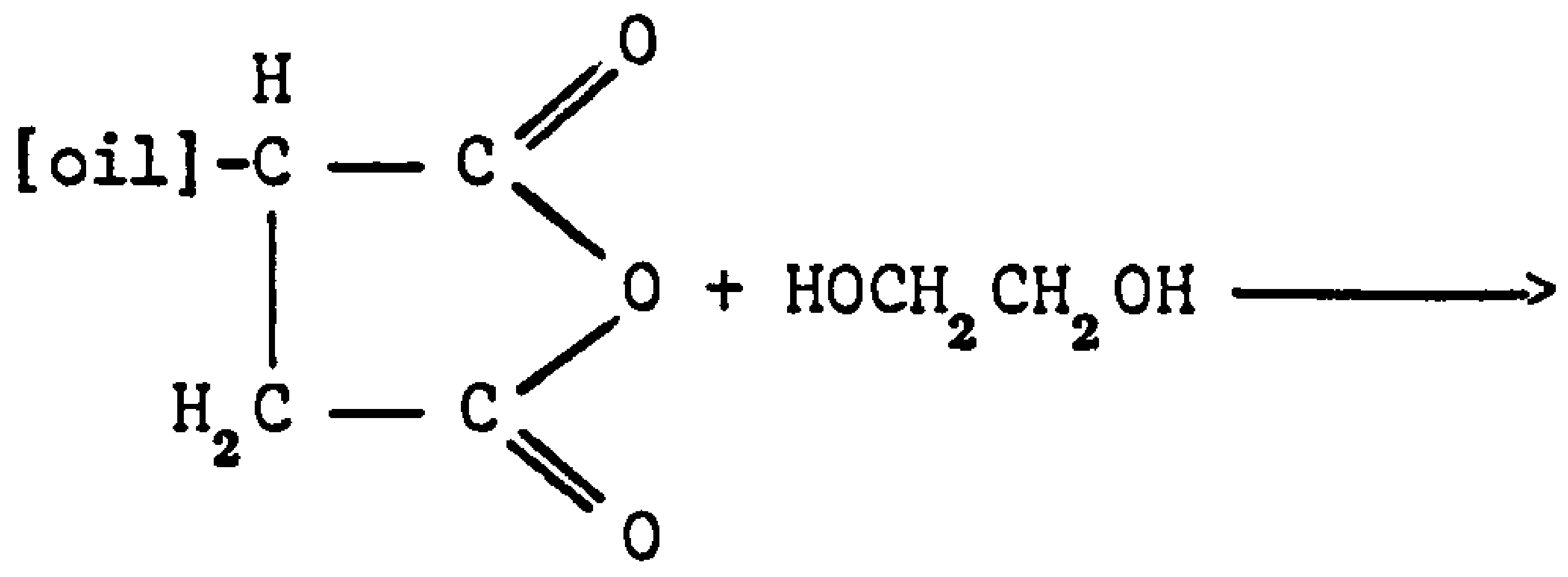
$ROOR \longrightarrow 2RO^*$

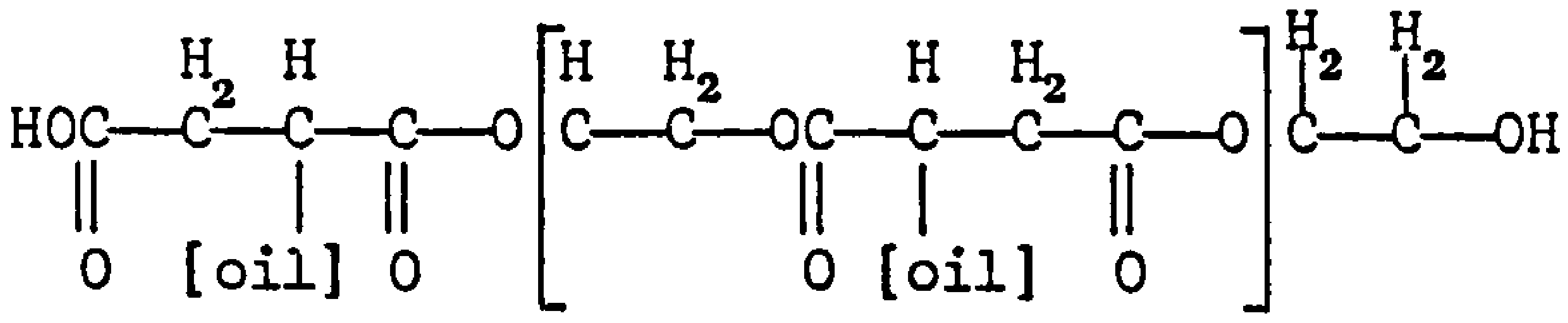


(6)

The physical and chemical constants of the catalyzed products are different from those induced by thermal treatment(86). However, when the catalyzed product is heated to 150°C or more, a change takes place in which the oil acquires the constants and properties of the thermally processed adduct.

The maleic anhydride substitution-addition products are acidic. The early workers considered this a disadvantage. Hence these derivatives were esterified with polyols, such as glycols, and glycerols and later a pentaerythritol. These esters are the most important derivatives of this group. These derivatives are difunctional with respect to acidity. Upon esterification with glycol, they will theoretically form a glycol oil-substituted succinate. This is a two-dimensional chain with oil molecules pendant on the succinyl radical.



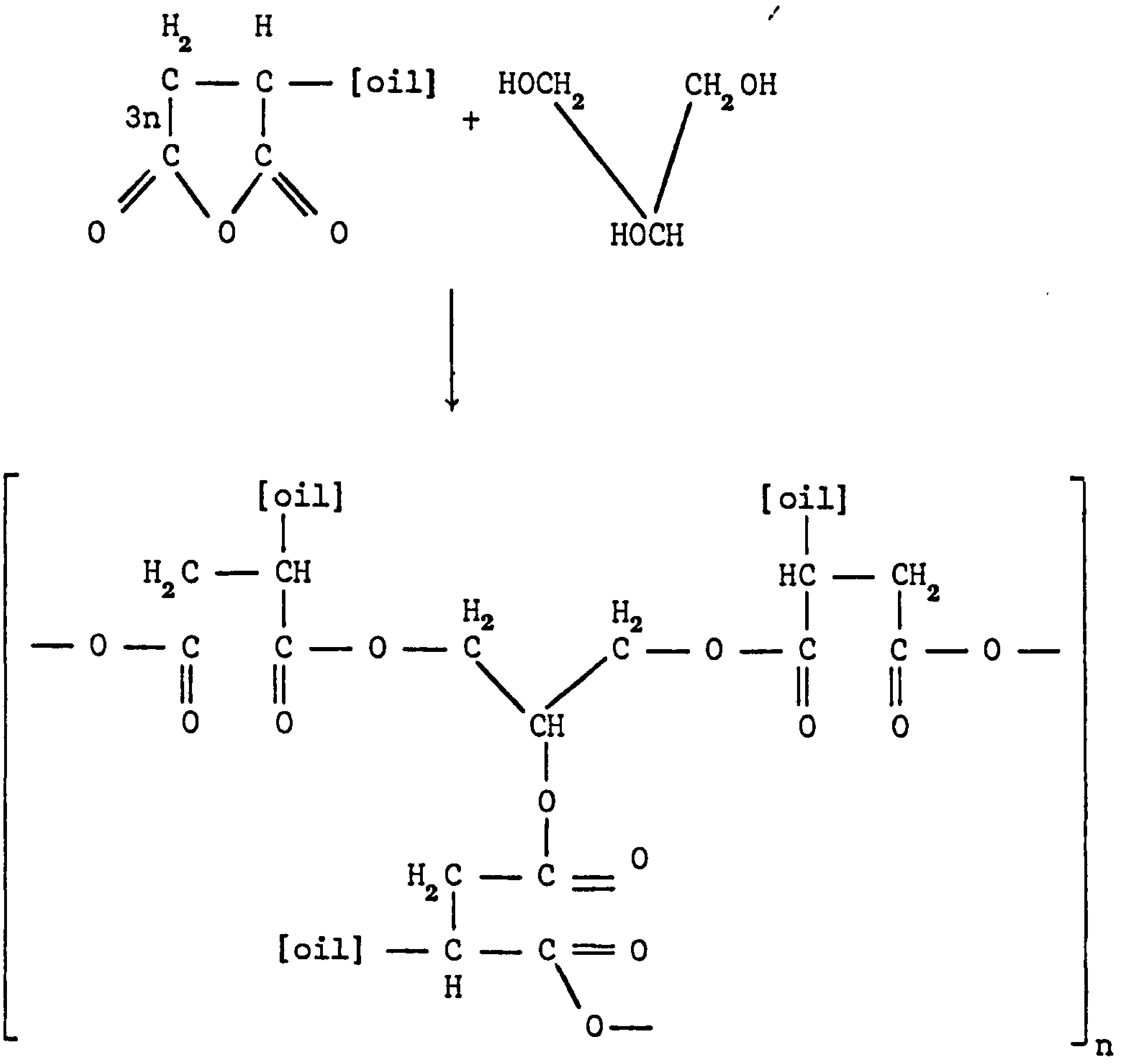


$$\mathrm{HO\underset{\underset{O}{\|}}{C}-\overset{H_2}{C}-\underset{[oil]}{\overset{H}{C}}-\underset{\underset{O}{\|}}{C}-O\left[\overset{H}{C}-\overset{H_2}{C}-O\underset{\underset{O}{\|}}{C}-\underset{[oil]}{\overset{H}{C}}-\overset{H_2}{C}-\underset{\underset{O}{\|}}{C}-O\right]\overset{H_2}{C}-\overset{H_2}{C}-OH}$$

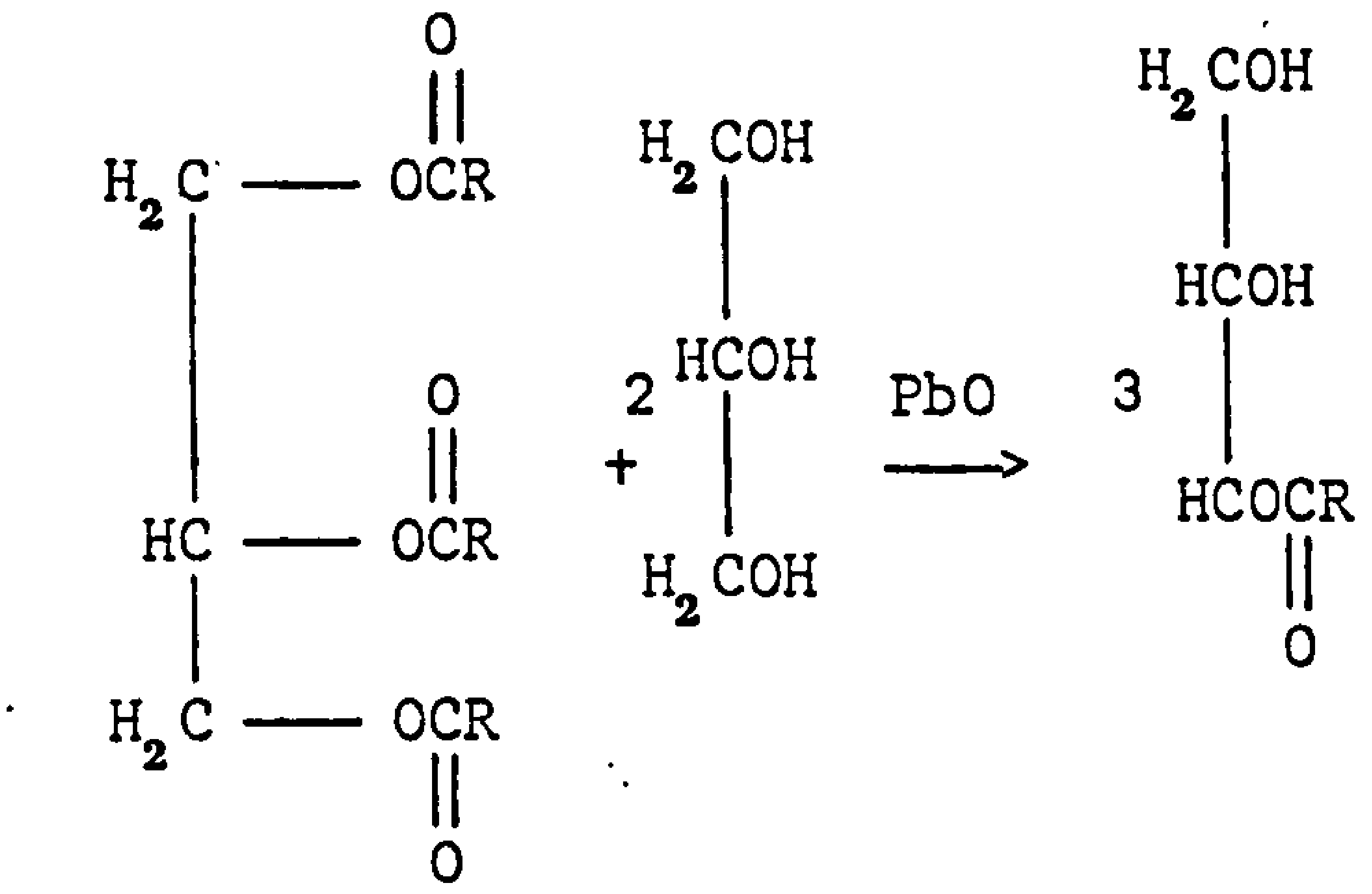
(7)

If glycerol or pentaerythritol are substituted for a glycol, a cross-linked polymer will be the result and chances of gelation are great. Gelation conditions are a function of the percent maleic anhydride modification and the functionality of the polyol.

A glycerol ester may have the theoretical trifunctional structure:

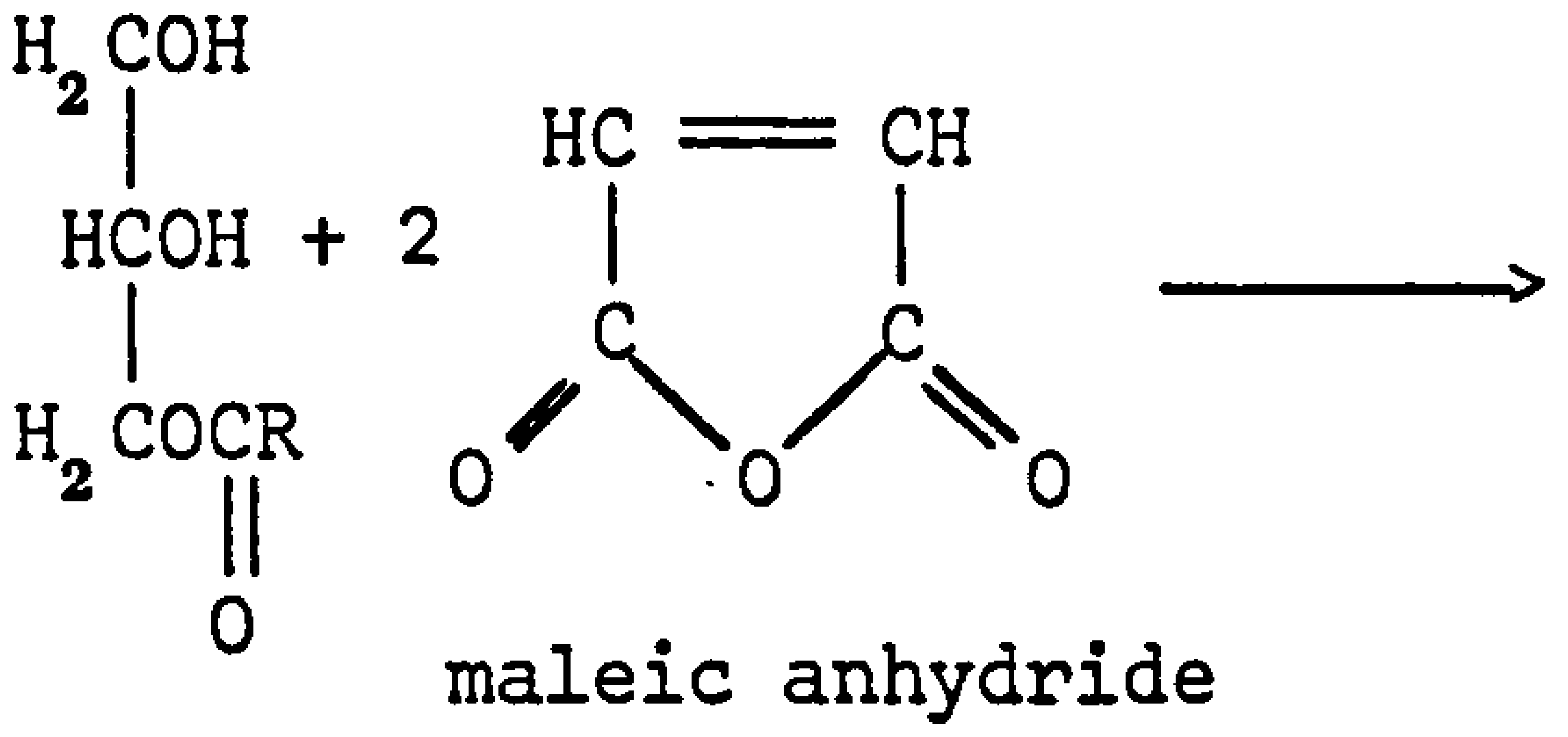


Maleated oil can also be prepared via alcoholysis of the oil with a polyol. The reaction is catalyzed with a base; lithium ricinoleate is usually preferred in place of litharge. The ideal reaction is as follows:

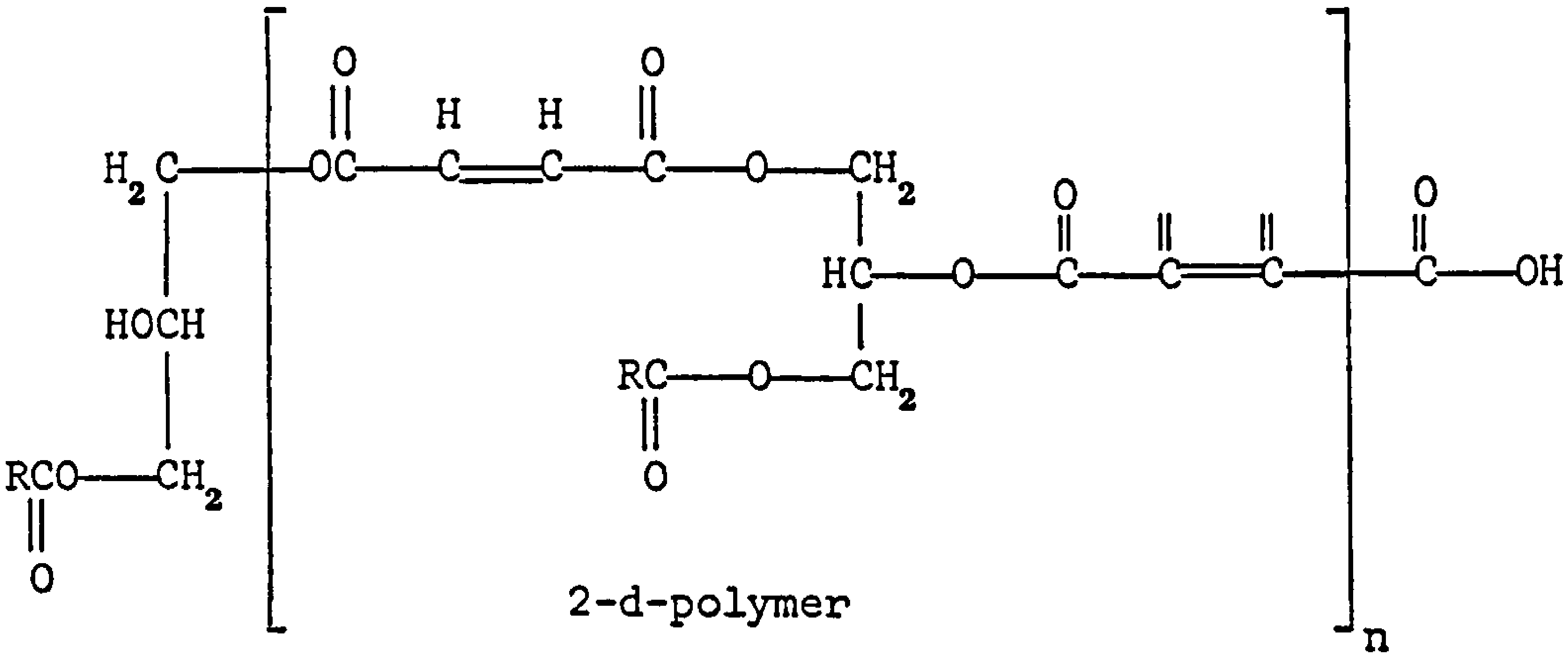


The alcoholysis product (theoretically a glycerol monoester) is difunctional with respect to hydroxyl.

Increased molecular weight is achieved by reacting the alcoholysis product with maleic anhydride as follows:



maleic anhydride



2-d-polymer

Because both maleic anhydride and the monoglycerol ester are difunctional, a two-dimensional polymer with pendant fatty acid groups is formed.

1.3.6 Autocatalytic Autoxidative Mechanisms

Antioxidants e.g. phenols and amines can reduce the rate of decomposition of free radicals. This led some earlier researchers on the topic to believe that a chain reaction was involved. It is now known that the activated molecules involved in such reactions are free radicals.

Bolland(87), Gee(47), Bateman(88) et al, Uri(89) and Stivala(90) and Reich have hypothesized the mechanism of autocatalytic autoxidation processes. The rate of autoxidation of ethyl linoleate was discovered to be directly proportional to its concentration and it increased linearly with the extent of oxidation above a certain level of oxidation(47). It was also suggested that the hydroperoxides themselves are the catalytic substances responsible for the autocatalytic nature of the reaction because virtually all of the absorbed oxygen appears as hydroperoxides.

Extrapolation of the straight-line relationship towards the y-axis by Bolland and Gee(47) gives a positive intercept with a finite rate of oxidation even at the very beginning of the reaction. Bateman et al.(88) have suggested that the initial rate of oxidation approximated zero. The rate of oxygen absorption by pure methyl linoleate shows that the initial rate of oxidation is zero. Various samples of methyl linoleate when subjected to pure oxygen at atmospheric pressure (40^{0}C) gave irreproducible induction periods of up to 8 hours during which no oxygen absorption takes place. Bolland(91) further found that the rate of oxidation varied with oxygen pressure. The rate of oxidation was found to be approximately proportional to the pressure at very low oxygen pressures. This was not so at the highest oxygen pressures. At high partial pressure of oxygen in the atmosphere the oxidation of ethyl linoleate (45^0C) is independent of pressure. The relationship between the rate of oxidation and the concentration of oxygen was given as:

$$-\frac{d[O_2]}{dt} = \frac{K_m[O_2]}{[O_2] - K_n[FA]}$$

where $[O_2]$ = oxygen concentration or pressure

K_m, K_n = constants

FA = fatty acid concentration e.g. linoleate.

A rate equation involving all the factors is as follows:-

$$-\frac{d[O_2]}{dt} = K\frac{[FOOH][FA][O_2]}{[O_2] - K_n[FA]} + f\{[O_2], [FA]\}$$

where [FOOH] = hydroperoxide concentration. The second term, an undefined function, is small compared with the first, except at very low hydroperoxide concentrations and may be considered negligible.

Certain other observations led to the formulation of a mechanism for the autocatalytic autoxidation:

(1) Spectrometric techniques reveal that shifts of double bonds occurred during autoxidation. This suggests that a free radical reaction is involved and a hydroperoxide is formed.

(2) The reactions in many respects, appear similar to certain auto-oxidation reactions in inorganic systems which involve chain reactions.

(3) Decomposition of hydroperoxide initiates the polymerisation and the reaction is bimolecular

$$ROOH \longrightarrow RO^* + O^*H \quad \text{or}$$

$$ROO^* + H^*$$

where ROOH = hydroperoxide.

A free radical chain mechanism was therefore proposed and it involves three distinct stages:-

Initiation
Propagation and
Termination.

Initiation can be brought about by an attack by any free radical upon unsaturated fatty acid. The most probable radicals to initiate chain reactions are those formed by decomposition of peroxidic compounds.

Highly purified linoleate has a long induction period with no measurable oxidation rate for several hours after exposure to oxygen(85). The first chain reaction must thus be initiated by some non-peroxidic free radicals or by stray radiation. Parallel oxidation chains are initiated by radicals formed by decomposition of hydroperoxides. The chain reaction is accompanied by the decomposition of hydroperoxide as oxidation proceeds. More free radicals are therefore generated and the reaction is autocatalytic.

Initiation:-

$$RH + O_2 \longrightarrow \text{Free radicals}$$

$$\left.\begin{array}{l} ROOH \\ (ROOH)_2 \end{array}\right] \longrightarrow \text{Free radicals (e.g. } R^*,\ RO^*,\ RO_2^*,\ HO^*,\ H^*\text{)}$$

Propagation:-

$$R^* + O_2 \longrightarrow RO_2^*$$

$$RO^* + RH \longrightarrow R^* + ROOH$$

Termination:-

$$\left.\begin{array}{l} R^* + R^* \\ R^* + RO_2^* \\ RO_2^* + RO_2^* \end{array}\right] \longrightarrow \text{stable (non-radical) end products}$$

Chain stopping is achieved by the reaction of two radicals as shown above.

If free radicals attack molecules of other substances present, some other products which neither decompose or favour the propagation are formed.

Maximum oxygen absorption of linseed oil and its related unsaturated fatty acids

Esters of unsaturated fatty acids such as linoleic acid when oxidized under conditions designed to eliminate the increasing influence of diffusion of oxygen on the rate of reaction show that the rate of oxidation expressed as oxygen consumption, accelerated without any preceding induction period. The rate of oxygen up-take varied linearly with the total amount of oxygen up-take. The dependence of the rate of oxidation on oxygen pressure may be expressed as:-

$$\frac{d[O_2]}{dt} = K[FA][FOOH]\ f(PO_2) = \frac{(PO_2)}{n + (PO_2)}$$

where [FA], [FOOH] are the concentrations of olefin and hydroperoxide respectively and $P(O_2)$ is oxygen pressure.

A substance capable of possessing singlet oxygen quenching ability is able to inhibit singlet-oxygen-initiated autoxidation of oils. Carson et al.(16) reported that α-tocopherol (a fat soluble vitamin e type) could quench singlet oxygen effectively and was found to be a poor inhibitor of photoxidative polymerization of oils. Other forms of tocopherols (γ-, δ-) are also singlet oxygen quenchers(92). Foote and Denny(93) have it that β-carotene possesses an efficient singlet oxygen quenching ability. The singlet oxygen quenching involves a route whereby the quencher (Q) either undergoes no ultimate chemical change (physical quenching), or a chemical reaction resulting in new products(94).

$$Q + I_{O_2} \longrightarrow Q + 3O_2 \left[\begin{array}{l}\text{Physical}\\ \text{quenching}\end{array}\right]$$

$$Q + I_{O_2} \longrightarrow Q_{O_2} \qquad \left[\begin{array}{l}\text{Chemical}\\ \text{reaction}\end{array}\right]$$

Because of the extremely high reaction rate constants encountered in free radical reactions, special techniques are required for evaluation of their kinetic parameters. One convenient technique for the study of peroxy radical and the reactions with antioxidants, is pulse radiolysis. This is based on monitoring of radiation-generated free radicals as a function of time with resolution as low as nanoseconds or even less. Some autoxidation processes occur in these systems by other spontaneous routes over a period of days, weeks or even months. This can be expressed by radiolysis into a sub-second region with a concentration of free radicals high enough to be studied by e.g. spectrophotometry, conductivity etc.(95)

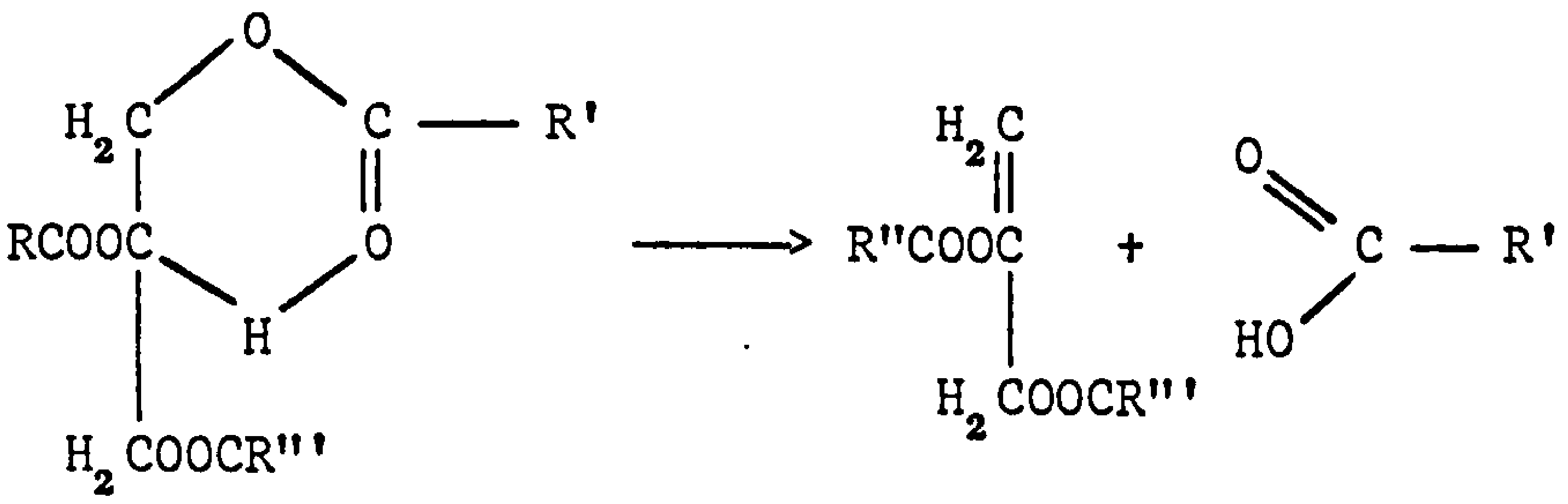
1.3.7 Autoxidation of Fats and Oils at Elevated Temperatures

The chemistry of lipid oxidation at high temperature is complex since both thermolytic and oxidative reactions or unchanged and rearranged material are simultaneously involved. Both saturated and unsaturated fatty acids undergo chemical decomposition when exposed to heat in the presence of oxygen. For a better understanding of the reactions which occur upon heating natural fats, thermal decomposition of saturated and unsaturated model systems of fatty acid esters and glycerides have been studied by Nawar and Witchwoot(96).

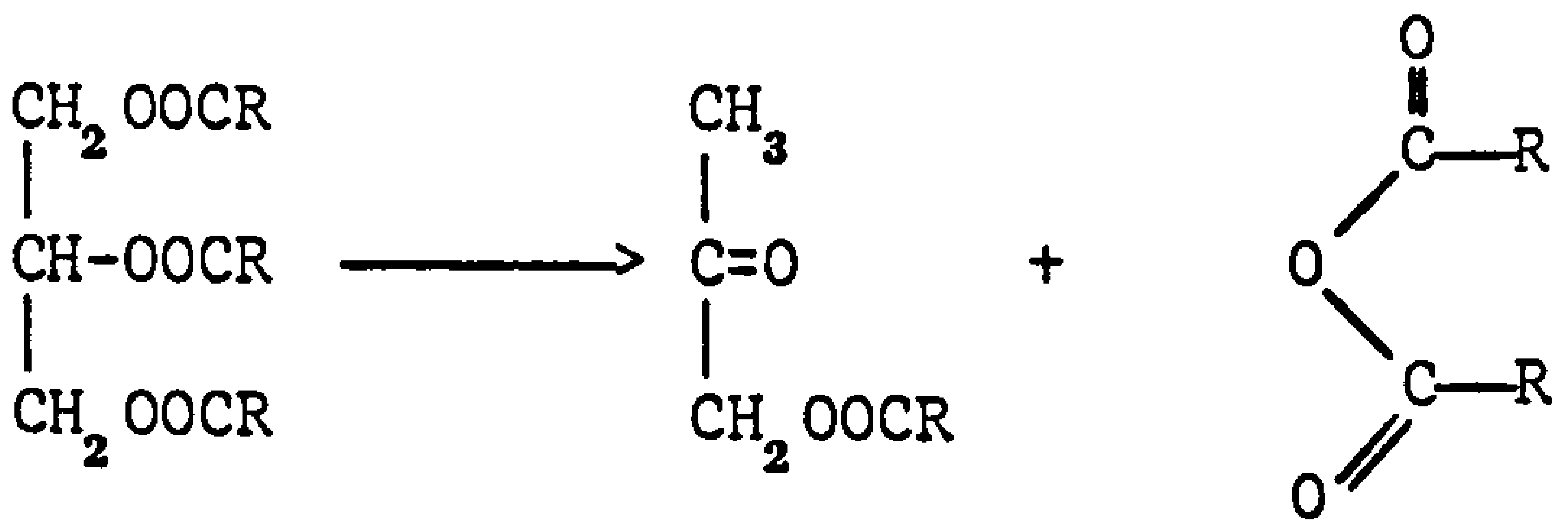
(i) Thermal non-oxidative reactions of saturated t~~h~~riacylglycerols

In general, higher temperatures of heating are required for detection of the non-oxidative decomposition products of saturated fatty acids. Thus, a number of investogators have heated saturated t~~h~~riacylglycerols and methyl esters of fatty acids in the absence of oxygen at temperatures ranging from 200-700°C to study their decomposition(97),(98). Trace amounts of thermolytic products can be detected in triacylglycerols after heating in a vacuum for one hour at 180°C using sensitive detection techniques.

The selection of substrates with short chain fatty acids facilitated the analysis of the higher-boiling decomposition products(99),(100),(101). Quantitatively, component fatty acids are the major compounds produced from thermolytic decomposition of thiacylglycerols. In the absence of moisture, the free fatty acid can be formed via a "six-atom-ring-closure" as shown below.



This mechanism also explains the formation of propenedioldiesters. Expulsion of the acid anhydride from the triacylglycerol molecule produces 1- or 2-oxopropyl esters and the acid anhydride.



Decomposition of 1-oxopropyl ester gives rise to acrolein and c_n fatty acid, while decarboxylation of the acid anhydride intermediate produces a symmetrical ketone. Free radical mechanisms similar to those proposed for the radiolysis of triacylglycerols may also play a significant role in the formation of thermolytic products, particularly when relatively high temperatures are used$^{(102),(101)}$.

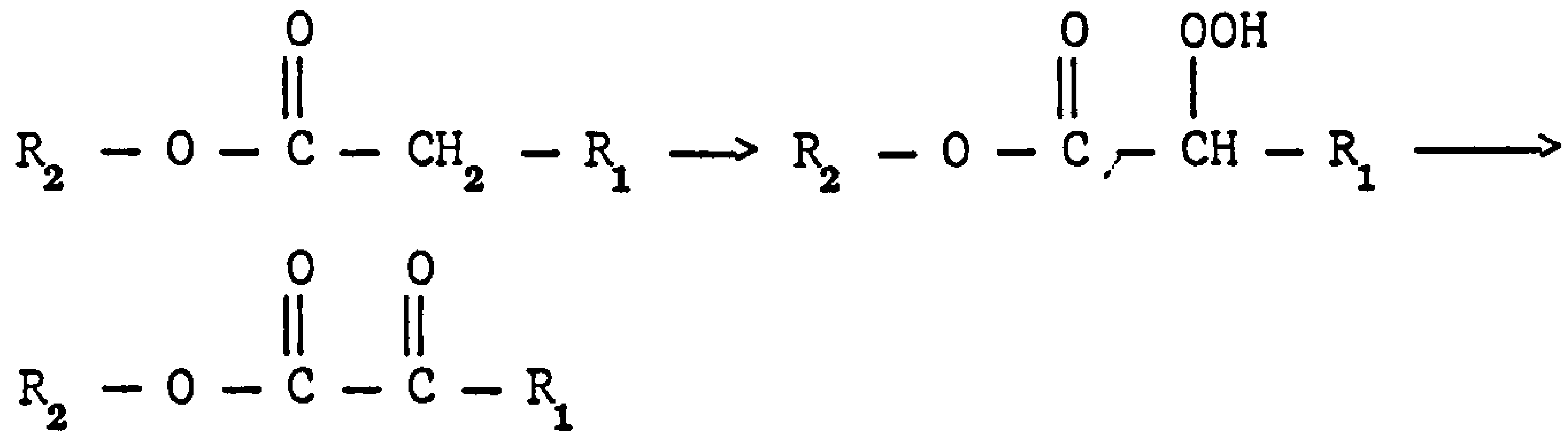
(ii) Thermal oxidative reactions of saturated triacylglycerols

Saturated fatty acids and their esters are considerably more stable than their unsaturated analogues. However, when heated in air at temperatures higher than 150°C, they undergo oxidation giving rise to a complex decomposition pattern. The major oxidative products consist of homologous series of carboxylic acids, 2-alkanones, n-alkanals, lactones, n-alkanes and 1-alkenes$^{(97),(102),(103),(104)}$.

In a recent study, a series of triacylglycerols containing the even numbered fatty acid chains c_6 to c_{16} were heated in air for one hour at 180°C and 250°C, and their oxidation products examined. Qualitatively, the oxidative pattern was similar for samples heated at the two temperatures. However, higher amounts of the decomposition products were formed at 250°C. The hydrocarbon series was the same as that produced in the absence of oxygen, but the amounts formed were much more significant under the oxidative conditions.

The principal mechanism in thermal oxidation of saturated fatty acids involves the formation of monohydroperoxides, and that oxygen attack occurs at all the methylene groups of the fatty acid$^{(104),(97),(106)}$. Controversy still exists whether hydroperoxide formation is favoured at certain locations along the alkyl chain.

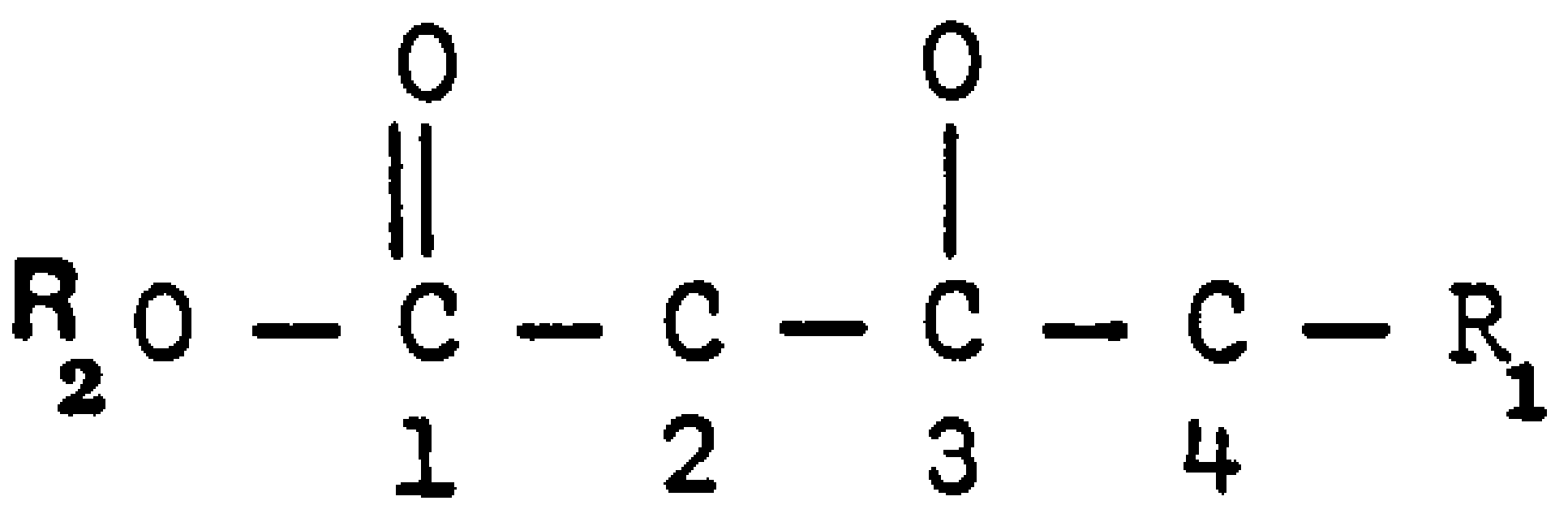
Many investigators have observed that the dominant oxidative products of saturated fatty acids are those with chain lengths near or equal to the parent fatty acids. This led to the conclusion that oxidation occurs preferentially at the alpha, beta and gamma positions(97),(100),(107). Alpha attack accounts for the formation of the C_{n-1} fatty acid via formation and decomposition of the α-keto acid.



$$R_2-O-\overset{O}{\overset{\|}{C}}-CH_2-R_1 \longrightarrow R_2-O-\overset{O}{\overset{\|}{C}}-\overset{OOH}{\overset{|}{CH}}-R_1 \longrightarrow R_2-O-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R_1$$

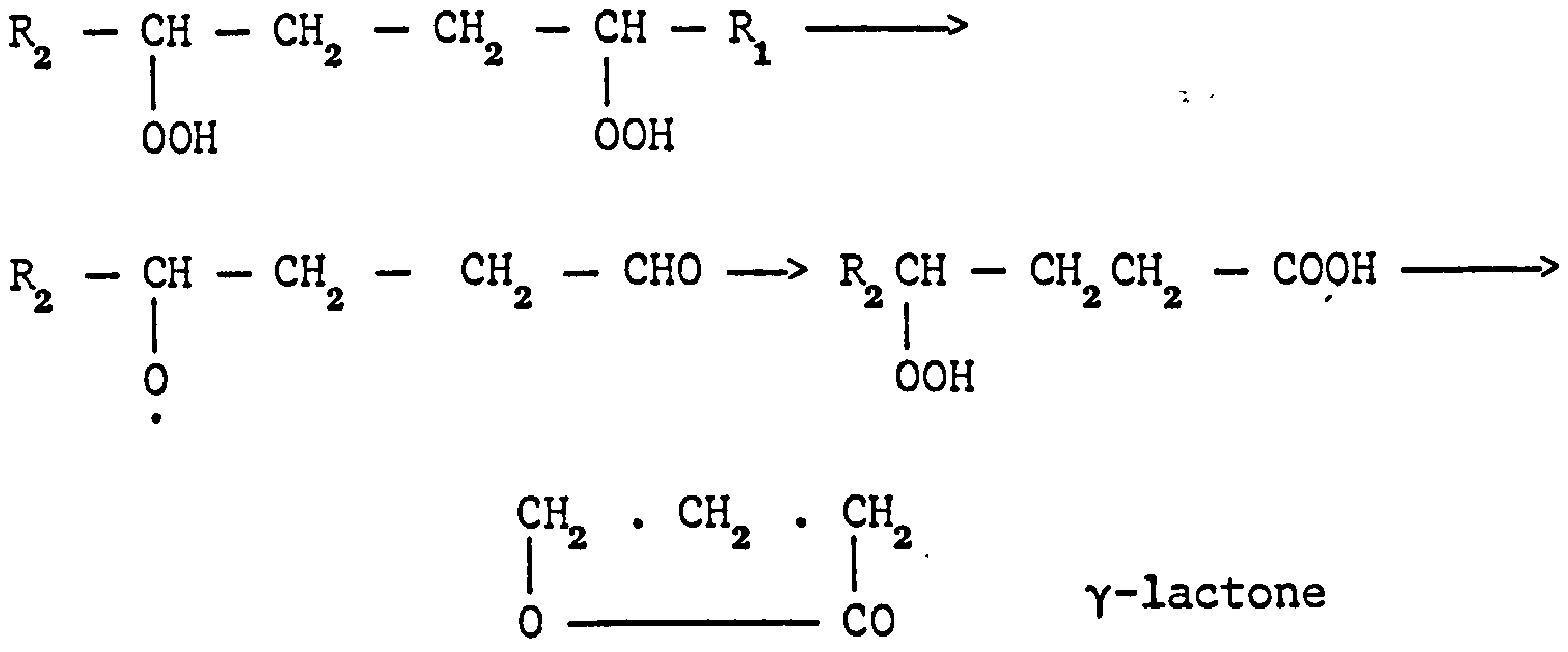
Further stepwise α-oxidations would produce the series of lower acids. Decomposition of the alkoxy radical intermediate may also account for the formation of the C_{n-1} alkanal and the C_{n-2} hydrocarbons. Oxidative attack at the β-carbon of the fatty acid results in the formation of β-ketoacids which are responsible for the formation of C_{n-1} methyl ketones.

Cleavage between carbons 2 and 3 of the alkoxy radical gives rise to the C_{n-2} alkanal while scission between carbons 3 and 4 produces C_{n-3} hydrocarbons.



$$R_2O-\underset{1}{\overset{O}{\overset{\|}{C}}}-\underset{2}{C}-\underset{3}{\overset{O}{\overset{|}{C}}}-\underset{4}{C}-R_1$$

Similarly, oxygen attack at the gamma position would give rise to the C_{n-3} alkanal, C_{n-2} methyl ketone and C_{n-4} hydrocarbons. In addition, hydroperoxide formation at the gamma position is believed to be responsible for the production of the C_n γ-lactones via cyclization of the resulting hydroxy acids. C_n δ-lactones can similarly result from oxidations at δ-positions. If the gamma methylene group of saturated fatty acids is a favoured site for oxygen attack, γ-lactones having shorter chains than the original acid can be explained on the basis of the further oxidation of the lower fatty acid series, produced by stepwise oxidation as mentioned above. Watanabe and Sato(108) proposed an alternative mechanism which involved the formation of dihydroperoxides:



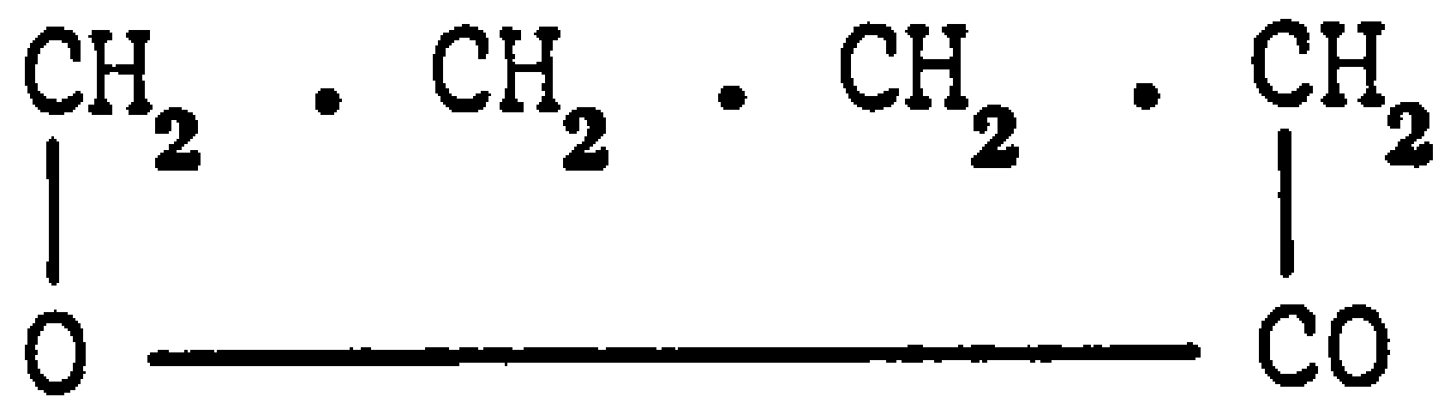
$$R_2-\underset{\text{OOH}}{\underset{|}{CH}}-CH_2-CH_2-\underset{\text{OOH}}{\underset{|}{CH}}-R_1 \longrightarrow$$

$$R_2-\underset{\underset{\bullet}{O}}{\underset{|}{CH}}-CH_2-CH_2-CHO \longrightarrow R_2\underset{\text{OOH}}{\underset{|}{CH}}-CH_2CH_2-COOH \longrightarrow$$

$$\begin{array}{lcl} CH_2 \cdot CH_2 \cdot & & CH_2 \\ | & & | \\ O & \text{———} & CO \end{array}$$

γ-lactone

It is not clear, why the only δ-lactones produced are those having a carbon chain length equal to that of the parent fatty acid



$$\begin{array}{lcl} CH_2 \cdot CH_2 \cdot CH_2 \cdot & & CH_2 \\ | & & | \\ O & \text{—————} & CO \end{array}$$

δ-valerolactone.

In contrast, to the above argument, preferential oxygen attack toward the centre of the fatty acid chain was concluded by Brodnitz et al.(106) who chemically cleaved the reduced esters of oxidized methyl palmitate and analyzed the resulting mono- and dibasic acids. Selke et al.(105) also heated tristearin in a stainless steel "microroom" and analyzed the volatiles by gas chromatography. The apparent contradiction may be due to the different oxidative conditions and analytical techniques employed by different investigators. Hydroperoxides decompose rapidly at elevated temperatures. Higher amounts of specific hydroperoxides collected after thermal oxidation may reflect their relative stability rather than their selective formation.

1.3.8 Thermal Non-Oxidative Reactions of Unsaturated Fatty Acid Esters

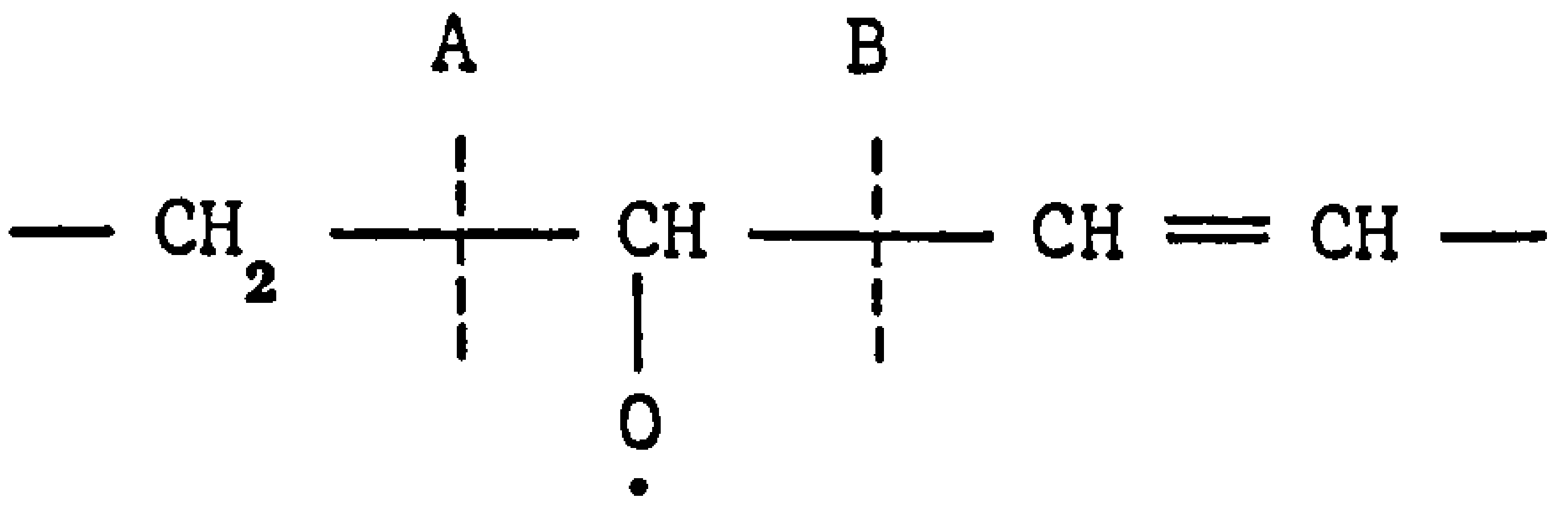
The formation of dimeric compounds appears to be the predominant reaction of unsaturated fatty acids when heated in the absence of oxygen. In addition, other lower molecular weight substances may be formed. Relatively severe heat treatment is required for such reactions. Sen Gupta(109) detected no significant decomposition of methyl oleate at temperatures below 220°C. The samples, when heated at 280°C for 65 hours under argon, he found hydrocarbons, short and long-chain fatty acid esters, straight-chain dicarboxylic dimethyl esters as well as dimers. Many of these compounds were explained on the basis of the formation and/or combination of free radicals resulting from homolytic cleavage of c-c linkages near the double bond(110),(111). The dimeric compounds, which included dicyclic monoene and diene dimers as well as saturated dimers with cyclopentane structure, are believed to arise via allyl radicals resulting from hydrogen abstraction at methylene groups alpha to the double bond. Such radicals may undergo disproportionation into monoenoic and dienoic acids, or inter- and intramolecular addition to c-c double bonds(109). Methyl linoleate, heated under the same conditions, produced a more complex mixture of dimers comprised of saturated tricyclic, mono-unsaturated bicyclic, diunsaturated monocyclic and triunsaturated acyclic dimers as well as dehydrodimers containing one or two double bonds(112).

1.3.9 Thermal Oxidative Reactions of Unsaturated Fatty Acid Esters

Unsaturated fatty acids are much more susceptible to oxidation than their saturated analogs. At elevated temperatures, their oxidative decomposition proceeds very fast. Although, certain differences between high and low temperature oxidations have been observed by some investigators, the evidence accumulated to date indicates that in both cases, the principal reaction pathways are basically the same. The formation and decomposition of hydroperoxide intermediates, predictable according to location of double bonds(113) appears to occur over a wide range of temperatures. A large number of decomposition products has been isolated by many investigators from heated fats(104),(114),(115). However, the major compounds are typical of those ordinarily produced from room temperature autoxidations.

Nawah et al.(116) has provided quantitative analysis of the major volatile compounds formed in corn, soybean and coconut oils after heating in air for two hours at 185 and 250°C. For all these fats, the volatile pattern obtained at the two temperatures reflected the autoxidation of their constituent linoleic and oleic acids. In the case of coconut oil however, significant quantities of lactones and methyl ketones, from the oxidation of its shorter chain saturated fatty acids were also formed.

The autoxidation of linoleates at elevated temperatures has been studied in some detail by Henderson et al.(117). Samples were distilled and the distillates pre-fractionated on silica before gas chromatographic analysis. There are speculations that the so-called "type B" scission of the alkoxy radical (cleavage of the c-c bond between a vinyl function and the oxygen-bearing carbon atom) is favoured at low temperatures, while "type A" cleavage (splitting of the c-c bond on the side away from the olefinic linkage) occurs preferentially at elevated temperatures.



$$-CH_2 - \underset{\underset{\dot{O}}{|}}{CH} - CH = CH -$$

Decadienal was considerably greater in vegetable oils heated to 185°C for 2 hours than in other oils heated to 250°C. The amounts of hexanal were approximately the same for both treatments.

There is no simple explanation to account for the quantitative differences in results observed at various temperatures of heating. At elevated temperatures, hydroperoxide decomposition and secondary oxidations occur at extremely rapid rates. The amount of a given decomposition product, at a given time during the oxidation process, is determined by the net balance between the complex effects of a number of factors. Hydroperoxide structure, temperature, the degree of autoxidation, and the stability of the decomposition products themselves, undoubtedly exert major influences on the final quantitative pattern. Significance of the heating time was emphasized in a recent study with linoleates(118). The picture is further complicated if the effects of such factors on c-c bond scission and on the large numbers of other possible decomposition reactions occurring simultaneously and in competition with c-c cleavage are considered. Such reactions include c-o scission which may lead to positional isomerization of hydroperoxides(119) epoxidation, formation of dihydroperoxides, intramolecular cyclization and dimerization.

The basic mechanisms of thermal and oxidative polymerization of unsaturated fatty acids have been reviewed(120). Heating in air at elevated temperatures leads to the formation of oxydimers or polymers possessing hydroperoxide, hydroxide, epoxide and carbonyl groups as well as ether and peroxide bridges. The precise structure of many of these compounds as well as the effects of the various oxidation parameters on the reactions leading to their formation, are still incompletely understood.

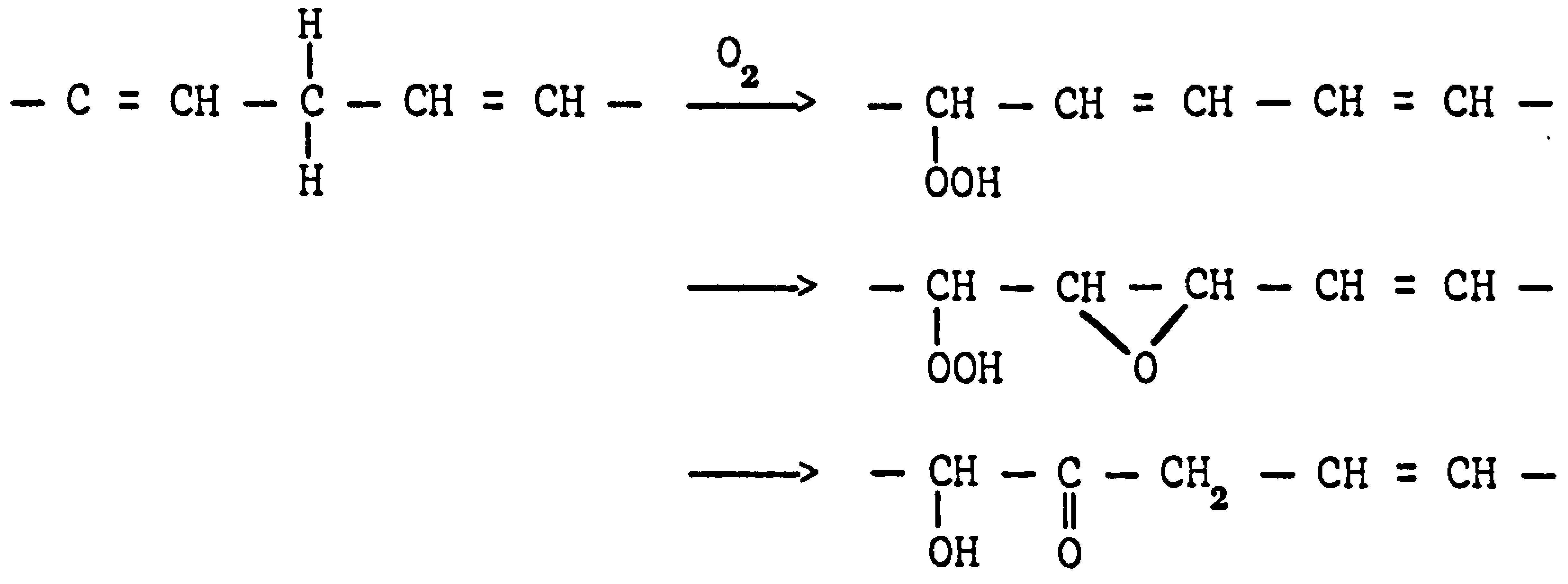
1.3.10 Thermal Decomposition of Saturated-Unsaturated Mixtures

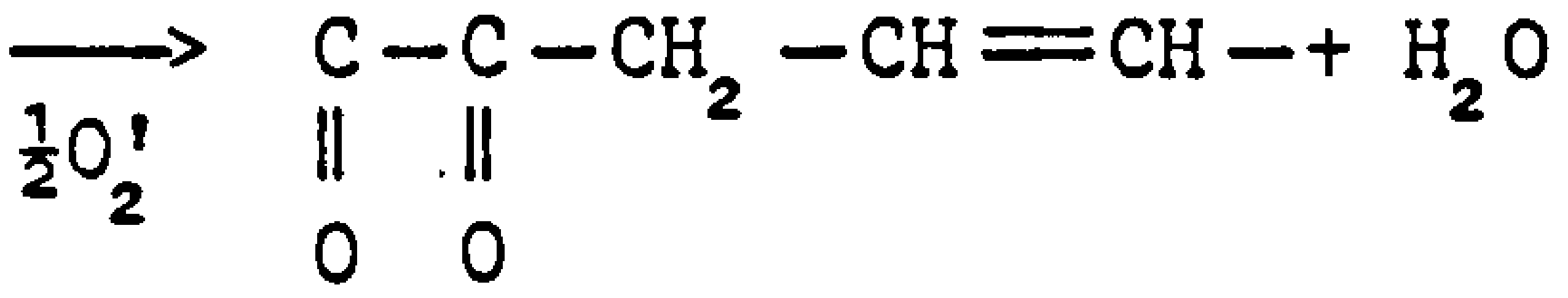
The effect of unsaturated fatty acids on the decomposition of saturated systems has recently been studied by Witchwoot et al.(121). The volatile pattern of the mixture was essentially the same as that of the unsaturated ester. The unsaturated acid is seen to provide an antioxidant effect inhibiting the autoxidation of the saturated chains. The presence of unsaturation does not appear to have a significant influence on non-oxidative reactions of the saturated system.

The interplay of reactions in complex mixtures, the interaction between oxidative and non-oxidative pathways and the influence of the conditions of oxidation on the quantitative pattern of decomposition products are critical areas worthy of closer examination in lipid autoxidation at elevated temperatures.

1.3.11 Secondary Products of Autoxidation

The secondary products of olefinic oxidation are low molecular weight polar compounds. According to Swern(122) the first products isolated and identified were hydroxy compounds and carboxylic acids. A typical composition of products revealed the presence of peroxides, hydroxy, oxirane, α, β-unsaturated carbonyl and other compounds. Chang and Kummerow(123) found that ethyl linoleate autoxidation gave rise to diketones amongst other products. They suggested the following sequence:

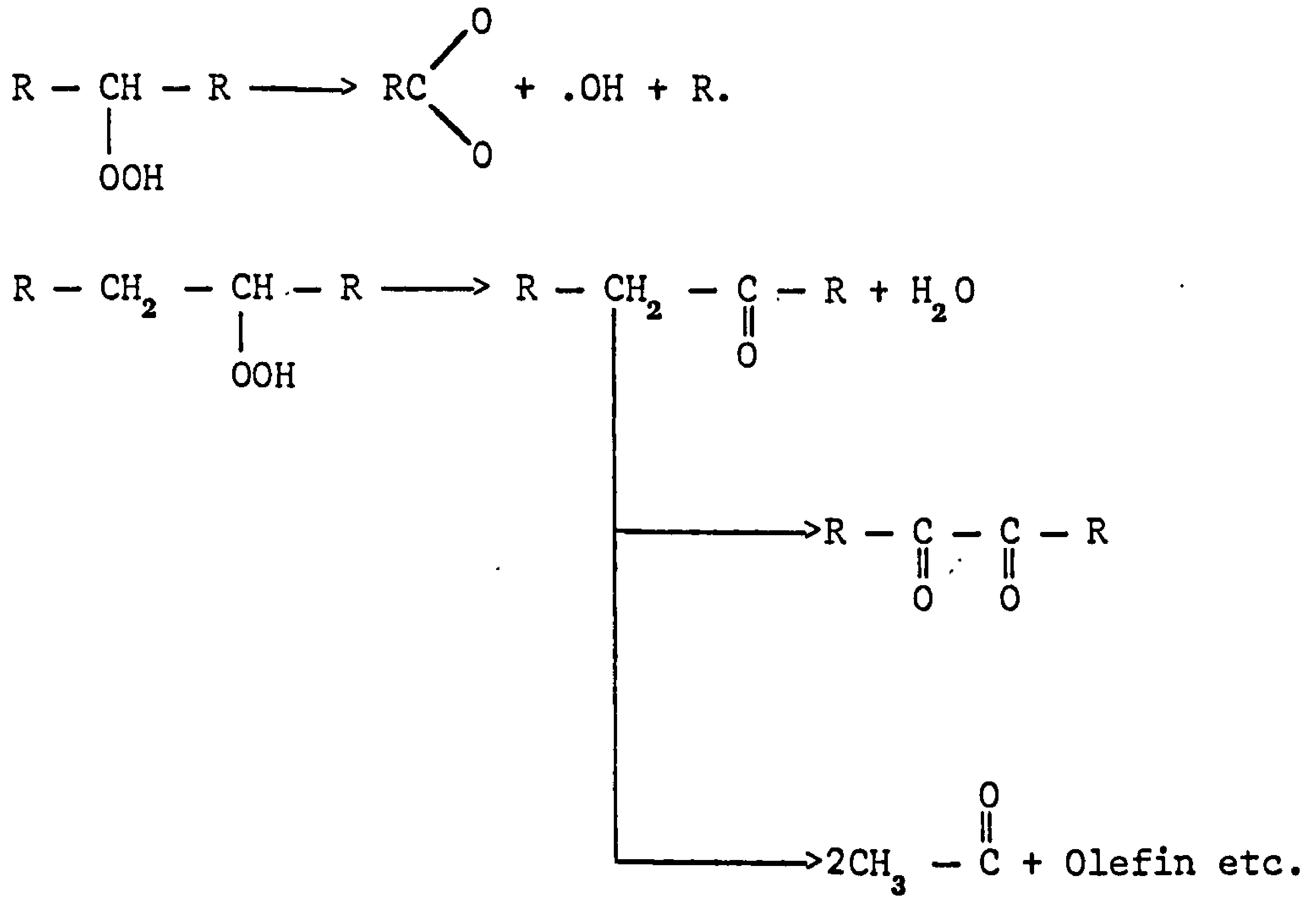




$$\xrightarrow[\frac{1}{2}O_2]{} \underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_2-CH=CH- + H_2O$$

The formation of ketols as intermediates has been confirmed by King(124). Lathlean(125) separated seven different aldehydes by paper chromatography from autoxidized methyl linoleate. Privett(126) and co-workers found out that only 20% of the products could be accounted for as hydroperoxides.

Carbonyl compounds have been identified as products of depolymerization reactions(127). Some of the reactions are as follows:-



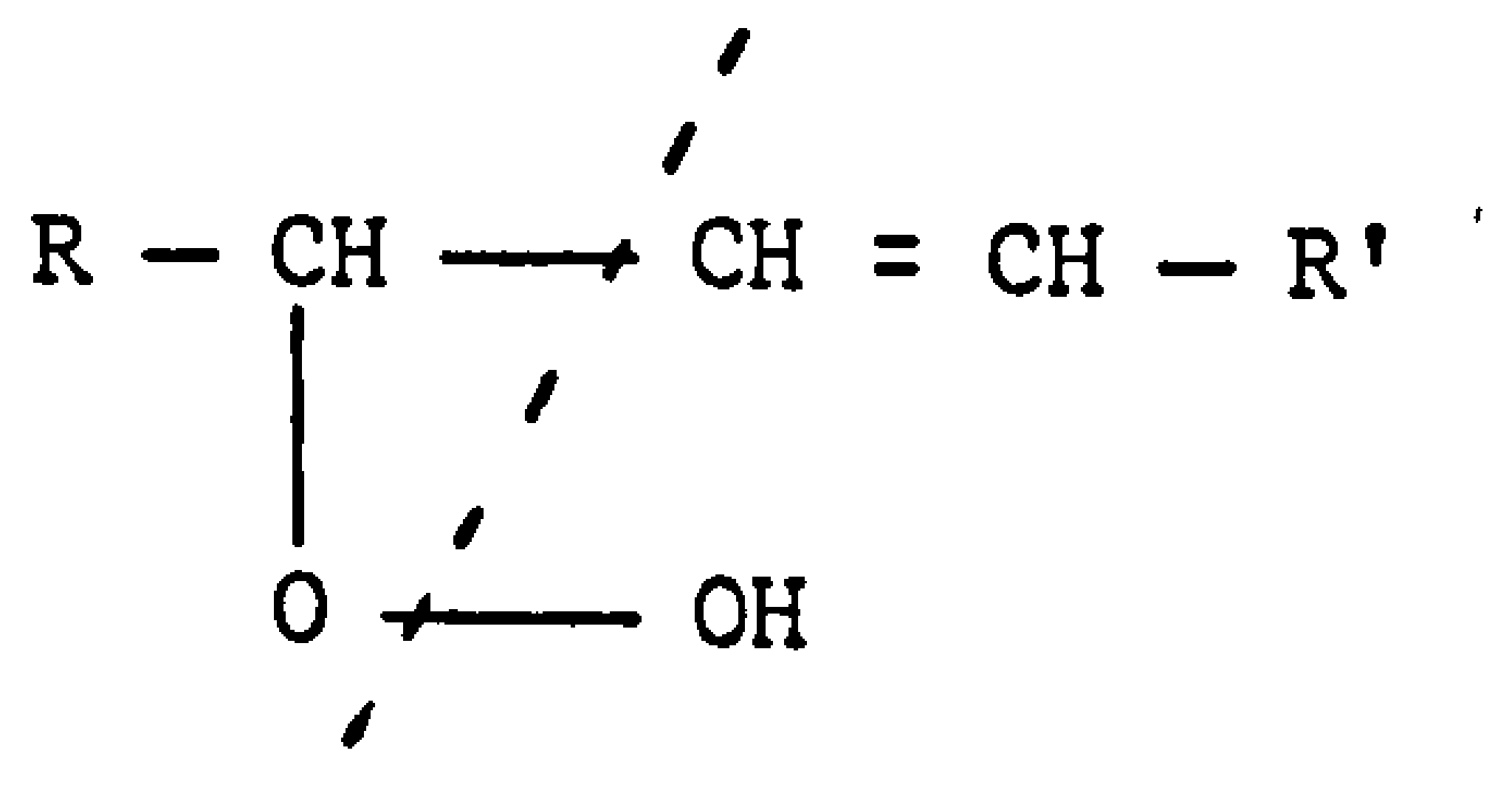
$$R-\underset{\displaystyle OOH}{\underset{|}{CH}}-R \longrightarrow RC\begin{smallmatrix}O\\O\end{smallmatrix} + .OH + R.$$

$$R-CH_2-\underset{\displaystyle OOH}{\underset{|}{CH}}-R \longrightarrow R-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-R + H_2O$$

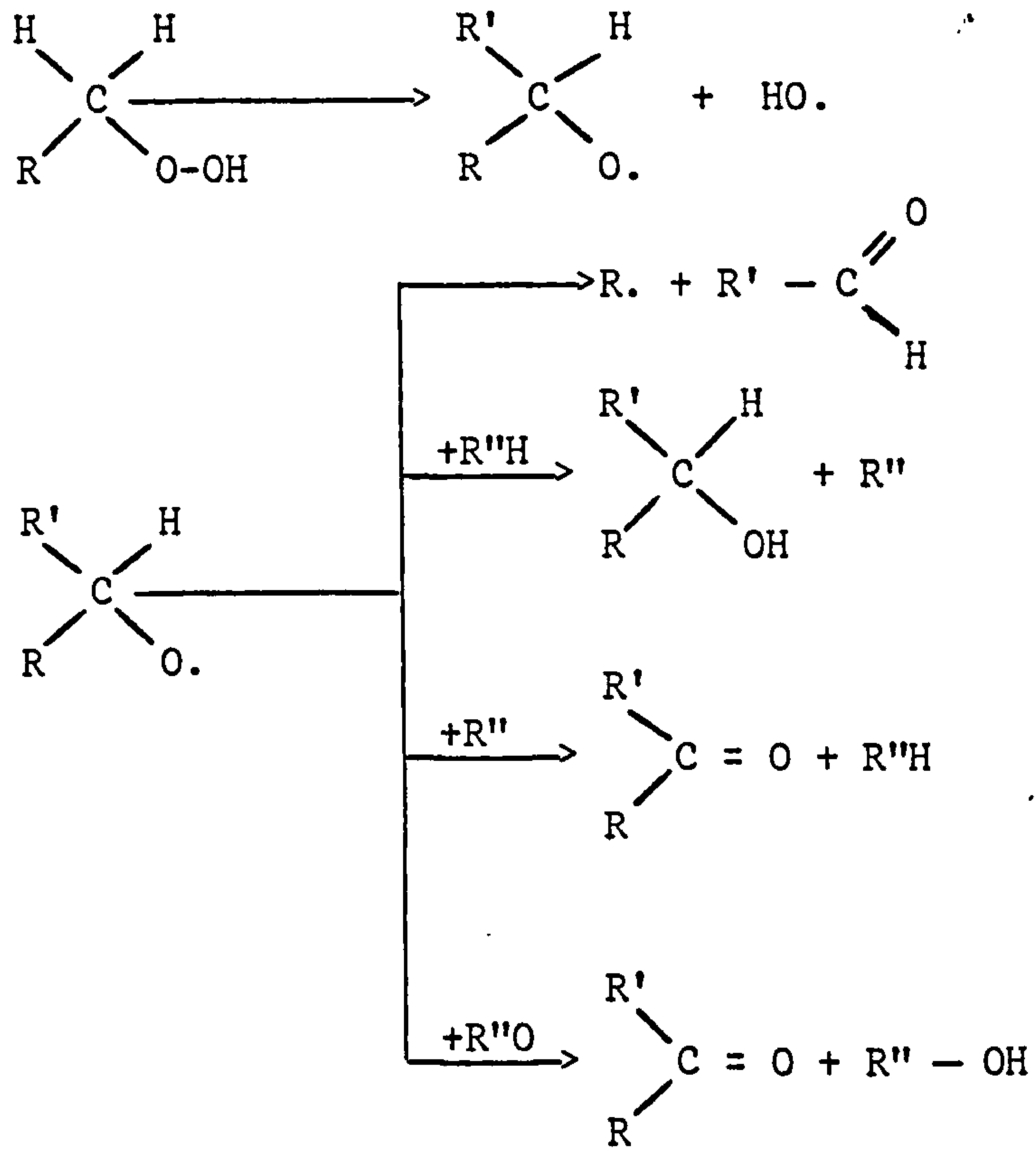
$$\longrightarrow R-\underset{\displaystyle O}{\underset{\|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}-R$$

$$\longrightarrow 2CH_3-\overset{\displaystyle O}{\overset{\|}{C}} + \text{Olefin etc.}$$

Badings(128) studied the oxidation of ammonium linoleate in the presence of copper catalyst at 37.2°C. The reaction was stopped when a half mole of oxygen per mole of linoleate was absorbed. Carbonyl compounds were released and on separation by column chromatography were identified as 2, 4-dinitrophenyl-hydrazones. The three main carbonyl compounds identified were n-hexanal, 2-octanal and 2, 4-decadienal. Badings postulated hydroperoxide formation, followed by cleavage as shown below, to produce the aldehydes.

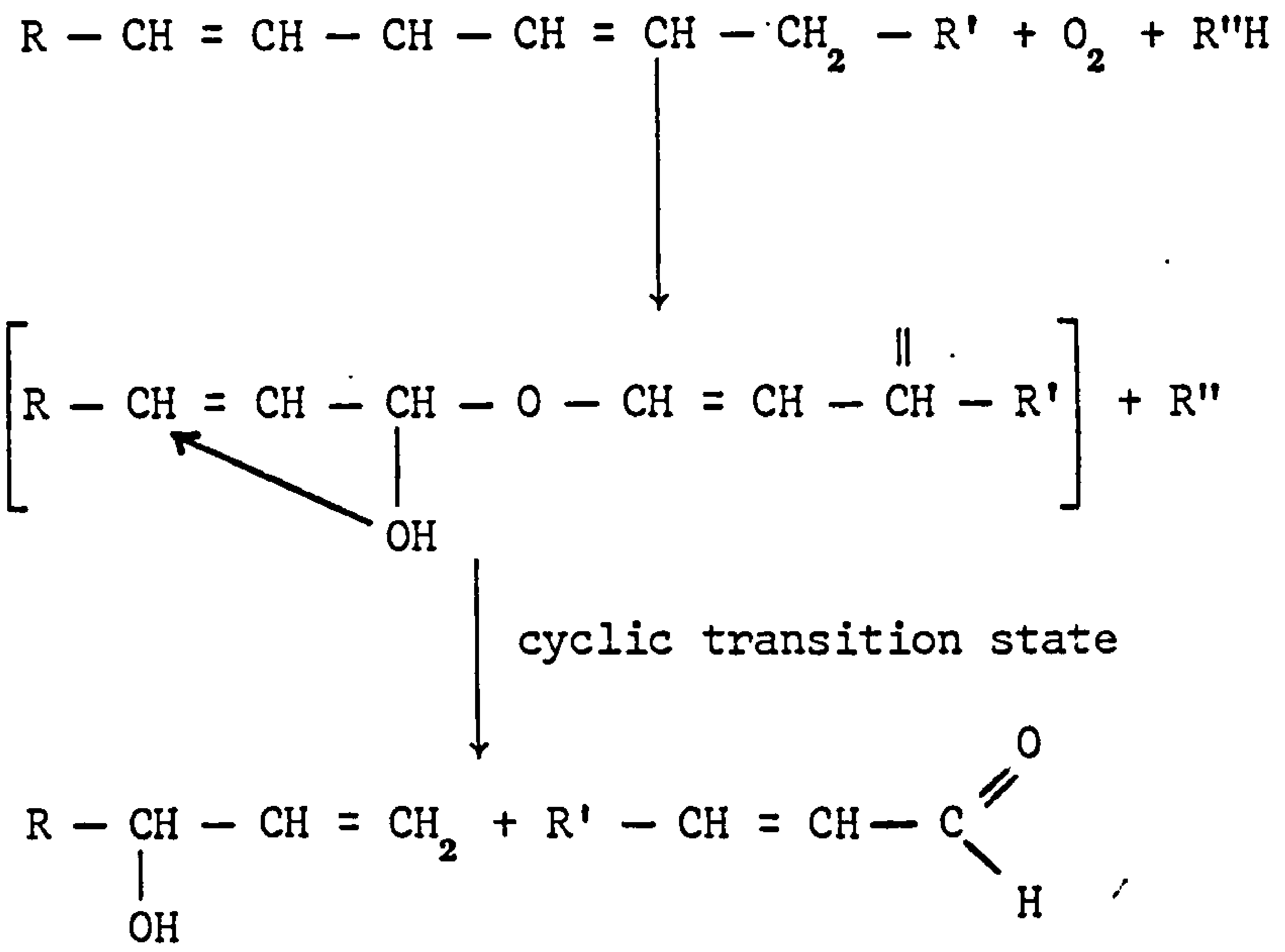


The position at which the initial hydroperoxide is formed determines the type of aldehyde resulting from this scission. The cleavage of hydroperoxides at O-O bond is seen as the precursor for the formation of other compounds.

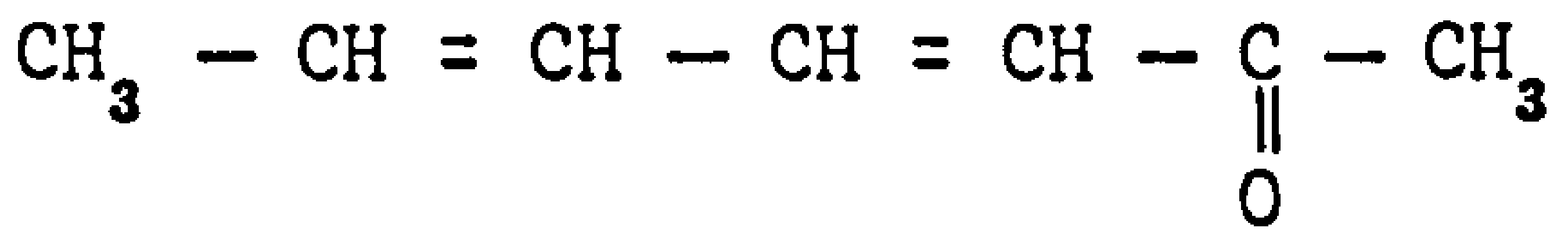


A C-C bond cleavage of free radicals resulting in low molecular weight aldehydes was proposed by Frankel(129) and co-workers.

Similar techniques were employed by Keith and Day(130) who studied the oxidation of polyunsaturated glyceryl esters. They identified carbonyl compounds of the types alk-2-enals and alk-2-4-dienals. Hoffman(131) studied methyl linoleate oxidation and found that besides aldehydes, an unsaturated secondary hydroxyl compound, was also formed. He proposed the formation of an intermediate hemiacetal which splits off to give an aldehyde and alcohol through a cyclic transition state.

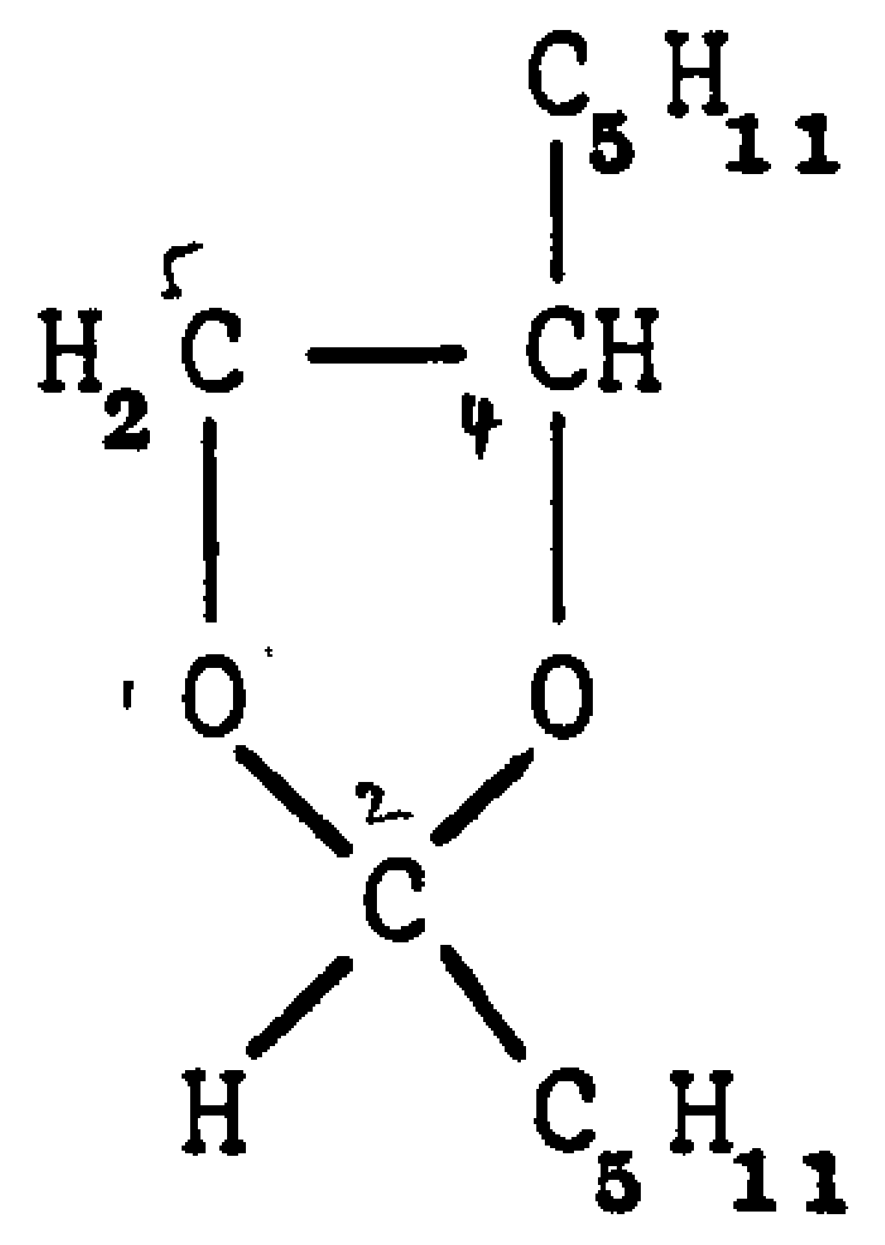


Skellon(132) found out that aldehydes, ketones, mono- and dicarboxylic acids, hydroxy and epoxy compounds, ketols and diketones were also formed. A seven carbon dienone was separated, characterized and found to be hepta-3, 5-dien-2-one(133).

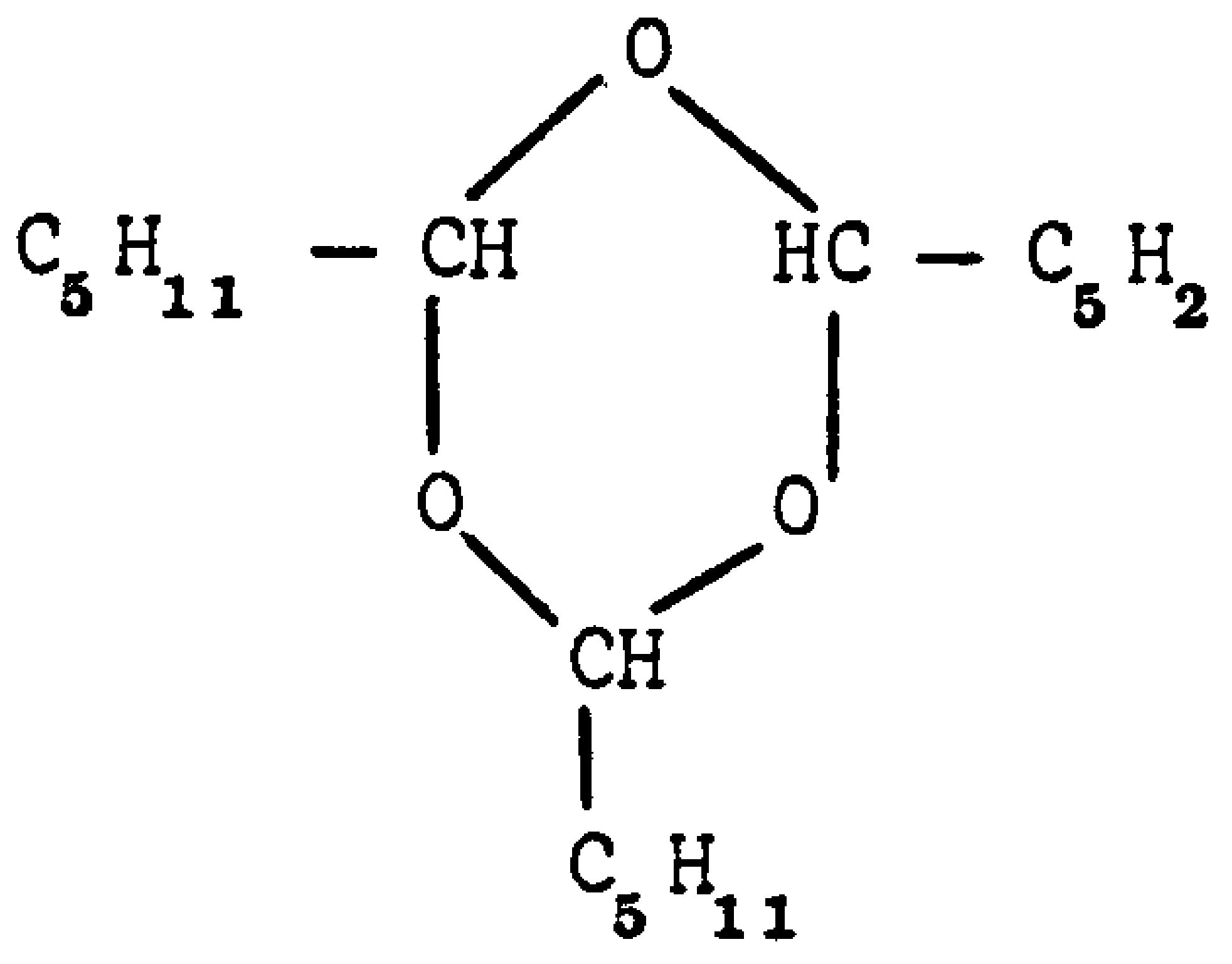


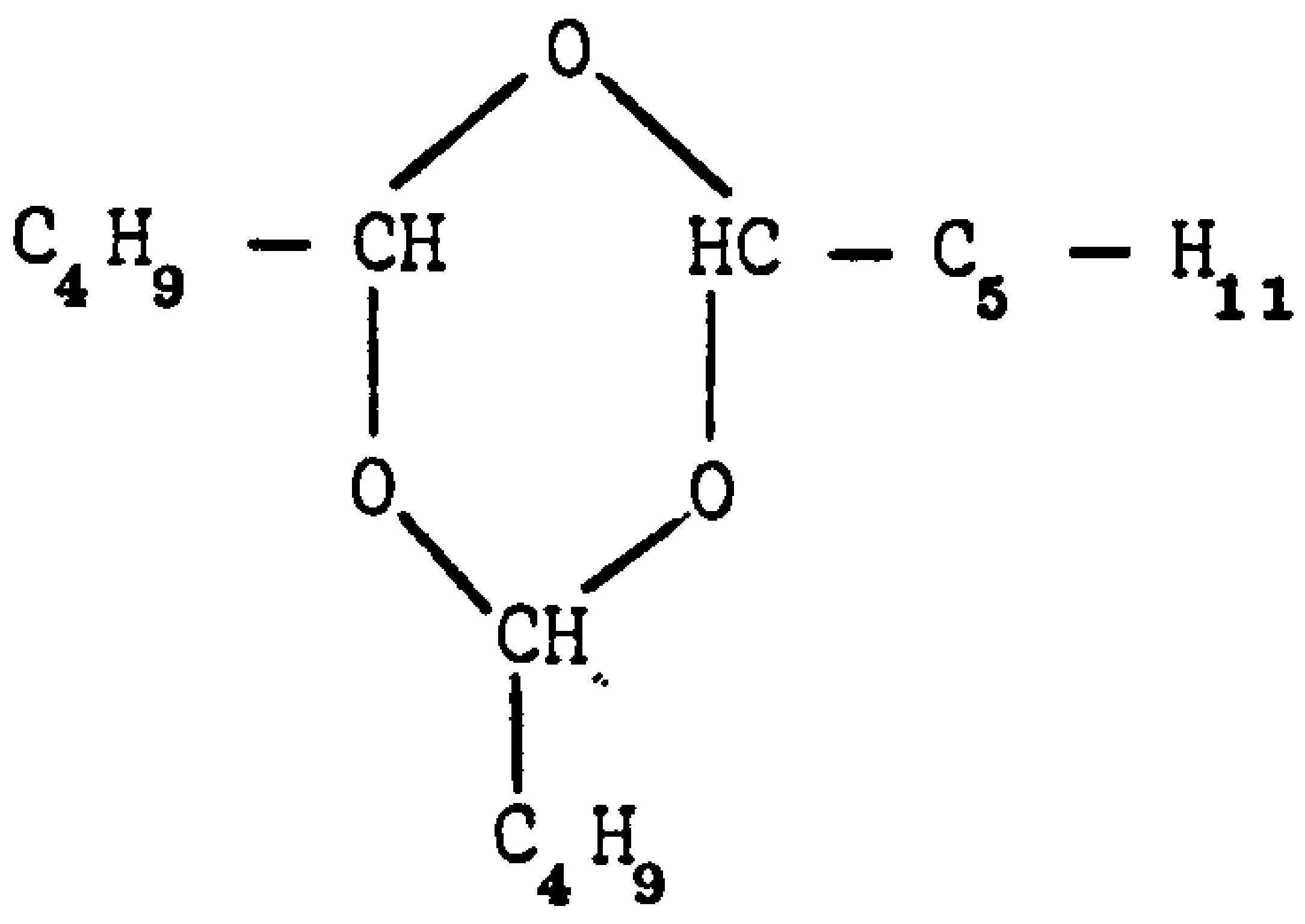
$$CH_3 - CH = CH - CH = CH - \underset{\underset{O}{\|}}{C} - CH_3$$

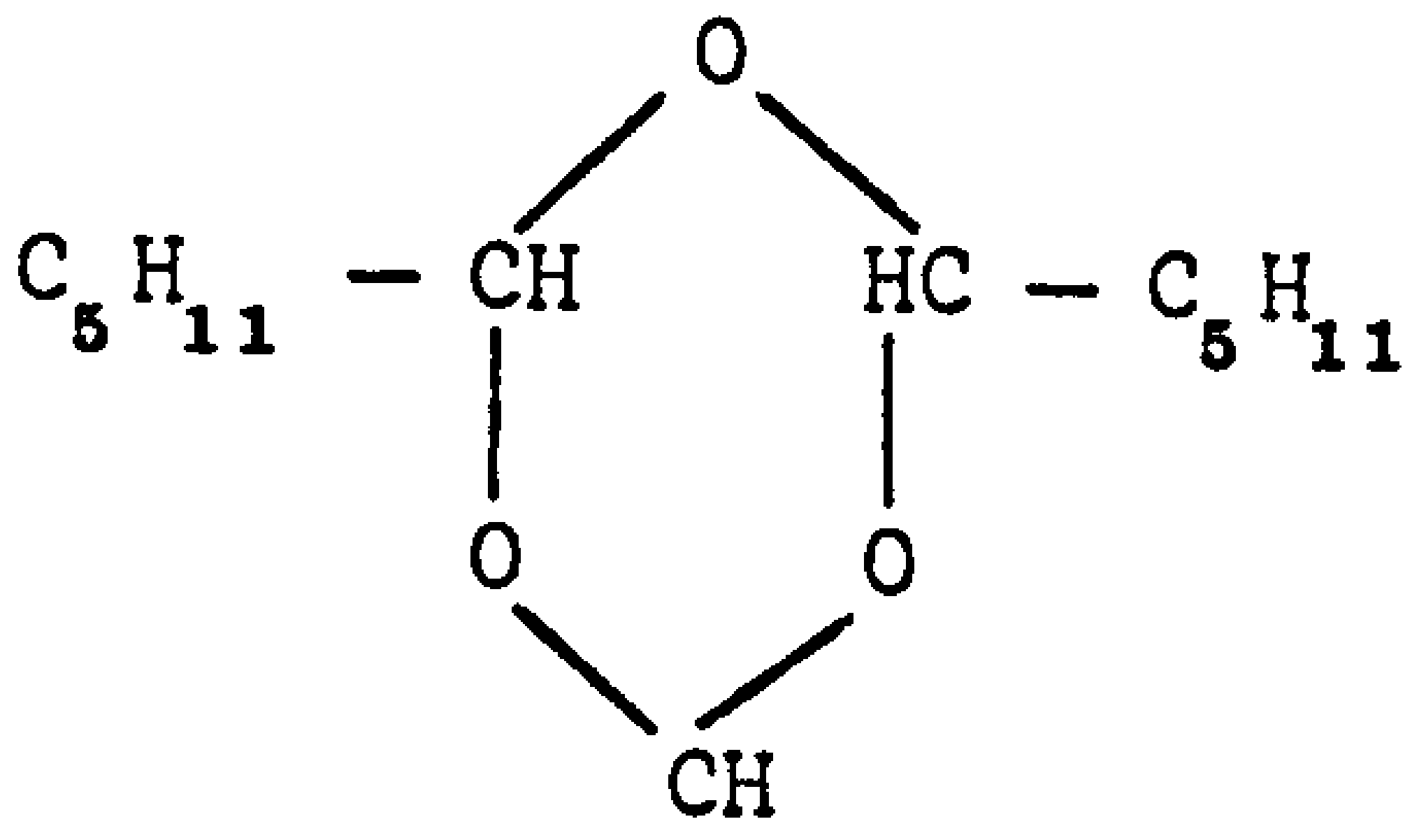
The presence of oxygenated cyclic compounds in highly oxidized methyl linoleate was reported by Horvat et al.(134). Mass spectroscopic analysis showed the formation of the following compounds during room temperature oxidation. They proposed the formation of these compounds through di- and trimerization of pentanals and hexanals.



2, 4-dipentyl, 1, 3-dioxolane







2, 4, 6-trialkyl trioxanes.

CHAPTER 2

AUTOXIDATION KINETICS

CHAPTER 2

AUTOXIDATION KINETICS

The various major reactions involved in autoxidation processes have been discussed to some extent in the previous chapter. Autoxidation reactions are influenced by various environmental factors and additives. Some of the agencies known to influence autoxidation reactions include metal salts, light, temperature, pressure, pH, impurities in substrate, etc. A more detailed account of how some of these factors affect autoxidation reactions is given in Chapter 3, section 3.5.0.

Also in the previous chapter, it was observed that decomposition of hydroperoxides gave rise to free radicals and other secondary products. Theories giving possibilities of a chain reaction were discussed. Further accounts of research evidences supporting the possibility of a free radical mechanism follow shortly.

AUTOXIDATIVE CHAIN REACTIONS

2.0.0 The Free Radical Mechanisms

The existence of a trivalent carbon was first reported by Gomberg(135),(136) as far back as 1900. He showed that hexaphenylethane $(C_6H_5)_3C-C(C_6H_5)_3$ could easily dissociate into two very reactive radicals $(C_6H_5)_3C^{*}$. The exact nature of free radicals remained obscure for some years after Gomberg's work, probably due to a vague definition given by Weiland(137). The definition was modified to read "A free radical is a chemical species which possesses an unpaired electron". During the study of the catalytic decomposition of hydrogen peroxide by ferrous and ferric ion, Weiss and Haber(138) proposed the following mechanism involving the free radicals OH^{*} and HO_2^{*}.

$$OH^{*} + H_2O_2 \rightarrow HOH + HO_2^{*}$$

$$HO_2^{*} + H_2O_2 \rightarrow O_2 + HOH + OH^{*}$$

The concept of chain reaction was first introduced by Bodenstein(139) following his work on hydrogen and chlorine gases. A chain reaction involves three distinct stages: initiation, propagation and termination. Kinetic features which distinguish chain reactions from other reactions are summarized as follows:

(i) The simple kinetic law:-

$$d[AB]/dt = K[A][B]$$

is not obeyed. In the autoxidation of a hydrocarbon represented here as RH;

$$[RH + O_2 \rightarrow ROOH].$$

The kinetic law is not as simple as:-

$$d[ROOH]/dt = K[RH][O_2]$$

(ii) From the collision theory of chemical kinetics, the rate constant of a bimolecular reaction is given by:

$$K = \sigma z_0 e^{-E/RT}$$

where E is the activation energy

z_0 is the Collison rate

σ is the probability factor.

The probability factor (σ) is sometimes so large that the only satisfactory explanation is one based on a chain reaction involving free radical intermediates.

(iii) A chain reaction initiated by light does not obey Einstein's law of photochemical equivalence and quantum yields may exceed unity by a large factor.

(iv) Stationary state kinetics are usually applicable to chain reactions. An assumption that the concentration of free radicals in the system is stationary at any given time is that:

$$d[\text{radical}]/dt = 0.$$

(v) Because chain reactions undergo initiation, propagation and termination stages, it is believed that catalysts and inhibitors are likely to affect the progress of the chain reactions.

2.1.1 Hydrocarbon Autoxidation

From the studies of Farmer(36),(37),(38), Bolland, Gee(47),(48) Bateman(88) and other workers on hydrocarbon autoxidation, certain conclusions were drawn: That the process involved a chain reaction with three distinct steps:-

$$\{\text{Initiator} \xrightarrow{r_1} \text{free radicals} \qquad (1a)$$

$$\begin{cases} R^* + O_2 \xrightarrow{K_2} RO_2^* & (2) \\ RO_2^* + RH \xrightarrow{K_3} ROOH + R^* & (3) \end{cases}$$

$$\left.\begin{cases} R^* + R^* \xrightarrow{K_4} \\ R^* + RO_2^* \xrightarrow{K_5} \\ RO_2^* + RO_2^* \xrightarrow{K_6} \end{cases}\right\} \begin{matrix} (4) \\ (5) \longrightarrow \text{stable products} \\ (6) \end{matrix}$$

where r_1 is the rate of free radical production. R^* and RO_2^* are radicals.

2.1.2 Initiation

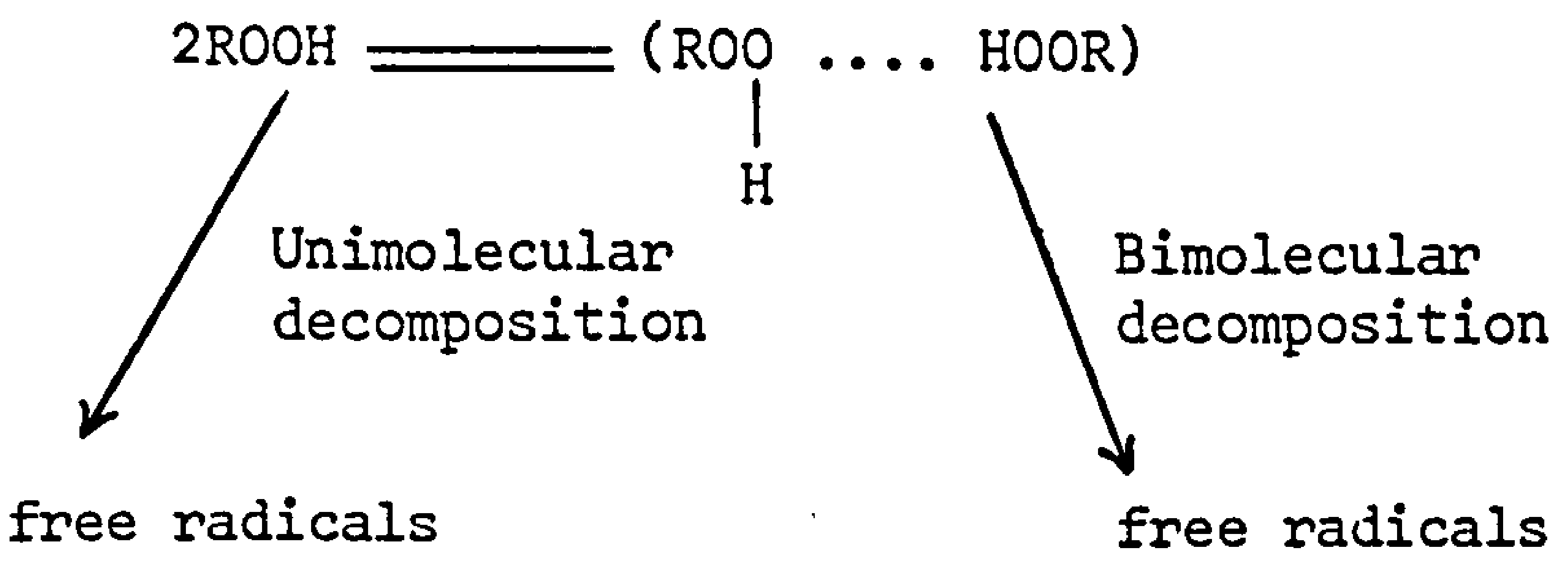
Autoxidation chain reaction can be initiated by a range of agents: light, heat, molecular oxygen, radiation etc. Kinetic studies of hydrocarbon autoxidation have revealed that subsequent oxidation of the substrate is autocatalyzed by the decomposition of hydroperoxides which produce radical chain carriers for the reactions(48),(140). The rate of hydroperoxide formation and the extent of decomposition bear a linear relationship. This implies that free radicals are produced in a bimolecular reaction.

$$2\mathrm{ROOH} \xrightarrow{K_1} \text{free radicals.}$$

Thus

$$d[\mathrm{ROOH}]/dt = K_1^{1/2}$$

The hydroperoxide decomposition has been found to be bimolecular above a certain concentration and unimolecular below it. This led to the suggestions that the bimolecular decomposition could be preceded by a molecular association of two hydroperoxide molecules in accordance with the equilibrium:



Infra-red spectroscopic evidence provided by Hughes and Bateman(141) supported the above assumptions.

Stannett and Mesrobian(142) obtained similar results for non-olefinic hydroperoxides. The decomposition was found to be a bimolecular second order reaction at 120°C for concentrations of 2 molar or above while changing gradually to first order at lower hydroperoxide concentrations.

Differences in the order of peroxide decomposition may not be mutually antagonistic(88).

2.1.3 Propagation

From the reaction scheme representing the chain reactions of hydrocarbon autoxidation, two reactions are possible during the propagation stage:

(i) Oxygen consumption (reaction 2)

$$R^* + O_2 \xrightarrow{K_2} RO^*$$

(ii) Hydroperoxide formation (reaction 3)

$$RO_2^* + RH \xrightarrow{K_3} ROOH + R^*$$

The rate constant K_2 defines the approximate quantitative relationship of the reactants and products during oxidation:

$$K_2 = [RO_2^*]/[R^*][O_2]$$

If after an interval of time dt, $[O_2]$ changes to $[O_2]'$ then the following changes are expected to occur within the time interval in order to maintain K_2.

$$[RO_2^*] \longrightarrow [RO_2^*]'$$

$$[R^*] \longrightarrow [R^*]'$$

If $[O_2]' > [O_2]$ then as $t \rightarrow \infty$, $[RO_2^*]/[R^*] \rightarrow \infty$, or as $[O_2] \rightarrow \infty$, $[R^*]/[RO_2^*] \rightarrow 0$. This means that at high oxygen pressure, $[R^*]$ may be neglected. Reaction (2) $R^* + O_2 \xrightarrow{K_2} RO_2^*$ is assumed to be very fast and the rate of oxidation becomes insensitive to further changes in oxygen pressure.

If $[O_2]' < [O_2]$, then with time, $[RO_2^*]/[R^*] \rightarrow 1$, or as $[O_2] \rightarrow 0$, $[R^*]/[RO_2^*] \rightarrow 1$. That is, at low oxygen pressure both $[R^*]$ and $[RO_2^*]$ are to be considered. Reaction (2) is slow and becomes dependent on the oxygen pressure. Decreasing the oxygen pressure is seen to decrease the overall rate of oxidation when reaction (2) is not incomparably faster than reaction (3) i.e. $[R^*]$ is not negligible compared with $[RO_2^*]$; and this occurs when $[RO_2^*]/[R^*] \to 1$.

The relationship between the reactants and products of reaction (3) $RO_2^* + RH \xrightarrow{K_3} ROOH + R^*$ is

$$K_3 = [ROOH]/[RO_2^*][RH]$$

During the time interval, dt, the change in $[RO_2^*]$ becomes s, where

$$s = \left\{[RO_2^*]' - [RO_2^*]\right\}$$

If within the same time interval, the reaction (3) can take up s_1 where $s_1 < s$, then there will be a build-up of excess $[RO_2^*]$ such that as $t \to \infty$,

$$[RO_2^*]/[R^*] \to \infty.$$

Only when the reactivities of both reactions (2) and (3) are nearly equal will $[R^*]$ remain appreciable and both $[R^*]$ and $[RO_2^*]$ must be considered.

The oxygen pressure at which the above condition prevails depends on the reactivity of the hydrocarbon. The lower the reactivity, the slower is reaction (3) and the lower the value of $[O_2]$ necessary to reduce the rate of reaction (2) accordingly.

Considering reaction (3) to be made up of two hydrocarbons R_1H and R_2H with rate constants K_{3a} and K_{3b} respectively. Let s_1 and s_2 be the amounts of excess $[RO_2^*]$ consumed by reaction (3) of R_1H and R_2H during the interval of time, dt.

If $K_{3a} > K_{3b}$, then $s_1 > s_2$ and there will be a more rapid build-up of excess $[R_2O_2^*]$ than $[R_1O_2^*]$ with time. To reduce this rate of build-up of excess $[R_2O_2^*]$, the ratio $[R_2O_2^*]/[R_2^*]$ must be reduced by decreasing the oxygen pressure, R_2H consequently consuming less oxygen. The radicals in the system are continuously consumed by reactions (4), (5) and (6).

RATE OF HYDROPEROXIDE FORMATION

The rate of hydroperoxide formation at low and high oxygen pressures has been briefly considered in the last section.

(i) At high oxygen pressure

Under this condition $[RO_2^*]$ is assumed to be much greater than $[R^*]$, i.e. $[R^*]$ is negligible. Termination reactions involving R^* may then be considered negligible.

Applying the stationary state conditions,

$$d[R^*]/dt = r_1 - K_2[R^*][O_2] + K_3[RO_2^*][RH]$$

$$d[RO_2^*]/dt = K_2[R^*][O_2] + K_3[RO_2^*][RH] - K_6[RO_2^*]^2$$

From above,

$$(d[R^*]/dt + d[RO_2^*]/dt = r_1 - K_6[RO_2^*]^2$$

The stationary state implies that at an instant the following assumptions are applicable:

$$d[R^*]/dt = 0$$

$$d[RO_2^*]/dt = 0.$$

But since $d[ROOH]/dt = K_3[RO_2^*][RH]$, the rate of hydroperoxide formation is obtained as:

$$d[ROOH]/dt = K_3(r_1/K_6)^{½}[RH].$$

Thus at high oxygen pressure, the rate of hydroperoxide formation is dependent on the substrate [RH] only.

(ii) At low oxygen pressure

At low oxygen concentrations, both $[RO_2^*]$ and $[R^*]$ are present in effective concentrations. The following assumptions may therefore be made.

$$K_2[R^*][O_2] = K_3[RO_2^*][RH]$$

$$K_4 = K_5 = K_6$$

Applying stationary state conditions

$$d[R^*]/dt = r_1 - K_2[R^*][O_2] + K_3[RO_2^*][RH] - K_4[R^*]^2 - K_5[R^*][RO_2^*]$$

$$d[RO_2^*]/dt = K_2[R^*][RO_2^*] - K_3[RO_2^*][RH] - K_5[R^*][RO_2^*] - K_6[RO_2^*]^2$$

Therefore

$$(d[R^*]/dt + d[RO_2^*]/dt = r_1 - K_4[R^*]^2 - 2K_5[R^*][RO_2^*] - K_6[RO_2^*]^2$$

The stationary state implies that:

$$d[R^*]/dt = 0; \quad d[RO_2^*]/dt = 0.$$

With the assumptions made above, the following relationships are obtained:

$$[RO_2^*] = (r_1/K_6)^{1/2} - [R^*]$$

$$[R^*] = K_3[RO_2^*][RH]/K_2[O_2]$$

and since

$$d[ROOH]/dt = K_3[RO_2^*][RH]$$

the following rate equation is then obtained

$$d[ROOH]/dt = K_3(r_1/K_6)^{1/2}[RH]\left(\frac{K_2[O_2]}{K_3[RH] + K_2[O_2]}\right)$$

This indicates that at low oxygen pressures, the rate of hydroperoxide formation is dependent on both the substrate and oxygen concentration.

From the work of Hargrave and Morris(143) it was shown that the hydroperoxide yield from ethyl linoleate accounts for 98% of the oxygen up-take. The rate of oxygen consumption can be approximated to the rate of hydroperoxide formation:

$$-d[O_2]/dt = d[ROOH]/dt$$

At high oxygen pressure:

$$-d[O_2]/dt = K_3(r_1/K_6)^{1/2}[RH]$$

This of course is dependent on the hydrocarbon concentration only.

At low oxygen pressure:

$$-d[O_2]/dt = K_3(r_1/K_6)^{1/2}[RH] \cdot \frac{K_2[O_2]}{K_3[RH] + K_2[O_2]}$$

and is dependent on both the hydrocarbon concentration and oxygen pressure.

Estimates of the constants for ethyl linoleate determined at 25^0C in $(\text{mole/l})^{-1}\text{sec}^{-1}$ are given below. Corresponding activation energies are also given in kilo calories.

Table 1·1

REACTION CONSTANT VALUES AND CORRESPONDING ACTIVATION ENERGIES

Time (hours)	2	4	5	6
K	1.0×10^6	20×10^6	50×10^6	20×10^7
E	0	0.4	-	2.6

An increase in rate constant for the chain propagation reaction K_3 increases the oxidation of a hydrocarbon.

THE CHAIN LENGTH

The kinetic chain length CHL (the average number of oxygen molecules consumed for each initiation act), is derived as follows:

$$CHL = \frac{d[ROOH]dt}{d[radicals]/dt} = \frac{K_3[RO_2^*][RH]}{r_1} = \frac{K_3[RO_2^*][RH]}{K_1[ROOH]^2}$$

At high oxygen pressure:

$$[RO_2^*] = (K_1/K_6)^{1/2}[ROOH],$$

and CHL is obtained as

$$CHL = \frac{K_3[RH]}{(K_1K_6)^{1/2}[ROOH]} .$$

The chain length here is found to be inversely proportional to [ROOH].

At low pressures of oxygen,

$$[RO_2^*] = (K_1/K_6)^{1/2}[ROOH]\left(\frac{K_2[O_2]}{K_3[RH] + K_2[O_2]}\right)$$

and

$$CHL = \frac{K_3[RH]}{(K_1K_6)^{1/2}[ROOH]} \cdot \left(\frac{K_2[O_2]}{K_3[RH] + K_2[O_2]}\right)$$

2.2.0 The Advanced Stage of Autoxidation

1.0 The Phenomenon of Maximum Rates

The rate representations given in the previous section apply only under mild conditions of oxidation where the chain lengths are long and where the amount of oxygen absorbed is approximately equal to the amount of hydroperoxide formed.

i.e. $-d[O_2]/dt = d[ROOH]/dt.$

The factors upon which the above assumption is based are disproportionately altered under more severe conditions e.g. high temperature, use of metallic activators (driers), long time intervals etc. The rate of hydroperoxide decomposition becomes appreciable under such conditions. The rate of oxidation, can no longer be equated to the rate of hydroperoxide formation.

(i) Rate of Hydroperoxide Formation

MAXIMUM RATES

Taking into account the hydroperoxide decomposition, a rate equation for the formation is:

$$d[ROOH]/dt = K_3(r_1/K_6)^{1/2}[RH] - r_1.$$

Since(48),(144) $r_1 = K_1[ROOH]^2$

$$d[ROOH]/dt = K_3(K_1/K_6)^{1/2}[ROOH][RH] - K_1[ROOH]^2$$

Assuming [RH] to be constant,

Let $a = K_3(K_1/K_6)^{½}[RH]$

$P = [ROOH]$

The above rate equation can be rewritten as

$$\frac{dP}{dt} = aP - K_1P^2$$

$$\int \frac{dP}{P(a - K_1P)} = \int dt$$

r_1 = rate of hydroperoxide formation

$$\frac{1}{a}\int\left(\frac{1}{P} + \frac{K_1}{a - K_1P}\right)dP = \int dt$$

$$\ell n\,\frac{P}{a - K_1P} = at + \text{constant}$$

Let $P = P_0$ when $t = 0$

$$\ell n\left(\frac{P}{P_0}\right)\left(\frac{a - K_1P_0}{a - K_1P}\right) = at$$

$$\left(\frac{P_0}{P}\right)\left(\frac{a - K_1P}{a - K_1P_0}\right) = e^{-at}$$

Let $P = P_\infty$ when $t \to \infty$

$$P_\infty = [ROOH]_\infty = a/K_1 = K_3[RH]/[K_1K_6]^{½}$$

$$\left(\frac{P_0}{P}\right)\left(\frac{P_\infty - P}{P_\infty - P_0}\right) = e^{-at}$$

On rearranging the expression for hydroperoxide concentration [ROOH] at any time t, it becomes

$$[ROOH] = \frac{[ROOH]_\infty}{1 - \left(1 - \left([ROOH]_\infty/[ROOH]_0\right)\right)e^{-at}}$$

When $\left([\mathrm{ROOH}]_\infty/[\mathrm{ROOH}]_0\right)$ is greater than unity, the time $t_{\frac{1}{2}}$ required for the hydroperoxide to reach one half its maximum value is:

$$t_{\frac{1}{2}} = \frac{1}{a}\,\ell n\left(\left([\mathrm{ROOH}]_\infty/[\mathrm{ROOH}]_0\right) - 1\right)$$

Since $[\mathrm{ROOH}]_\infty = K_3[\mathrm{RH}]/(K_1K_6)^{\frac{1}{2}}$, it can be seen that the value of $[\mathrm{ROOH}]_\infty$ will vary with temperature according to the magnitude of the expression;

$$E_3 - \tfrac{1}{2}(E_1 - E_6)$$

where E_3, E_1 and E_6 are the activation energies of reactions 3, 1 and 6 respectively. If this quantity is negative, then the steady state concentration of hydroperoxide will decrease with the increase in temperature and also $t_{\frac{1}{2}}$ will decrease very rapidly with increasing temperature.

(ii) Rate of Oxygen Consumption

If the amount of oxygen consumed is assumed to be equal to the gross quantity of hyroperoxide formed (i.e. no loss due to decomposition) then the rate expression for oxygen consumption is:

$$-d[O_2]/dt = K_3(K_1/K_6)^{\frac{1}{2}}[\mathrm{ROOH}][\mathrm{RH}]$$

On integration, the total amount of oxygen absorbed as a function of time is obtained as:

$$-d[O_2] = [\mathrm{ROOH}]_\infty at + [\mathrm{ROOH}]_\infty \ell n\left\{\frac{1 - \left(1 - \left([\mathrm{ROOH}]/[\mathrm{ROOH}]_\infty\right)\right)e^{-at}}{1 - \left(1 - \left([\mathrm{ROOH}]_\infty/[\mathrm{ROOH}]_0\right)\right)}\right\}$$

when $t \to \infty$ approaches the limiting value of

$-[O_2] = [\mathrm{ROOH}]_\infty\left(at - \ell n[\mathrm{ROOH}]_\infty/[\mathrm{ROOH}]_0\right)$.

Using the definition (γ) at any time during the oxidation for the chain length as the rate of oxidation divided by the rate of initiation, the following expression is obtained:

$$\gamma = \frac{K_3 RO_2^{*}[RH]}{K_1[ROOH]^2} = \frac{K_3(K_1/K_6)^{1/2}[ROOH][RH]}{K_1[ROOH]^2}$$

$$= \frac{[ROOH]_\infty}{[ROOH]}$$

Tobolsky(54) pointed out that the chain length which could be very large during the initial stages of autoxidation, becomes unity when the steady state concentration of hydroperoxide is reached. At the point where γ is unity, the propagation reaction (3) in the chain reaction proceeds at the same rate as the initiation reaction (1) and that of oxidation approaches a steady value which is maximum if $[ROOH]_0 < [ROOH]_\infty$.

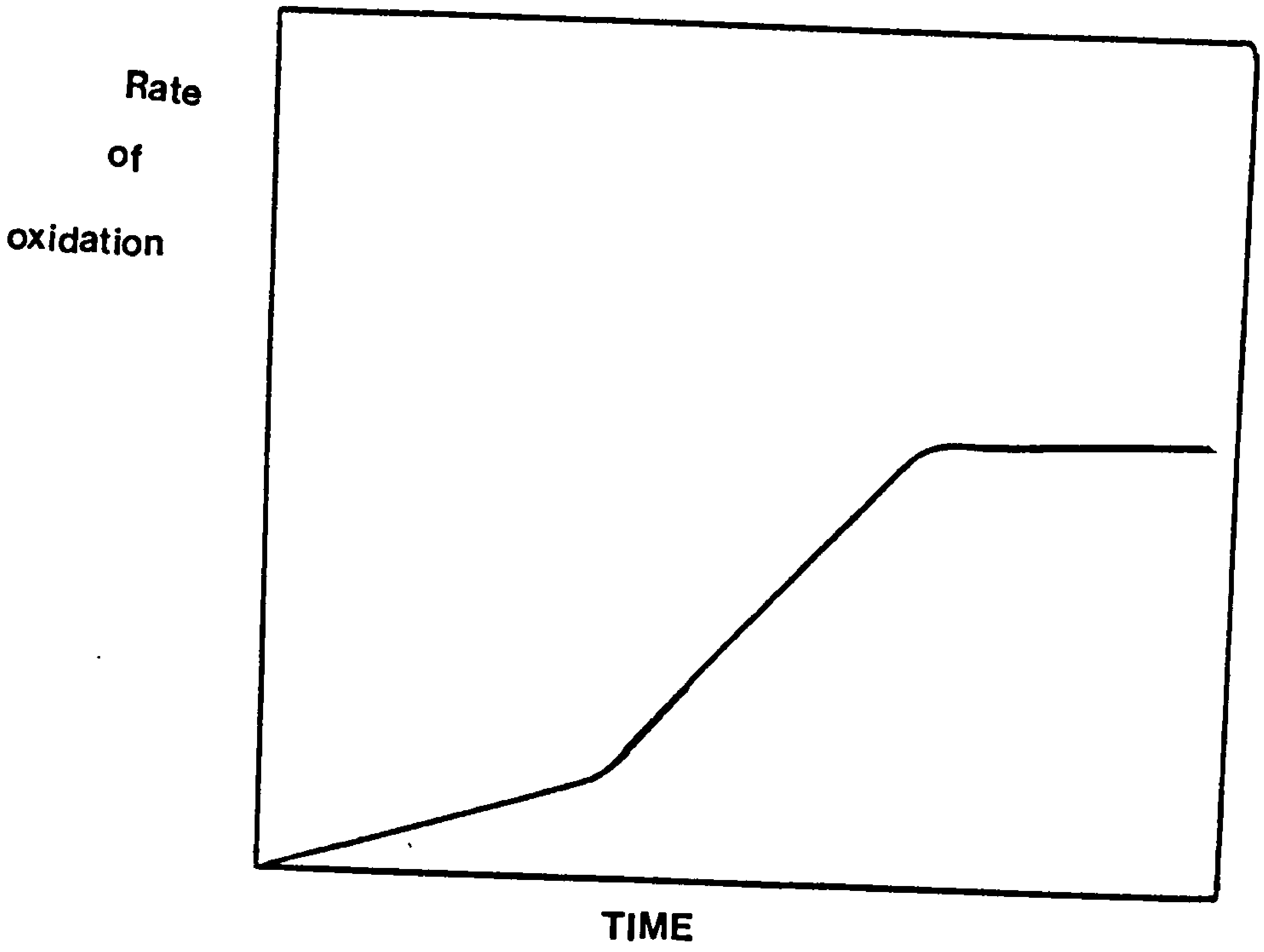
The steady state rate of oxidation (when the hydroperoxide has reached limiting concentration) is:

$$-d[O_2]/dt = K_3^2[RH]^2/K_6.$$

Fig 1·0

THE DECELERATION PERIOD

The sketch below is a rough representation of the rate of oxidation according to Tobolsky(144) et al.



Rate of oxidation of ethyl linoleate versus time

Bauman and Maron(145) gave a different representation resulting from their studies of the autoxidation of polybutadiene.

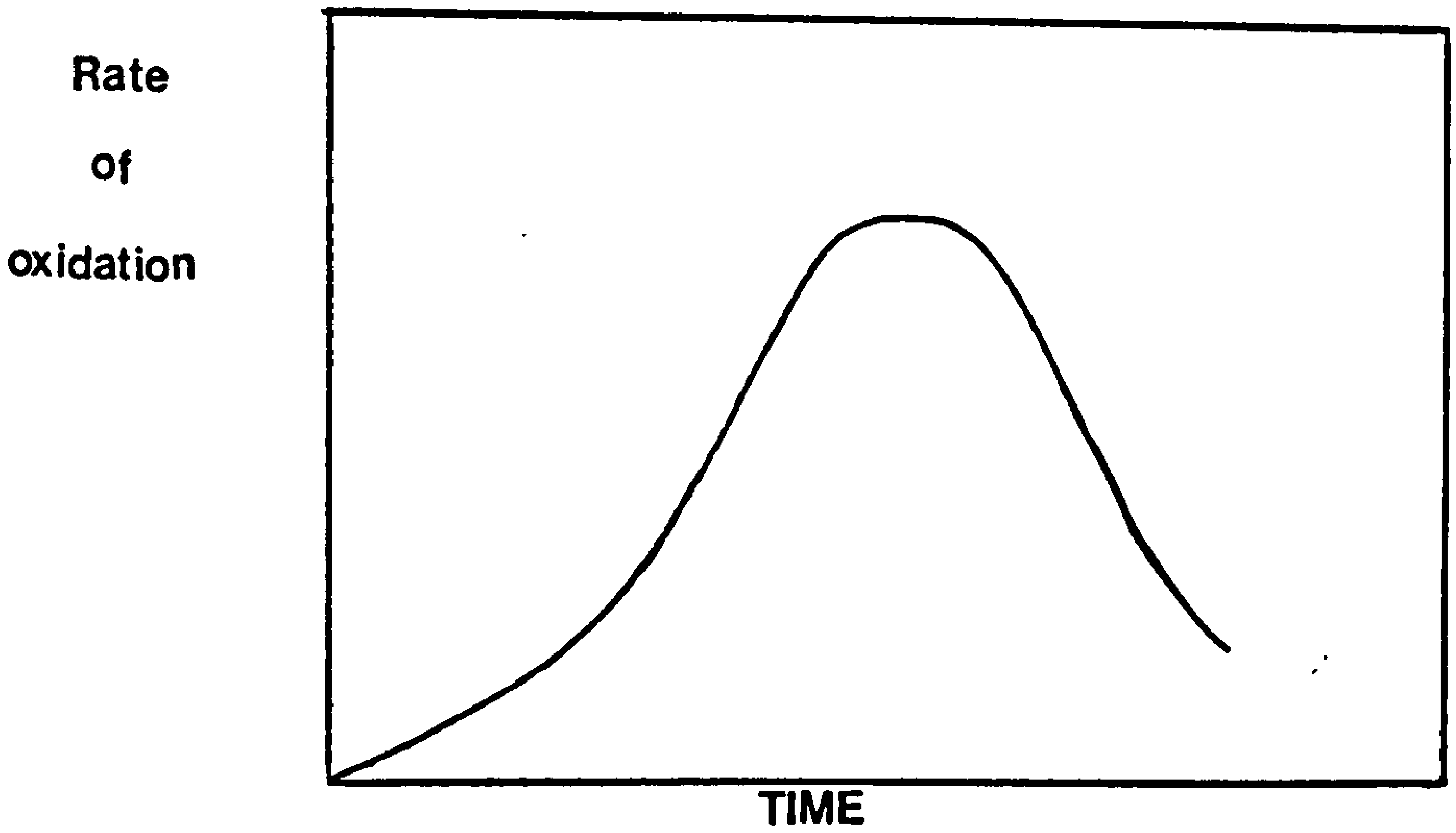


Fig 1·1 Oxidation of polybutadiene at 50°C.

Maron and Bauman in defending their results argued that the constant rate suggested by Tobolsky was not the maximum rate reached at the later stages of autoxidation; such results were typical only of stocks containing antioxidants. Their argument was based on an earlier report by Winn and Shelton(146), who working on the oxidation of a tread type RG-S vulcanizate showed that there are three stages in the oxidation.

(a) An initial rapid absorption, of apparently first order at constant pressure, which is of short duration.

(b) A constant rate of reaction, of apparent zero order at constant oxygen pressure, which would extend over most of the useful life of the vulcanizate in service. (An observed linear rate for the second stage would justify an assumption that a change in concentration of the remaining oxidizable groups is too small to affect the rate over the range. Thus, at constant oxygen concentration it takes the form of a zero order reaction.)

(c) An autocatalytic reaction, beginning after a given stock has absorbed a definite amount of oxygen that is independent of the temperature at which the absorption takes place. Maron and Bauman divided the rate curves into four regions viz.: the induction period, acceleration, deceleration and final periods.

Noting that the maximum steady-state rate of Tobolsky occurs at oxygen absorption levels similar to the constant rate period reported by Winn and Shelton, they pointed out that Tobolsky's rate equations may predict and represent rates up to the acceleration period, but are inadequate to define or predict the maximum rate.

Their main concern appears to have been the effect of assuming that the concentration of oxidizable hydrocarbon is constant as was done by Tobolsky. Apart from radical termination, deceleration may be caused in other ways. Two or more may be acting simultaneously. Possible causes include decrease in substrate concentration, hydroperoxide decomposition and diffusion limitation of the oxidation rate.

(iii) <u>Decreasing Substrate Concentration</u>

If [RH] is the initial concentration of the hydrocarbon, $[RH]_0$ the concentration present at any time, t, during the autooxidation process, and [ROOH] is the concentration of hydroperoxide formed during the process, then the following expression may be applied

$$[RH]_0 = [RH] - [ROOH]$$

Bauman and Maron[145] modified the equation

$$d[ROOH]/dt = K_3(K_1/K_6)^{1/2}[ROOH][RH] - K_1[ROOH]^2$$

to obtain on integration

$$[ROOH] = \frac{[ROOH]_\infty}{1 - \left\{1 - \left([ROOH]_\infty/[ROOH]_0\right)\right\}e^{-a't}}$$

where $a' = K_3(K_1/K_6)^{1/2}[RH]_0$ and

$$[ROOH]_\infty = \frac{a'}{K_3(K_1/K_6)^{1/2} - K_1}$$

Modifying the equation

$$-d[O_2]/dt = K_3(K_1/K_6)^{1/2}[ROOH][RH]$$

to $$-d[O_2]/dt = K_3(K_1/K_6)^{1/2}[RH]_0[ROOH] - K_3(K_1/K_6)^{1/2}[ROOH]^2;$$

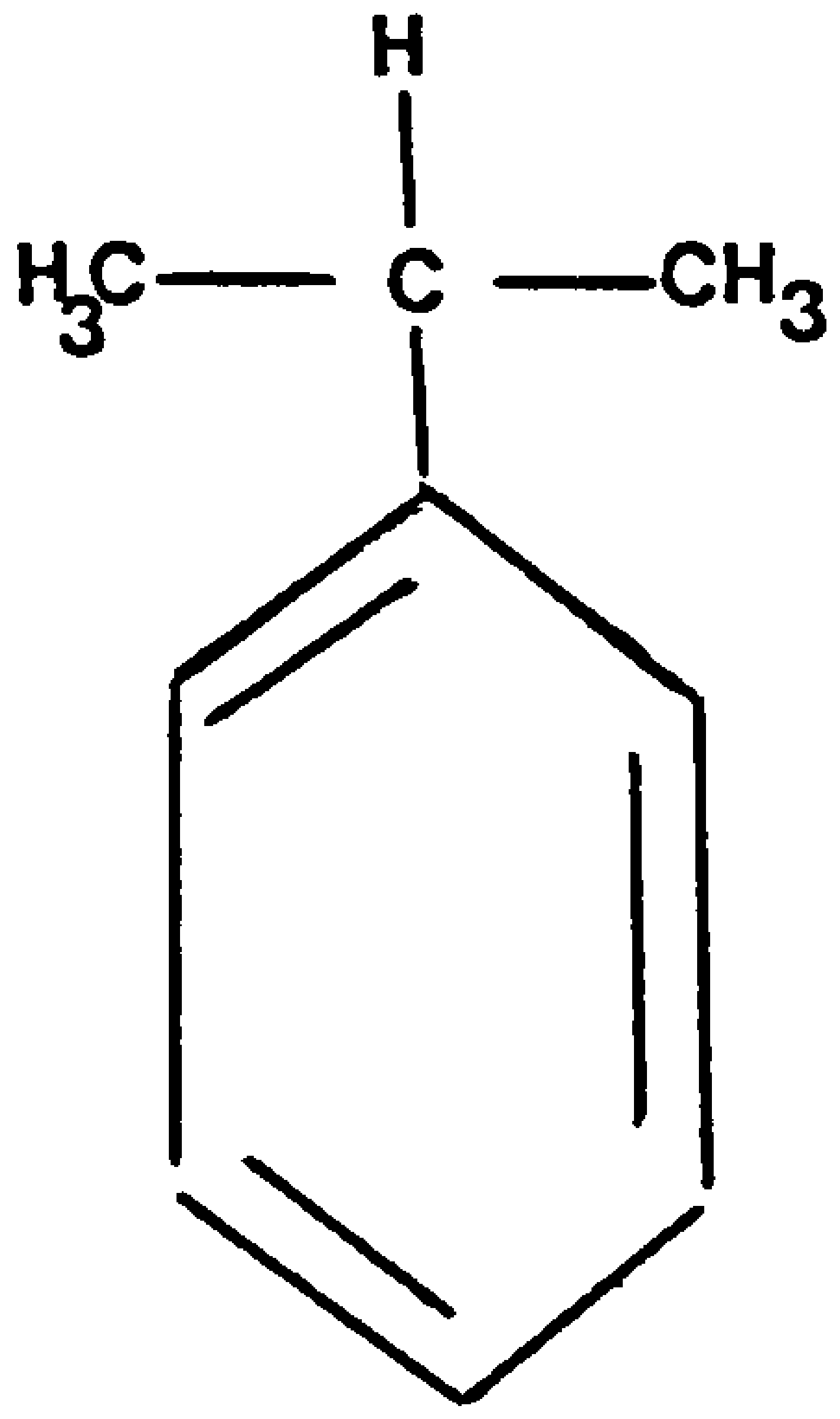
it is clear that a decrease in the hydrocarbon concentration could lead to a rate of oxygen consumption which can increase to a maximum and then decrease.

Bauman and Maron(145) in their results showed that the rate of oxidation at high temperatures is diffusion controlled and that the extent of oxidation would then depend on the thickness of the paint or oil film.

2·1·4 COOXIDATION

All drying and semi-drying oils contain fatty acids (saturated or unsaturated or both). The effects of these fatty acids on the drying characteristics have been mentioned (see section 1·3·3, 1 3 4)

Hilditch and Gunstone(147) studied the oxidation of methyl oleate, linoleate or linolenate at various temperatures. They found that peroxide formation and decomposition varied with time. These results do not give an accurate representation of the oxidation of linseed oil which contains three unsaturated fatty acids all reacting simultaneously. Competitive oxidation of two or more hydrocarbons is a very complex process. Russel(148) and some other workers(149) have studied the competitive oxidation of two hydrocarbons. Studies made by Russel(148) highlighted the effects of small amounts of reactive hydrocarbons (e.g. indan, cyclohexene, styrene and tetralin) present during the oxidation of cumene.



The following scheme represents the propagation stage, cumene and tetralin being represented by R_cH and R_tH respectively.

$$R_t^{*} + O_2 \xrightarrow{K_{2t}} R_tO_2^{*}$$

$$R_c^{*} + O_2 \xrightarrow{K_{2c}} R_cO_2^{*}$$

$$R_tO_2^{*} + R_tH \xrightarrow{K_{3tt}} R_tO_2H + R_t^{*}$$

$$R_tO_2^{*} + R_cH \xrightarrow{K_{3tc}} R_tO_2H + R_c^{*}$$

$$R_cO_2^{*} + R_cH \xrightarrow{K_{3cc}} R_cO_2H + R_c^{*}$$

$$R_cO_2^{*} + R_tH \xrightarrow{K_{3ct}} R_cO_2H + R_t^{*}$$

Applying steady-state conditions, the following expressions are obtained:

$$-d[R_tH]/dt = d[R_tO_2H]/dt$$

$$-d[R_cH]/dt = d[R_cO_2H]/dt$$

and

$$\frac{d[R_tH]}{d[R_cH]} = \frac{[R_tH]\left((K_{tt}/K_{3tc})[R_tH] + [R_cH]\right)}{[R_cH]\left((K_{3cc}/K_{3ct})[R_cH] + [R_tH]\right)}$$

The above equations indicate that the ratios K_{3tt}/K_{3tc} and K_{3cc}/K_{3ct} can be derived from a knowledge of the products formed from the competitive oxidation of mixtures having different initial hydrocarbon concentrations.

The values obtained by Russel at 90°C indicate that the rate of attack of a tetralylperoxy radical on a tetralin molecule is 16 times higher than that on a cumene molecule. For a cumylperoxy radical this factor is 23. These results show that there are differences in the reactivities of the α-hydrogen atoms of cumene and tetralin respectively. Tetralin has more α-hydrogen atoms than cumene.

Under similar conditions, the autoxidation of cumene and tetralin occur with the rate for tetralin expected to be greater than that of cumene. During cooxidation, the additions of small amounts of tetralin to cumene lowered the overall rate of the process. The following termination steps were devised to explain this mechanism (R^* is assumed to be negligible and therefore termination steps involving it (R^*) are neglected).

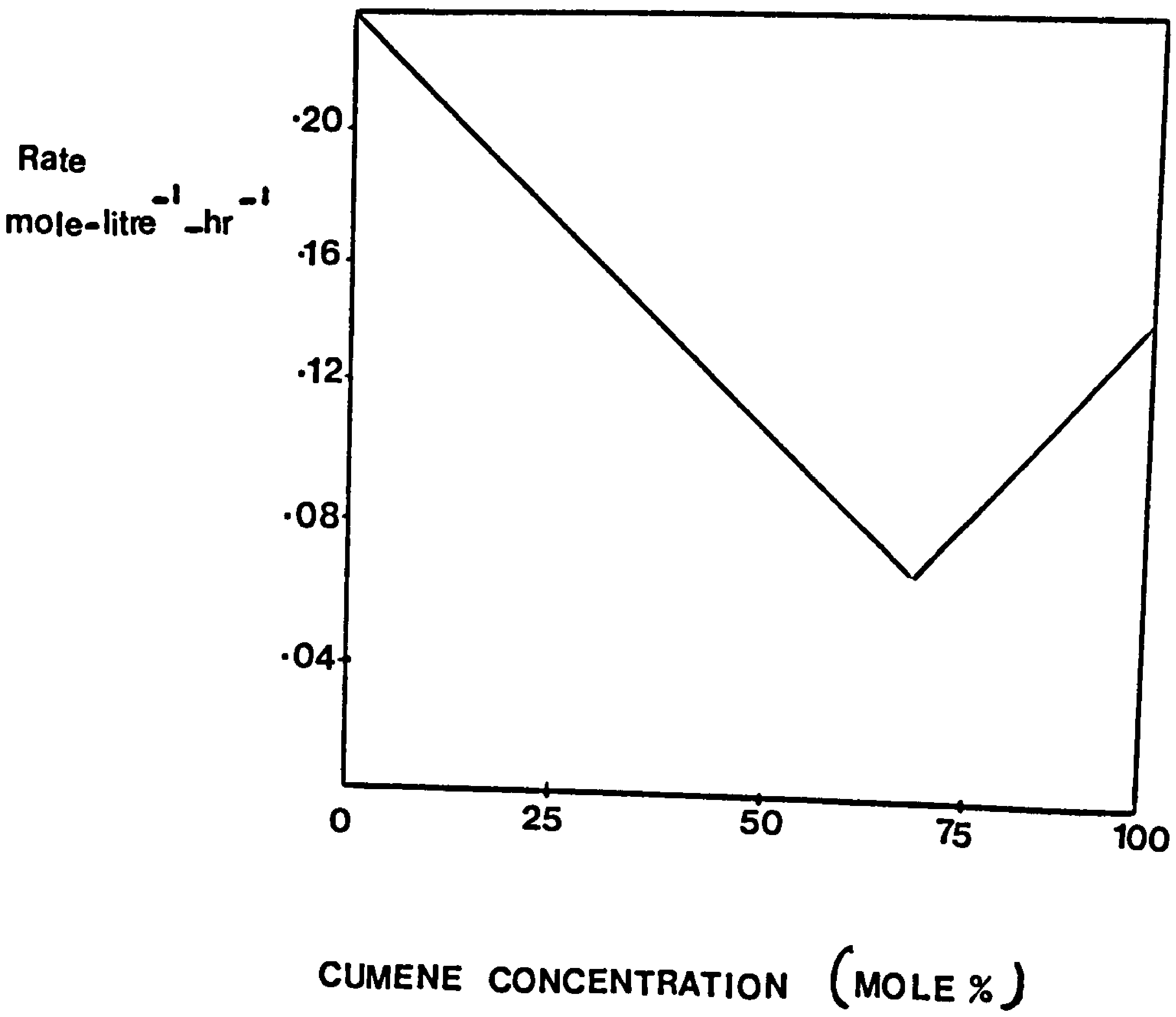
$$\left.\begin{array}{l} 2R_cO_2^* \xrightarrow{K_{6cc}} \\ R_cO_2^* + R_tO_2^* \xrightarrow{K_{6ct}} \\ 2R_tO_2^* \xrightarrow{\hspace{2cm}} \end{array}\right\} \text{stable products}$$

The values of the termination rate constants K_{6cc}, K_{6ct} and K_{6tt} have been calculated at 90°C(90),(150),(151) and it was found that they were in approximate ratios

$$K_{6cc} : K_{6ct} : K_{6tt} = 1 : 150 : 500$$

Because of the relatively high value of K_{6ct}/K_{6cc}, the cross-termination reaction must be playing a significant role in the lowering of the oxidation rate when tetralin was added to cumene. The high value of K_{6tt} serves to outweigh the greater tetralin activity until it (tetralin) is present in at least moderate concentrations.

Fig.12 gives a representation of Russel's results.



AUTOXIDATION OF A MIXTURE OF CUMENE AND TETRALIN AT 90°C.

Other workers(152),(153),(149) have reported the cooxidation of hydrocarbons. They estimated the kinetic parameters in a more comprehensive scheme than those employed by Russel. Various termination steps were considered and only peroxy radicals were assumed to be present due to the rapid oxidation of the other free radicals, (R^*) by oxygen.

If R_1H and R_2H are two different hydrocarbons, then their scheme can be represented as:

$$R_1O_2^* + R_1H \xrightarrow[O_2]{K_{3a}} R_1O_2H + R_1O_2^*$$

$$R_1O_2^* + R_2H \xrightarrow[O_2]{K_{3b}} R_1O_2H + R_2O_2^*$$

$$R_2O_2^* + R_1H \xrightarrow[O_2]{K_{3c}} R_2O_2H + R_1O_2^*$$

$$R_2O_2^* + R_2H \xrightarrow[O_2]{K_{3d}} R_2O_2H + R_2O_2^*$$

$$\left.\begin{array}{ll} 2R_1O_2^* & \xrightarrow{K_{6a}} \\ R_1O_2^* + R_2O_2^* & \xrightarrow{K_{6b}} \\ 2R_2O_2^* & \xrightarrow{K_{6c}} \end{array}\right\} \longrightarrow \text{stable products}$$

If R is the overall change in the rate of oxidation, then

$$-d([R_1H] + [R_2H])/dt = R$$

and upon addition of substances A_2 to A_1, the reaction may be written as:

$$dR = \frac{\partial R}{\partial A_1} \cdot dA_1 + \frac{\delta R}{\delta A_2} \cdot dA_2$$

Retardation occurs when

$$dR < 0 \quad \text{and} \quad \left[\frac{\partial R}{\partial A_1} \cdot A_1\right] < \left[\frac{\partial R}{\partial A_2} \cdot dA_2\right]$$

It can thus be seen that retardation is connected with large values of K_{6b}/K_{6a}. Inhibiting has been negated by the large values of K_{3c} in comparison to K_{3b}.

Thus if $\alpha_1 = K_{6a}/K_{3b}^2$; $= K_{6b}/K_{3b} \cdot K_{3c}$;

and $\gamma_1 = K_{3a}/K_{3b}$

then the retardation as proposed by Tsepalov(69) was the inequality

$$(\beta/\alpha_1) - (2/\gamma_1) > 1$$

Acceleration occurs when

$$dR > 0$$

and

$$\left| \frac{\partial R}{\partial A_1} \cdot dA_1 \right| < \left| \frac{\partial R}{\partial A_2} \cdot dA_2 \right|$$

The oxidation rate has been determined as the inequality

$$(2/\gamma_2) - (\beta/\alpha_2) > 1$$

where $\alpha_2 = K_{6c}/K_{3c}^2$

$\gamma_2 = K_{3d}/K_{3c}$.

Here again, the main factor responsible for the acceleration is K_{6b}/K_{6c}.

CHAPTER 3

DRIERS

CHAPTER 3

DRIERS

3.0.0 GENERAL DESCRIPTION

A drier is any material which promotes or accelerates the drying, curing or hardening of oxidizable coatings vehicles. A drier is different from other curing agents which react chemically or condense with the vehicle components and become an integral part of the final polymer. The main driers of importance to the paint technologist are a group of heavy-metal soaps of monocarboxylic acids. The acids used in the preparation of these soaps are such as to confer solubility of the metal compound in the vehicle system to be cured. A summary of the stages in drier development has been given in the historical preamble. For a soap to be used as a satisfactory drier, certain requirements must be met(9) :-

(1) The soap must be compatible in vegetable oils, preferably cold. The metal should be in a form capable of dispersing in the vehicle. The closer the dispersion approaches the molecular subdivision, the more effective is the cation. Thus, the acid radical is important in affecting solubility. The soap must be permanently soluble.

(2) The cost necessary to obtain adequate drying time should be low i.e. small amounts of drier should be effective.

(3) The soap should be stable on exposure in the concentrated form, neither causing a fire hazard nor becoming excessively oxidized.

(4) The soap should cause neither skinning nor discolouration of the paint.

(5) Driers should not be absorbed or adsorbed excessively by pigments.

(6) The active metal content should not vary during storage. This is necessary so that the precise amount of catalysts give predictable results.

(7) Drying throughout the film should occur, rather than surface drying or skinning as it is called. This depends on choosing the correct metal or combination of metals.

(8) The metal of the soap must be capable of existing in at least two stages of oxidation. Apparently the cation of higher valence should be stable in oxygen, but unstable in oil. Thus the metal will tend to oxidize to the higher valence under influence of oxygen or air, but will then be reduced by the oil with its simultaneous oxidation. The metal thus returns to a lower valence. The process will be repeated indefinitely.

The last of these requirements must in some cases be accepted with reservations. This is because some metals such as zinc, although having one valence state, do improve the catalytic effectiveness of other metals e.g. cobalt. Zinc alone does not act as a drier. In combination with cobalt, zinc probably acts synergistically in some way other than direct catalysis.

Most of the requirements stated above are for driers for vegetable oils and similar products. Some of the requirements such as high solubility and for many purposes, the existence of a soap metal in more than one valence, are applicable to catalysts in general(9). It has been suggested that those soaps of metals possessing only one valence which apparently catalyze reactions do so by promoting the solubility of immiscible phases. If metallic oxides are used in conjunction with a soap, the reaction is promoted by making possible a more intimate contact of solid and liquid. Most metals which function as driers and those which do not, are used as catalysts for numerous other processes though not combined as soaps.

As far as the ability to accelerate the drying of linseed oil is concerned, Van Wuellen-Scholten(155) has grouped the metals as follows: Cobalt (best), manganese, cernium, lead, iron, copper, nickel, vanadium, chromium, calcium, aluminium, cadmium, zinc and tin (poorest). Another worker(156) has classified them thus: Cobalt, vanadium, manganese, lead, iron, nickel, copper, and zinc. Other investigators have reported slightly different results. Their results are similar even though soaps possessing dissimilar anions or uncertain amounts of impurities were used. Variable drying conditions, different grades of linseed oil, different vehicles and variable temperatures all affect the effectiveness of a metal drier.

The functions of driers in paints can be outlined as follows:

(i) To cause a decrease in the maximum total oxygen absorption of the oil film. This would seem to indicate that the course of the reaction, as well as its velocity had been altered.

(ii) To cause solidification of the oil film at a much lower oxygen content.

(iii) To cause a marked shortening of the induction period before any obvious reaction occurs.

(iv) To accelerate the oxidation and polymerization of the oil.

The exact mechanism of how driers function is not fully understood. It is however believed that the induction period is shortened by counteracting inhibitors or antioxidants naturally present in the oil.

3.1.0 ORGANIC DRIERS

A number of natural prooxidants for drying oils have been studied. Their efficiency is low compared to metallic driers. Kaufman(157),(158) has investigated the use of carotenoids for drying oils. He observed that at least a doubling of drying speed was achieved with the addition of 0.005% carotene. Chlorophyl has been reported as a drying catalyst and a number of workers have investigated hemin(159),(160),(161). The activity as drying catalysts of these latter compounds appears to be related to their ability to complex metals.

Aldehydes(162) and carbonyl(163) compounds have been reported as driers but in most cases their performance is low except when used in conjunction with other conventional driers. There has been considerable work on various diamines and schiffs bases(164) as complexing agents. 1, 10-phenanthroline is one such compound that has attained commercial importance. The performance of these compounds varies not only with the coating system but also with the drier metal. Manganese increases in activity up to a point comparable to cobalt; iron increases but not to such an extent as manganese. The activity of cobalt is not affected with such additions. An optimum ratio of metal to accelerator exists and is in most instances a complex formation.

Although these compounds improve the drier performance, their use is limited due to high cost, effects on the original colour (discoloration) and due to complex formation in preference to the drier metals in systems containing zinc.

3.1.1 Manufacture of Metal Soaps

Three general techniques are commonly used to prepare metal soap driers. Commercial driers are a solution of designated metal soap in a hydrocarbon solvent such as mineral spirit.

(i) Fussion Process: This involves the direct reaction of the metal oxide or hydroxide with the chosen organic acid. Other metal salts which would produce a volatile by-product could also be used as the source of the metal. Lead, zinc, and calcium driers are commonly prepared by the fusion process. The oxides of these metals represent a relatively low-cost source of the metal.

The desired acid is dissolved in a hydrocarbon solvent and the metal oxide is slurried into the solution. The mixture is heated to reaction temperature, at which point the soap is formed and water is evolved.

(ii) Double-Decomposition Process: This process involves the reaction of the sodium salt of the chosen acid with a water-soluble soap of the desired metal. Some of these water-soluble soaps include cobalt, ceric or zirconyl sulphates etc. The reaction occurs in the presence of a solvent. Since the metal soap is not soluble in water layer, it is taken up in the solvent portion. At the completion of the reaction, the water and solvent layers are physically separated. Sodium sulphate or other sodium salt is formed as a by-product. For this reason, it is necessary to wash the solvent-layer with water to extract the salts before drying to the final product. The separation of the two phases is not always readily accomplished, since an excess of the sodium soap, one of the starting components can lead to problems of emulsification. Temperature control and other operational factors are also important if clean phase separation is to be obtained.

(iii) The DMR Process: The direct metal reaction process (DMR process) is a general method for the preparation of hydrocarbon solutions of metal soaps. With some modifications the process can be adapted for the preparation of metal salts of weak acids directly from the metal.

The DMR process consists of suspending finely divided metal in hydrocarbon solution of the acid, with a small amount of water present. The slurry is then air blown, or oxygen may be used for faster reaction at elevated temperatures.

The actual reactions may be viewed as a rapid corrosion of the metal to either the oxide or the hydro-oxide, followed by an immediate reaction of the oxide surface layer of the particle with the acid. The thin layer of newly formed oxide reacts quickly with the acid, thus exposing new metal surfaces to further oxidation. The principal advantages of the process are manufacturing and materials economies as well as the absence of extraneous salts in the finished product.

Although the DMR process is applicable to most metals, some metals produce water as by-product and others produce hydrogen. This potential hazard therefore places some limitations on the versatility of the method.

3.2.0 CATALYSTS FOR PAINTS

CATALYSIS

From thermodynamic calculations, it may be possible to determine whether at certain pressures and temperatures, certain reactions are thermodynamically possible with maximum yields at equilibrium. Unfortunately, thermodynamics give no indication of the time necessary for equilibrium to be attained. Many reactions are slow and therefore need agents to accelerate them. These agents are called catalysts. Also, there is usually a reduction in the process either occurring simultaneously or preceedingly.

Catalysts do not affect the maximum thermodynamic yield. The reaction is accelerated so that the result is obtained in a shorter time. The speeds of two reactions are rarely affected to the same degree; one is possibly accelerated while the other is inhibited. Consequently, a predominance of one compound may be formed if, as is often the case, the system is not given enough time to come to equilibrium.

Because catalysts have the ability to further reactions selectively, they are of tremendous importance for use in industries. A catalyst must possess a high degree of subdivision to obtain a large surface area and great reactivity.

(i) Positive Oxidation Catalysts

Soaps used in the paint and varnish industry (driers or siccatives) are at the present time the most important of positive oxidation catalysts. Driers have been treated in Chapter 2, section 2.1.5.

(ii) Negative Oxidation Catalysts

Whereas some of the metallic soaps earlier mentioned act as positive oxidation catalysts, some others influence the oxidation process quite negatively. They owe their importance by being capable of inhibiting the oxidation of organic materials particularly petroleum hydrocarbons. Strangely enough, some of the metallic soaps suggested as antioxidants have been used to promote oxidation e.g. naphthenates and oleates. A number of suggestions have been put forward to explain the mechanism. Brands(165) observed that the function of soaps in preventing or promoting oxidation of petroleum oils appears to be a function of temperature. At low temperatures an antioxidant effect is observed, while at high temperatures a prooxidant mechanism seems predominant. Tanaka, Kobayashi, and Furihata (166) found out that some substances which acted as antioxidants under certain conditions may be prooxidants in oils with other characteristics. They further proposed that these results could be explained by the formation of a peroxide of the antioxidazable substance, A, which could react with the addition agent, B:

$$AO_2 + B \underset{K_2}{\overset{K_1}{\rightleftharpoons}} BO_2 + A$$

where K_1 and K_2 are the reaction velocity constants in the directions shown. The effectiveness of B as an antioxidant is greater the higher the ratio K_1 to K_2.

The naphthenates and oleates of metals such as zinc, lead, manganese, tin, chromium, copper, cobalt, aluminium and calcium are mentioned in the literature as having varying degrees of effectiveness. Some of the work has been done on lubricating oils and transformer oils.

(iii) Polymerization and Condensation Catalysts

The drying of vegetable oils and compounds in which they are combined seems to be a combination of polymerization and condensation, though the polymerization effect is usually stressed. Polymerization appears to occur because of an inherent reactivity closely associated with free energy and is affected by such factors as the size and mobility of the molecules. Small quantities of catalysts effectively influence the reaction negatively or positively. Some metallic soaps act as oxidation as well as polymerization catalysts. The two effects are quite difficult to separate. The use of various soaps such as cobalt, manganese, iron and calcium to accelerate the polymerization of drying oils has been reported in the literature(167),(168).

(iv) Hydrogenation Catalysts

Hydrogenation or reduction occurs when hydrogen is combined with a compound and oxygen or its equivalent (i.e. elements such as sulphur, carbon, halogens or nitrogen) is withdrawn. The hydrogen for reduction may be generated from several sources; and is often active enough to reduce the compound without catalytic aid if generated in situ. Because molecular hydrogen from water gas, coke oven gas or similar sources is cheap, it is often used in preference to the atomic hydrogen generated by chemical methods. The catalyst in this instance, functions by causing gaseous hydrogen to combine with the substances capable of adding hydrogen to its molecular structure.

Metallic soaps acting as hydrogenation catalysts function in two ways:

(i) The soaps may be decomposed by the hydrogen to produce a finely divided metal and a compound from the reduced anion(221). In this case, it is questionable whether it is the soap which has the catalytic activity or the finely divided metal functioning in its usual manner. The polyvalent metals such as chromium, nickel, iron and copper are good examples of hydrogenation catalysts.

(ii) Soaps may be used in conjunction with other metallic oxides in liquid-phase hydrogenation. Under these conditions, the soaps seem to promote contact between the oxide catalyst and the organic compound. Nickel, copper, and iron soaps are good examples but the environment is not so strongly reducing as to decompose the soap.

That new paths are opened by catalysts, the contributions from which resulted in increased rates of reactions has earlier been mentioned. These new paths can be created in the following ways:-

(i) By assistance to those reaction paths which operate in the absence of the catalysts for example during the decomposition of hydroperoxides in a chain reaction. The following uncatalyzed path is illustrative:

$$\text{ROOH} \xrightarrow{K_1} \text{free radicals}$$

$$\text{Cat} + \text{ROOH} \xrightarrow{K_1} \text{free radicals} + \text{cat}$$

Here the catalyst assists by entering as a reagent, undergoes some chemical transformation and is ultimately regenerated so that its concentration remains constant.

(ii) By stabilising those reaction paths which could otherwise be very unstable in an uncatalyzed reaction. In this context, the effect of the catalyst may be the stabilisation of the intermediate stage of the corresponding uncatalyzed reaction path. The stabilizing effect is necessarily greater than that of the reactants.

e.g. $\text{ROOH} + \text{Cat} \text{ ——— } [\text{Complex}] \longrightarrow \text{radicals} + \text{Cat.}$

All active metal catalysts are transition metals. Coordination compounds of transition metals play important catalytic roles in a variety of reactions including oxdiation-reduction, substitution, addition and isomerization reactions of unsaturated molecules such as olefins. A number of recognizable factors contribute to this catalytic versatility in transition metals:

(i) The ability of transition metals to stablise a great variety of ligands through coordinations. Examples of these coordinations are σ-bonded ligands (H' and alkly groups); π-bonded ligands such as olefins, acetylenes, polyenes, allyl groups, etc.

(ii) The existence of relatively stable and highly reactive complexes of transition metals, notably the low spin d^7 and d^8 which by virtue of their electronic and structural properties exhibit high degrees of reactivity closely related to those of the "reactive intermediate" namely the free radicals.

(iii) The accessibility of different oxidation states and coordination numbers (a feature not entirely restricted to but most frequently exhibited by coordination compounds of transition metals).

Influencing the kinetic behaviour of an autoxidation reaction process implies that the catalysts can readily employ one, or a combination of the above factors. The way in which the catalysts are employed and the extent of their influence though of great technical significance, are still largely unexplained. There are suggestions that metal catalyzed autoxidation exhibits characteristic features similar to those described for chain reaction(154).

In a chain reaction catalyzed by metals, the relative concentrations of radicals present in the systems play a central role in defining the overall rate of autoxidation.

INITIATION:

The decomposition of hydroperoxides is the major initiation reaction

$$\mathrm{ROOH} \xrightarrow{K_1} \text{free radicals}$$

It is believed that metal catalysts employ their redox potential to interact with hydroperoxides, with primary reaction products being radicals.

$$\mathrm{ROOH} \xrightarrow{M^{(n+1)+}} \mathrm{RO_2^{\cdot}} + M^{n+} + H^+ \qquad (7)$$

$$\mathrm{ROOH} \xrightarrow{M^{n+}} \mathrm{RO^{\cdot}} + M^{(n+1)+} + OH^- \qquad (8)$$

$$\mathrm{2ROOH} \xrightarrow{M^{(n+1)+}/M^{n+}} \mathrm{RO_2^{\cdot}} + \mathrm{RO^{\cdot}} + H_2O \qquad (9)$$

Metal catalysts can therefore be broadly grouped as either:

(i) Strong oxidising agents e.g. lead,

(ii) Strong reducing agents e.g. iron,

or (iii) Equally oxidising and reducing agents e.g. cobalt.

(i) Strong oxidizing agents

With strong oxidizing agents such as lead, reaction (7) is dominant. Gunther and Bartlet(169) reacted lead tetraacetate with t-butyl hydroperoxide at -70^{0}C. They suggested that peroxy radicals RO_2^* were formed in the process.

$$ROOH + Pb(OAc)_4 \longrightarrow RO_2^* + AcOH + Pb(OAc)_3$$

Other investigators found that the rate of Pb^{4+} disappearance was a function of the square of the hydroperoxide concentration. They postulated that Pb^{4+} and the hydroperoxide interacted to form a complex:

$$Pb^{4+} + ROOH \text{ ——— } [Pb^{4+} . ROOH]$$

This complex is capable of interacting with a molecule of ROOH:

i.e. $$[Pb^{4+} . ROOH] + ROOH \longrightarrow .....$$

(ii) Strong reducing agents

Under this condition, reaction (8) is dominant. Kharasch and co-workers(170) have provided evidence for the existence of alkoxy radicals RO* during the decomposition of t-butyl hydroperoxide in the presence of butadiene at 0^{0}C. RO* and butadiene react to form stable products

$$2RO^* + 2H_2C = CHCH = CH_2 \rightarrow 2(ROC_4H_6)^* \rightarrow \{\text{stable products}$$

The kinetics of reaction between cumene hydroperoxide; its derivatives with ferrous salts in dilute aqueous solutions have been studied by researchers such as Williams and Fordham(171) and Orr and Williams(172). They proposed that

$$Fe^{2+} + ROOH \xrightarrow{K_{8a}} Fe^{3+} + RO^{*} + OH^{-} \qquad (8a)$$

The rate of disappearance of ferrous ions may be expressed as

$$-d[Fe^{2+}]/dt = K_{8a}[Fe^{2+}][ROOH]$$

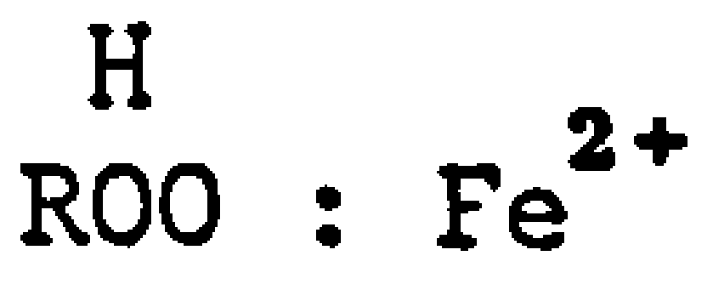
In the presence of oxygen and alkoxy radicals, the rate of ferrous ion disappearance was found to be second order at the initial stages and of different order at the later stages. The difference was explained by the assumption that the radicals were capable of forming hydroperoxides which further reacted with ferrous ions. The decomposition was carried out under a nitrogen atmosphere in the presence of acrylonitrile to prevent various side reactions. The acrylonitrile is capable of trapping RO^{*} radicals. The reaction is of second order:

i.e. $-d[Fe^{2+}]/dt = K_{8a}[Fe^{2+}][ROOH] = K_{8a}[Fe^{2+}]\{a - b + [Fe^{2+}]\}$

where $a = [ROOH]_0$, $b = K_{8a}[Fe^{2+}]_0$ or the initial concentrations

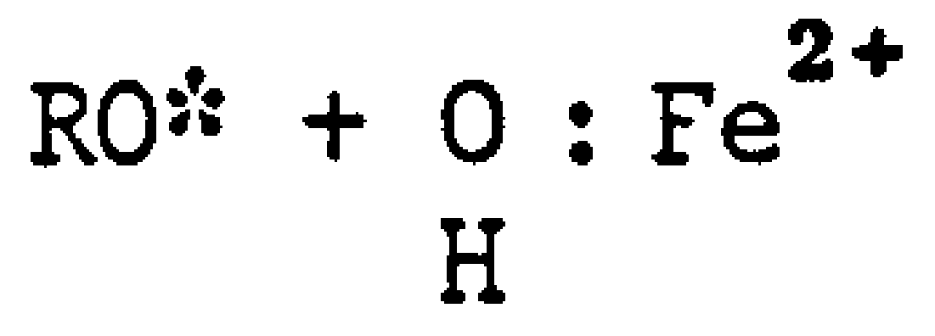
$$\ell n\left(1 + (a - b)/[Fe^{2+}]\right) = (a - b)K_{8a}t + \ell n\, a/b$$

Orr and Williams(172) investigated the kinetics of the reaction between isopropyl cumene, tertiary butyl cumene hydroperoxide and iron (11) in dilute aqueous solutions in the absence of oxygen and in the presence of a radical trap such as acrylonitrile. The activation energies of the thermal decomposition of hydroperoxides in the presence and absence of metal catalyst showed a substantial decrease in the former. Based on this fact, a reaction mechanism was suggested involving the donation of an electron by the iron to form a coordination of the iron with the oxygen adjacent to the hydrogen before reacting to form a complex of the type



$$\overset{H}{ROO} : Fe^{2+}$$

The excess electron at the O-O linkage should cause a more rapid rate of dissociation. The complex therefore dissociates immediately to



$$RO^{\ast} + \underset{H}{O} : Fe^{2+}$$

(iii) Equally oxidising and reducing agents

Cobalt and manganese are the most important in this group, e.g.

$$ROOH + Co^{2+} \longrightarrow RO^{\ast} + Co^{3+} + OH^{-} \qquad (9a)$$

$$ROOH + Co^{3+} \longrightarrow RO^{\ast} + Co^{2+} + H^{+} \qquad (9b)$$

The existence of $RO_2^{\ast}$ and $RO^{\ast}$ radicals was proved(173) by using butadiene as solvent and cobalt salts. Bickell and Kooyman(174) and Horswill and Ingold(175) have provided further evidence for the formation of $RO_2^{\ast}$ and $RO^{\ast}$ radicals. Besides reacting with hydroperoxides as simple metal ions, various complexes between metal salts and hydroperoxides have been postulated in order to explain kinetic results obtained by various investigators.

Skirrow and Dean(176) have it that an equilibrium association occurs between Co ions and t-butyl hydroperoxide in acetic acid.

$$ROOH + Co^{2+} \text{ ——— } [Co^{2+} . ROOH]$$

$$[Co^{2+} . ROOH] \longrightarrow Co^{3+} + RO^{\ast} + OH^{-}$$

Korsum and co-workers(177) studied the catalytic decomposition of ethylbenzene hydroperoxide by cupric stearate in chlorobenzene. The following reactions were suggested:

$$CuSt_2 + ROOH \text{ ——— } [CuSt_2 . ROOH]$$

$$CuSt_2 . ROOH \longrightarrow CuSt + RO_2^{\ast} + HSt$$

Complex formation between copper and hydroperoxides was further reported by other investigators(178),(179),(180).

Kamiya and co-workers(181) observed that during the cobalt (II) catalyzed autoxidation of tetralin in nonpolar media e.g. chlorobenzene, the initial hydroperoxide concentration only affected the maximum oxidation rate up to a certain limiting concentration. This implied that the rate determining chain initiation reaction was not a simple bimolecular reaction but a rate controlling step which involved the slow decomposition of a rapidly formed complex. The same observation was made for manganese(181) i.e.

$$ROOH + Mn^{3+} \overset{\text{fast}}{\rule{3em}{0.4pt}} [ROOH \, . \, Mn^{3+}]$$

$$[ROOH \, . \, Mn^{3+}] \xrightarrow{\text{slow}} RO_2^{\ast} + Mn^{2+} + H^{+}$$

Uri(89) postulated the following equations to explain the rate expression obtained during the cobaltous stearate catalyzed oxidation of methyl linoleate in benzene

$$Co^{2+} + O_2 \;\rule{3em}{0.4pt}\; [Co^{2+}O_2]$$

$$[Co^{2+}O_2] + Co^{2+}(XH) \longrightarrow Co^{2+} + Co^{3+} \, . \, X^{-} + H_2O$$

(XH) = substrate or solvent.

The formation of radicals during the reaction of oxygen with styrene and cobalt (11) stearate in chlorobenzene using α-naphthylamine as inhibitor has been observed by Denisova et al.(182). They postulated a complex between oxygen and Co^{2+} followed by radical formation

$$Co^{2+} + O_2 \;\rule{3em}{0.4pt}\; [Co^{2+} \, . \, O_2]$$

$$[Co^{2+} \, . \, O_2] + CH_2 = CHR \longrightarrow Co - O_2 - \overset{\ast}{C}H - R$$

Elvidge and Lever(91) observed that manganese porphyrin complex forms reversible oxygen complexes. The oxidation of tetralin at 70°C catalyzed by cobalt naphthenate showed that the addition of hydroperoxide inhibited the reaction(183). This observation led the researcher to suggest that the main chain initiation reaction involved a metal oxygen complex. Iron in haemoglobin forms a well known metal-oxygen complex.

3.3.0 TERMINATION

In metal catalyzed reactions only the oxy RO^{*} and the peroxy RO_2^{*} radicals may be considered useful. This is because in most accelerated reactions, R^{*} is negligible.

Oxy radicals

The decomposition of α-cumyl hydroperoxide by aqueous solutions of ferrous salts has led Kharasch et al.(184) to suggest that one of the steps involved the reaction between ferrous ions and cumyloxy radicals:

$$C_6H_5(CH_3)_2Co^{*} + Fe^{2+} \xrightarrow{H_2O} C_6H_5(CH_3)_2COH + Fe^{3+}$$

Similar reactions were observed for cobaltous salts(151),(177),(185) and cuprous salts .

$$C_6H_5Co^{*} + CuCl \longrightarrow C_6H_5CoCuCl$$

Cuprous chloride is capable of reacting with a benzoyloxy radical to form a trapped radical.

Peroxy radical: RO_2^{*}

Kharasch et al.(75),(94),(95) have in addition suggested a reaction whereby the oxygen liberated is accounted for during metal salt catalyzed decomposition of hydroperoxides:

$$RO_2^{*} + M^{(n+1)^+} \longrightarrow R^{*} + M^{n+} + O_2$$

Reaction with substrate

Bawn and Sharp(190) studied the reaction between various unsaturated hydrocarbons such as Octane-1 and cobalt salts in polar media. They proposed that:

$$RCH = CH_2 + Co^{3+} \longrightarrow R\overset{*}{C}H - \overset{+}{C}H + Co^{2+}$$

Bawn and Jolley(187) showed that metal-substrate interaction was a major interaction for olefins during the induction period; [ROOH] = 0.

The addition of hydroperoxide or its initial presence as an impurity enhances the catalytic activity of cobalt salts in polar media by reacting with the hydroperoxides(188).

Twigg and Wise(189) studied the reaction between ferrous ions and cumene hydroperoxide in dilute acid (aqueous) in the absence of oxygen and a radical trap. They expressed the ratio R_1, the number of moles of ferrous ion oxidized per mole of peroxide consumed, as

$$R_1 \equiv \frac{d[Fe^{2+}]}{d[ROOH]}$$

At low ferrous ion concentrations, R_1 was found to be independent of ferrous and peroxide concentrations. At high ferrous ion concentrations, R_1 tended towards the value of 2.

The effect of varying concentrations of different catalysts on autoxidation processes has also been studied by other workers(190). They reported that at high catalyst concentrations:

$$-d[O_2]/dt = K[RH]^2[Cat]^{\frac{1}{2}}$$

and $$[ROOH] \propto [RH]^2$$

and at low catalyst concentration:

$$-d[O_2]/dt = K[RH]^2[Cat]$$

and $$[ROOH] \propto [RH^2][Cat].$$

The rates are more dependent on catalyst concentration at low catalyst concentration levels than at high concentration levels. Studies(191),(192) have been made to explain this dependence at low catalyst concentrations. Kamiya and co-workers(192) working on cobalt-catalyzed autoxidation of tetralin in a non-polar medium observed that the oxidation rate decreased after reaching its maximum value. The lower the cobalt concentration, the lower the extent of oxidation.

Reactivation by metal catalyst-hydroperoxide interaction has been considered and suggestions have been made as to what factors influence the deactivation process(192):

(i) Non-polar medium (when polar medium was employed cobalt deactivation was not observed).

(ii) Precipitation of metal compounds formed during autoxidation(192).

(iii) Interaction between the metal and the substrate(193).

Side reactions may contribute to deactivation(191). Examples of such side reactions include:

$$\begin{aligned}
&\mathrm{ROOH} + \mathrm{CoA_2} &&\longrightarrow \mathrm{RO^*} + \mathrm{CoA_2OH}\\
&\mathrm{ROOH} + \mathrm{CoA_2OH} &&\longrightarrow \mathrm{CoA(OH)}\downarrow + \mathrm{AH} + \mathrm{RO_2^*}\\
&\mathrm{ROOH} + \mathrm{CoA(OH)} &&\longrightarrow \mathrm{CoA(OH)_2}\downarrow + \mathrm{RO^*}\\
&\mathrm{ROOH} + \mathrm{CoA(OH)_2} &&\longrightarrow \mathrm{Co(OH)_2}\downarrow + \mathrm{AH} + \mathrm{RO_2^*}\\
&\mathrm{ROOH} + \mathrm{Co(OH)_2} &&\longrightarrow \mathrm{Co(OH)_3}\downarrow + \mathrm{RO^*}
\end{aligned}$$

where A is an anion (decanoate, stearate, naphthenate, etc.).

Kamiya employed the concept of deactivation to explain the kinetic orders of results previously obtained by other workers for low concentrations of cobalt ($< 2 \times 10^{-4}$ M). At these low concentrations, a significant fraction of cobalt may become deactivated when relatively little of the hydroperoxide has been decomposed. First order plots of hydroperoxide decomposition would therefore show marked curvature and the measured rate constant may appear to decrease rather than increase as cobalt concentration is increased.

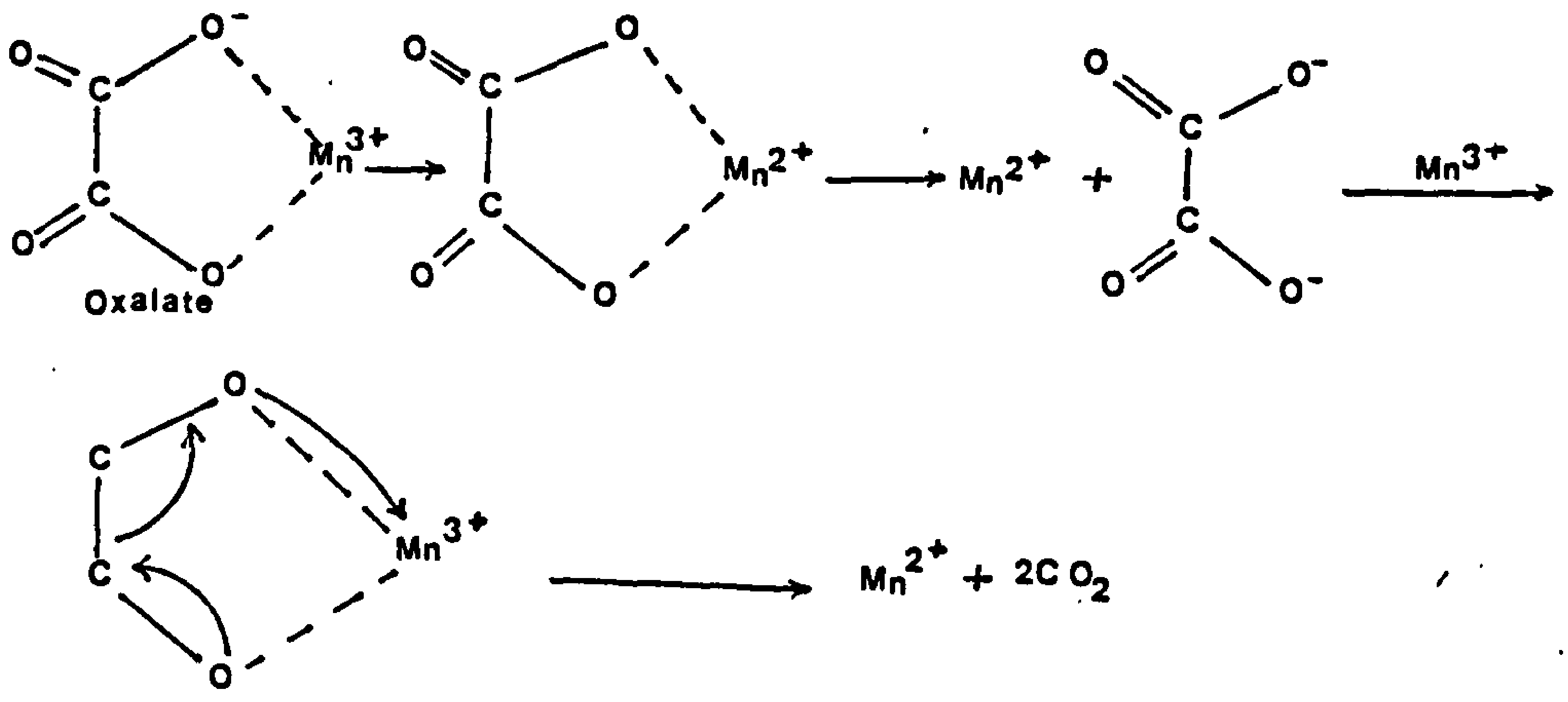
3.4.0 METAL-CATALYZED OXIDATION OF ORGANIC SUBSTRATES: DIOXYGEN COMPLEXES AS INTERMEDIATES

The oxidation of organic substrates by molecular oxygen in the presence of metal ions may occur by direct oxidation through an inner sphere electron transfer from the ligand to the metal ion in solution. In some cases, evidence has been found for a concerted (joint) reaction involving a metal-ligand dioxygen complex. In many systems, the presence of an oxygen complex as an intermediate has been inferred through a study of reaction kinetics. Such complexes are usually unstable and exist in solution in trace and undetectable amounts. The recent advances in the synthesis of a wide variety of metal ions complexes (primarily cobalt (ii)) has made possible the study of direct oxidation of organic substrates by dioxygen complexes. Arthur Martell(194) studied such reactions as models for oxidase and oxygenases enzyme systems. He believed that redox reactions of dioxygen complexes could provide analogous reactions in which a dioxygen complex occurred only as a reactive intermediate at very low concentrations.

Typical examples of the direct oxidation of an organic ligand by a coordinated metal ion are given in plate (i). Early kinetic work by Duke(195) and Taube(196),(197) is illustrated by the oxidation of oxalate in a manganese (iii) oxalate complex. The kinetics of the reaction involves two successive one-electron transfers from the oxalate to the manganese (iii). This is followed by a second one-electron transfer to give the final products comprising two moles of

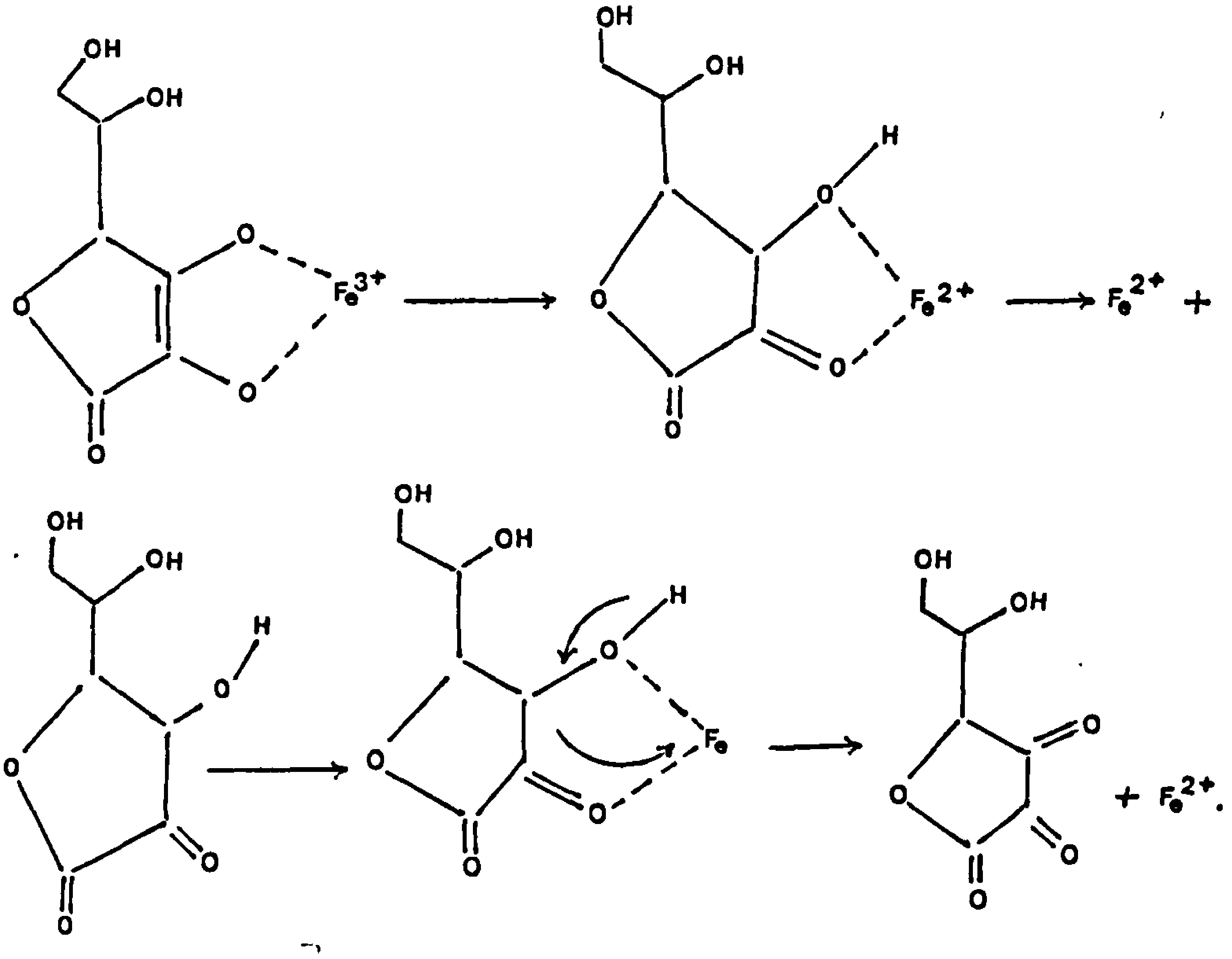
Plate 1

Direct Oxidation Of Ligand By Metal Ion.



Scheme 2

Ascorbic Acid



carbon dioxide and two manganous ions. Scheme 2 shows the oxidation of the monoanion as ascorbic acid by coordinated ferric ion. The sequence of reactions is similar with two ferric ions required for a two-electron reduction of ascorbic acid to dehydroascorbic acid. The formation of a free radical intermediate and the dissociation of reduced metal ion is followed by recombination of the intermediate with an additional Fe (iii) ion. The kinetics of this and similar reactions have been described(198) and the oxidation of glycols by cernium (iv)(199),(200) and ethylenediamic and glycine by copper (ii) and other metal ions have been reviewed by Martell(201).

(i) Effect of Molecular Oxygen

Most redox reactions of metal ions involve one electron transfer. Molecular oxygen may be reduced to some stable species by a two-electron transfer to peroxide or by a transfer of four electrons to water. The interacting organic substrates are generally oxidized to stable species in two electron steps. There are a few cases where one electron oxidations produce stable intermediates for example semi-quinones in which the intermediate free radical is resonance stabilized.

Hamilton proposed a scheme in which the metal ion may catalyze a smooth transfer of two electrons from an organic reducing agent to dioxygen (plate 2). The first reaction between a catechol and an azo compound producing a quinone and a substituted hydrazine, occurred with some difficulty. The electron transfer only took place through the formation of high energy free radical intermediates. Similar reactions could occur in an intramolecular fashion, the two groups, the oxidant and the reductant being bound together within the same molecule.

Another way of bringing the reducing and oxidizing groups together is through simultaneous coordination with a metal ion as shown in plate (3). The metal provides a smooth pathway for electron transfer from the reductant to the oxidant without the formation of free radical intermediates in appreciable concentration. This reaction pathway is lower in energy and therefore faster, regardless of whether the electron transfer occurred by ionic fashion or by two-electron steps.

(ii) Metal-Ion Catalysis

The performance of certain metallic compounds of lead, cobalt, nickel, copper, iron, etc. as oxidation catalysts has been mentioned earlier.

Figure 1·3 shows the linear dependence on copper (ii) concentration of the pseudo first order oxidation of ascorbic acid by molecular oxygen at various pH values. The hydrogen ion dependence on the reaction indicated that the reactive intermediate was a monophotosated copper (ii) ascorbate chelate. The second order rate constants calculated from the same data were found to be proportional to the dioxygen concentration in the solution. At low concentrations of dioxygen, this dependence was found to level off indicating a change in reaction mechanism. Since the rates observed were much higher than those measured for the oxygen free system (plate 1), the evidence indicates the formation of an intermediate ascorbate-copper-dioxygen complex in which electron transfer is more facile than is possible in a simple ascorbate copper (ii) complex. A possible mechanism for this type of catalysis is as shown in plate 3. The stability of the intermediate copper-ascorbate-dioxygen complex would be enhanced by resonance structure illustrated. The copper (ii) is coordinated to the superoxide anion and the ascorbate free radical from which one electron has been removed. Other resonance forms capable of stabilizing the intermediate dioxygen complex are possible. This mechanism may involve two-electron transfers instead of the usual single two-electron transfers. The

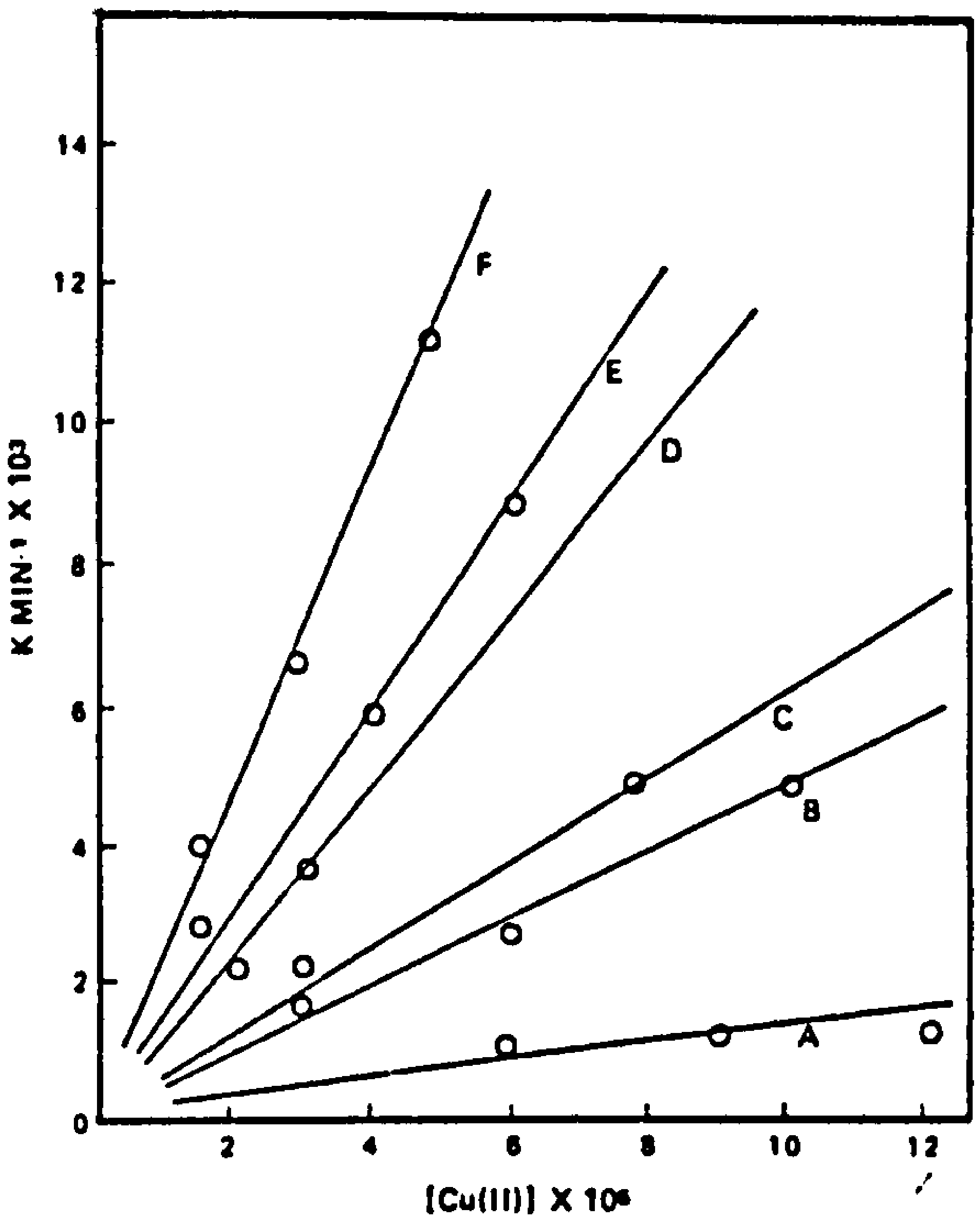


Fig. 1.3 Catalytic effect for the oxidation of ascorbic acid in the presence of Cu(II) ion at 25°, at -log $[H^+]$ values of: A, 1.50; B, 2.00; C, 2.25; D, 2.50; E, 2.85; F, 3.45. $\mu = 0.10$ M KNO_3.

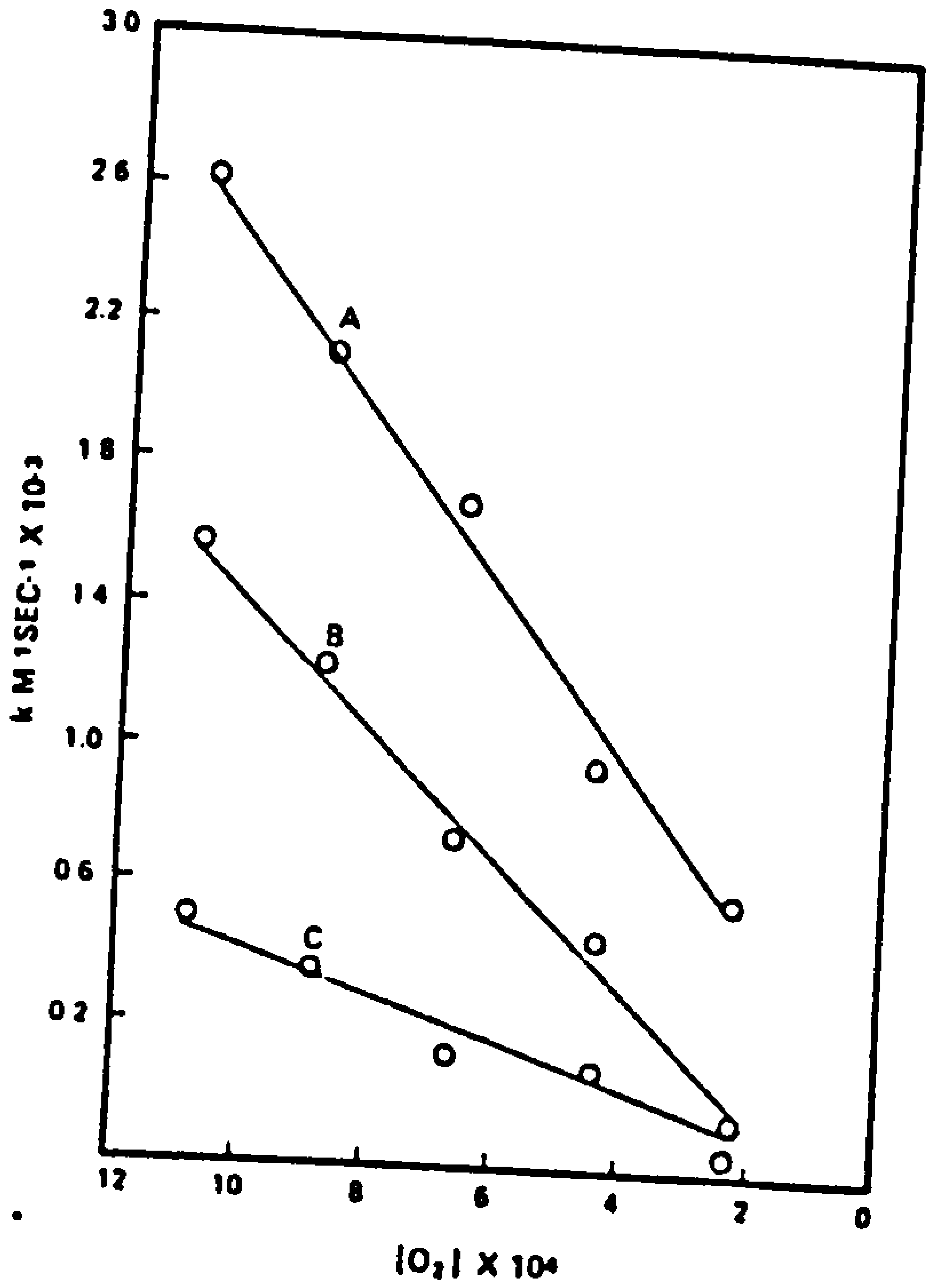


Fig.1.4 Dependence of the specific rate constants k on oxygen concentration for Fe(III) ion catalyzed oxidation of ascorbic acid at 25°; -log $[H^+]$ values of: A, 3.85; B, 3.45; C, 3.00; $\mu = 0.10$ M (KNO_3).

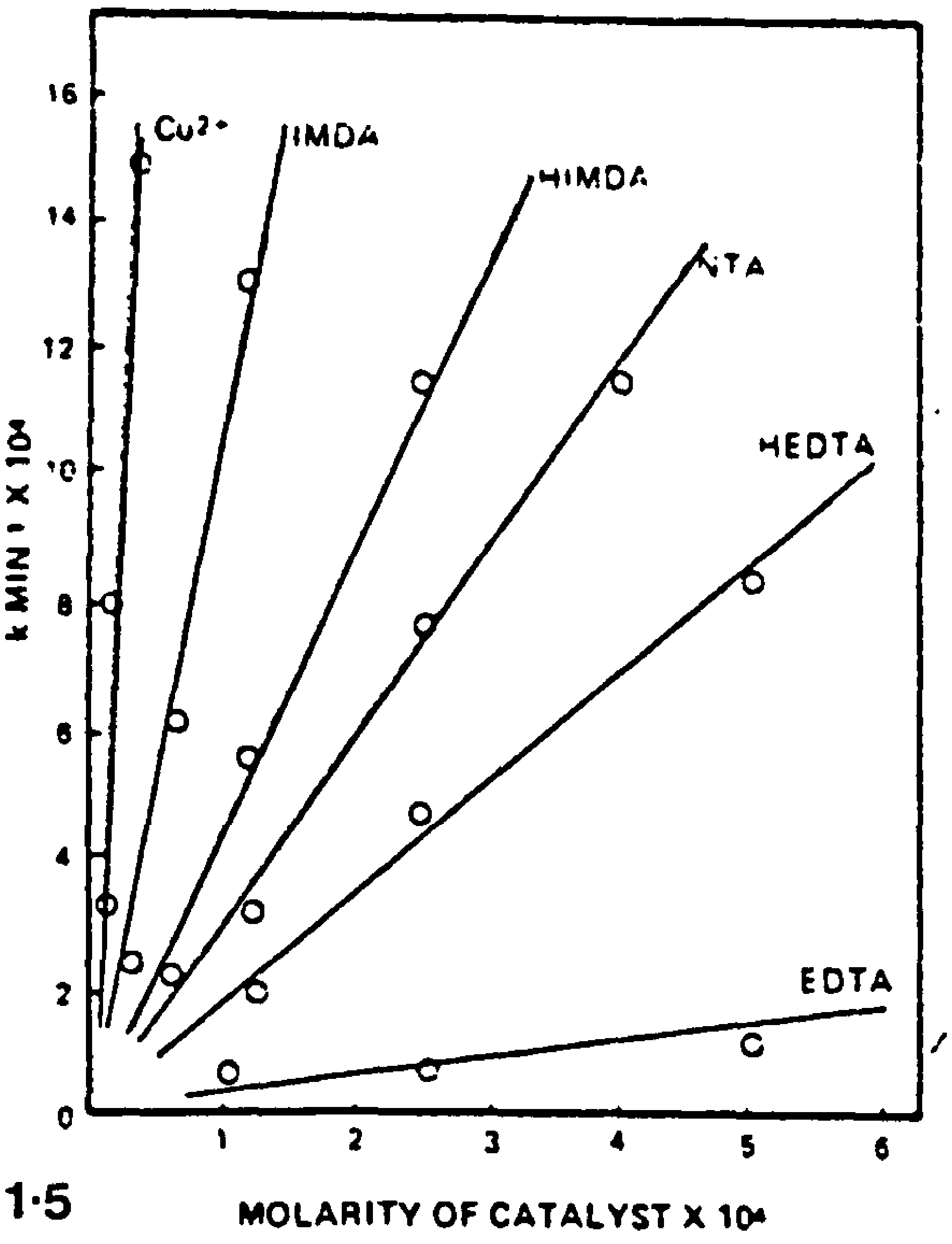
catalytic nature of this system is obvious since the copper (ii) ion is regenerated for participation in subsequent reaction cycles.

Catalysis of this type may be promoted by the presence of other metal ions. One such example is the dependence of iron (iii)-catalysed oxidation of ascorbic acid (fig. 2). The mechanism of such a reaction is similar to that in plate 3 for copper (ii) catalysis. The oxidation rates are considerably higher than those reported by Taqui Khan and Martell(198).

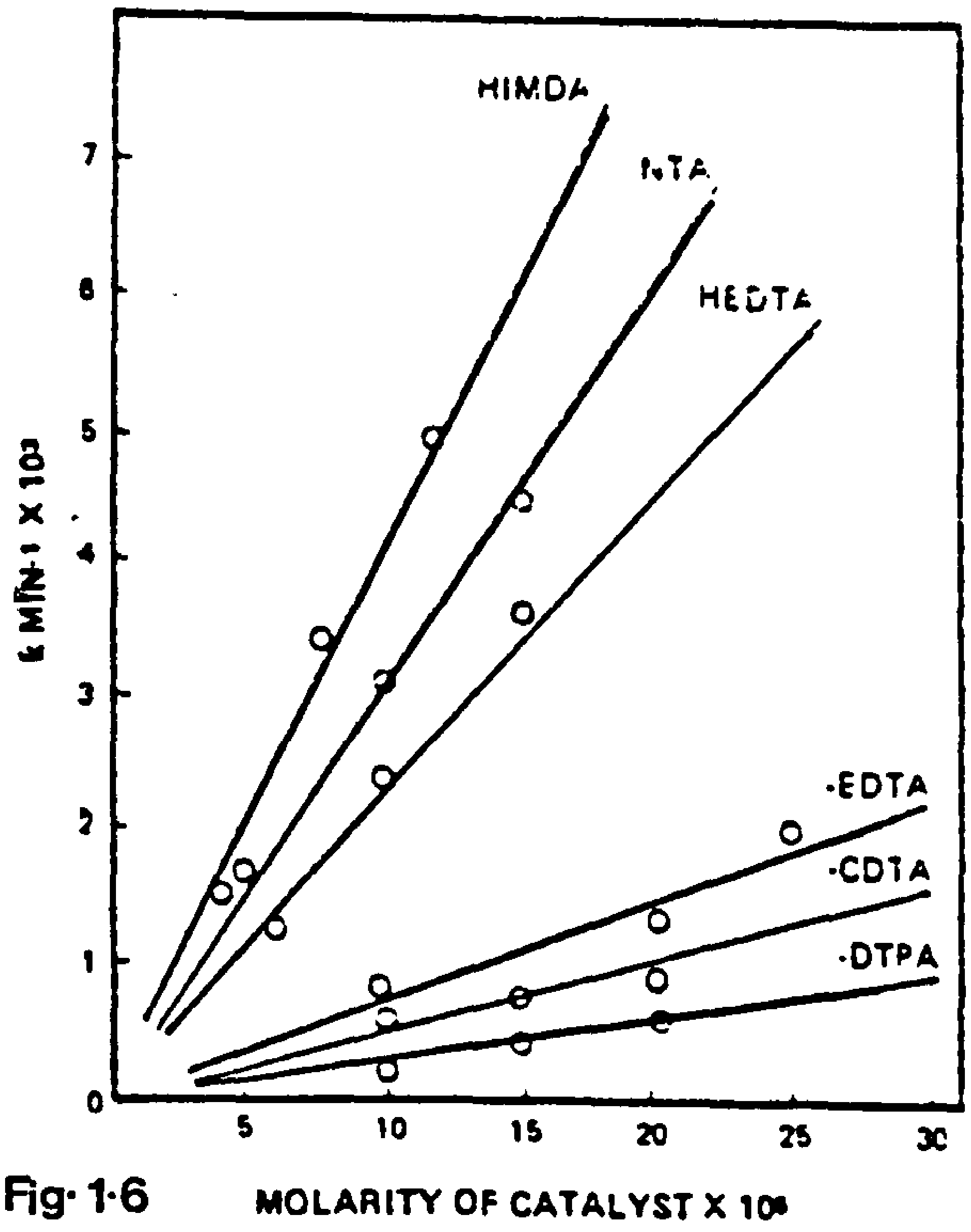
(iii) Metal Chelate Catalysis

Figures 1·3 and 1·4 illustrate the results obtained for copper (ii) and iron (iii) chelate catalysis for the oxidation of ascorbic acid(202). The rate constants shown are independent of concentration of molecular oxygen and are much lower than those observed for catalysis by free aquo ions such as those of copper and iron. These reactions are expected to proceed through single electron transfer steps, each transfer being followed by dissociation of the lower valent form of the metal chelate. Complete oxidation of the intermediate requires recombination with the metal ion in its higher oxidation state to give dehydroascorbic acid as the final two-electron oxidation product. Reoxidation of the metal chelate in solution by molecular oxygen and recombination with the substrate completes the catalytic cycle.

The slopes of the lines (figs. 1·3 and 1·4) show that pseudo first order rate constants decrease rapidly as the stabilities of metal chelates increase. The possibility that this observation may indicate some form of dissociation in which the free metal ion in the catalyst was explored by attempting to correlate the observed rates with the concentrations of free metal ion in equilibrium with the various chelates was investigated. The lack of such a correlation indicated


k MIN⁻¹ X 10⁴
0
2
4
6
8
10
12
14
16
Cu²⁺
IMDA
HIMDA
NTA
HEDTA
EDTA
1
2
3
4
5
6
MOLARITY OF CATALYST X 10⁴

Fig·1·5

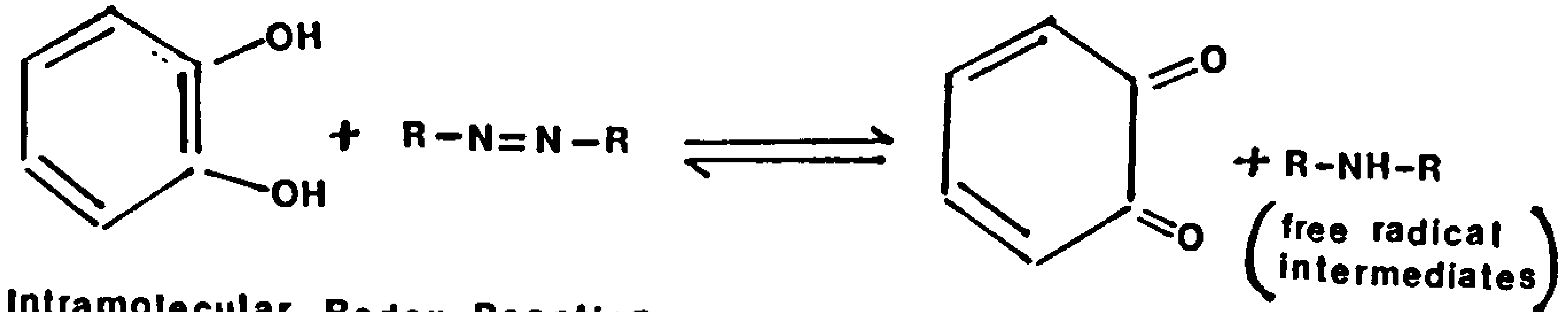

k MIN⁻¹ X 10³
0
1
2
3
4
5
6
7
HIMDA
NTA
HEDTA
EDTA
CDTA
DTPA
5
10
15
20
25
30
MOLARITY OF CATALYST X 10⁶

Fig·1·6

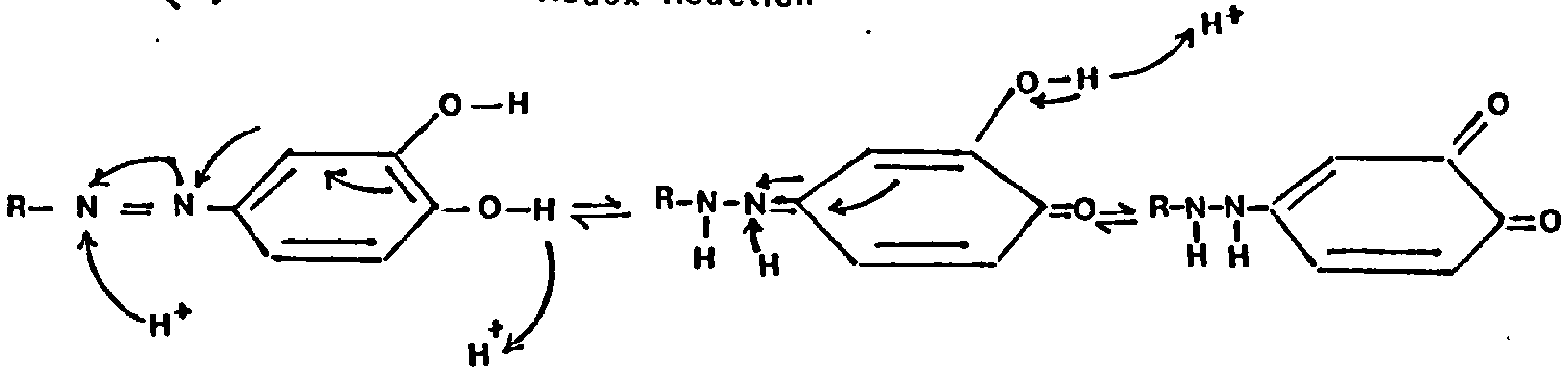
PLATE 2

Catalysis Of Two-electron Transfer Reactions By Metal Ions·

(i) Intermolecular Redox Reaction·



(ii) Intramolecular Redox Reaction·



(iii) Intramolecular Electron Transfer Reaction in a Metal Complex·

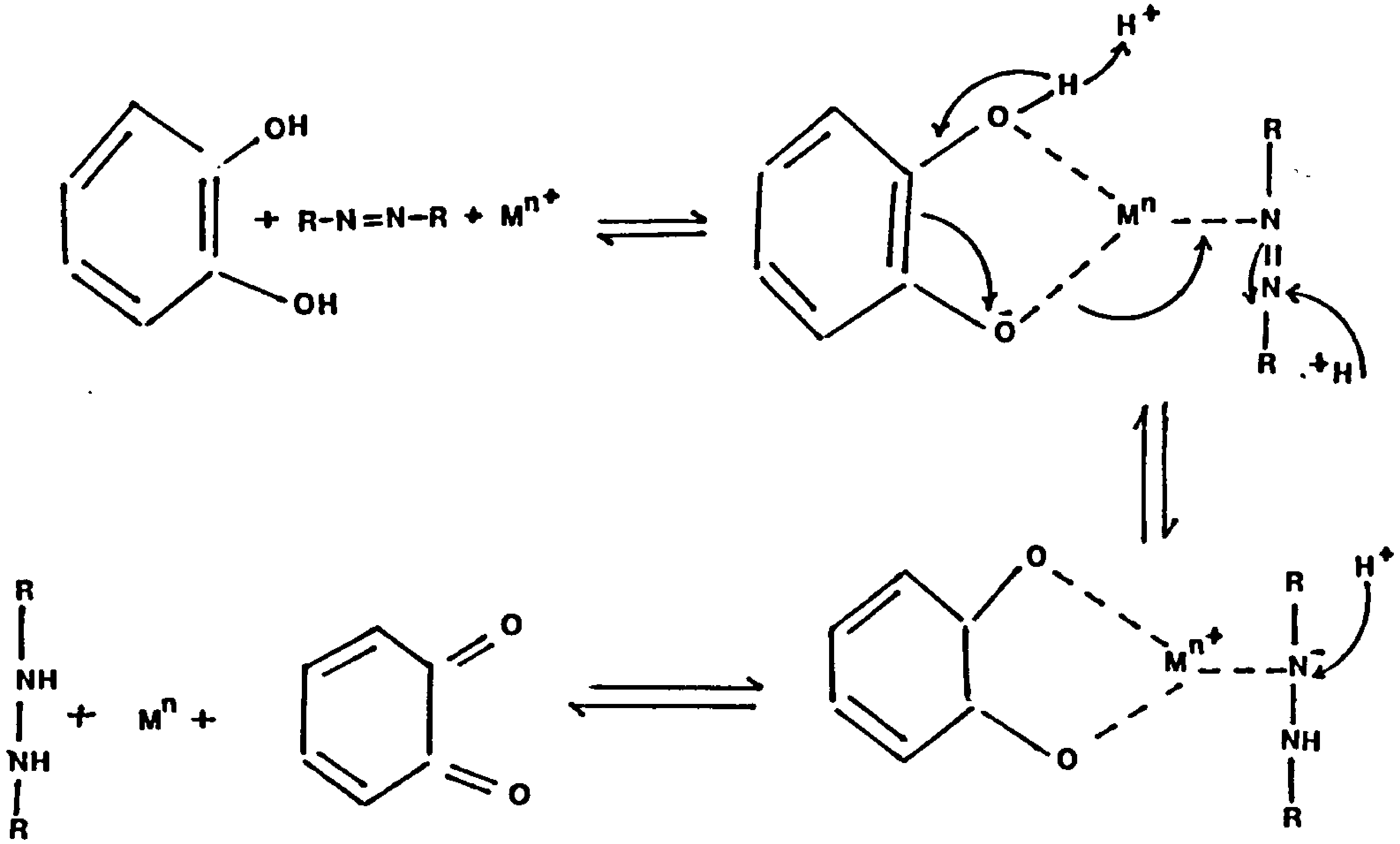


PLATE 3

COPPER II ION-CATALYZED OXIDATION OF ASCORBIC ACID

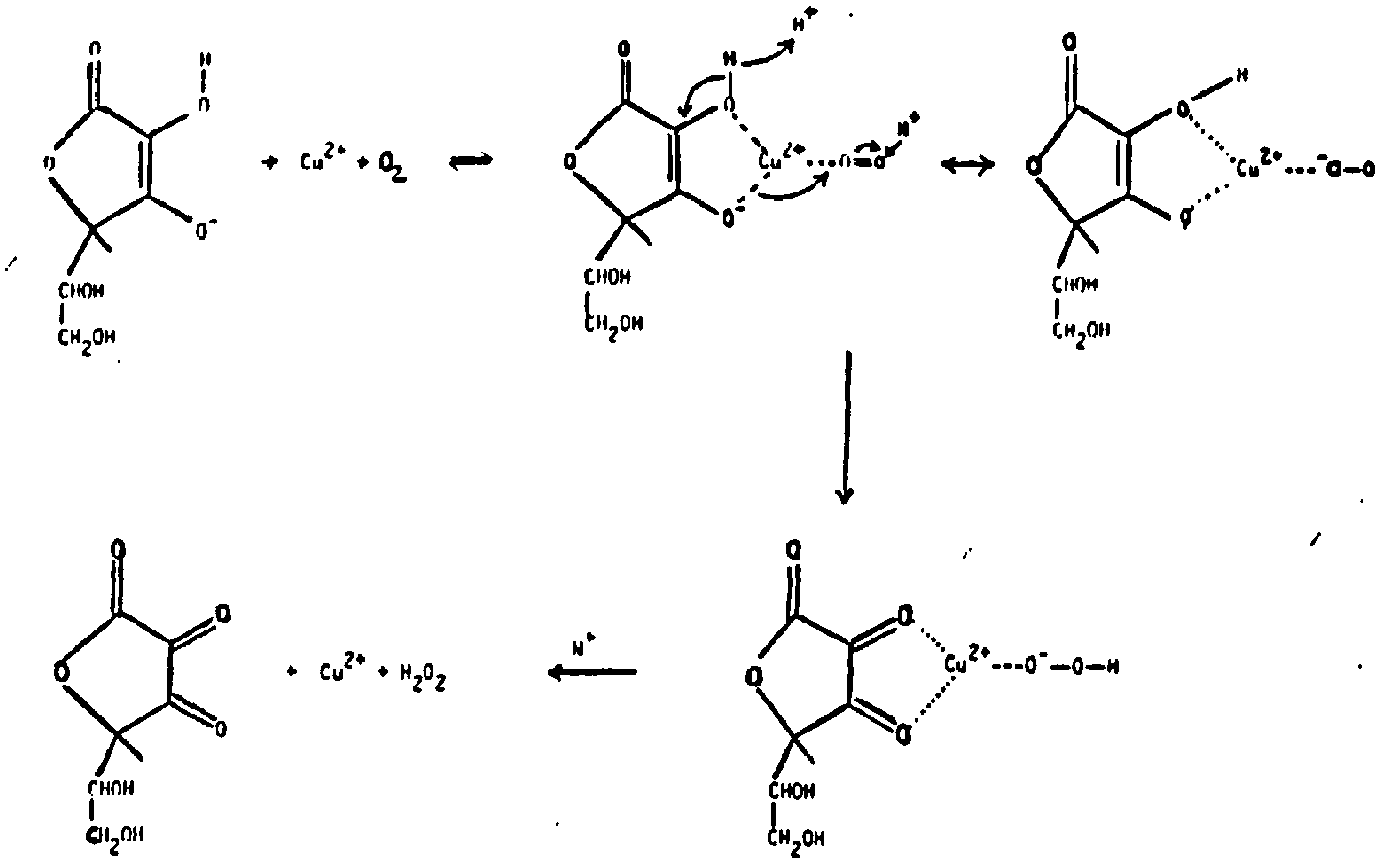
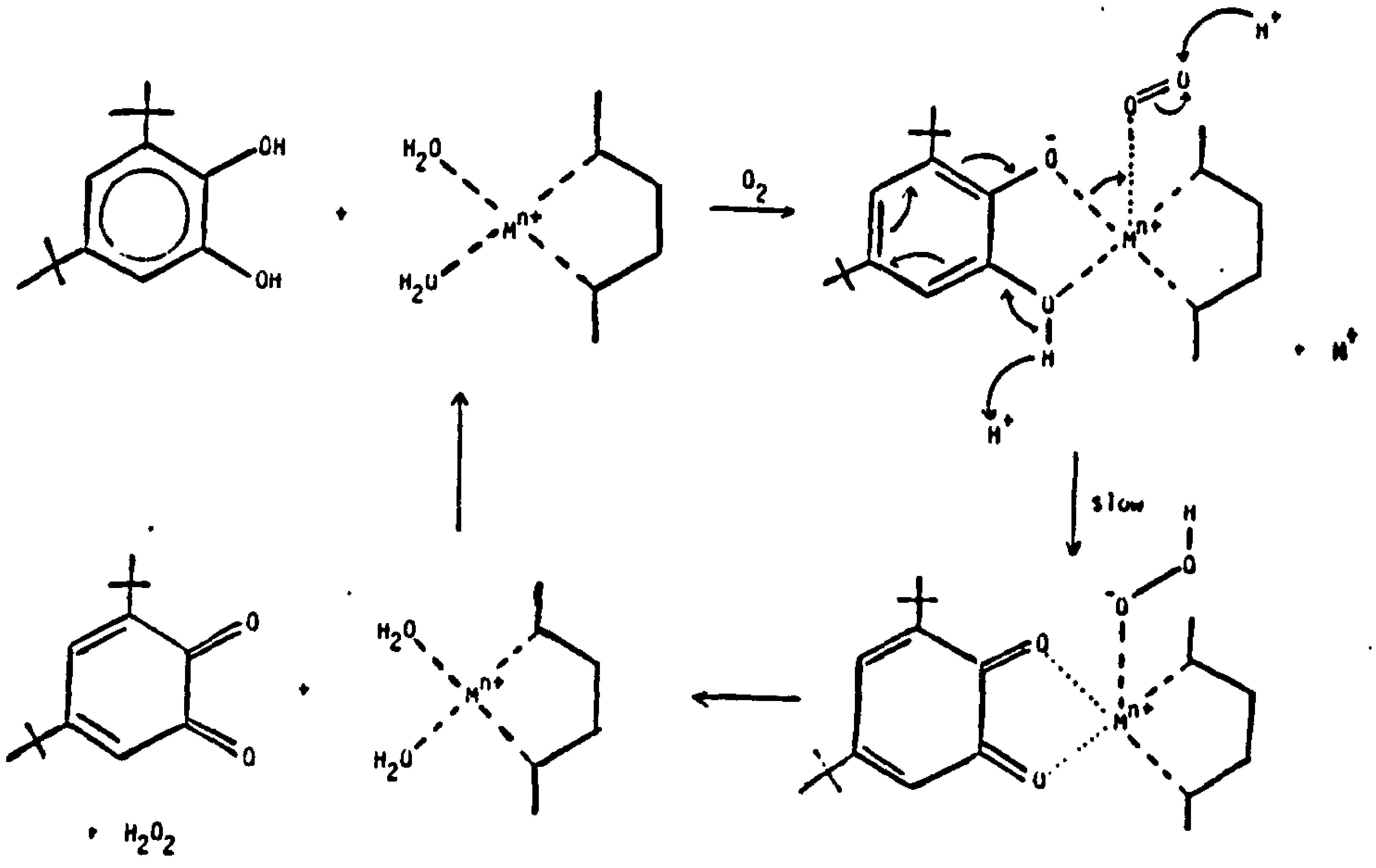


PLATE 5

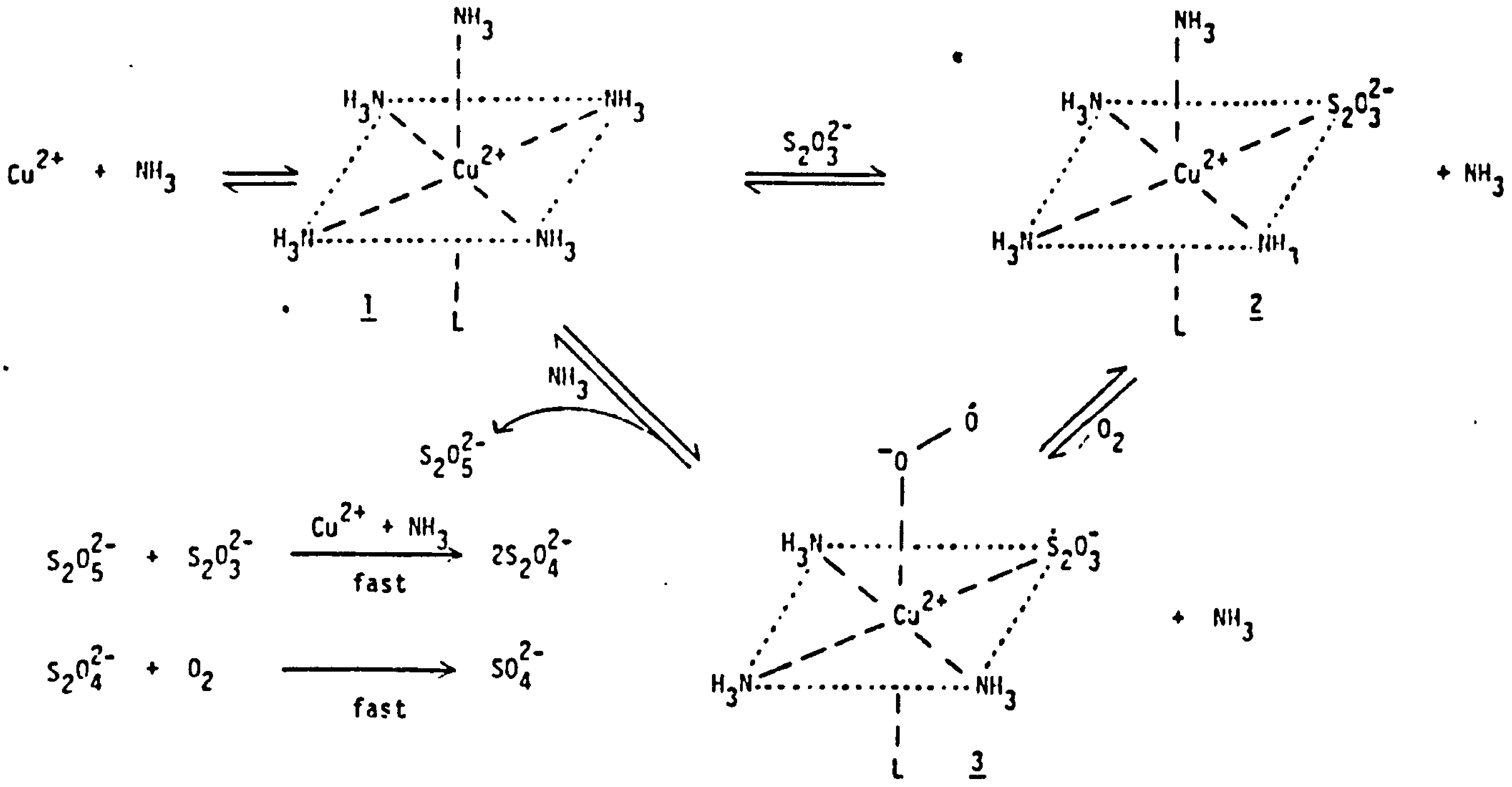
METAL CHELATE CATALYZED OXIDATION OF DITERTIARYBUTYL CATECHOL.



Mn(II) > Co(II) > Fe(II) > Cu(II) > Ni(II)

PLATE 8

PROPOSED MECHANISM FOR COPPER(II)-AMMINE CATALYZED OXIDATION OF THIOSULPHATE BY DIOXYGEN



$$\text{Rate Law:}\quad \frac{-d[O_2]}{dt} = \frac{kK_1K_2[Cu_T^{2+}][O_2][S_2O_3^{2-}]}{[NH_3] + K_1 + K_1K_2[O_2]}$$

that these reactions probably proceeded via electron transfers to the metal ion in the chelate itself. The metal chelates remain intact in both oxidized and reduced forms through the entire catalytic cycle. The variation in the observed reaction rates must therefore depend on the redox potential of the metal chelate which controls the rate of electron transfer from the substrate to the metal chelate. There is no doubt an additional steric factor in that the more stable metal chelates have structures with the ligands more effectively surrounded by the metal ion to prevent contact between the central metal and the ascorbate anion. This case is important for the higher multidentate ligands such as diethylenetriaminepentaacetic acid (DTPTA), ethylenediaminetetraacetic acid (EDTA), and N-(2-hydroxethyl) ehtylenediame-N, N', N'-triacetic acid (HEDTA).

It is interesting to note that while the more highly effective chelating agents can greatly reduce the catalytic activity of the metal ion, the observed rates are never reduced to zero. Thus the use of chelating ligands such as EDTA and DTPA to prevent autoxidation of ascorbic acid may be highly effective. The rate of oxidation is slowed down but goes to completion over a long period of time.

(iv) Model Systems

The oxidation of catechols by metal ions and metal chelates have been studied by Grinstead(203) and by Tyson and Martell(204) . They observed that first row transition metal ions are strongly catalytic with relative activities as indicated in plate 5. For these metal ions to be kept in solution under the conditions employed in the reaction, they were usually bounded to a ligand as bidentate (plate 5). The rates were found to be first order in substrate and in molecular oxygen. This indicated the probable formation of an intermediate quaternary metal ligand dioxygen substrate complex in which the electron transfer process occurred. The hydrogen peroxide was not formed in stoichiometric amounts probably because of disproportionation to oxygen and water through a catalase type reaction. Attempts to find any free radicals in the reaction mixtures were unsuccessful. This indicated that an ionic type mechanism of the type illustrated in plate 5 could be a possibility.

3.5.0 FACTORS AFFECTING METAL CATALYST ACTIVITY

Autoxidation processes in the presence of metal catalyst is affected by various factors:

[1] Solvents

The autoxidation of tetralin catalyzed by cobalt salts has shown a considerable change on the oxidation kinetics resulting from changes in the solvent. For example, a change from acetic acid as solvent to hydrocarbon caused catalyst deactivation and a decrease in catalyst solubility (both of which affect oxidation kinetics).

Recent research work on the effects of fatty acid solvents on metal catalyzed oxidation of tetralin with cobalt decanoate as catalyst using various media as solvents indicated that the rate of tetralin oxidation against cobalt concentration was in each case found to reach a limiting value at some cobalt concentration. Such solvents included acetic acid, propoionic, butyric, pentanoic, octanoic, decanoic, etc. acids. The limiting value depended on the dielectric constant of the acid. The lower the dielectric constant, the lower the limiting rate. However, the order of the oxidation rate was completely reversed at low catalyst concentrations. This was attributed to the effect of a higher initiation rate brought about by the fatty acids of lower dielectric constant.

[2] Temperature

The effect of increase in temperature on various metal catalysts has been studied by Arrhenius(191). At relatively low reaction temperatures, the oxidation rate of active catalysts vary more rapidly than the non-active catalyst-catalyzed oxidation rate. A rise in temperature causes the difference in the oxidation rates to be reduced. This is because at high temperatures, the chain oxidation process develops rapidly and becomes a limiting reaction. Several factors may be responsible including:

(i) Diffusion effect, and

(ii) Increased activation energy resulting from increase in temperature.

Catalyst decactivation is very great at high temperatures of reaction. The apparent activation energy for the overall catalyzed oxidation may be higher than the true values (and should approach the activation energy for uncatalyzed oxidation under similar conditions). A significant high temperature reaction capable of causing increased water formation is given below:

$$2ROOH \xrightarrow{M^{n+}/M^{(n+1)+}} RO^{*} + RO_2^{*} + H_2O$$

Measured rates at high temperatures can quite reflect the rate at which oxygen diffuses through the resulting water vapour which has formed over the substrate rather than the rate at which oxygen reacts with the substrate.

[3] Effect of Type of Metal

(i) The initiation of hydrocarbons involving oxidation-reduction shows that the higher the redox potential, the more active is the catalyst. Such a correlation was observed(205) during the autoxidation of 2, 5-dimethylhexane in the presence of various metal stearates. The metal-catalyzed autoxidation of cyclohexene in non-polar media revealed similar results(206).

(ii) Valency variables.

The different valence states of a metal catalyst could vary by an extent to which they enhance catalyst activity at different stages of autoxidation processes. Freidin(207) showed that divalent manganese and cobalt salts were converted to their trivalent states during the induction periods. The induction periods ended at the points associated with the highest concentration of trivalent states.

[4] Effect of Metal Salt Anions

The iron salt-catalyzed decomposition of cumene hydroperoxide in xylene has been studied by Wallace et al.(208) and the table below is a reprint of their results:**Table 1·2**

	% cumene hydroperoxide decomposed		
CATALYST	½ hour	1 hour	2 hours
Iron octoate	37.3	56.7	83.7
Iron naphthenate	25.8	47.6	75.4
Iron oleate	15.9	22.1	35.1
Iron acetylacetomate	-	18.0	28.0
Octonoic acid	-	2.7	2.7
Oleic acid	-	-	6.3
No catalyst (blank)	Not reported	Not reported	Not reported

Iron octoate and naphthenate are reactive catalysts while oleate and acetylacetonoate are moderate catalysts under the prescribed conditions. The moderate activities due to oleate and acetylacetonoate were due to their low redox potential(208).

[5] Effect of Additives

(i) Water

The effect of water at high reaction temperatures on oxygen diffusion was mentioned (see temperature effects).

At relatively low reaction temperatures, water could enhance catalytic activity by increasing the solubility and dispersion of the metal catalyst in the medium. It was observed that the addition of 10% by volume of water caused an increase in the oxidation rate(209) of tetralin in non-polar medium (manganese, copper, and nickel as catalysts). Water may be capable of lowering the rate of hydroperoxide decomposition by coordinating with the metal thus interfering with the formation of the metal-hydroperoxide complex e.g. in the cobalt-catalyzed decomposition of hydroperoxides(196),(210),(211).

(ii) Presence of organic acids

The addition of organic acids e.g. decanoic acid is found to lower the rate of oxidation of tetralin in non-polar media in the presence of manganese, copper, and nickel salts. Metal-acid complexes are readily formed and interfere with metal-hydroperoxide complex formation similar to the effects of water. The addition of decanoic acid increased the rate of cobalt-catalyzed oxidation due to increased solubility.

(iii) Mixing of metal catalysts

The oxidation of cyclohexene in non-polar media using a mixture of iron (ii) and copper (ii) heptanoates produced a synergistic effect on oxidation(206). Synergism is a phenomenon where the mixed effect of two influences is greater than the sum of the two influences acting separately.

Antagonistic effects have also been encountered where the activity of cobalt was very much lowered by mixing it with manganese during the oxidation of tetralin in acetic acid(212). The antagonistic effect is attributed to the interaction between manganese (ii) and peroxy radicals which resulted in chain termination. Antagonism is an unusual phenomenon of a negative action where the blending of two or more influences produces an unacceptable system whose total effect is less than the sum of the individual parts.

S. Panush(213) worked on pigment synergism and antagonism in automotive paints. He found that synergism occurs in automotive enamels under specific conditions determined by the pigments, their levels and value of the colour. Altering the relationship of the pigments in the synergistic system by increasing the level of one or the other; decreasing or increasing the reducing pigments e.g. aluminium trioxide (metallics); titanium dioxide (non-metallic); or adding other coloured pigments can totally negate the synergistic effects of the pigments in the initial colour. The possibility of pigment combinations acting synergistically to fill the voids of unusable colour areas has led to a wide variety of pigment blends. Synergism is normally predictable but the unique effects of antagonism are not planned for; and in many cases, occur as a complete surprise. Colour is the easiest and most readily determined form of antagonism. Other forms of antagonism include gloss, moisture, sensitivity and exposure durability. These however, are not easily detectable, being subtle and requiring more time to develop.

The dependence of iron (iii)-catalyzed oxidation of ascorbic acid(198) with a synergistic feature is given by figure 2. In this system the oxidation rates are considerably higher than those reported by Taqui, Khan and Martell(198) for iron (iii) catalysis. The mechanism of this redox reaction is similar to that in plate 3 for copper (ii) catalysis. In addition to the copper (ii)- and Fe(iii)-catalyzed oxidation of ascorbic acid by molecular oxygen, vanadyl[9] and uranyl[10] ion have been employed.

[6] Effect of Oxidation Products

The effect of hydroperoxides on catalyst concentration causing deactivation of the reaction system has been mentioned earlier.

Oxidation products such as alcohols and ketones could compete with the hydroperoxides for coordination with metal catalysts thereby causing a reduction in the autocatalytic behaviour of such a system(216).

The metal catalyst may not necessarily maintain a steady-state concentration for each particular valence during the autoxidation of hydrocarbons e.g. $d[M^{n+}]/dt = 0$.

It was observed that during the oxidation of n-decane[115], the concentration of manganese (iii) passed through a maximum when about 20-30% existed in its trivalent state. During the oxidation of cumene and tetralin, manganese was completely converted to the trivalent state(217).

The difference in these two reactions arose from differences in the composition of the oxidation products and their differing reducing actions on manganese (iii).

Cobalt (iii) is capable of oxidising formaldehyde and methyl alcohols in aqueous acid solutions. The cobalt (iii) is reduced to its lower valency state(218) (219). The period of rapid reduction of cobalt (iii) to its lower valency state corresponds with the appearance of aldehydes during cobalt-catalyzed oxidation of cyclohexene(220).

CHAPTER 4

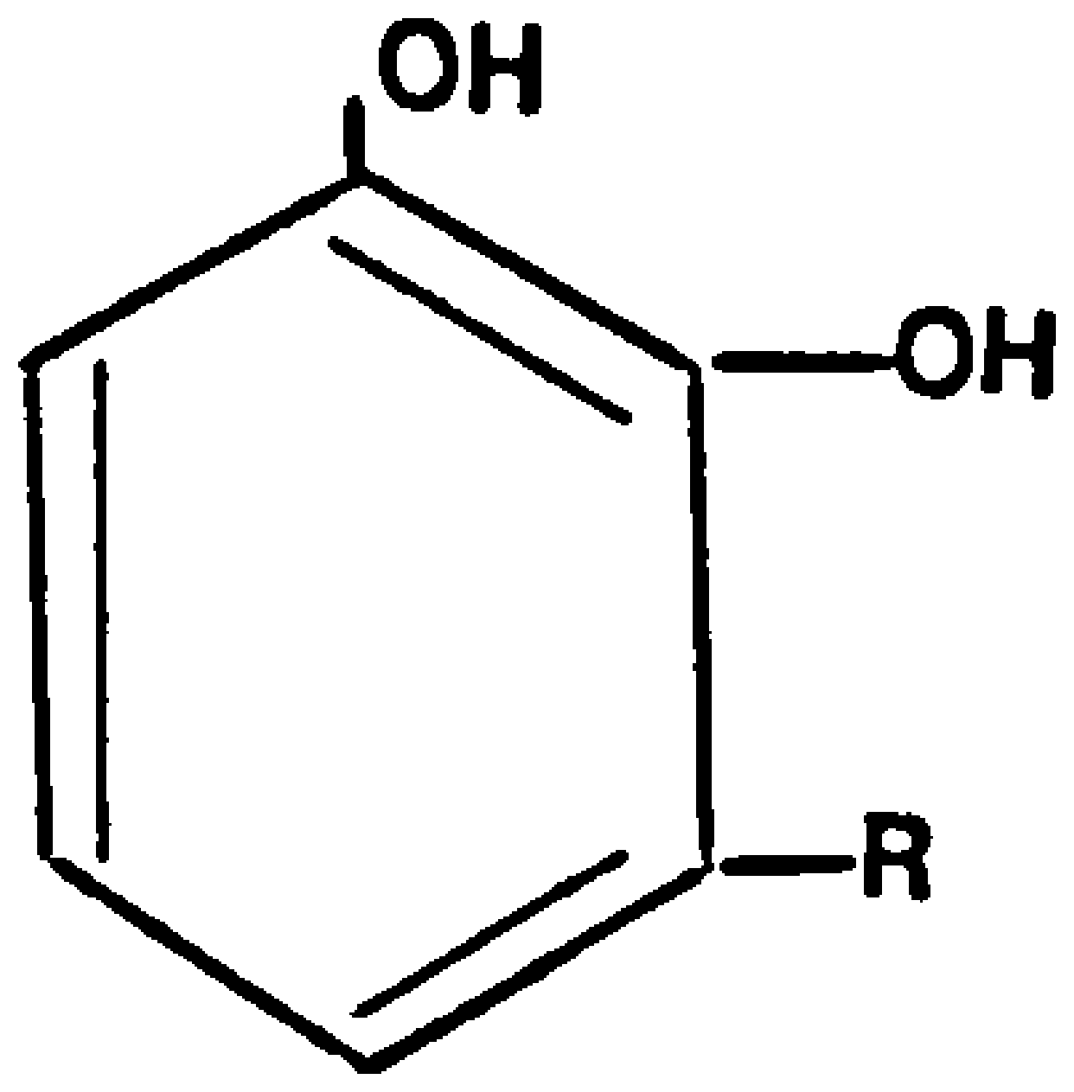
STOVING PROCESSES

CHAPTER 4

STOVING PROCESSES

Stoving systems other than autoxidation types have not been mentioned e.g. systems based on amino-aldehyde condensation etc.

The drying of films of surface coatings is a process which remained unchanged for thousands of years. Until this century, almost all films of surface coatings were simply allowed to dry by themselves. The only exception from earlier times was the drying of oriental lacquer where the process was carried out in special rooms where a high humidity was maintained. Oriental lacquer is produced from the milky emulsion sap tapped from the tree Rhus vernicifera - a native of China. After various purification processes including the removal of water, the product from the milky emulsion sap is a liquid very similar to boiled linseed oil in appearance and consistency. The main component of the liquid is an unsaturated phenol called Urushiol.



R consists of four different straight chains with 15 carbon atoms. The dominant chain (ca 50%) is

$$-(CH_2)_7CH = CHCH_2CH = CHCH = CHCH_3.$$

Two out of the three double bonds are conjugated. The urushiol is associated with lesser amounts of gum and nitrogenous substances. The latter include an enzyme which catalyses the oxidative drying of the phenol.

Towards the end of the 19th century, the use of black japans and stoving varnishes started and were cured in simple ovens.

The industrialization of the painting process raised the demand for a shortening of the time required for drying. This demand has been met in two ways:-

(i) By the development of finishes which dry spontaneously in much shorter times than the old oil paints, and

(ii) By the development of finishes whose rate of drying is either dependent on or is greatly accelerated by the provision of energy such as heat (stoving catalysts).

4.1 FORCED CURING

The curing of a normal air-drying finish may be accelerated by raising the temperature, since the breakdown of the active compounds, such as hydroperoxides into radicals is a temperature-dependent process. Such an acceleration, where the temperature does not exceed about 80^0C, is usually known as forced drying.

However, a stage is soon reached where the rate of reaction becomes dependent on the formation rather than on the breakdown of active compounds. At this stage the process is regulated by oxygen availability and not by temperature. Furthermore, an increase in temperature will often unbalance the drying process so that the labile compounds formed at the air/film interface break down before they can diffuse into the film resulting in surface or skin drying. The result of unbalanced drying processs at higher temperatures is utilised in the formation of surface texture of wrinkle finishes (246).

In the case of coatings which dry by simple loss of solvent, a moderate acceleration of the drying process may also be achieved by forced drying. This, too, has its dangers since entrapped solvent may give rise to blistering, while the more rapid solvent evaporation will aggravate any tendencies to floating and flooding and may result in the formation of orange-peel or other surface imperfections.

4.2 STOVING TECHNIQUES

In general, the curing effect of an increase in temperature can only be fully exploited where the curing reaction takes place at the same rate throughout the depth of the film. The curing reaction is characterized by a certain activation energy and for curing to occur in a reasonable time, there will be a threshold temperature which must be exceeded. The transfer of heat energy to the coating may be achieved in the following ways:-

(i) Convection Oven Stoving

In convection oven stoving systems, the heat is transferred to the coating from the heat source by means of air which acts as a heat-transfer fluid. The air may either move by natural convection or may be circulated forcibly by means of a fan or fans. The heat source may range from open gas flames to electric resistance heaters.

Convection ovens may be either batch ovens or tunnel ovens in which the workpieces (solvents and fumes given off) are carried by means of a conveyor.

Air is a rather poor heat transfer fluid owing to its low heat capacity. The heat capacity of air determines the rate of heat transferred from the heat source to the reaction site - the film. The low heat capacity of air has several practical consequences in stoving:

(a) Most objects which are stove-dried are metallic. This means that the rate of heat transfer will be so slow and the conductivity of the object is very high thus requiring that the whole object must be raised to the stoving temperature.

(b) A rapid air circulation is therefore necessary which can only be achieved in any but the smallest ovens, by the use of fans.

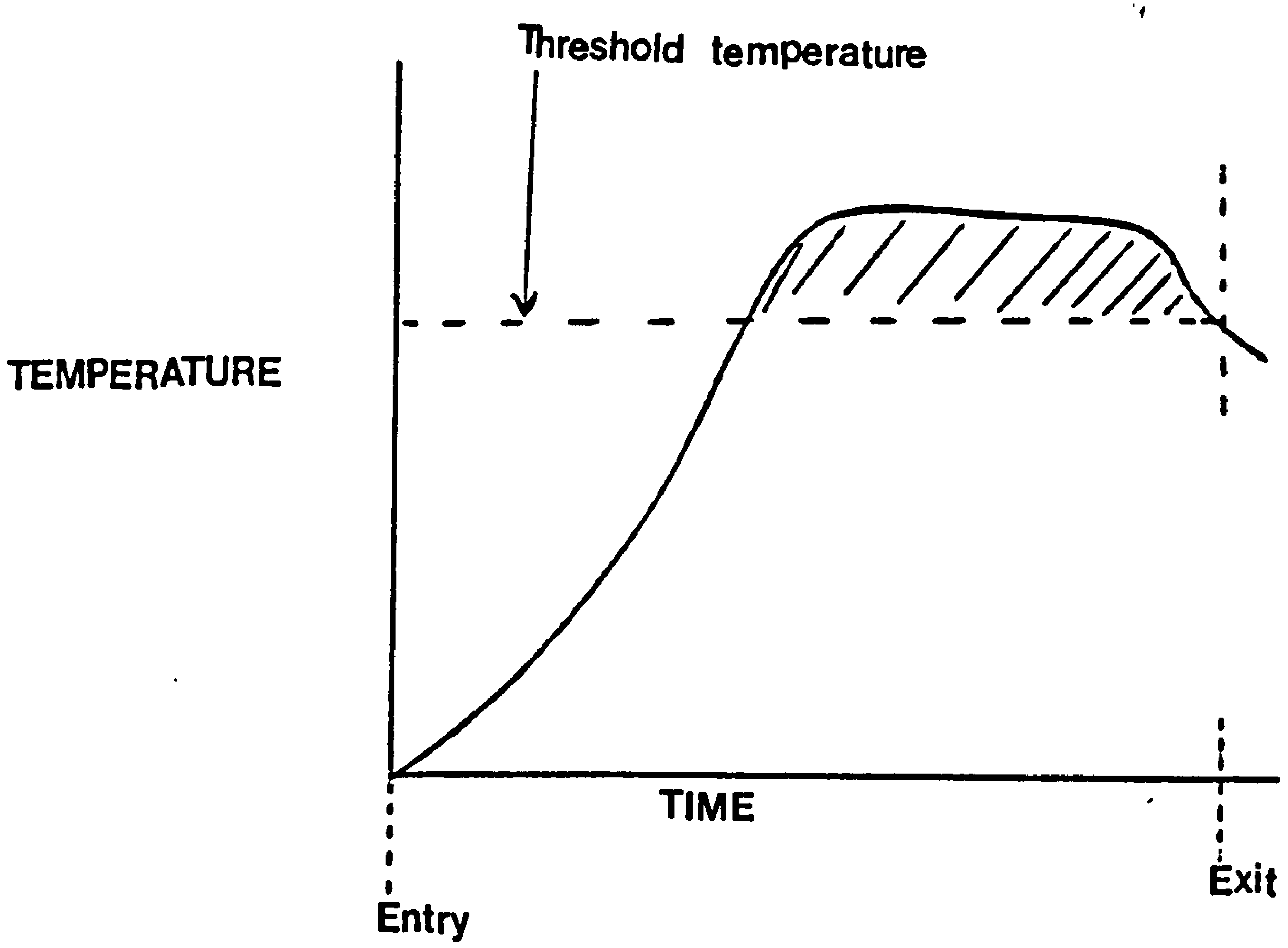
(c) The entry of fresh, cold air must be restricted to the minimum necessary to carry away the fumes given off during the stoving process for economic reasons.

Convection oven stoving processes are generally slow. In continuously operating ovens, precautions must therefore be taken to avoid the entry of excess cold air along the workpieces if the heat is to be efficiently utilised. Excessive cold air is prevented from entering the workpieces by arranging the oven on two levels. The goods enter the oven at a lower level, move up along an inclined portion to a higher horizontal section and are moved down a second sloping portion before leaving the oven at the lower level. By this arrangement, the hot air is trapped in the upper portion and does not mix with the colder air at the entry and exit points. This type of conveyor oven is called a camel-back oven and for even greater efficiency, an air-lock may be fitted at the entry and exit points.

Temperature measurement of the film during its passage through a conveyor oven reveals a temperature-time curve of the form shown Fig. 1.7

Very little will be known about the temperature reached by the film even if a thermometer is placed at the hottest part of the oven. The technique of stating paint curing characteristics as x min at y^0 is misleading in extreme when attempts are made to translate the information into practice. Equally misleading to the paint technologist

Fig·17



Temperature — time curve in a convection oven.

is the information that a certain curing schedule used in a paint drying oven is x min at y^0 and can be used to formulate such a paint system.

The only technique is to determine a temperature-time curve for the surface of the particular workpiece and actual or dummy production run where the workpiece is both preceded and followed by others. A knowledge of the threshold temperature of the paint (the area under the temperature-time curve above this temperature) may be used as a measure of the stoving effect. Where different stoving schedules are to be investigated it may be necessary to use some function of the temperature which gives a more accurate picture of the effect of different temperatures. Such a function can be derived empirically from laboratory tests on the paint.

Temperature-time curves may be obtained by using one or more thermocouples attached to the workpiece to register the temperature outside the oven or by sending a suitable temperature registering instrument along with the workpiece.

In some cases, paint defects appear on the production scale even though they have not been apparent in laboratory tests. This is very often due to the fact that the atmosphere surrounding the workpiece in the production oven is much more contaminated with solvent and fumes than is the case in laboratory stoving processes. Results of experiments performed on laboratory scale may be very difficult to explain and are in most cases impossible to reproduce unless the air circulation is very good and the oven is correctly loaded.

(ii) Radiant Stoving

Instead of raising the temperature of the coating via air as the heat-transfer medium, the energy for stoving may be transferred from the heat source directly by radiation. This is known as infrared stoving since the main part or in some cases the entire energy is radiated in the infrared region. In order to have a sufficiently high flux of infrared energy, the source temperature must be higher than the walls of a convection oven.

The earliest infrared stoving equipment consisted of arrangements of electric bulbs in reflectors. Such arrangements of bulbs were capable of concentrating the energy in the zone where the workpiece was placed or allowed to pass through. Special lamps with thicker filaments than the ordinary lighting lamps have also been used. These operated at lower colour temperatures and the energy emitted as visible light was low. Reflectors were originally gold-plated. Gold is the most efficient reflector of infrared energy followed by highly polished aluminium. Other elements such as those used in electric fires, preferably of the type enclosed in a quartz tube, ceramic radiators heated directly by gas, and simple steel panels heated to 500 - 700^{0}C have all been used as sources of infrared energy. In general, infrared stoving is used in connection with conveyor belt production, the infrared oven forming a suitably shaped tunnel through which the painted articles pass.

The following are some of the advantages of radiant stoving over convection stoving:

(1) Greater speed. Radiation heat transfer is instantaneous. If the surface receiving the radiation is a good absorber, its temperature could rise very rapidly. Stoving times of 1 - 2 min are possible in favourable cases.

(2) More efficient use of energy is made. No energy is lost in heating the oven as is the case with convection stoving.

(3) Readiness for use. The electric-lamp types of oven are ready for use as soon as they are switched on, while other types take only a few minutes for the emitters to reach operating temperature.

(4) Simplicity and flexibility. Since the air is not heated, there is no need for elaborate arrangements to conserve the hot air. The emitters may be readily moved to give different profiles to suit different workpieces.

(5) Small portable emitters may easily be brought into action to heat limited areas, e.g. in touching-up or repairing automobile finishes etc.

Disadvantages of Infrared Stoving:

(1) In the electric-lamp types of equipment, the reflectors and lamps become contaminated with fumes from the work and, unless regular cleaning is carried out, their efficiency falls rapidly.

(2) The temperature reached at a point on the surface of the equipment will depend on the shape of the workpiece. Shadowing effects must be avoided to produce evenly stoved coatings. Some objects cannot be stoved successfully on account of their shape.

(3) The most serious disadvantage of radiant stoving is that the amount of energy transferred, and hence the stoving time, is strongly dependent on the nature of the coating, i.e. its infrared absorbency. A matt black or red oxide paint may absorb more than 90% of the incident energy. A glossy white paint may absorb only 10% and it is even less with aluminium-based paint. Widely differing colours cannot be stoved successfully on the same line at the same time.

(4) Very short stoving times have a minor disadvantage. Small voltage changes or changes in gas pressure may cause over- or under-stoving unless the equipment is under accurate and instantaneous control.

In suitable cases, the use of infrared stoving can give great savings in time and is widely employed in many industries.

(iii) Induction Stoving

Induction heating can be employed for curing coatings for specialised uses. In the case of magnetic substrates such as steel, normal mains frequency may be used. The energy losses in the alternating field appear as heat. In the case of non-magnetic substrates e.g. a copper wire, it is necessary to use radiofrequencies to produce eddy currents which also appear as heat energy.

Induction stoving does not appear to have widespread application in the coatings industry. It is in regular use for curing synthetic adhesives in the furniture and allied industries.

(iv) Other Stoving Techniques

It is possible to cure practically all types of stoving finish by carefully heating the surface with a blow lamp after a suitable time has elapsed for the evaporation of volatile solvents. Some skill is necessary to attain some good results, hence the process is little known and used.

It has been proposed to cure coatings on pipes by passing the pipe continuously through a ring burner or series of burners. Flame curing has much the same advantages as infrared curing in that high rates of energy transfer are possible.

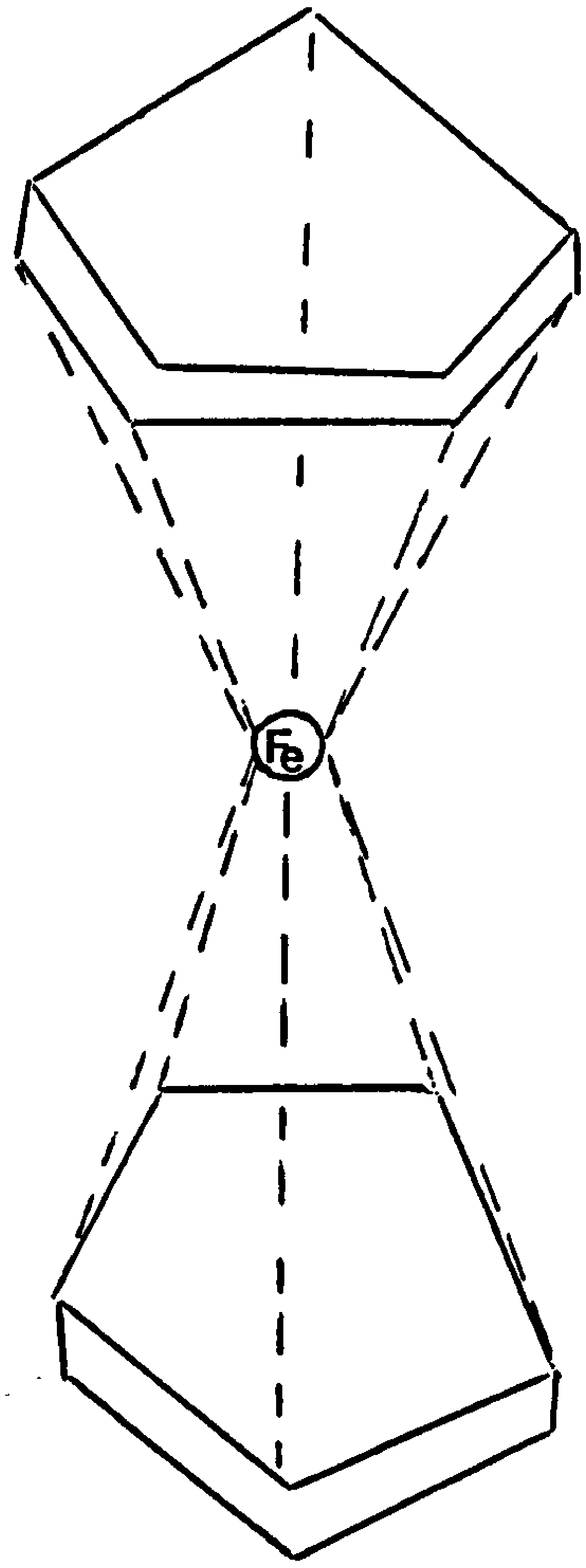
Since polymerization processes are generally dependent on the formation of radicals, it should be possible to accelerate polymerization by the use of high energy radiation e.g. ultraviolet radiation. Such methods do not appear to have been used in curing surface coatings, but they have found limited application in initiating polymerization in other industries.

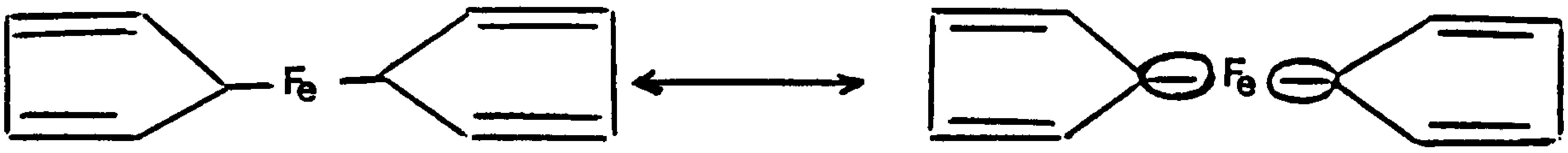
4.3 POTENTIAL IRON-BASED STOVING CATALYSTS

Iron is the fourth most abundant element in the earth's crust. In the elemental state, it occurs very rarely. It combines with most non-metals on heating. Iron has a very ancient history, being first used by man some 6000 years ago (iron from meteorites). Pure iron finds no great industrial use. Compounds based on iron and in particular ferrocene were employed in this work to study their catalytic efficiencies.

Ferrocene (biscyclopentadienyl iron), the parent compound in this work, is an organometallic derivative of iron.

1. FERROCENE (Iron biscyclopentadienyl)



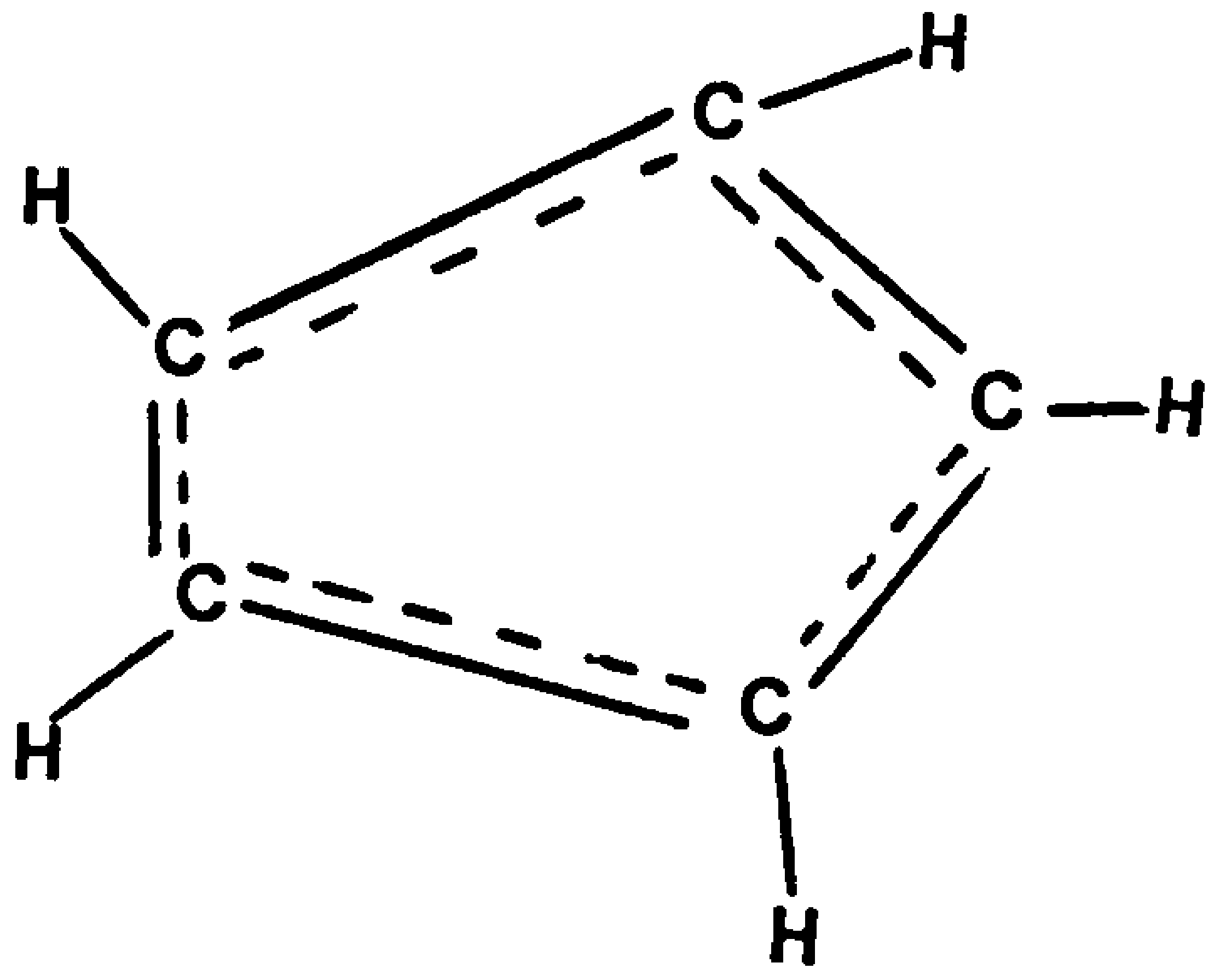


(1a) (1b)

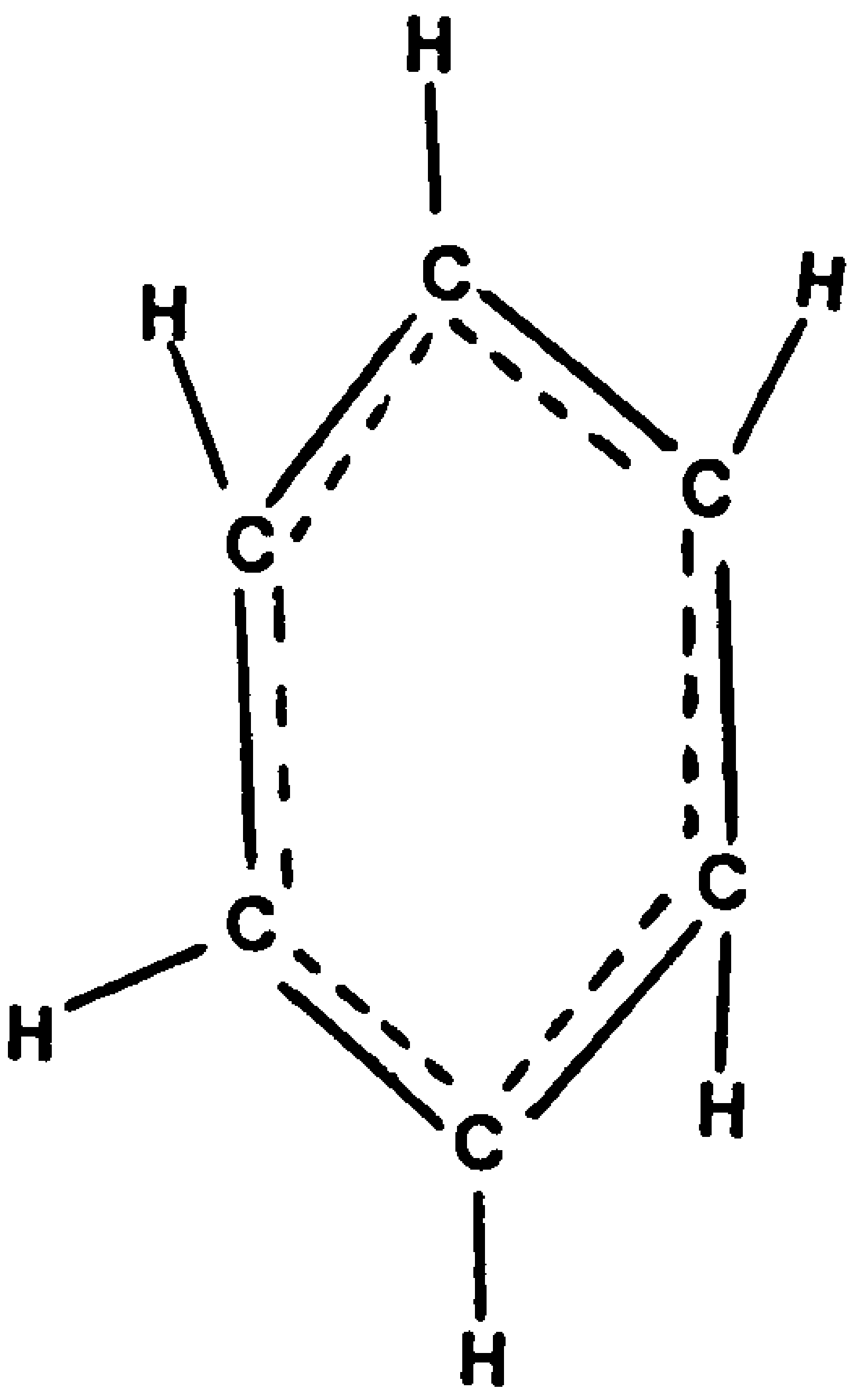
Kealy and Pauson$^{(223)}$ were among many researchers who worked on the preparation of stable organo-iron compounds with some useful results. They formulated a compound $C_{10}H_{10}Fe$ dicyclopentadienyl iron.

Wilkinson and co-workers(224) carried out further investigation with due attention to the facts presented by Kealy and Pauson. They considered whether the structure (1a↔1b) had some resemblance to Kealy and Pauson's compound. The equal unsaturation of each of the carbon atoms of the cyclopentadienyl anion suggested that two such units might form covalent bonds to ferrous iron symmetrically as in 1. Iron biscyclopentadienyl is diamagnetic with $X_{\text{mole}}^{25^\circ} = -125 \times 10^{-6}$ cgsu. The infrared absorption spectrum contains in the 3 - 4μ region a single sharp band at 3.25μ which indicates the presence in the compound of C-H bonds of only one type.

Woodward and co-workers(225) confirmed that iron biscyclopentadienyl molecule contains two rings, each of five equivalent C-H groupings. Considering one of the carbo-cyclic rings alone, then the situation might be represented as in (ii).



(II)

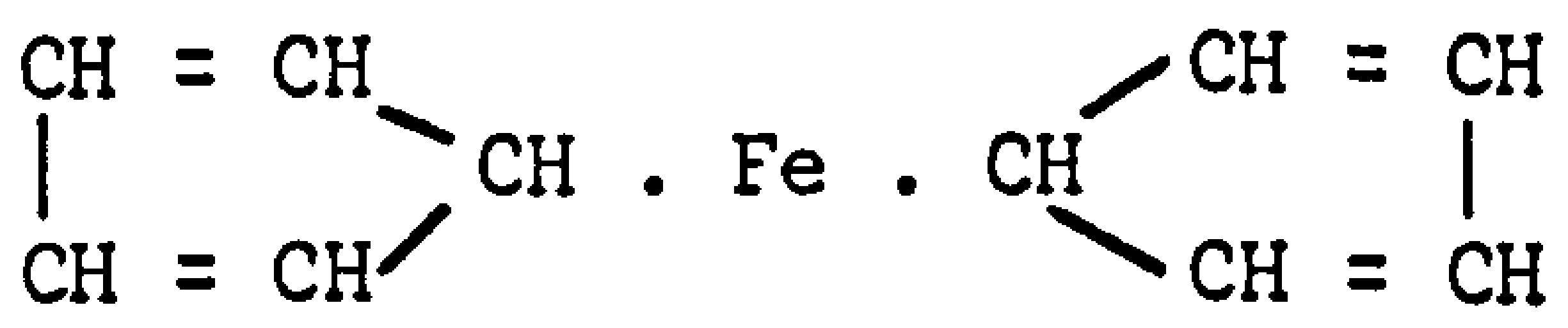


(III)

The very similar circumstances obtaining in the case of benzene (iii) led the researchers to believe that iron biscyclopentadienyl (ferrocene) might behave as an aromatic compound. Some reactions which demonstrate typical aromatic properties in ferrocene are as follows:

In spite of its high degree of formal unsaturation, ferrocene does not possess properties typical of pohyolefinic compounds. It does not react with maleic anhydride in boiling benzene and is not hydrogenated under normal conditions over reduced platinum oxide. It is resistant to basic and acidic reagents and has great thermal stability, a factor which has prompted its investigation as a possible stoving finish catalyst in this work.

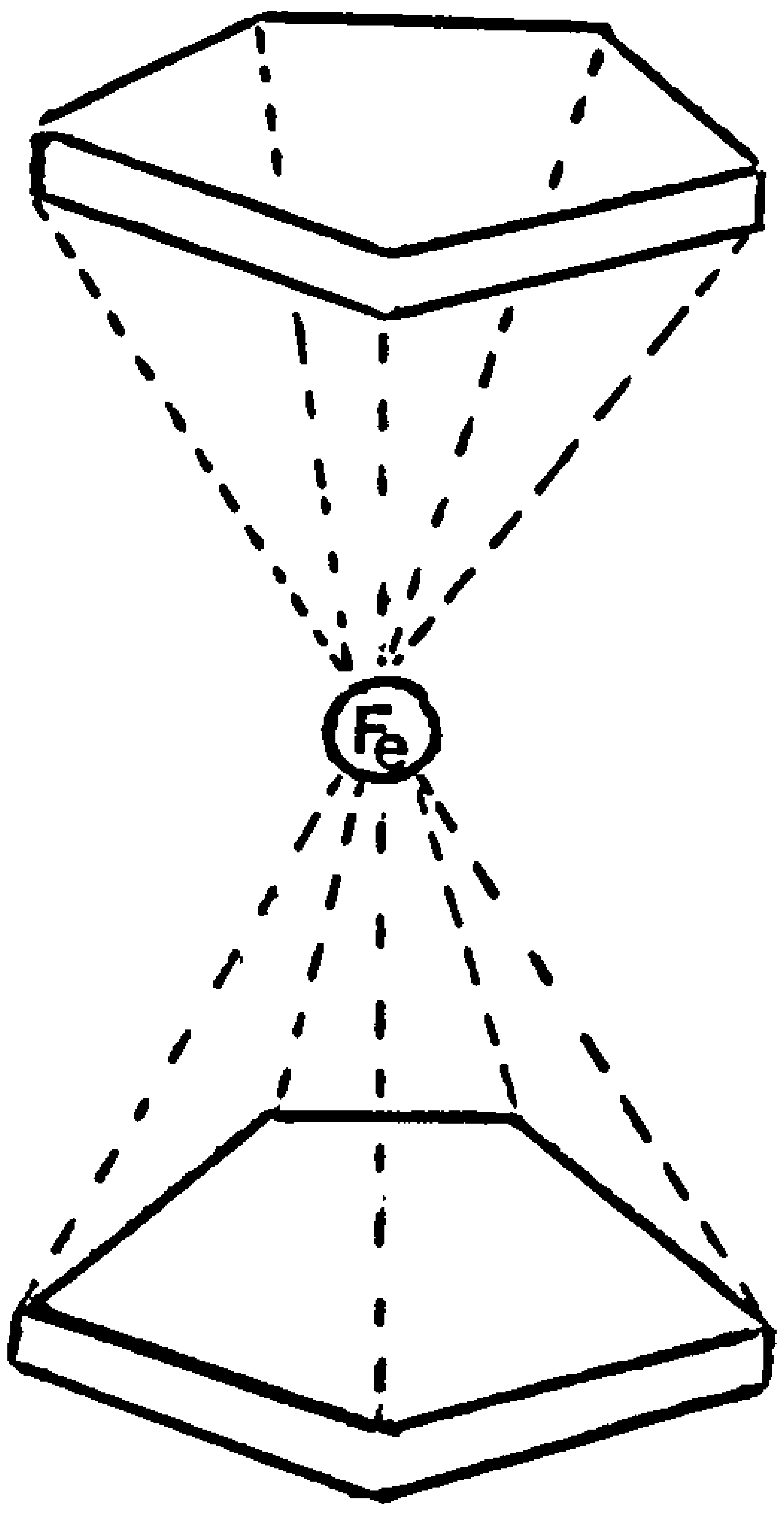
The iron in dicyclopentadienyliron is bivalent because treatment of a carbon tetrachloride solution of the material with bromine gives a dark green precipitate. The green precipitate dissolves in water to give a blue solution containing ferrous and bromide ions. By anology with the well-known cyclopentadienyl-potassium, it is believed that substitution occurs at the methylene group and the compound can be represented as shown below:



Dicyclopentadienyliron melts without decomposition at 172.5 - 173^0 and sublimes readily, still without decomposition. It is steam volatile. It is charred by and reduces sulphuric acid and decolorises acid potassium permanganate. It has a detectable vapour pressure at 0^0C and resists pyrolysis at 470^0. Iron biscyclopentadienyl is readily oxidized to a blue cation $[FE(C_5H_2)]^+$ ferricinium cation. Polarographic studies indicate an oxidation-reduction potential of -0.59V. The cation has been isolated as the crystalline tetrachlorogallate

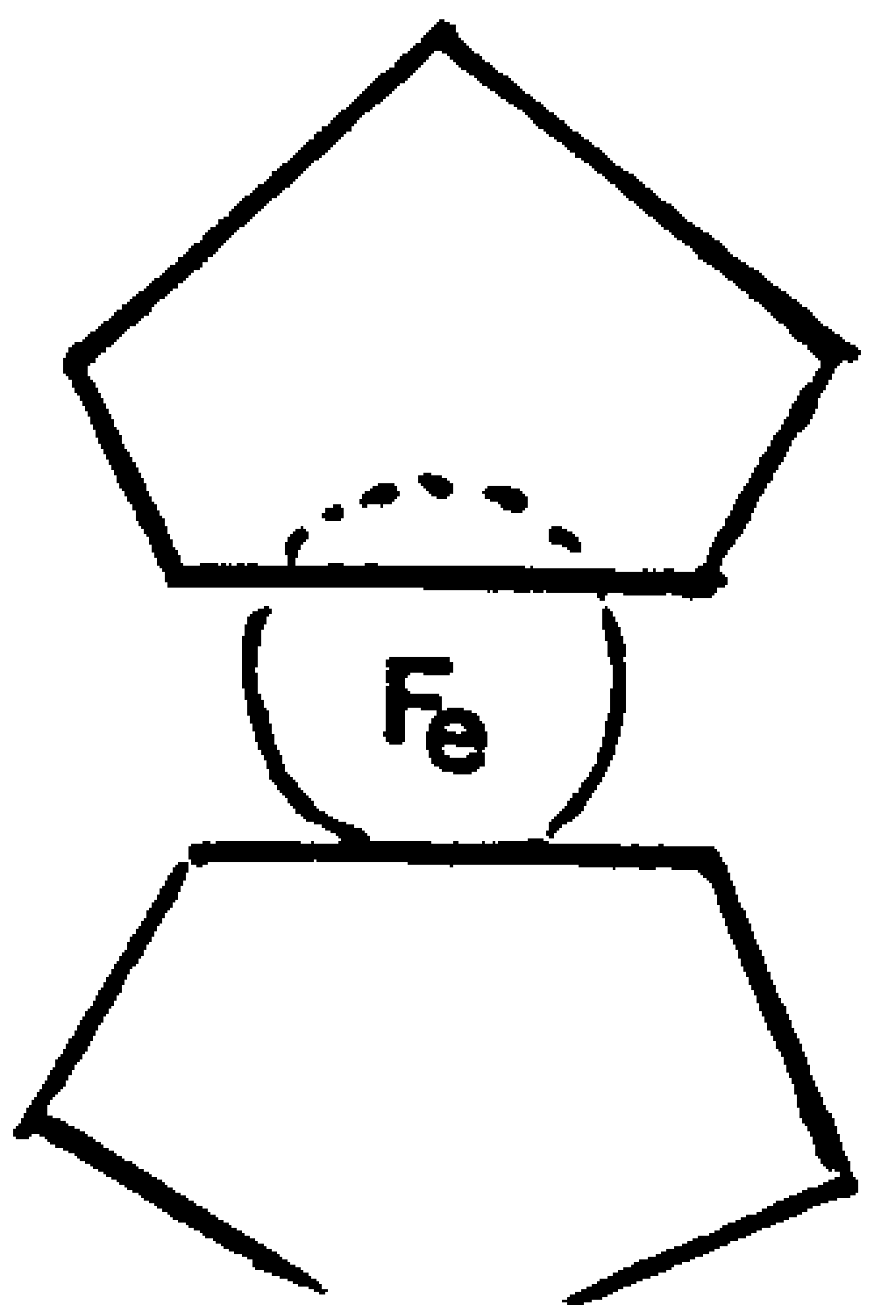
$$C_{10}H_{10}FeGaCl_4.$$

In view of the unique character of the iron compound, and of the inherent difficulties in the precise formulation of the covalent complexes of the transition metals, particularly those with unsaturated hydrocarbons, detailed proposals with respect to the electronic structure of iron biscyclopentadienyl cannot be given without some reservation. The number of electrons available (but not necessarily used) for iron to carbon binding, is eighteen (five-π electrons for each cyclopentadienyl unit, plus the eight electrons of the iron atom). Thus the effective atomic number of the central iron atom is thirty-six (krypton structure) as in the ferricyanide ion and in iron pentacarbonyl. Details of hybridization will determine the precise geometry of the molecule. Although formulated as a pentagonal anti-prism, a prismatic structure - Fig. 1c - is also possible.



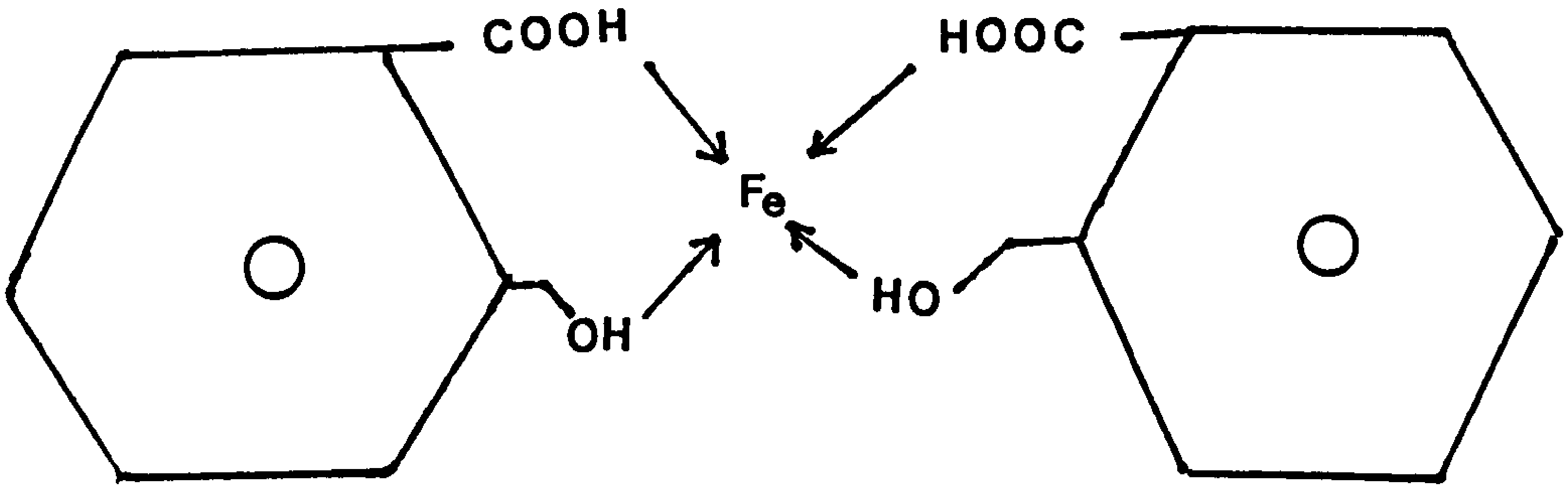
1c

The ferrocene is best considered as a "sandwich-like" structure as shown below:



2. Ferrocene dicarboxylic acid

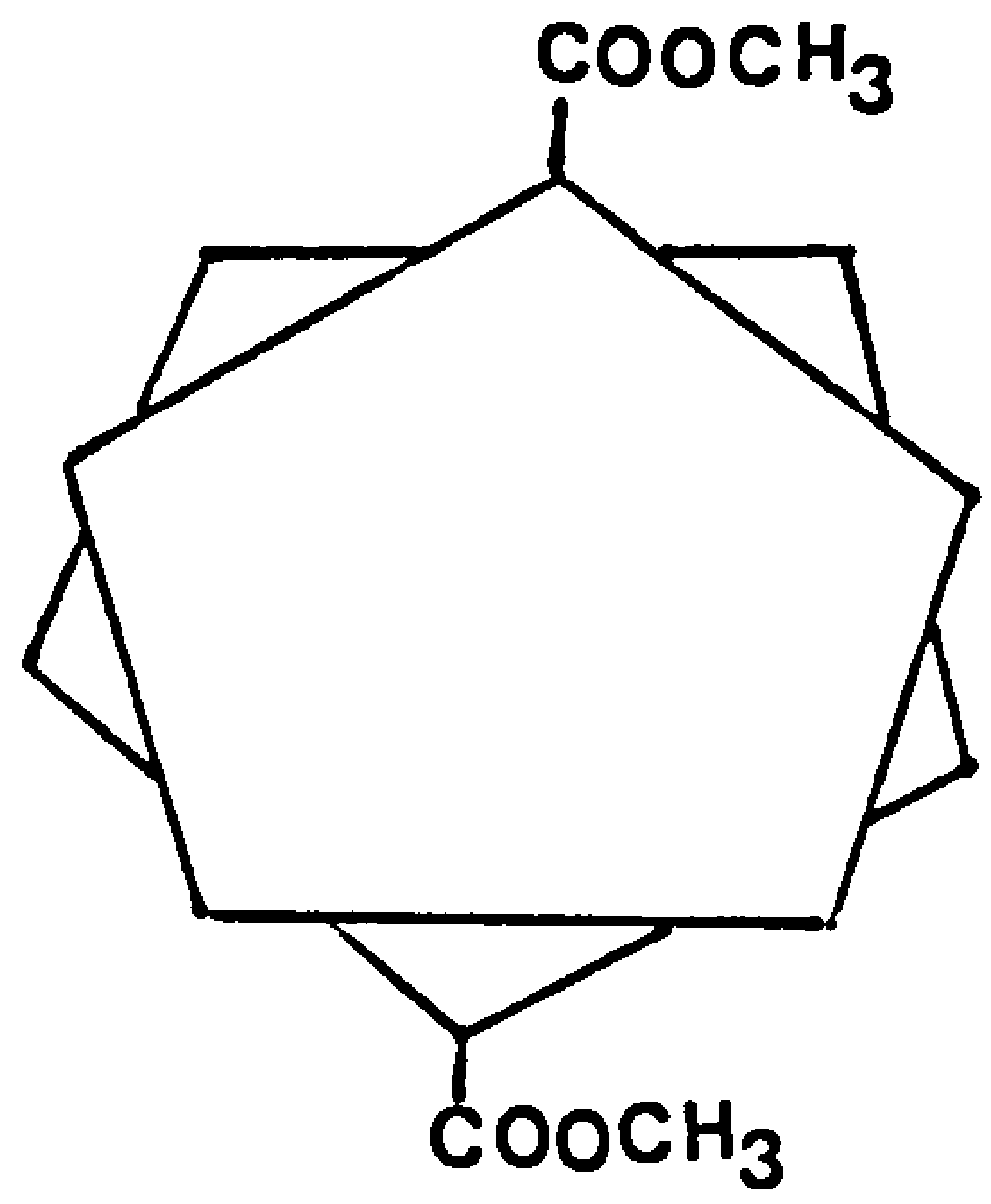
Treatment of ferrocene in carbon bisulfide with acetyl chloride (aluminium chloride present) gives rise to diacetyl derivative which on oxidation by hypoiodite forms ferrocene dicarboxylic acid. $C_{12}H_{10}O_4Fe$ (sublimes unchanged above 230°C).



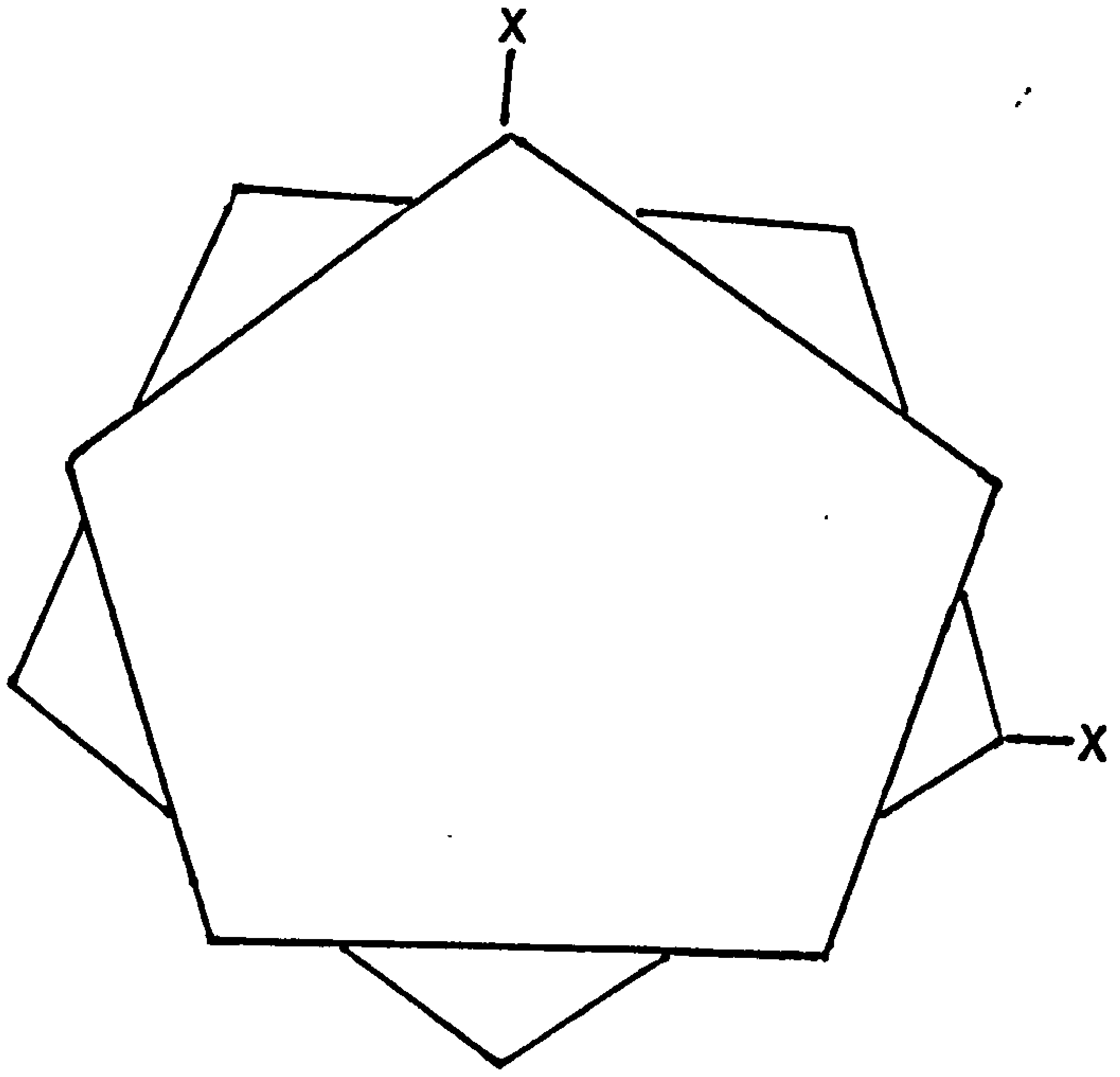
Acylferrocenes dissolve readily in acids with marked halochromism. They are photoliable and so far, cannot be converted into isolable derivatives of ferricinium cation

$$[(C_5H_5)_2Fe]^+$$

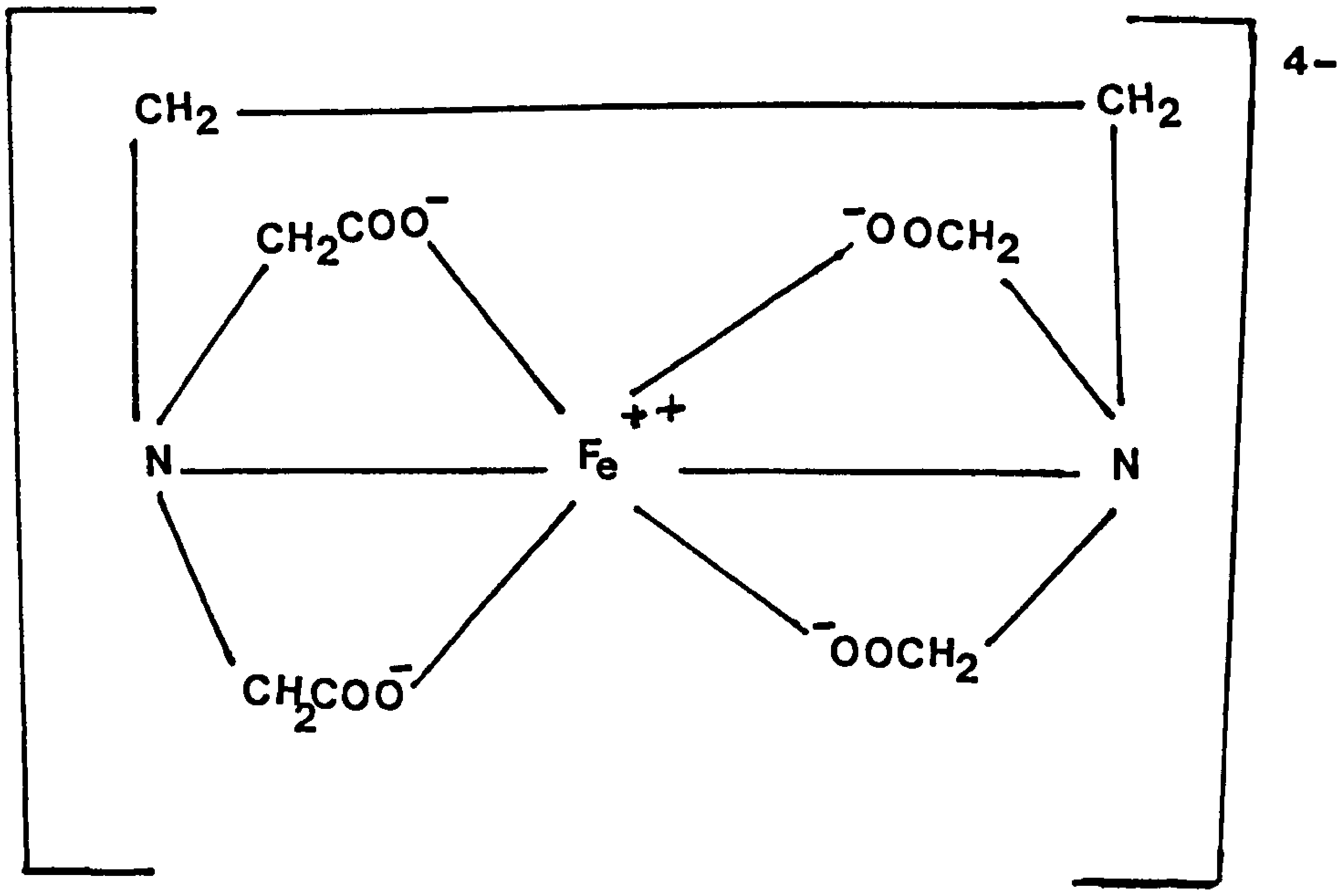
In diacetylferrocene the aceyl group is attached to a different ring (fig. d). It has not yet been confirmed whether the barrier in the way of rotation of one ring with respect to the other is sufficient to permit the existence of isomeric disubstituted ferrocenes as in (e).



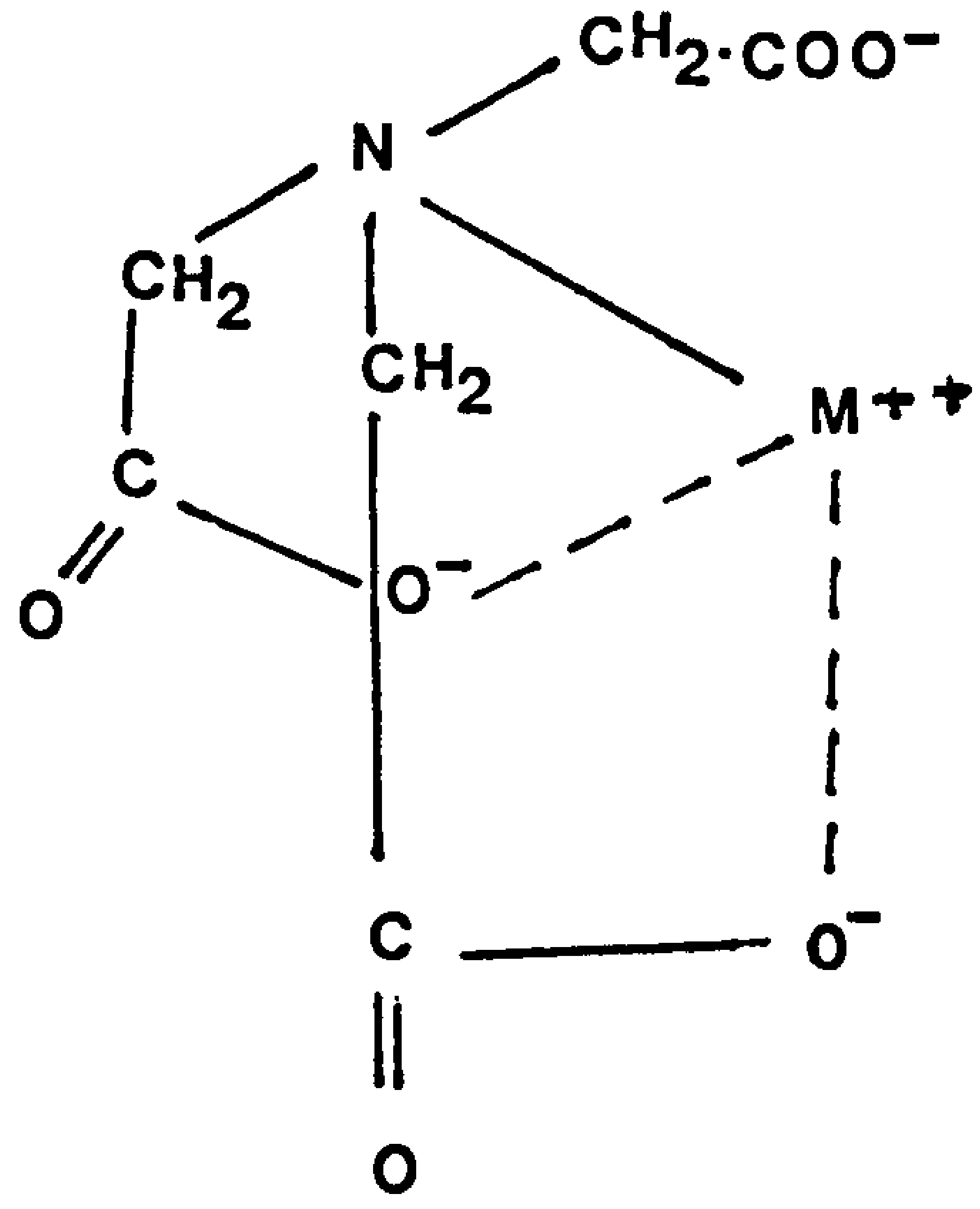
(e)



3. Fe/EDTA COMPLEX



4. Fe/TRILON A COMPLEX

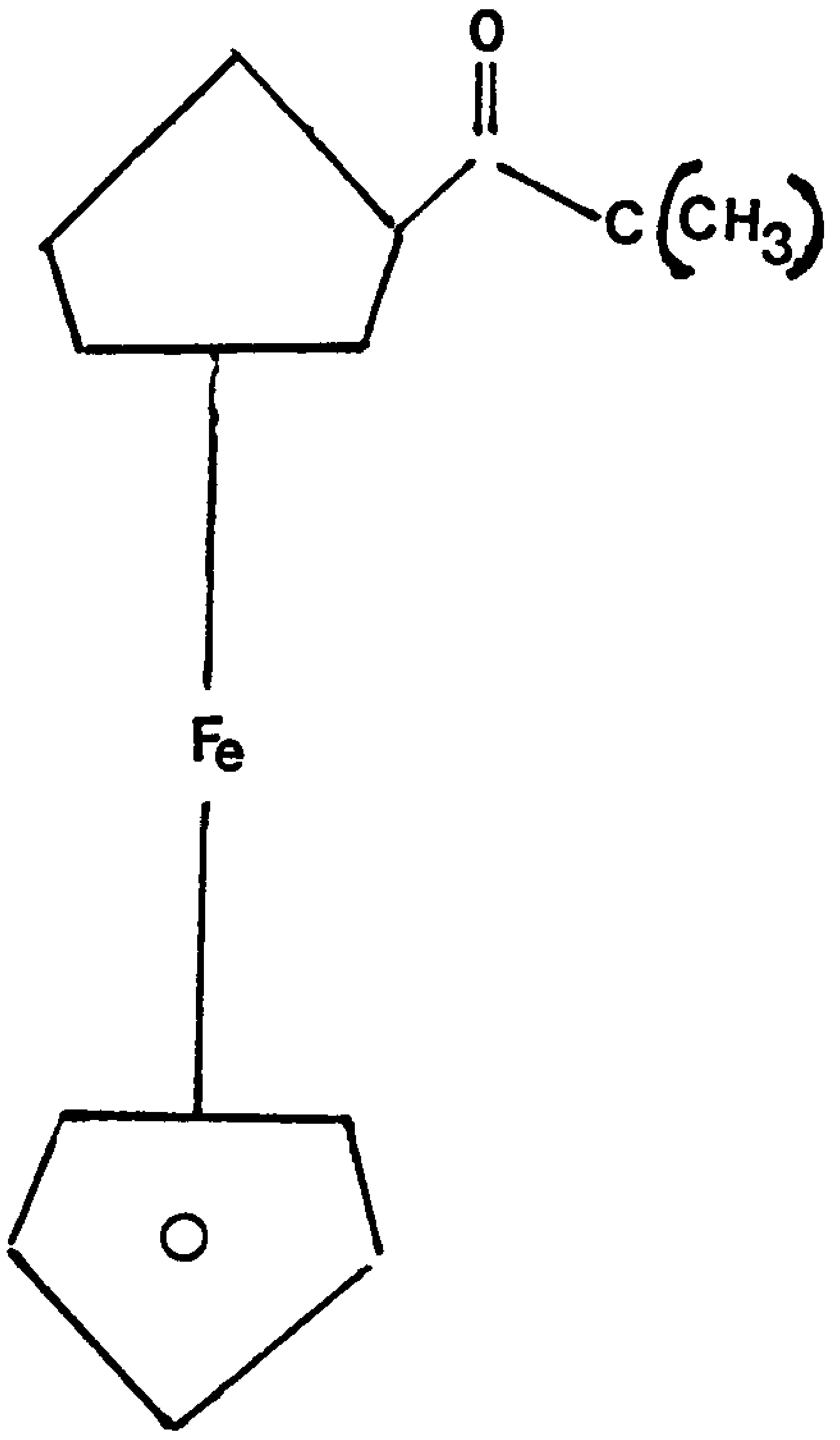


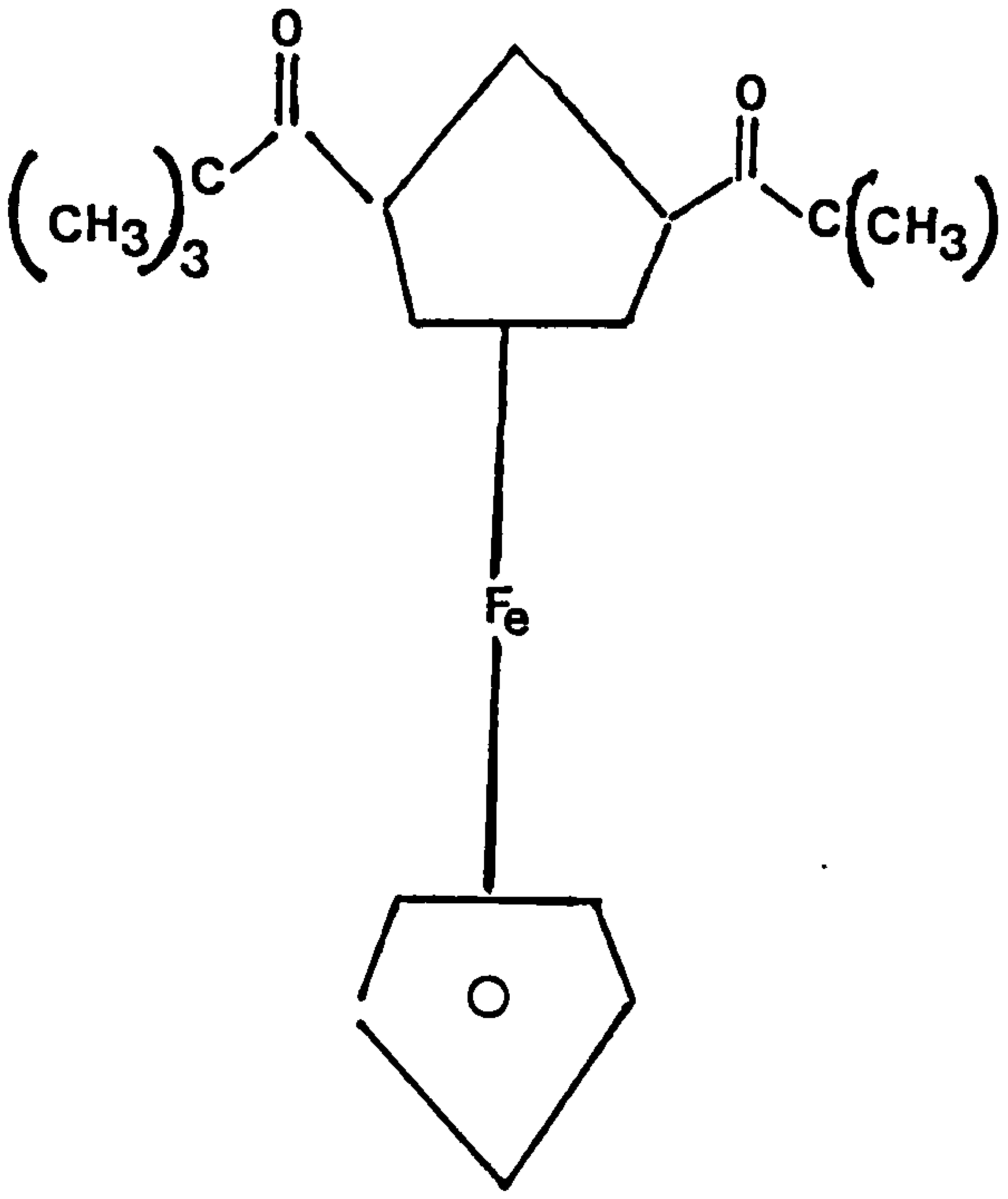
5. Ferrous salicylate

$Fe^{2+}(ortho\text{-}HOC_6H_4COO^-)_2$

6. Monopivaloylferrocene

7. Dipivaloylferrocene





8. Ferrous Stearate

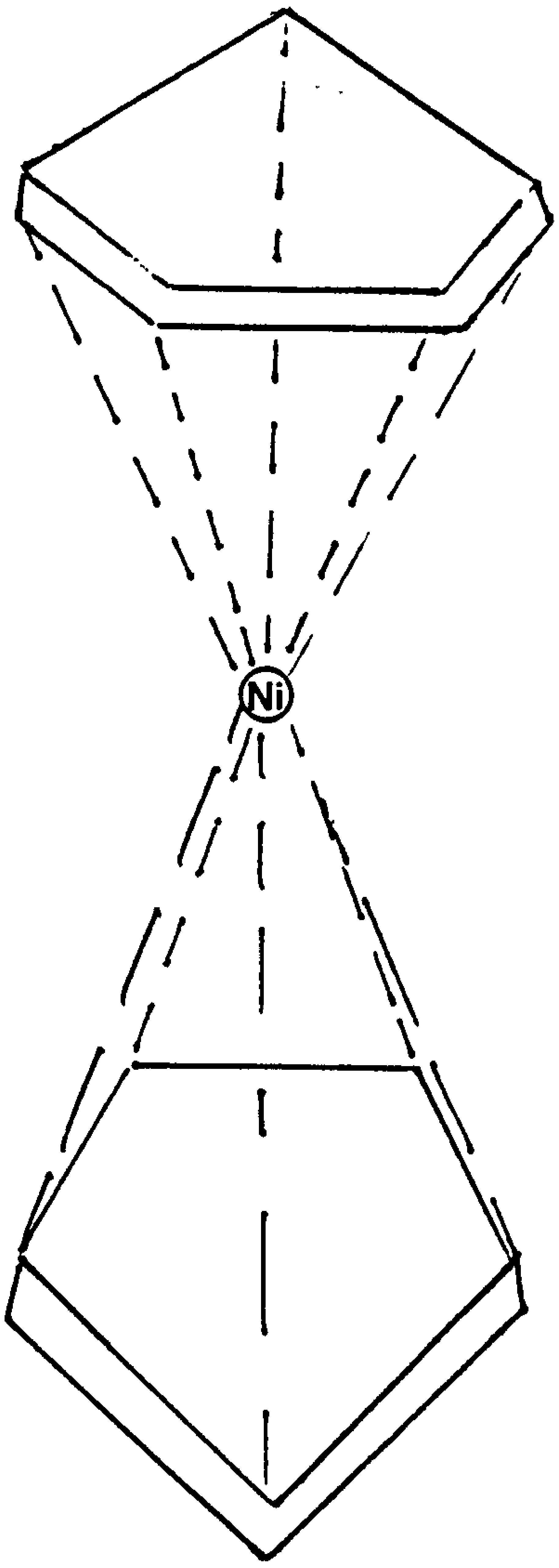
$Fe(OOC\text{-}C_{17}H_{35})_2$

9. Ferrous Octoate

$Fe(OOC_7H_{15})_2$

10. NON-FERROUS COMPOUNDS

Nickelocene (Dicyclopentadienylnickel)



11. Nickel Octoate

$Ni(OOC-C_7H_{15})_2$

12. Cobalt Stearate

$Co(OOC-C_{17}H_{35})_2$

13. Cobalt Octoate

$Co(OOC-C_7H_{15})_2$

14. Cotalt Oleate

$Co(OOC-C_{17}H_{33})_2$

15. Lead Oleate

$Pb(OOC-C_{17}H_{33})_2$

16. Lead Stearate

$Pb(OOC-C_{17}H_{35})_2$

17. Lead and Cobalt naphthenates (with undefined formulae).

CHAPTER 5

EXPERIMENTAL

5.0 PREPARATION OF MONOPIVALOYL AND DIPIVALOYL FERROCENES

The mono- and dipivaloyl ferrocenes were prepared as specified in B.P. 861833 Example 3. A mixture of four parts of ferrocene and 24 parts of pivaloyl chloride (Trimethylacetyl chloride) $(CH_3)_3CCOCl$ and one part of magnesium powder was heated under reflux for 30 minutes and poured into cold distilled water. The mixture was extracted with diethyl ether and extract was washed with dilute aqueous sodium hydroxide and water and dried over anhydrous sodium sulphate. The solvent was removed by evaporation and the residue was dissolved in petroleum ether (b.p. 40-60°C) and passed through a column of alumina.

The column was eluted with a mixture of chloroform-acetone 1 : 2 for monopivaloyl ferrocene and chloroform-acetone-diethyl ether for dipivaloyl ferrocene.

The first eluent was evaporated and used as monopivaloyl ferrocene m.p. 93°C, dark brown powder, soluble in methyl ethyl ketone.

Further elution of the column provided dipivaloyl ferrocene on evaporation m.p. 128°C brown powder, soluble in methyl ethyl ketone.

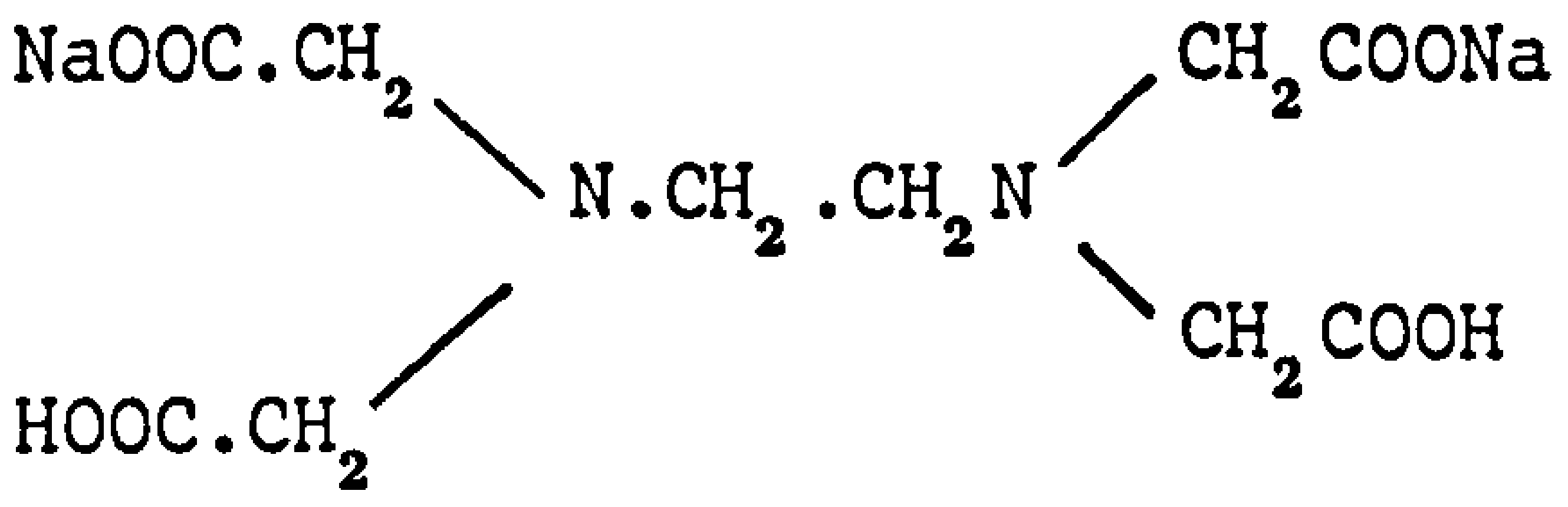
Quantities used

24 g	Ferrocene
6 g	Magnesium powder
145 g	Trimethylacetyl chloride (density = 1 g/ml)

5·1 PREPARATION OF FERROUS/ETHYLENEDIAMINE TETRA-ACETIC ACID COMPLEX (Fe/EDTA)

Materials:

Disodium EDTA



Molecular weight	372
Purity	98%
Ferrous sulphate	$FeSO_4.7H_2O$
Molecular weight	278
Purity	98%
Isopropanol	$HO-CH-(CH_3)_2$
Molecular weight	60

Equimolar quantities of reactants and reagents were used taking into account their respective percentage purities.

7.5750 g Ferrous sulphate was dissolved in 60 mls of distilled water. Drops of concentrated sulphuric acid were added to this solution until all the ferrous hydroxide had redissolved.

20.2578 g sodium EDTA was weighed out and dissolved in 150 mls of warm distilled water. The ferrous salt solution was added slowly to the sodium-EDTA solution with constant stirring. A clear solution, slightly yellowish green, was obtained.

One litre of isopropanol was added to the yellowish-green solution to cause the complex to precipitate out. The precipitate was left to settle out overnight. The liquor was decanted off and the solids collected, washed with isopropanol and dried in an oven at 50-60°C. The product was ready for use.

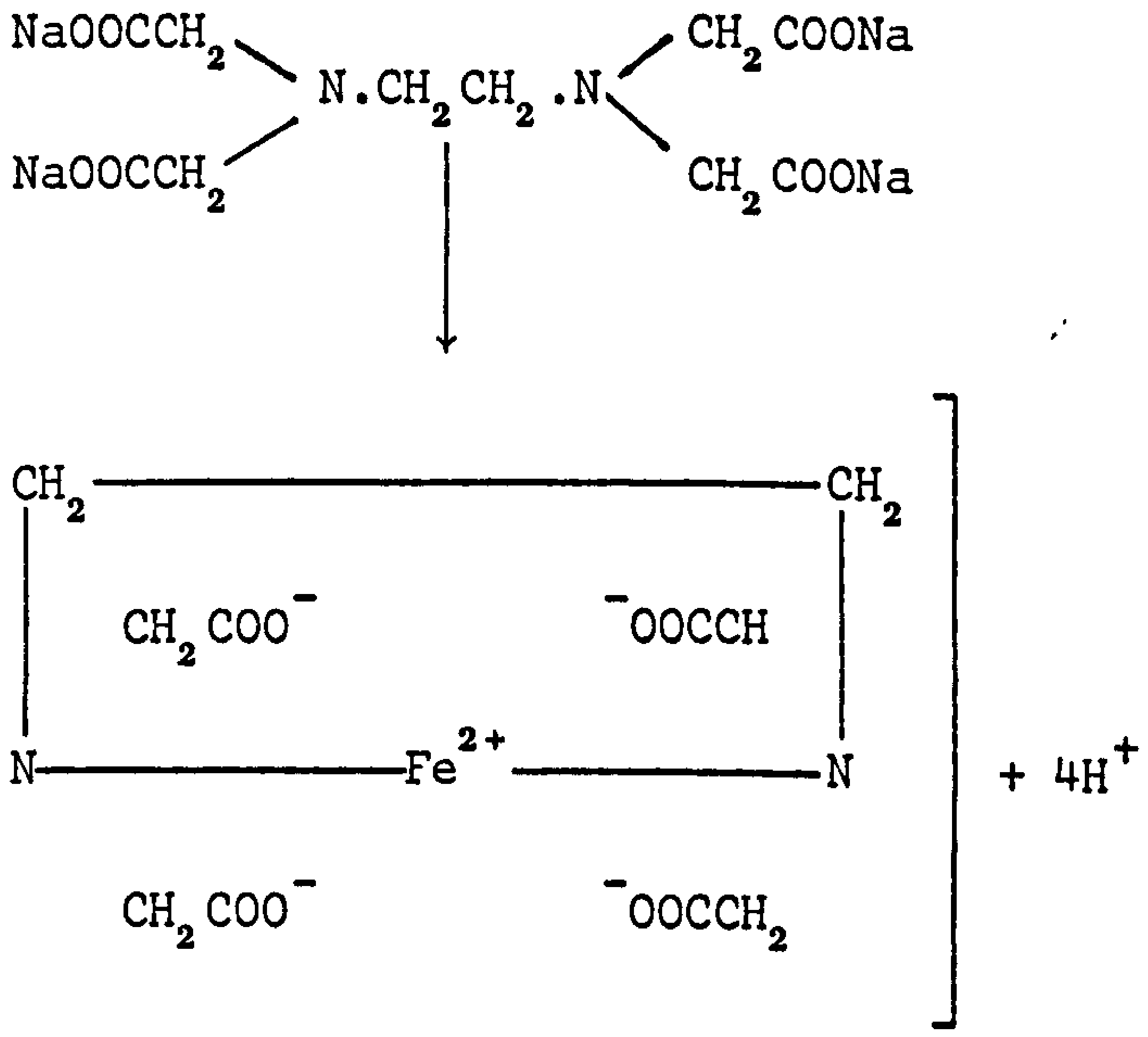
Properties Yellow powder,

m.p. 242°C

Soluble in methyl ethyl ketone.

$Na_2[H_2EDTA] \xrightarrow{Fe^{++}} Na_2[Fe\ EDTA] + 2H^+$

Similarly



Fe/EDTA COMPLEX

5·2 PREPARATION OF FERROUS/NITRILOTRIACETIC ACID

(Fe/NTA or Fe/Trilon A)

Materials:

Disodium salt of nitrilotriacetic acid

$N(CH_2.COO)_3Na_2H$

Molecular wt	234
Minimum assay	99% (acidimetric)
Melting point	245°C (with decomposition)

Ferrous sulphate	$FeSO_4.7H_2O$
Molecular wt	278
Purity	98%
Isopropanol	$HO{-}CH{-}(CH_3)_2$
Molecular wt	60

Equimolelar quantities of reagents and reactants were used taking into account their respective percentage purities.

3.7825 g $FeSO_4.7H_2O$ was dissolved in 30 mls distilled water. Concentrated sulphuric acid was added in drops to this solution until all the ferrous hydroxide (seen as a white solid) redissolved.

3.10 g Nitrilotriacetate was weighed out and dissolved in 75 mls of warm distilled water. The ferrous salt solution was added slowly to nitrilotriacetate solution with constant stirring.

One litre of isopropanol was added to the mixture of ferrous sulphate and nitrilotriacetate solution to cause precipitation of the complex. The precipitate was left to settle overnight. The liquor was decanted, the solids were collected, washed with 200 mls isopropanol and allowed to dry in an oven at 50-60°C. The product was ready for use.

Properties - Grey powder, m.p. 224°C, soluble in methyl ethyl ketone.

5·3 PREPARATION OF FERROUS SALICYLATE

Materials:

Ferrous sulphate, salicylic acid, ethanol at pH 8.

11.12 g of ferrous sulphate was dissolved in 50 mls distilled water with slight warming.

44.16 g salicylic acid was dissolved in 400 mls absolute ethanol. The dissolved salicylic acid was brought to boil and the ferrous sulphate solution was added dropwise with constant stirring. The pH of the resulting solution was adjusted with sodium hydroxide to pH 8. A white precipitate was formed and this was filtered off from the purple solution. Barium chloride was used to test for the absence of sulphate ions confirming the formation of salicylate.

The ethanolic solution was then evaporated to dryness. The dry product (ferrous salicylate) was purified by differential solubility in chloroform and water. Salicylic acid is insoluble in water but soluble in chloroform. The ferrous salicylate dissolves in water to form a purple solution. The two phases were separated. The aqueous phase was evaporated to dryness to isolate the ferrous salicylate.

The product was ready for use in this work.

$$\mathrm{Fe^{2+}SO_4^{2-} + 2(ortho\text{-}HOC_6H_4COOH)}$$

$$\Big\downarrow \text{ Ethanol pH 8}$$

$$\mathrm{Fe^{2+}(ortho\text{-}HOC_6H_4COO^-)_2}$$

Ferrous salicylate

5·4 PREPARATION OF STEARIC ACID SALTS FOR USE AS DRIERS

Salts of stearic acid were prepared from cobalt, nickel, iron and lead.

Stearic acid salts are generally prepared from the sodium salt of the acid. Most stearic acid salts are insoluble in water. The soap derivatives appear as a scum of insoluble salts.

$$nC_{17}H_{35}COONa + M(X)_n \longrightarrow$$
$$(C_{17}H_{35}COO)_nM + nNaX$$

TABLE 1·3 SPECIFICATION OF SOLUBLE METALLIC SALTS USED IN PREPARING THE STEARATES

Soluble Metal Salt	* (a)	* (b)	Manufacturer
$CoCl_2.6H_2O$	24	10	Halewood Chemicals
$NiCl_2.6H_2O$	18	12	" "
$FeSO_2.7H_2O$	24	6	" "
$(CH_3COO)_2Pb.3H_2O$	18	12	BDH

$\overset{*}{(a)}$ and $\overset{*}{(b)}$ are the the number of grams sodium stearate (manufactured by BDH) and the metallic salts respectively.

The required weights $\overset{*}{(a)}$ and $\overset{*}{(b)}$ were weighed as accurately as possible in a suitable weighing machine. The sodium stearate $\overset{*}{(a)}$ was dissolved in 200 ml distilled water at 70 C in a 1 litre beaker with constant stirring. The soluble metallic salt $\overset{*}{(b)}$ was dissolved in 40 ml of distilled water at 68°C in a separate 500 ml beaker. This solution was gradually added to the sodium stearate solution with constant stirring while maintaining the temperature 68 - 70°C. Shortly after mixing the two solutions, the contents of the beaker were immediately filtered in a Buchner funnel. The stearic acid salt was washed twice with 100 mls water at 68°C, followed by 100 mls of diethyl ether. The product, the required metal stearate was dried in the oven at 50°C after which it was ready for use.

The preparation of oleates and octoates followed the same pattern except that sodium oleate and sodium octoate are used as the soluble acid salts respectively. The oleates are prepared at 40 - 42°C.

Tables 1·4 & 1·5

preparation of metal oleates and octoates.

1·4

Soluble Metal Salts	$(\overset{*}{a})_1$	$(\overset{*}{b})_1$
$CoCl_2.6H_2O$	72	30
$NiCl_2.6H_2O$	54	36
$FeSO_4.7H_2O$	72	30
$(CH_3Coo)_2Pb.3H_2O$	$67\frac{1}{2}$	45

Table 1·5

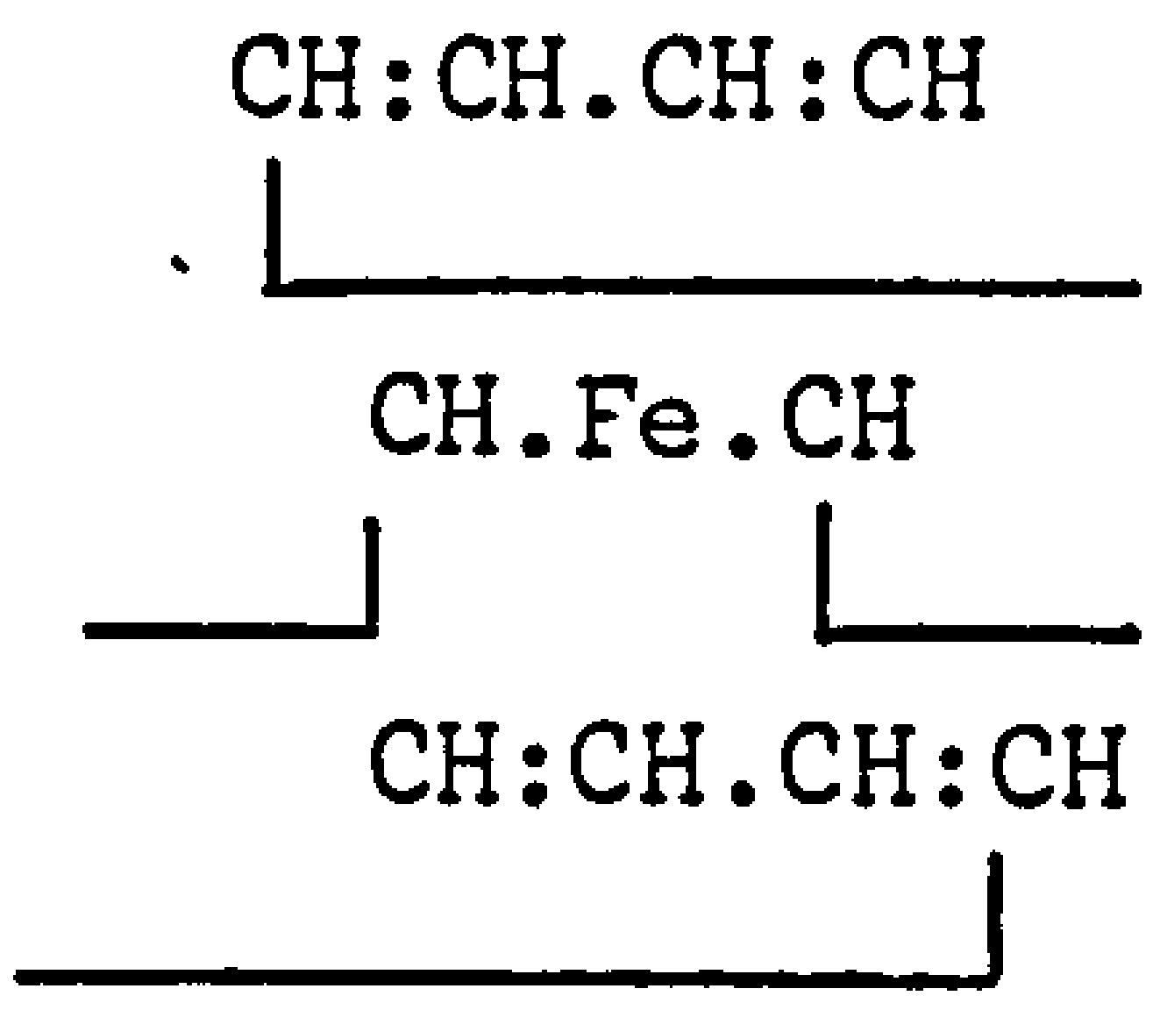
Soluble Metal Salts	$(\overset{*}{a})_2$	$(\overset{*}{b})_2$
$CoCl_2.6H_2O$	50	40
$NiCl_2.6H_2O$	72	48
$FeSO_4.7H_2O$	72	40
$(CH_3Coo)_2Pb.3H_2O$	72	60

$(\overset{*}{a})_1$ and $(\overset{*}{b})_1$ are grams of pure sodium oleates and soluble metal salts respectively.

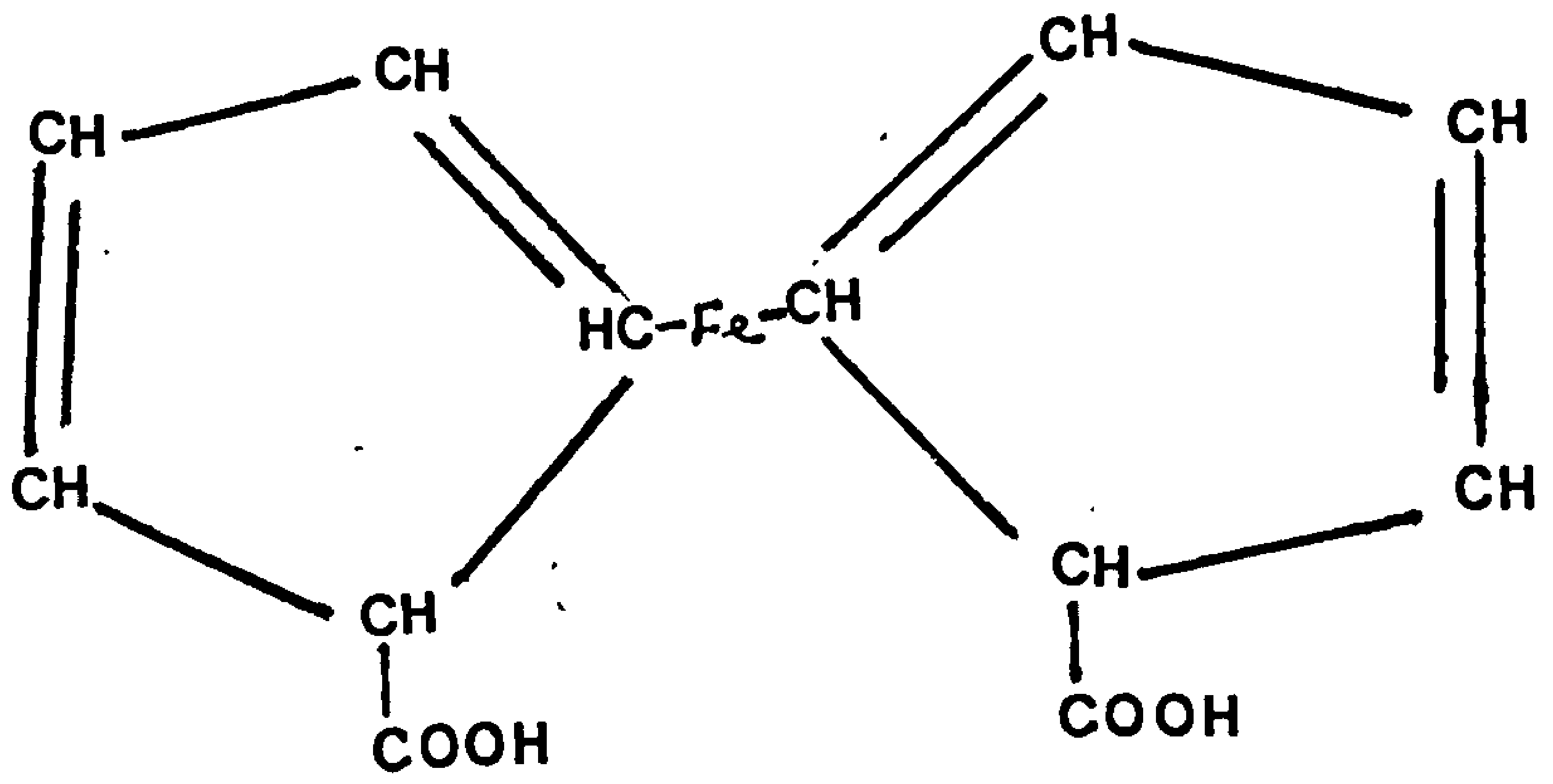
$(\overset{*}{a})_2$ and $(\overset{*}{b})_2$ are grams of pure sodium octoates and soluble metal salts respectively.

The following compounds were ordered and used as prepared by the manufacturers.

(i) Ferrocene (dicyclopentadienyliron) manufactured by BDH Chemicals Ltd.



(ii) 1, 1'-Ferrocenedicarboxylic acid manufactured by Lancaster Synthesis Ltd.



(iii) Lead Napthenate (24%) manufactured by Holbrook and Illingworth Ltd.

(iv) Cobalt Napthenate (6%) was also manufactured by Holbrook and Illingworth Ltd.

Drier solutions containing 5% iron on the weight of metal were prepared using the equation:

$$\frac{PM}{E} \text{ per 100g solution.}$$

where P = Percentage metal concentration required.

M = Molecular weight of the drier.

E = Equivalent weight of iron (56).

For each drier, the required weight to give a 5% iron stock solution was weighed out in a sensitive balance and dissolved in a suitable solvent.

Where dissolution was not good enough with some solvents, other solvents were employed as can be seen in the case of Fe/EDTA and Fe/Trilon A complexes.

Because this work involved a comparative catalytic behaviour of various driers, it was necessary to ensure that equal amounts of dissolved drier were put into the reaction vessel and that approximately equal weight and volume of the reacted sample was removed for analysis. This was achieved by the use of 100 µl labpipette and 100 µl plastic tips. Equal weights of linoleic acid were used in each case.

Variable weights of driers were employed in one series of experiments to determine if high or low concentrations of the driers affected the rate of drying.

For each of the driers, experiments were carried out at room temperature, 60°C, 80°C and 120°C.

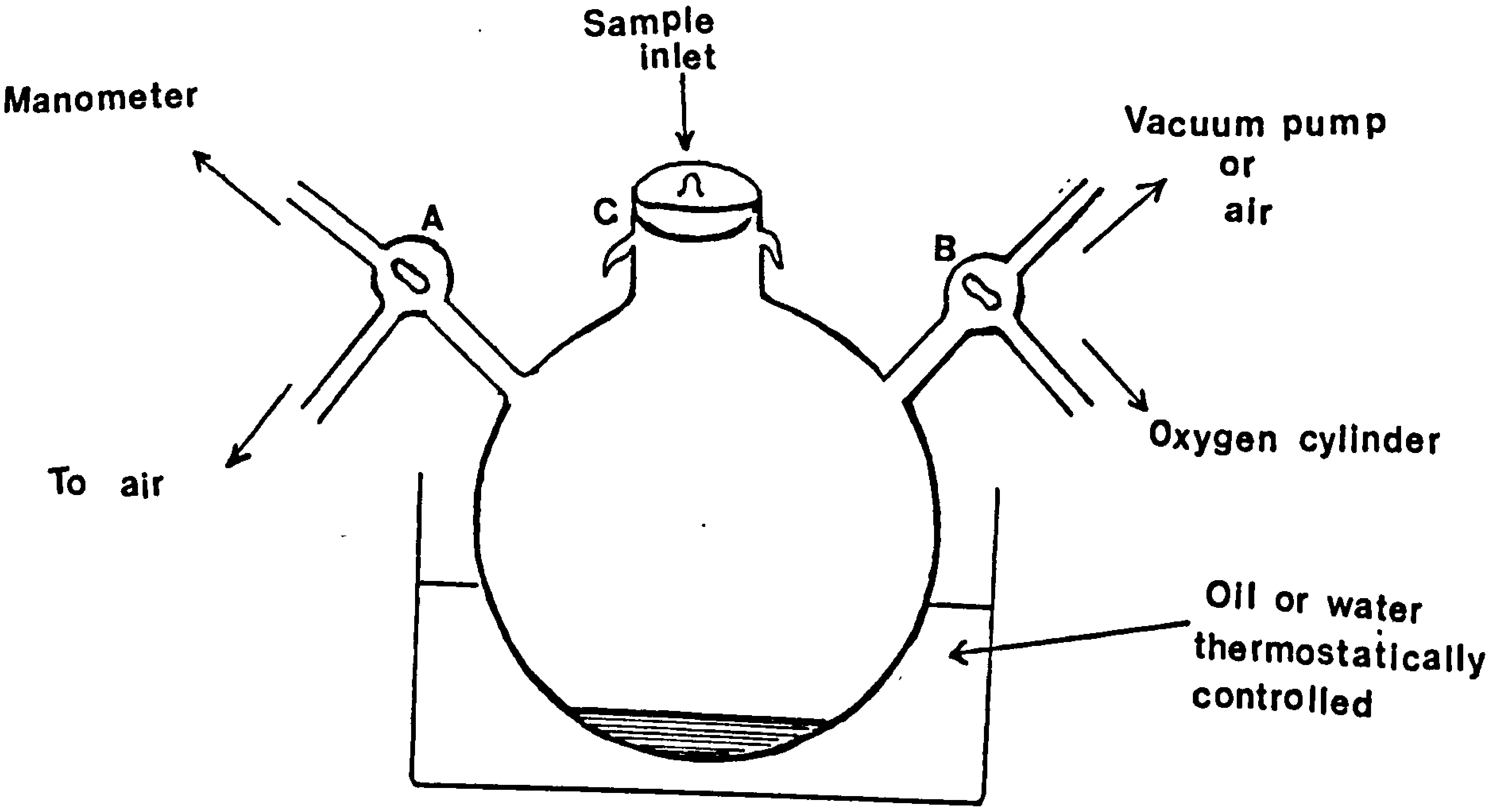
The duration for each experiment was limited to 60 hours (in most cases) above which the high temperature samples gelled and polymerized thereby became sticky and difficult to remove to the exact weight. Consequently, the results no longer became comparative as accuracy could no longer be maintained in sampling.

5·5 OXYGEN ABSORPTION

The rate of oxygen absorption of cis 9, cis 12-octadecadienoic acid in the presence or absence of driers was measured as follows:-

Apparatus

1000 cm^3 flasks fitted with two 3-way taps as shown in plates 1A and 1B. Also see the diagram of the apparatus below.



For room temperature, and 60-80°C experiments, a thermostat covered by styrene foam pellets was used.

For 120°C experiments, a thermostat filled with glycerine was used.

For pressure measurement, manometers were attached to one 3-way tap, having a trap (glass bulb filled with Pora-Pak a) fitted between flask and manometer to absorb volatile products of autoxidation. The third arm of the tap was open to the atmosphere and kept open during admission of oxygen for purging and to provide the oxygen for the absorption experiment (A).

Oxygen was admitted via the second 3-way tap from a B.O.C. oxygen cylinder fitted with pressure reducing valves and gauges (B).

Materials and samples were added or transferred from the neck C, which was fitted with a greased glass stopper held in place by rubber bands fitted to glass hooks on the stopper and the neck of the flask.

Method

The stock solutions were used to give either 0.05% iron or 0.25% iron on the weight of linoleic acid from 100 µl plastic tip attached to a Labpipette. From the 5% stock solution prepared for each drier, 100 µl of the stock gave 0.05% iron in 10 mls of linoleic acid. Also 500 µl i.e. 100 µl × 5 gave 0.25% iron in 10 mls of linoleic acid.

The chart below shows the drier, its molecular weight and solvent used.

DRIER	MOL WEIGHT	SOLVENT	Wt/100 mls STOCK SOLUTION
Ferrous stearate	622	2-methoxyethanol	55.536
Ferrous salicylate	332	"	29.6429
Cobalt stearate	625	xylene	55.8036
Ferrocene	186	methyl/ethyl/ketone	16.607
Cobalt octoate	345	xylene	30.8036
Ferrous octoate	342	white spirit	30.5357
Cobalt oleate	621	xylene	55.4464
Lead oleate	769	xylene	68.6607
Nickel octoste	342	xylene	30.5375
Lead stearate	773	white spirit	69.0179
Nickelocene	189	methyl/ethyl/ketone	15.890
Fe/EDTA	448	"	40.00
Fe/NTA	524	"	46.7857

The bath was set to the required temperature. Glass wool (1 gm) was teased out and put into the 1000 cm^2 flask to increase the surface area. The stock solution was warmed up to ensure dissolution. 100 or

500 µl of appropriate drier solution was added using a 100 µl disposable plastic tip on a Labpipette to 10 mls of linoleic acid. The mixture was poured into the 1000 cm^3 flask. The flask was stoppered and oxygen purged through the vessel via tap B to expel the air from the vessel. Tap A was open to the air during the operation which took about 1½ minutes. Tap B was then closed and Tap A used to connect the vessel to the manometer. At this stage the pressure in the vessel was atmospheric i.e. both limbs of the manometer were level.

The reading of the barometer attached to the wall gave the atmospheric pressure at that particular time. The rise in the column of the manometer connected to the flask was read after specific intervals. For each reading the ambient atmospheric pressure was noted.

The results were expressed as the change in pressure ΔL corrected for atmospheric pressure (mm Hg).

5.6 IODINE VALUE

The iodine value of a fat is the number of grams of iodine absorbed by 100 g of the fat.

Fats which are esters of saturated acids will not absorb iodine. A fat which is an ester of unsaturated acids will absorb iodine. The mass of iodine absorbed is a measure of the degree of unsaturation.

A molecule of triolein would, for example, absorb three molecules of iodine.

$$\begin{array}{lcl} \mathrm{CH_2OOCC_{17}H_{33}} & & \mathrm{CH_2OOCC_{17}H_{33}I_2} \\ \mathrm{CHOOCC_{17}H_{33}} + \mathrm{3HI} & \longrightarrow & \mathrm{CHOOCC_{17}H_{33}I_2} \\ \mathrm{CH_2OOCC_{17}H_{33}} & & \mathrm{CH_2OOCC_{17}H_{33}I_2} \end{array}$$

The term unsaturation refers to the number of double bonds in an acid. From the above equation, the molecular mass of pure triolein is 884.

6 moles of iodine weigh 762 g

∴ 100 g triolein will absorb

$$\frac{762}{884} \times 100 \text{ g iodine}$$

$$= 86 \text{ g iodine.}$$

All drying and semi-drying oils contain fatty acids with double bonds. Linseed oil (a major vegetable oil used in plant manufacture) contains five different fatty acids, three of which are unsaturated.

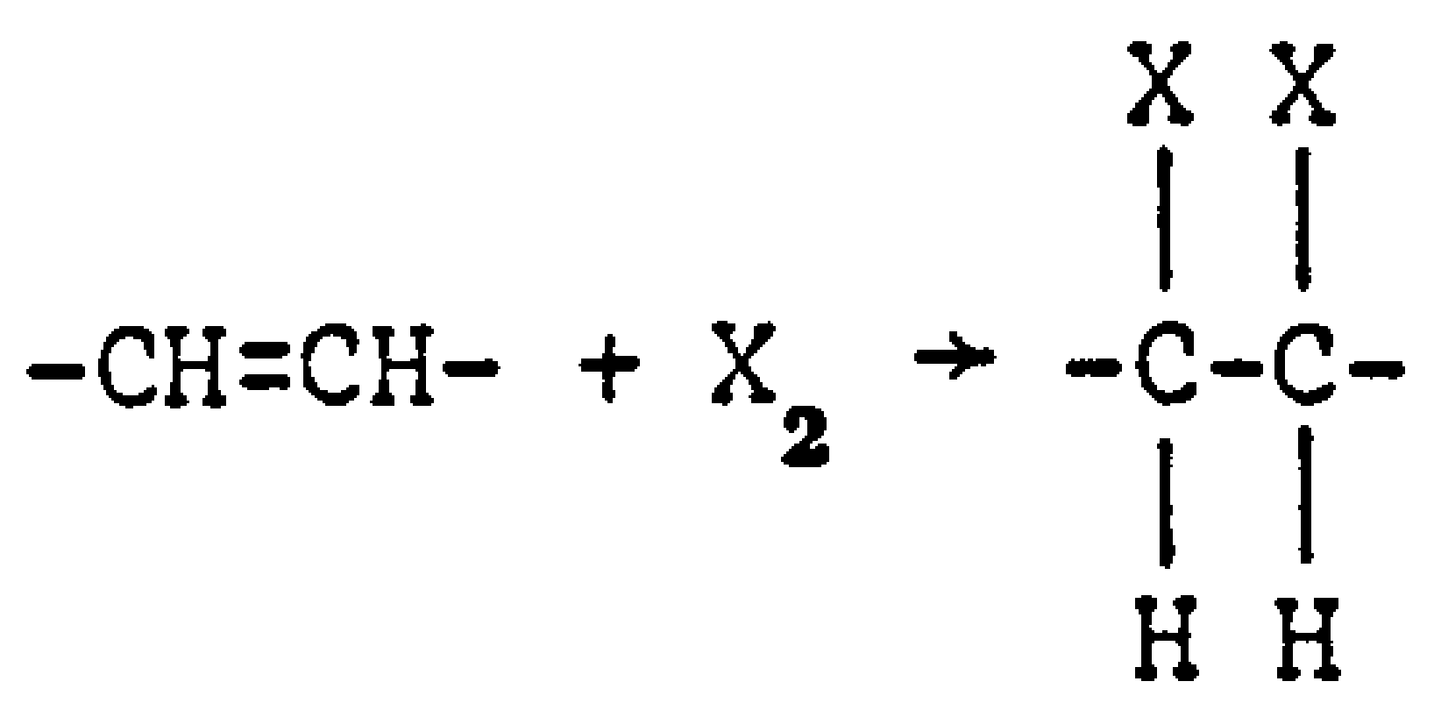
Table 1·6

FATTY ACIDS OF LINSEED OIL

FATTY ACID	FORMULA	MOL. WT.	IODINE VALUE
PALMITIC	$CH_3(CH_2)_{14}COOH$	256.5	0
STEARIC	$CH_3(CH_2)_{16}COOH$	284.6	0
LINOLEIC	$CH_3(CH_2)_4CH{=}CH{-}CH_2{-}CH{=}CH(CH_2)_7COOH$	280.5	180
OLEIC	$CH_3(CH_2)_7COOH$	282.5	90
LINOLENIC	$CH_3{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}$ $CH{=}CH{-}(CH_2)_7COOH$	278.5	274

For a list of other saturated and unsaturated fatty acids, the reader is referred elsewhere(226).

In general, the average amount of unsaturation of an oil is determined by adding an excess of the halogen to the oil and measuring the amount of absorbed halogen under specified conditions. Variables such as time, solvent, amount of reagent, effect of light and nature of unsaturation all affect the amount of halogen absorbed.



$$-CH{=}CH- + X_2 \rightarrow -\overset{X}{\underset{H}{C}}-\overset{X}{\underset{H}{C}}-$$

Hubl(227) was among the first investigators to put forward techniques of determining iodine value. He suggested the use of a solution of iodine and mercuric chloride in ethanol as the halogenating agent.

The Wij's(228) and also the Hanus technique soon followed. The Hanus method used iodine monobromide in acetic acid. The Wij's technique which employs iodine monochloride in acetic acid is the most commonly used method, being preferred to other techniques because of the relative stability of the reagents used.

The official method of A.S.T.M. and B.S. is the Wij's method. In this work, however, Wij's technique was used according to B.S. 243 with some modifications to accelerate the work and improve accuracy.

DETERMINATION OF IODINE VALUE

Apparatus: Conical flasks with ground glass stoppers of 250 ml capacity. A one-litre boiling flask, with a rubber stopper. The stopper has two holes bored, through which two bent glass tubes are inserted to allow the entry of oxygen and escape of air from the vessel (see Plate 3). A 100 µl labpipette and 100 µl plastic tips. Burette, stand, beakers (50 ml).

Reagents: Distilled water was used in preparing solutions where the use of water was required .

(i) Sodium thiosulphate 0.1N or 0.2N.

(ii) Potassium iodide 10% (w/v) solution free from iodates and iodine.

(iii) Starch solution (0.5 g/100 ml).

(iv) Carbon tetrachloride solution.

This was ordered from May and Baker Ltd., Dagenham, England.

(v) Glacial acetic acid (not less than 99% w/w, also manufactured by May and Baker.

(vi) Iodine trichloride.

Preparation of Starch Solution

The starch solution was prepared by dissolving 5 g of soluble starch in one litre of water at the boil for 2 - 3 mins. The solution was stirred continuously and allowed to cool. Three or four drops of mercuric iodide were added to improve the storage characteristic of the solution

Preparation of Wij's Solution

For most part of the work, Wij's iodine solution was ordered from BDH Chemicals, Pool. Initial work was carried out with samples prepared as follows:

8 g ICl_3 was dissolved in a mixture of 600 mls glacial acetic acid and 300 mls carbon tetrachloride (the latter being free from reducing agents). This was confirmed by shaking one mililitre of carbon tetrachloride and one drop of saturated potassium dichromate in the presence of concentrated sulphuric acid. No green colour was observed.

The halogen content of the iodine trichloride solution was measured by the addition of 5 mls ICl_3 solution to 5 mls of potassium iodide solution (10% w/v) and 30 mls of distilled water. The mixture was titrated against a standard 0·1 or 0.2N sodium thiosulphate solution in the presence of starch solution as an indicator. Approximately 8 g of powdered iodine was added and dissolved in the iodine trichloride solution until the halogen content reached 1.5 times the value of the first determination. This was to reduce the probability of side reactions and increase the stability of the solution. The solution was diluted with a mixture of glacial acetic acid and carbon tetrachloride (3 : 7 v/v). This was stored in the dark, the dark brown bottle containing the solution was wrapped with a black piece of cloth.

5 mls of the above solution should require approximately 10 mls of sodium thiosulphate (0.1N or 0.2N for titration).

Experimental Procedure: Approximately 1 - 2 g of glass wool was put into the 1000 cm^3 flask after being teased out to increase its volume. 10 mls of linoleic acid was pipetted and poured onto the glass wool. A labpipette with a 100 µl plastic tip attached was used to extract 100 µl of stock solution, the latter having been warmed up over an electric heater. This was done to ensure that the stock solution was a homogeneous system before the extraction of samples. The 100 µl stock solution was poured into the flask. The flask was sealed with the stopper. Pure oxygen was purged through the flask. The flask was immersed in the water-bath or oil bath as the case might be. Samples taken as soon as the flask was immersed in the bath were used as reference. These and the samples taken at subsequent intervals were poured into a clean dry bottle labelled A with a tight-fitting stopper. The sample was dissolved in 15 mls carbon tetrachloride. 25 mls Wij's solution was added and the bottle was sealed with a stopper moistened with potassium iodide to prevent the evaporation of iodine. The bottle A was stored in the dark at 20 - 25°C.

After two hours, 20 mls potassium iodide (10% w/v) solution and 150 mls distilled water were poured into a 500 ml quickfit flask labelled B. The contents of A were emptied into B, care being taken to avoid spillage. Some 20 - 30 cm^3 extract from B were used to rinse bottle A to ensure minimum loss of reagents.

The contents were titrated with standard sodium thiosulphate (0.1N or 0.2N) solution in the presence of starch solution as an indicator. The starch solution (2 - 3 drops) was added when the yellow colour of the iodine had almost disappeared. The solution turned blue on the addition of starch solution. Titration was continued until the blue colouration disappeared. A parallel procedure was carried out for a blank omitting the linoleic acid. The experiments were repeated using the various driers or combinations at the various reaction temperatures earlier mentioned.

Calculation: In Wij's technique, the iodine value can be calculated from the equation

$$1.V = 12.69(T_1 - T_2)N/M$$

where T_1 = required volume of sodium thiosulphate for sample (mls)

T_2 = required volume of sodium thiosulphate for blank (ml)

N = normality of sodium thiosulphate solution

M = mass of the sample (grammes)

12.69 = grammes of iodine required per 100 ml of sodium thiosulphate solution (N/10).

5·7 PEROXIDE VALUE

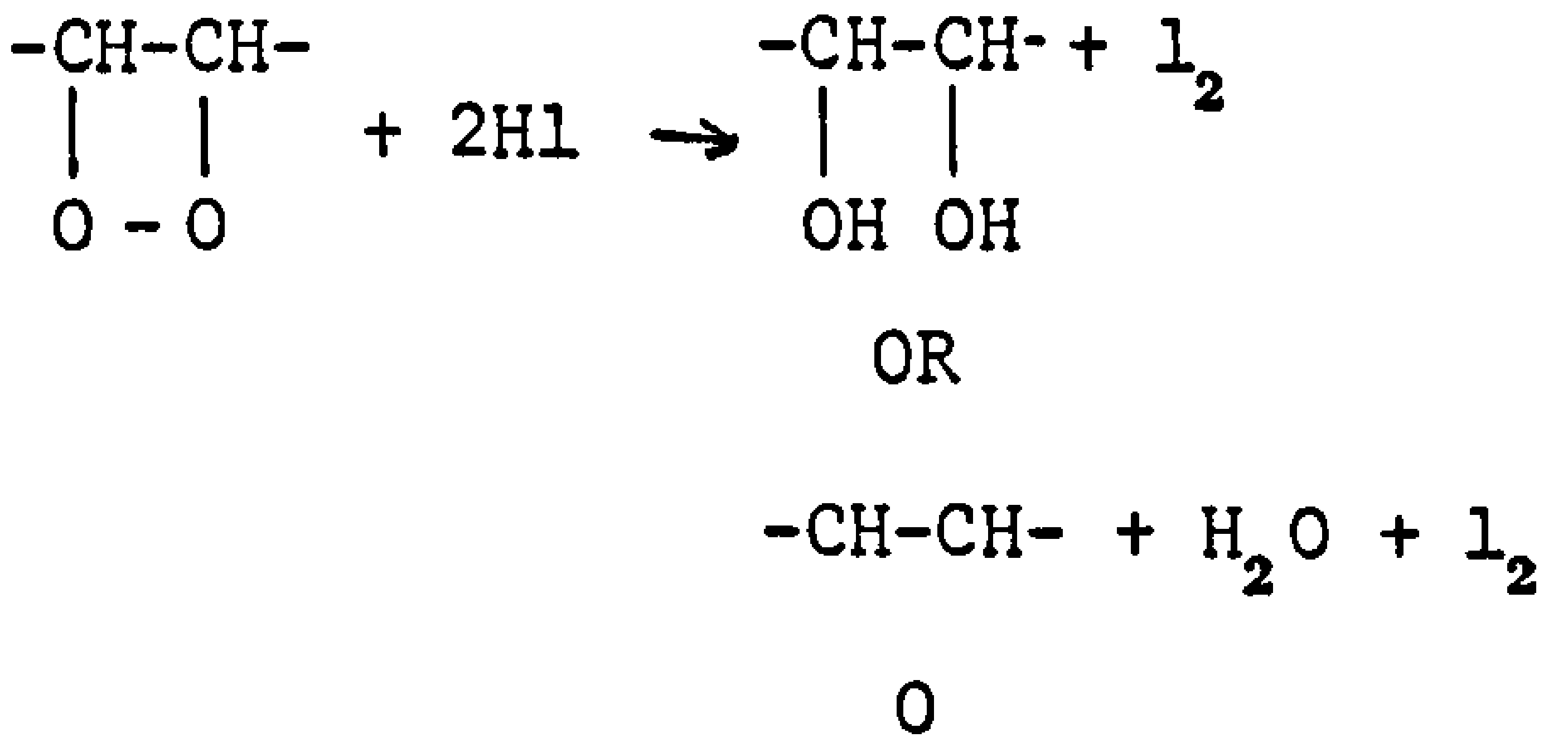
The peroxide value is a measure of deterioration in fats. During the oxidation of fats, the double bonds in the unsaturated systems are attacked. Peroxides are produced which in turn break down to produce secondary oxidation products. The fatty acid at this stage becomes rancid.

Peroxide value can therefore be used to estimate oxidation. However, as the compounds formed are unstable, as oxidation proceeds further, the peroxide value does not give a complete measure of oxidation and if employed in isolation may give misleading conclusions.[230]

DETERMINATION OF PEROXIDE VALUE

The estimation of peroxide content of oils or fats has been categorised into two main groups by various investigators.

(a) One technique involves the liberation of iodine from potassium iodide or iodic acid by oxidation by fatty peroxides.



$$\underset{\text{O - O}}{\text{-CH-CH-}} + 2\text{H1} \rightarrow \underset{\text{OH OH}}{\text{-CH-CH-}} + 1_2$$

$$\text{OR}$$

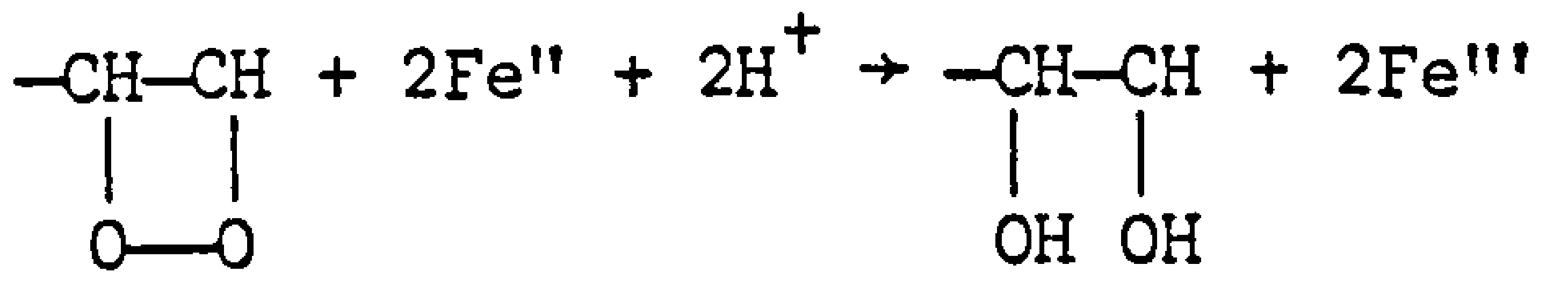
$$\underset{\text{O}}{\text{-CH-CH-}} + H_2O + 1_2$$

1.0

The iodine liberated is titrated with thiosulphate. Several disadvantages are involved even though the various modifications of the technique have found widespread technical application. For example, the technique cannot detect very small amounts of peroxide, and iodine has a tendency to combine with any double bonds present. Problems are therefore involved in the estimation of peroxide content of unsaturated oil or where highly unsaturated fatty acids are present(176). Published techniques differ in their choice for solvent, sample size, temperature and the use of aerobic and anaerobic conditions.

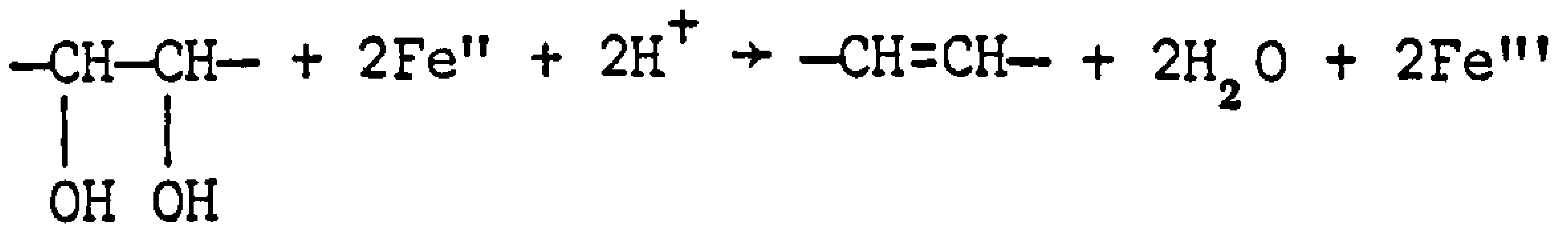
(b) The second technique of peroxide content determination of oils or fats involves the oxidation of ferrous iron, the ferric ion produced being estimated colorimetrically(229),(147) or volumetrically(230).

The destruction of peroxide by ferrous ions could be explained under two possible mechanisms:

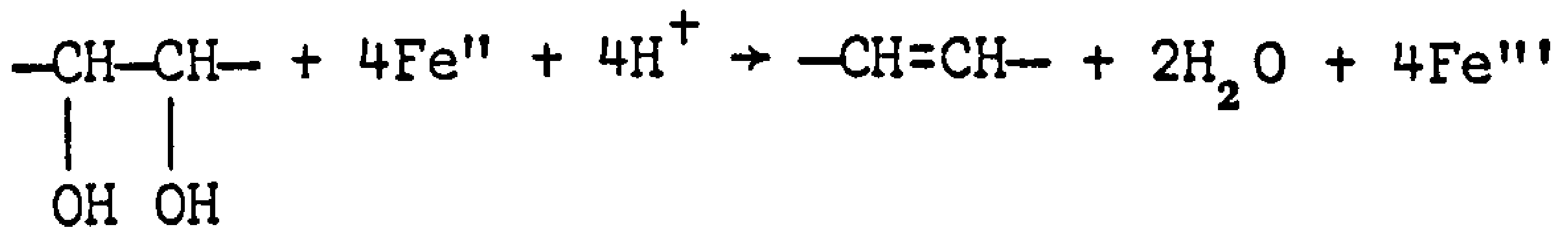
1. 

$$-\underset{|}{\mathrm{CH}}-\underset{|}{\mathrm{CH}}\ (\mathrm{O{-}O}) + 2Fe'' + 2H^+ \rightarrow -\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\mathrm{OH}}{\mathrm{CH}} + 2Fe''' \qquad 1.1$$

then



$$-\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\mathrm{OH}}{\mathrm{CH}}- + 2Fe'' + 2H^+ \rightarrow -CH=CH- + 2H_2O + 2Fe''' \qquad 1.2$$

2. 

$$-\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\mathrm{OH}}{\mathrm{CH}}- + 4Fe'' + 4H^+ \rightarrow -CH=CH- + 2H_2O + 4Fe''' \qquad 1.3$$

Reaction 1.1 would indicate a two electron transfer reaction, comparable with reduction of peroxide by iodide (reaction 1.0).

Other Techniques:

Stannous chloride(90) has been used to determine tert-butyl, cyclohexene and tetralin hydroperoxide in different solvents with variable pH and sample sizes.

Hamm et al.(231) have reported a sensitive quantitative technique for the determination of the peroxide value of fats and oils. Their work was based on the colour reaction of diphenylcarbohydrazide discovered by Hamm.

The use of I.R. spectroscopy for the determination of methyl octadecadienoate hydroperoxides has been reported(232). The —OOH group in the system can be quantitatively estimated even in very small quantities of oxidised oil.

ESTIMATION OF PEROXIDE VALUE IN LINOLEIC ACID BY THE FERRIC THIOLYANATE TECHNIQUE

HILLS TECHNIQUE

Hills technique(233) was used in the determination of peroxide value, although the Lips method(234) could have been used.

The solvent consisted of a mixture of 70 vols of benzene and 30 vols of absolute alcohol. The benzene was redistilled prior to use. The alcohol was refluxed for four hours with bright magnesium ribbon and distilled.

Ferrous Chloride Solution

One gramme of hydrated barium chloride was dissolved in 50 mls of distilled water and added slowly with constant stirring to another solution containing one gramme hydrated ferrous sulphate dissolved in 50 mls water and 4 mls of ION hydrochloric acid. A precipitate of barium sulphate was formed and allowed to settle. The clear top layer of solution was decanted into a bottle. The bottle, dark brown in colour, was wrapped around with a piece of dark cloth to protect the solution from light. The ferrous chloride solution prepared as described above is known to have a stability of approximately one week, hence a new stock was prepared weekly throughout the course of the experiment.

Ammonium Thiosulphate Solution

Ammonium thiosulphate solution was prepared by dissolving 30 g of ammonium thiocyanate in distilled water and diluting to the 100 ml mark in a graduated flask.

CALIBRATION CURVE

The calibration curve was prepared according to the method of Chapman and Mackay(231). The standard solution was made by dissolving a known quantity of hexahydrated ferric chloride (98% purity) in a mixture of benzene-methanol. Different concentrations of this solution were made (0.2 - 3 μgr/ml) in separate volumetric flasks. One drop of ammonium thiocyanate was added to each flask and diluted to 10 ml with benzene-methanol. Their optical densities were measured using a Unican SP600 spectrophotometer at 520 nm.

EXPERIMENTAL PROCEDURE

The design of the apparatus is the same as that used in the determination of iodine value. Approximately 1 - 2 g glass wool was put into the flask and 100 μl or 500 μl of stock solution containing 5% iron was poured onto the glass wool. 10 mls of 9, 12-octadecadienoic acid was pippetted into the flask. The bath was set to the required temperature with the reaction flask in air. This was done to avoid undue heating of the reactants before the complete setting up of the experiment. The flask was lowered into the thermostat and pure oxygen was purged in through one end of the glass. A sample taken at the start of the experiment gave a reading at zero hours.

At subsequent intervals, a Labpippette with 100 μl tip attached was used to extract 100 μl of the sample after stirring to ensure a homogeneous system. The sample was put into a 50 ml volumetric flask, and made up to the mark with benzene-methanol solution. The volumetric flask was shaken vigorously. 1 ml of the solution was extractdd into a 10 ml volumetric flask. One drop of ammonium thiocyanate solution and one drop of ferrous chloride solution were added and the mixture diluted to the 10 ml mark with benzene-methanol solution. The flask was shaken and placed in a 80°C water bath for a minute. It was then cooled to 25°C and the intensity of the colour was measured at 520 nm. In most of the sample prepared, it was necessary to dilute further. This was so because, most solutions were too deeply coloured to be analysed by the spectrophotometer at the given wavelength (520 nm) at this dilution. The extent of dilution is indicated on the Tables for Peroxide Values as

D. A blank was used containing all reagents except linoleic acid. The peroxide value was calculated as milliequivalent of O_2 per kg of linoleic acid as follows:

$$P.V. \;=\; \frac{A.D.X}{C \times 55.84}$$

where A = micrograms of Fe'' in 10 mls of Fe''' in 10 mls of blank solution

X = primary dilution of extract (50 ml)

D = secondary dilution of extract (D)

C = weight of sample (gr)

55.84 = equivalent weight of iron

In all the experiments, the sample weight was assumed constant. This was arrived at after taking samples from the prepared stocks using a labpippette and a 100 µl tip. The weights were totalled. The average weight was determined with a 10% allowance for error. This gave a figure (0.1262 gr) which was used as the sample weight in all cases where weight of sample extracted by the Labpippette was mentioned.

The peroxide value was expressed either as ΔPV where initial peroxide values were very different, or as PV where initial peroxide values were similar.

On the oxygen absorption charts, the symbols employed to indicate the weather conditions were self-devised and the assessment of the weather was non-instrumental but on personal judgement.

The following symbols were used to describe the weather conditions:

*	Bright and sunny
○	Wet, rainy with sunny intervals
○—○	Dry and clear
△	Wet, dull and windy
●	Dull and dry
▼	Dull and wet

M = morning; D = day; E = evening; N = night.

5·8 DIFFICULTIES ENCOUNTERED

The stock solution had to be warmed up in most cases before use to ensure a complete solution.

Another source of error arose from the use of the 100 μl plastic tips for extracting the samples. The plastic tips are very good at room and low temperatures of reaction. At high temperatures, some tips deformed on immersion in the sample and in some cases extracted less than the required 100 μl of sample. In such a case, another plastic tip was employed to extract exactly 100 μl volume of sample.

The main reason for using plastic tips was to avoid the problem associated with extraction and weighing of sample. The technique was quick, reliable and the tendency of the extracted sample to undergo further reaction during weighing was eliminated.

Some of the problems associated with convection stoving techniques (Chapter 4, Section 4.2(i)) are likely to affect the exact rate of reaction during oxygen absorption experiments.

Plate (2-A) A view of the apparatus used in O_2 absorption

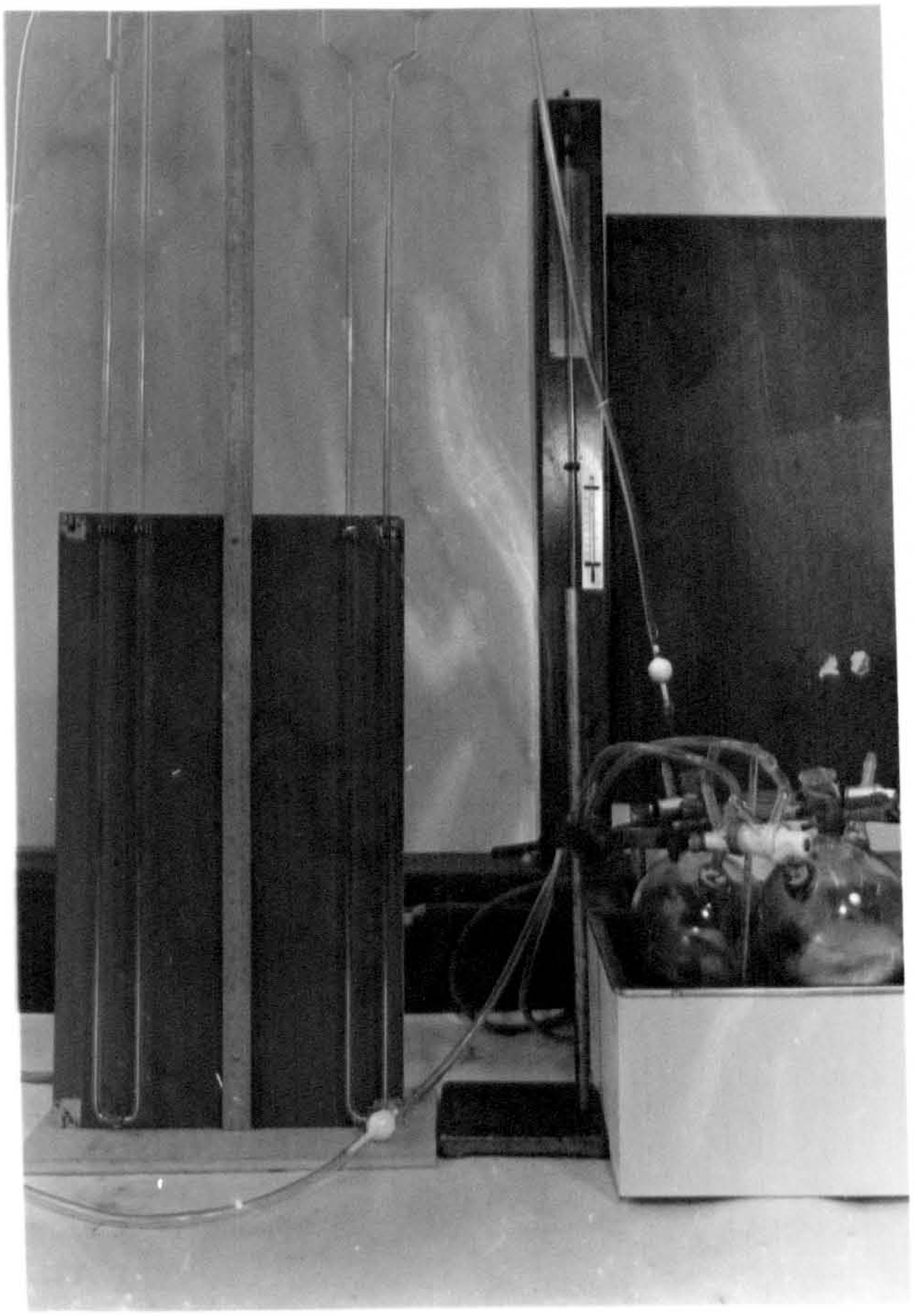


Plate (2-B) Water-bath with lagging to maintain constant temperature

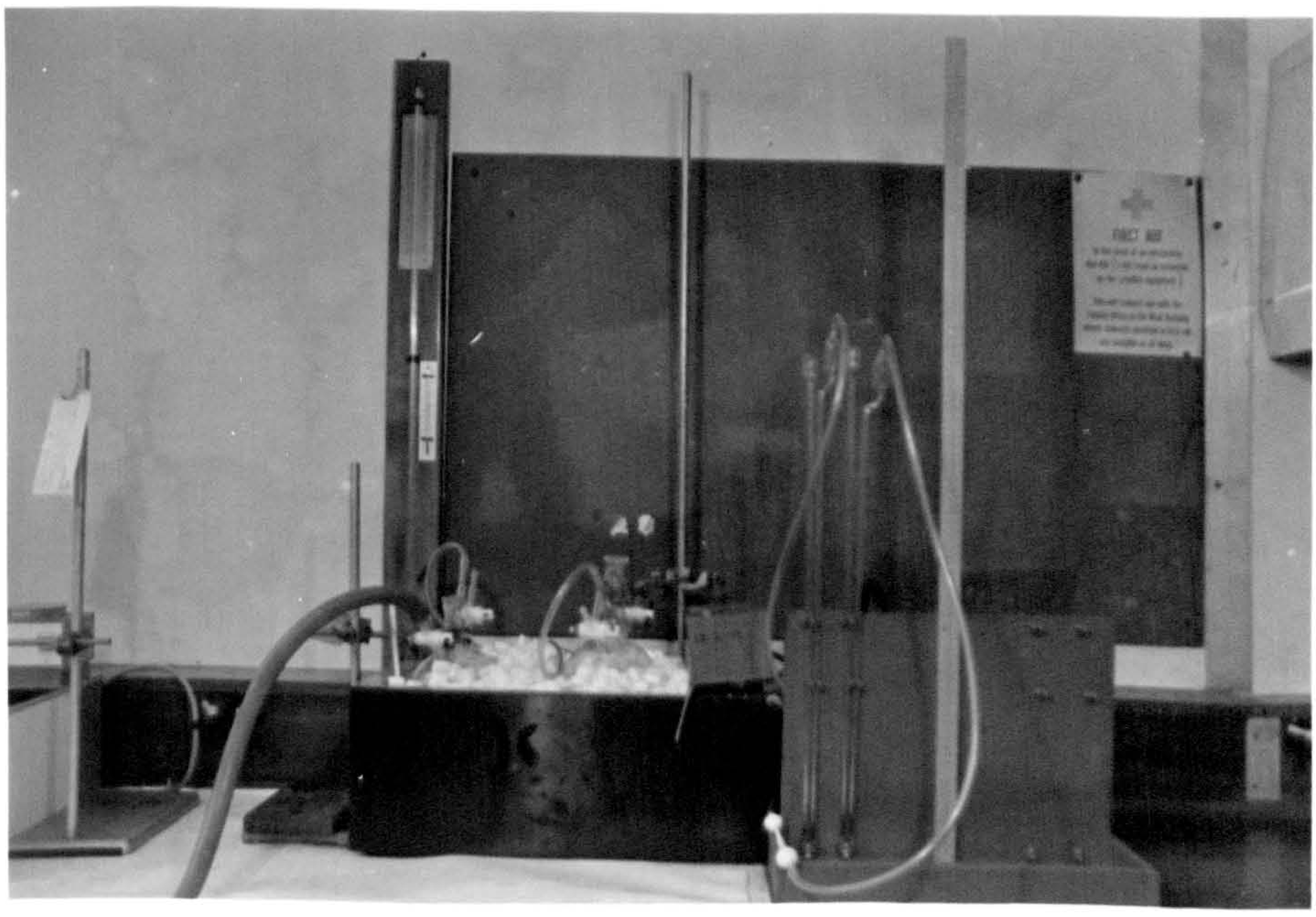
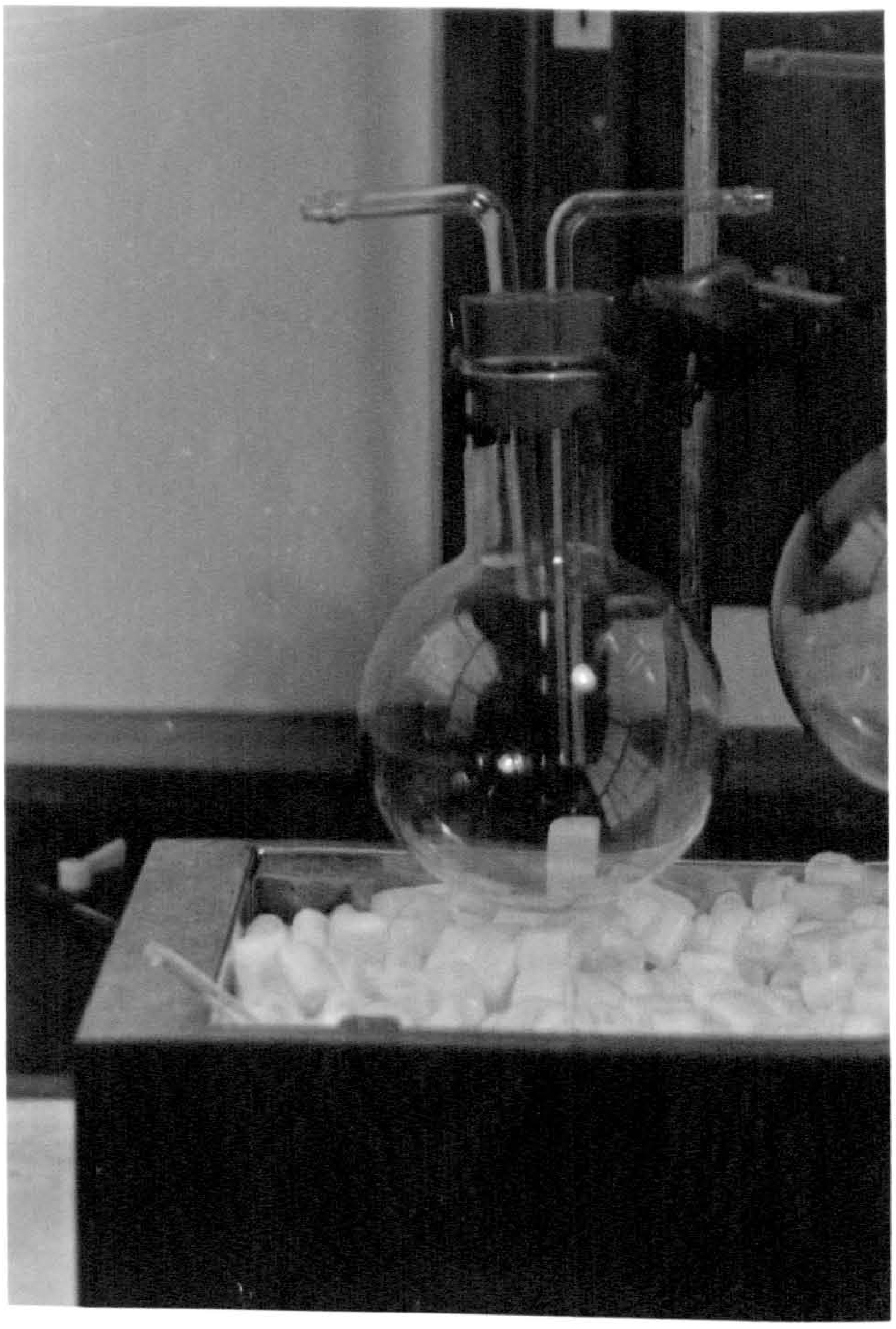


Plate (3-A) Apparatus employed for I.V. and P.V. determination



3-A

Table 1·7

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% Iron on the weight of acid (ferrous octoate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	763	0	O—OM
3	0	763	0	✻D
5.5	0.4	763	0.4	✻D
10	0.7	763	0.7	O—ON
22	0.8	760	3.8	● M
30	1.0	760	4.0	▼N
60	1.2	760	4.2	▼N
90	1.3	760	4.3	O—ON
146	1.3	760	4.3	O—ON

Table 1·8

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% Iron on the weight of acid (lead oleate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	763	0	O—ON
3	0.7	763	0.7	✻D
5.5	0.8	763	0.8	✻D
10	0.9	761	2.9	O—ON
22	0.9	761	2.9	✻M
30	1.0	760	4.0	▼N
60	1.1	760	4.1	▼N
90	1.2	760	4.2	O—ON
146	1.2	761	3.2	O—ON

Table 1·9

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid [ferrous-Trilon A complex (HCl solvent)]

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	759	0	O—ON
3	0	763	4	O—ON
12	0	767	7	*M
36	0	766	6	O—ON
48	0	766	6	O—ON
60	0	762	3	*M
72	0	765	6	*M
96	0	761	3	*M
120	0	763	4	O—ON

Table 2·0

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid [ferrous-EDTA complex (HCl as solvent)]

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	759	0	O—ON
3	0	763	4	O—ON
12	0	767	7	*M
36	0	766	6	O—ON
48	0.1	762	2.9	O—ON
60	0.1	765	4.9	*M
72	0.1	761	1.9	*M
96	0.1	763	5.9	*M
120	0.1	765	5.9	O—ON

Table 2·1

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron, monopivaloylferrocene

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	751	0	*M
1	0	751	0	*M
1.5	0	752	+1	*M
2	0	751	0	*M
3.75	0	750	0	*D
5	0	751	0	*D
15	0	751	0	O—ON
23	0	757	-6	*M
30	0	758	-7	*D

Table 2·2

Rate of O_2 absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron, dipivaloylferrocene

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	751	0	*M
1	0	751	0	*M
1.5	0	752	+1	*M
2	0	751	0	*M
3.75	0	750	-2	*D
5	0	751	0	*D
12	0	751	0	O—ON
15	0	751	0	O—ON
23	0	757	-6	*M
30	0	758	-7	*D

Table 2·3

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid (ferrous dicarboxylic acid)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	750	0	○M
3	0	747	3	✿M
4	0	747	3	✿M
6	0	750	0	○D
12	0	751	1	▼N
24	0	750	0	▼M
36	0	753	3	▼N
40	0	753	3	▼M
60	0	754	4	✿N
72	0	750	0	✿M

Table 2·4

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% nickel on the weight of acid (nickelocene)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	758	0	✿M
1	0	758	0	✿M
2	0	757	1	✿M
3	0	757	1	✿M
4	0	757	1	✿D
8	0	758	0	✿E
12	0	757	1	●N
15	0	757	1	O—ON
18	0	757	1	O—ON

Table 2·5

Oxygen absorption of linoleic acid during autoxidation at 35^0C ± 2^0C in the presence of 0.025 g ferrous octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	737	0	○D
22	1.3	749	-10.7	✻D
34	4.0	752	-11.0	△D
123	14.0	753	-2.0	△D
147	20.0	753	4.0	△D

Table 2·6

Oxygen absorption of linoleic acid during autoxidation at 35^0C ± 2^0C in the presence of 0.02 g ferrous stearate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	749	0	○D
16	0.2	777	-27.8	✻D
20	0.2	775	-25.8	△D
23	0.2	775	-25.8	△D
40	1.5	725	25.8	△D

Table 2·7

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid (ferrocene)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	756	0
10	0	756	0
23	0	754	2
32	0.7	751	5.7
70	1.0	751	6.0
90	1.1	751	6.1
120	1.1	751	6.1

Table 2·8

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% cobalt on the weight of acid (cobalt octoate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	756	0
10	0	756	0
23	0.2	751	5.2
32	0.4	751	5.4
70	0.4	751	5.4
90	0.7	751	5.7
120	0.8	751	5.8

Table 2·9

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid [ferrocene - Trilon A complex (H_2O as solvent)]

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	750	0	O—OD
10	0	752	-2	O—ON
23	0	754	-4	O—OM
73	0.2	754	-3.8	▼D
90	0.4	754	-3.6	✿D
120	0.6	757	-6.4	✿D

Table 3·0

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid (ferrous salicylate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	750	0	✿D
10	0	754	-4	O—ON
23	0.2	754	-3.8	O—OM
73	0.3	754	-3.7	▼D
90	0.6	757	-6.4	✿D
120	1.2	757	-5.8	✿D

Table 3·1

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.523 g cobalt naphthenate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	738	0	O—OE
18	16.1	738	16.1	✿M
21	16.2	738	16.2	✿M
24	20.1	742	16.2	O—OD
43	30.5	742	26.5	O—OD
46	30.5	742	26.5	● N

Table 3·2

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.6 g lead naphthenate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	745	0	✿M
½	0	745	0	✿M
3	12.9	743	14.9	O—OM
5	19.7	742	22.7	O—OD
6	19.9	743	21.9	●D
21	25.7	743	27.7	○M
27	25.7	743	27.7	○N
43	25.7	743	27.7	△M
46	25.7	743	27.7	△D

Table 3·3

Oxygen absorption of linoleic acid during autoxidation at 35°C ± 2°C in the presence of 0.02 g ferrous octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	749	0	○ D
16	4.6	747	6.6	✽D
20	4.6	775	8.6	△D
23	4.7	775	8.7	△D
40	5.5	725	29.5	✽D
42	5.9	728	26.9	△D

Table 3·4

Oxygen absorption of linoleic acid during autoxidation at 60°C in the presence of 0.05% nickel on the weight of acid nickelocene

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	756	0	✽M
1	0	756	0	✽M
3	0	756	0	✽M
6	1	756	1	▼D
9	1	756	1	▼N
12	1.3	757	0.3	○N
15	1.4	756	1.4	○N
18	1.6	757	2.6	●M

Table 3·5

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.042 g ferrous stearate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	748	0	○D
1	1.1	747	2.1	○D
4	7.3	749	6.3	○—○N
8	6.9	750	4.9	△N
10	6.1	751	3.1	○—○N
26	1.7	757	-7.3	●D
28	1.7	757	-7.3	●D

Table 3·6

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.90 g lead linoleate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	748	0	○D
1	0	748	0	○D
4	16.7	748	16.7	○—○N
8	15.1	750	13.7	△N
10	15.2	751	12.2	○—○N
26	9.6	757	0.6	●D
28	9.6	757	0.6	●D

Table 3·7

Oxygen absorption of linoleic acid during autoxidation at 60^0C in the presence of 0.451 g cobalt naphthenate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	745	0	○M
0.5	14.8	745	14.8	○M
3	14.5	743	16.5	▼M
5	14.5	742	17.5	▼M
6	13.5	743	15.5	O—OD
21	14.5	742	17.5	✿M
27	14.5	742	17.5	✿D

Table 3·8

Oxygen absorption of linoleic acid during autoxidation at 60^0C in the presence of 0.5 g cobalt octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	738	0	○M
18	16.1	738	16.1	○M
21	16.2	738	16.2	○M
24	20.2	742	16.2	✿D
43	30.5	742	26.5	✿M
46	22.2	742	18.2	▼M
50	22.3	742	18.3	✿D

Table 3·9

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.0493 g nickel octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	753	0	*M
3	1.5	753	1.5	*M
9	3.6	752	2.6	O—ON
12	4.3	749	8.3	O—ON
36	4.7	750	7.7	●M
48	4.8	745	12.8	*N
60	5.9	750	8.9	*M
72	6.9	751	8.9	O—ON

Table 4·0

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.039 g nickel stearate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	760	0	○M
3	1.4	760	1.4	○M
12	1.6	759	2.6	●N
24	1.9	759	2.9	△M
36	2.9	760	2.9	△N
48	3.9	761	2.9	○M
60	4.0	761	3.0	▼N
72	4.0	761	3.0	△M

Table 4·1

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.6 g lead naphthenate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	745	0	✻M
0.5	0	745	0	✻M
3	11.9	743	13.9	✻M
5	18.7	742	21.7	O—OD
6	18.9	742	21.9	O—OD
21	24.7	743	26.7	● N
27	23.5	744	25.7	● N
45	17.5	738	24.5	✻M

Table 4·2

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.03 g lead stearate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	761	0	✻M
3	0.30	761	0.30	✻M
9	0.90	760	1.90	O—ON
12	1.00	759	3.00	O—ON
24	1.40	758	4.40	○ M
36	1.80	759	3.80	△N
48	2.10	758	5.10	O—OM

Table 4·3

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.60 g lead naphthenate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	745	0	✻M
1/12	0	745	0	✻M
3	12.9	743	14.9	✻M
5	19.7	742	22.7	○—○D
6	19.9	743	21.9	○—○D
21	25.7	745	25.7	△N
27	25.5	745	25.7	△N
40	25.5	745	25.7	✻M

Table 4·4

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.030 g lead stearate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	761	0	○—○M
3	0.3	761	0.30	○—○M
9	0.9	761	0.90	●D
12	1.0	759	3.00	○N
24	1.4	758	4.40	○M
36	1.8	759	3.80	○—○N
48	2.1	758	5.10	○M
60	2.3	760	3.30	△N
72	2.4	760	3.40	○M

Table 4·5

Rate of O_2 absorption of linoleic acid during autoxidation at 60^0C in the presence of 0.05% iron, monopivaloylferrocene

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	758	0	O—OD
2	0	760	-2	O—OE
3	0	759	-1	O—ON
5	1.9	759	0.9	O—ON
18	8.2	757	9.2	*M
19	8.8	757	9.8	*M
21	9.7	758	9.7	*M
23	10.2	758	10.2	O—OD
25	11.0	758	11.0	O—OE
26	11.2	758	11.2	O—OE

Table 4·6

Rate of O_2 absorption of linoleic acid during autoxidation at 60^0C in the presence of 0.05% iron, dipivaloylferrocene

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	757	0	*D
1	1	758	0	*D
3	1.3	758	0.3	*D
4	4.0	758	3.0	O—OE
10	12.9	757	12.9	O—ON
15	13.5	758	12.9	O—ON
21	13.5	758	12.9	*M
27	13.5	758	12.9	*D
30	13.5	758	12.9	*E

Table 4·7

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.05% iron on the weight of acid [ferrous-Trilon A complex (HCl as solvent)]

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	757	0
0.5	0	757	0
1	0	757	0
2	0	757	0
4	0	756	-1
6	0	756	-1
8	0	757	0
12	0	757	0
20	0	756	-1
40	0	757	0

Table 4·8

Oxygen absorption of linoleic acid during autoxidation at 60 C in the presence of 0.05% iron on the weight of acid [ferrous EDTA complex (HCl as solvent)]

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	757	0
0.5	0	757	0
1	0.20	757	0.2
2	2.10	756	3.1
4	4.80	757	4.8
6	4.90	756	5.9
8	5.00	757	5.0
12	5.20	757	5.2
20	5.30	757	5.3
40	5.50	757	5.5

Table 4·9

Oxygen absorption of linoleic acid during autoxidation at 60^0C in the presence of 0.05% **lead** on the weight of **acid** (lead oleate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	759	0
1	1.80	759	1.80
3	3.20	759	3.20
6	4.80	760	3.80
12	5.20	761	3.20
24	6.80	758	7.80
36	7.20	759	7.20
48	8.20	759	8.20
50	8.20	759	8.20
60	8.30	759	8.30

Table 5·0

Oxygen absorption of linoleic acid during autoxidation at 60^0C in the presence of 0.05% **cobalt** on the weight of **acid** (cobalt octoate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	746	0
½	2.40	746	2.40
1	6.00	746	6.00
3	7.40	747	6.40
12	10.60	745	11.60
24	11.00	745	12.00
36	11.80	746	11.80
48	12.00	746	12.00
60	12.00	746	12.00
70	12.00	746	12.00

Table 5·1

Oxygen absorption of linoleic acid during autoxidation at 60^0C in the presence of 0.05% **iron** on the weight of **acid** (ferrous salicylate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	731	0
3	0	730	-1
4	0	730	-1
12	2.00	730	-3
24	5.80	733	3.80
36	6.20	732	5.20
48	6.80	732	5.80
60	8.00	731	8.00
72	8.60	731	8.60

Table 5·2

Oxygen absorption of linoleic acid during autoxidation at 60^0C in the presence of 0.05% **lead** on the weight of **acid** (lead octoate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	746	0
3	1.20	747	0.20
4	1.40	746	1.40
12	2.30	745	3.30
24	3.40	745	4.40
36	4.40	745	5.40
48	4.80	746	4.80
60	5.10	746	5.10
72	5.20	745	6.20

Table 5·3

Oxygen absorption of linoleic acid during autoxidation at 60°C in the presence of 0.05% cobalt on the weight of acid cobalt naphthenate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	731	0
3	1.60	731	1.60
4	2.00	730	3.00
12	8.20	730	9.20
24	10.20	731	10.20
36	12.80	733	10.80
48	12.80	732	11.80
60	13.00	732	12.00
72	13.00	732	12.00

Table 5·4

Oxygen absorption of linoleic acid during autoxidation at 60°C in the presence of 0.05% iron on the weight of acid (ferrocene dicyclopentadienyl)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	732	0
2/3	6.80	732	6.80
2	8.20	732	8.20
6	8.80	732	8.80
12	10.00	731	11.00
24	11.20	732	11.20
36	11.80	732	11.80
48	12.20	732	12.20
60	12.20	732	12.20
72	12.20	732	12.20

Table 5·5

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.05% nickel on the weight of acid nickel octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	750	0
3	3.00	747	6.00
4.5	3.30	747	6.30
12	4.90	750	4.90
24	7.40	751	6.40
36	10.20	752	8.20
46	10.80	750	10.80
60	10.80	750	10.80
72	10.80	750	10.80

Table 5·6

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.05% iron on the weight of acid ferrocene dicarboxylic acid

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	750	0
3	0	747	3
4.5	0	747	3
12	0	750	0
24	0	751	-1.0
36	0.1	752	-1.9
46	0.2	750	0.2
60	0.3	750	0.3

Table 5·7

Oxygen absorption of linoleic acid during autoxidation at 60^0C in the absence of driers

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	765	0	○M
3	1.4	765	1.4	○M
5	3.6	765	3.6	○D
23.5	10.3	765	10.3	△M
27	10.1	765	10.1	●M
31	13.1	765	13.1	▼D
35	15.4	765	15.4	△N

Table 5·8

Oxygen absorption of linoleic acid during autoxidation at 80^0C in the absence of driers (no oxygen was purged into the vessel)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	765	0	○M
1	0	765	0	○M
3	0	765	0	○D
21	0	762	3	△M
24	0	763	2	△M
30	0	761	4	▼N
45	0	757	8	●M

Table 5·9

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.042 g ferrous stearate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	748	0	OD
4	7.3	748	7.3	ΔN
8	9.0	750	7.0	ΔN
10	11.1	751	8.1	ΔN
26	18.1	757	9.1	*M
28	18.1	757	9.1	*D

Table 6·0

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.90 g lead linoleate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	748	0	OD
4	16.7	748	16.7	ΔN
8	18.7	750	16.7	ΔN
10	19.7	751	16.7	ΔN
26	25.7	757	16.7	*M
28	25.7	757	16.7	*M

Table 6·1

Oxygen absorption of linoleic acid during autoxidation at 60°C in the presence of 0.5 g cobalt naphthenate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	745	0	*M
1/12	14.8	745	14.8	*M
3	14.5	743	16.5	*M
5	14.5	752	7.5	O—OD
21	13.5	743	15.5	O—ON
27	12.5	744	13.5	*M

Table 6·2

Oxygen absorption of linoleic acid during autoxidation at 60°C in the presence of 0.041 g ferrocene dicyclopentadinyl

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	755	0	O—O
16	5.0	753	7.0	*M
23	6.1	745	16.1	O—ON
43	2.0	743	14.0	O—OD
64	4.1	739	20.1	O—OD

Table 6·3

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.0411 g cobalt octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	755	0	○—○N
16	1.3	753	3.3	✻M
23	1.5	745	11.5	○N
43	0.5	734	21.5	△D
64	1.0	739	17.0	○M

Table 6·4

Oxygen absorption of linoleic acid during autoxidation at 60^{0}C in the presence of 0.048 g dicyclopentadinyl iron

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	763	0	○D
2	0	763	0	○N
20	5.9	749	19.9	✻D
25	5.5	740	28.5	○—○
42	3.7	734	32.7	✻M
50	3.5	738	28.5	○—○N

Table 6·5

Oxygen absorption of linoleic acid during autoxidation at 80°C in the presence of 0.025 g ferrous octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	765	0	● M
1.5	11.3	765	11.3	● M
4	15.4	767	13.4	● D
18	17.2	765	17.2	△ N
28	19.0	763	21.0	○ M
52	19.2	763	21.2	* M

Table 6·6

Oxygen absorption of linoleic acid during autoxidation at 80°C in the presence of 0.014 g ferrocene dicarboxylic acid

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	765	0	● M
1.5	0	765	0	● M
4	0	767	2	● D
18	13.8	765	13.8	△ N
28	15.2	763	17.2	● M
52	15.8	763	17.8	○ M
60	15.8	763	17.8	● M

Table 6·7

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.05% cobalt on the weight of acid (cobalt oleate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	753	0	*D
1/10	7.0	753	7.0	*D
1/4	10.3	753	10.3	*D
1/2	12.0	753	12.0	*D
1	14.0	751	16.0	*D
3	16.0	752	17.0	*D
6	19.4	751	21.4	*D
12	20.2	753	20.2	O—ON
24	20.8	753	20.8	*M
36	*			

* overflow of mercury

Table 6·8

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.05% iron on the weight of acid (ferrous octoate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	753	0	*D
1/10	3.6	753	3.6	*D
1/4	5.0	753	5.0	*D
1/2	7.4	753	7.4	*D
1	9.0	751	11.0	*D
3	12.0	752	13.0	*D
6	12.2	752	13.2	*D
12	13.6	753	13.6	O—ON
24	14.0	753	14.0	*D
36	14.3	752	15.3	*D

Table 6·9

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.025 g ferrous octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	765	0	●M
1.5	12.3	765	12.3	●M
4	16.4	767	14.4	●D
18	18.2	765	18.2	●N
28	18.2	763	20.2	●N
52	18.2	763	20.2	*N
60	18.2	763	20.2	*D

Table 7·0

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.014 g ferrocene dicarboxylic acid

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	765	0	●M
$1\frac{1}{2}$	0	765	0	●M
4	0	767	2	●D
18	13.8	765	13.8	●N
28	15.2	763	17.2	●N
52	16.0	763	18.0	*M
60	16.0	763	18.0	*D

Table 7·1

Oxygen absorption of linoleic acid during autoxidation at 80°C in the presence of 0.05% lead on the weight of acid lead oleate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	759	0	*D
2/3	2.2	759	2.2	*D
3	5.6	760	4.6	*D
6	7.0	761	5.0	O—ON
12	8.0	760	7.0	*D
24	8.6	761	6.6	*D
36	9.0	762	6.0	O—O
48	9.4	761	7.4	*D
60	10.3	760	9.3	*D
72	10.8	760	9.8	*D

Table 7·2

Oxygen absorption of linoleic acid during autoxidation at 80°C in the presence of 0.05% nickel on the weight of acid nickel octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	750	0	OD
1	3.2	750	3.2	OD
3	7.8	744	13.8	Δ
4½	9.0	747	12.0	Δ
6	10.8	748	12.8	O—ON
24	13.6	751	12.6	*D
36	14.2	750	14.2	O—ON
48	*			

* overflow of mercury in manomer

Table 7·3

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.05% iron on the weight of acid, ferrous salicylate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	731	0	*D
1	5.6	731	5.6	*D
3	11.0	730	12.0	*D
5	12.6	731	12.6	O—ON
12	14.2	732	13.2	O—ON
24	16.3	731	16.3	*M
36	18.8	731	18.8	●N
48	20.6	733	18.6	△M
60	21.3	731	21.3	△N
72	21.3	731	21.3	▼M

Table 7·4

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.05% iron on the weight of acid (ferrocene dicarboxylic acid).

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	731	0	*D
1	4	731	4	*D
3	10.0	730	11.0	*D
5	11.2	731	11.2	O—ON
12	12.6	730	13.6	O—ON
24	15.7	731	15.7	*M
36	18.0	731	18.0	●N
48	20.0	733	18.0	△M
60	20.0	733	18.0	△N
72	20.0	733	18.0	▼M

Table 7·5

Oxygen absorption of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid [ferrous-trilon A complex (H_2O as solvent)]

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	732	0	✿D
2/3	3.0	732	3.0	✿D
2	6.0	731	7.0	✿D
5	7.6	730	9.6	▼D
12	8.6	731	9.6	▼N
24	9.3	731	10.3	▼M
36	10.4	732	10.4	✿M
48	10.8	732	10.8	✿M
60	11.2	732	11.2	✿M
72	11.6	732	11.6	✿M

Table 7·6

Oxygen absorption of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid (bicyclopentadinyl iron)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	732	0	✿D
2/3	6	732	6	✿D
2	9	731	10.0	✿D
5	9.3	730	11.3	▼D
12	10.0	731	11.0	▼N
24	11.4	731	12.4	▼M
35	11.8	732	11.8	✿M
48	12.2	733	11.2	✿M
72	13.1	732	13.1	✿M

Table 7·7

Oxygen absorption of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, lead oleate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	759	0	*D
2/3	3.2	759	3.2	*D
3	6.1	759	6.1	*D
6	7.1	761	5.1	O—ON
28	7.5	761	5.5	O—ON
48	7.8	761	5.8	*D

Table 7·8

Oxygen absorption of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid nickel octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	750	0	ΔD
1	3.2	750	3.2	ΔD
3	8.0	744	14.0	ΔD
4½	9.4	747	12.4	ΔD
6	11.3	748	13.3	*D
21	13.4	751	12.4	*M
36	14.2	750	14.2	*M
40	overflow			

Table 7·9

Oxygen absorption of linoleic acid during autoxidation at 120^{0}C in the presence of 0.05% iron on the weight of acid cobalt oleate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	753	0	*D
1/10	7.8	753	7.8	*D
1/4	10.7	853	10.7	*D
1/2	12.0	753	12.0	*D
1	16.0	851	18.0	*D
3	18.0	752	19.0	*D
6	20.0	751	22.0	O—ON
12	21.4	752	22.4	O—OM
36	21.8	753	21.8	O—OM
46	22.4	753	22.4	O—OM

Table 8·0

Oxygen abosrption of linoleic acid during autoxidation at 120^{0}C in the presence of 0.05% iron on the weight of ferrous octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	753	0	*D
1/10	4.2	753	4.2	*D
1/4	6.3	753	6.3	*D
1/2	8.2	853	8.2	*D
3	12.1	753	12.1	*D
6	12.6	751	14.6	O—ON
12	14.2	752	15.2	O—OM
36	16.2	755	14.2	*M
46	16.8	753	16.8	*M

Table 8·1

Oxygen abosrption of linoleic acid during autoxidation at 120^{0}C in the presence of 0.05% iron on the weight of acid Fe/Trilon A (HCl as solvent)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	757	0	*D
½	3.6	757	3.6	*D
1	10.2	754	13.2	*D
2	13.5	756	14.5	*D
4	16.0	757	16.0	O—ON
6	16.7	756	17.0	O—ON
8	16.9	757	16.9	*M
12	17.1	757	17.1	O—OD
20	19.6	756	20.1	O—ON
24	20.0	757	20.0	O—ON

Table 8·2

Oxygen abosrption of linoleic acid during autoxidation at 120^{0}C in the presence of 0.05% iron on the weight of acid Fe/EDTA complex (HCl as solvent)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	757	0	*D
½	2.6	757	2.6	*D
1	6.0	757	6.0	*D
2	10.9	756	11.9	O—ON
4	114.	757	11.4	O—ON
6	15.3	756	16.3	O—ON
8	15.6	756	16.6	O—ON
12	15.9	757	15.9	*M
20	16.4	756	17.4	O—ON
24	18.8	757	18.8	O—ON

Table 8·3

Oxygen absorption of linoleic acid during autoxidation at 120^{0}C in the presence of 0.05% iron on the weight of acid, ferrous salicylate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	731	0	ΔM
1	7.7	730	8.7	O—OD
3	15.0	730	16.0	O—OD
4	16.7	730	17.7	ΔD
5	19.7	733	17.7	ΔD
21	20.0	731	20.0	*M
36	21.3	731	21.3	*D
46	21.3	731	21.3	*M
60	21.3	731	21.3	*N

Table 8·4

Oxygen absorption of linoleic acid during autoxidation at 120^{0}C in the presence of 0.05% iron on the weight of acid, ferrocene dicarboxylic acid

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	731	0	ΔM
1	4.5	730	5.5	O—OD
3	11.7	730	12.7	O—OD
5	16.7	733	14.7	ΔD
21	19.6	731	19.6	ΔD
36	20.2	731	20.2	*M
48	20.8	731	20.8	●N
60	21.2	731	21.2	*M

Table 8·7

Oxygen absorption of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, ferrous - Trilon A complex

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	732	0	△M
2/3	4.3	732	4.3	△M
2	7.5	731	8.5	●D
5	8.2	731	9.2	●D
10	9.4	731	10.4	●D
12	9.6	731	10.6	● N
23	9.8	731	10.8	*M
30	11.2	732	11.2	△M
36	11.6	733	10.6	△M
40	11.8	732	11.8	*M
46	12.0	732	12.0	*D
54	12.0	732	12.0	*D

Table 8·8

Oxygen absorption of linoleic acid during autoxidation at 120°C in the presence of ferrocene (0·05% iron)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	732	0	△M
2/3	7.9	732	7.9	△M
2	9.1	731	10.1	●D
5	9.3	730	11.3	●D
10	10.3	731	11.3	●N
12	10.6	731	11.6	●N
23	11.4	732	11.4	*M
30	11.8	732	11.8	*D
36	12.1	733	11.1	△D
40	12.3	732	12.3	△D
46	12.3	732	12.3	△D
52	12.3	732	12.3	O—ON

Table 8·9

Oxygen absorption of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid , lead octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	746	0	O M
½	2.3	746	2.3	O M
1	6.0	746	6.0	O M
3	6.9	745	7.9	O—O D
5	8.6	745	9.6	O—O D
12	9.2	743	12.2	● N
24	9.9	744	11.9	* M
36	10.0	745	11.0	O—O N
48	10.1	745	11.1	O—O M
60	10.3	746	10.3	O N
72	10.3	745	11.3	Δ M

Table 9·0

Oxygen absorption of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid cobalt octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	746	0	O M
½	2.7	746	2.7	O M
1	7.2	746	7.2	O M
3	7.8	745	8.8	O—O D
5	10.4	745	11.4	O—O D
12	10.8	743	13.8	● N
24	11.2	744	13.2	* M
36	11.8	745	12.8	O—O N
48	12.0	745	13.0	O—O M
60	12.8	746	12.8	O N
72	13.2	745	14.2	Δ M

Table 9·1

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.0486 g cobalt octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	758	0	*M
3	2	760	0	*M
9	4.5	760	2.5	*D
12	4.8	761	1.8	O—ON
24	6.0	761	3.0	O—OM
36	6.4	760	4.4	*D
48	6.8	759	5.8	O—OM
60	6.9	759	5.9	*M
72	7.2	759	6.2	● M
84	7.2	759	6.2	● M

Table 9·2

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.05% nickelocene

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	758	0	● M
$\frac{1}{2}$	2.2	757	3.2	● M
1	4.4	757	5.2	○ M
4	7.7	757	8.7	*D
5	7.9	757	8.9	O—OD
12	8.0	757	9.0	O—ON
18	9.4	757	10.4	● N
21	10.1	757	11.1	O—OM

Table 9·2·1

Oxygen absorption of 9, 12-octadecadienoic acid during autoxidation at 120°C in the presence of equal weights (0.05%) iron on the weight of acid, mono- and dipivaloylferrocenes.

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	738	0	▼ D
0.333	4.9	740	6.9	▼ D
0.500	7.6	740	9.6	▼ D
1.000	12.6	740	14.6	▼ D
1.333	16.0	740	18.0	▼ D
2.000	19.2	741	22.2	▼ N
2.500	20.4	741	23.6	▼ N

Table 9·2·2

Oxygen absorption of 9, 12-octadecadienoic acid during autoxidation in the presence of equal weights (0.05%) iron on the weight of acid, mono- and dipivaloylferrocenes at 80°C.

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	738	0	▼ D
0.33	0	740	2	▼ D
1.00	1.2	740	3.2	▼ D
1.33	2.0	740	4.0	▼ D
2.00	4.5	741	7.5	○—○ D
2.50	5.5	744	11.5	○—○ E
4.00	6.0	744	12.0	○—○ N
5.00	6.2	746	14.2	○—○ N
7.00	6.5	746	14.5	○—○ N
8.00	6.7	748	16.7	▼ N

Table 9·3

Oxygen absorption of linoleic acid during autoxidation at 80^0C in the presence of 0.05% iron on the weight of acid, ferrous - Trilon A complex (HCl as solvent)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	757	0	*D
½	3.4	757	3.4	*D
1	10.0	754	13.0	*D
2	13.2	756	14.2	*D
4	16.0	757	16.0	O—ON
6	16.3	756	17.3	O—ON
12	16.8	757	16.8	*M
24	18.4	757	18.4	*M
36	19.0	756	20.0	*M
48	20.6	756	21.6	*D
60	*			

* overflow of mercury

Table 9·4

Oxygen absorption of linoleic acid during autoxidation at 80^0C in the presence of 0.05% iron on the weight of acid, ferrous - ethylenediamine-tetracetic acid complex (HCl as solvent)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	757	0	*D
½	2.6	757	2.6	*D
1	6.0	757	6.0	*D
4	11.4	757	11.4	O—ON
12	15.8	756	16.8	*M
24	17.8	757	17.8	*D
36	18.8	756	19.8	*D
48	20.2	756	21.2	*D
60	*			

* overflow of mercury

Table 9·5

Rate of O_2 absorption of linoleic acid during autoxidation at 80^0C in the presence of 0.05% monopivaloylferrocene on wt. of acid·

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	757	0	*M
1	1.6	758	2.6	*M
3	7.4	758	8.4	*M
4	7.6	758	8.6	*D
10	16.0	757	16.0	O—ON
15	17.5	757	17.5	O—ON
21	18.2	758	19.2	*M
27	19.2	757	19.2	*D
30	19.2	757	19.2	*D

Table 9·6

Rate of O_2 absorption of linoleic acid during autoxidation at 80^0C in the presence of 0.05% dipivaloylferrocene on wt. of acid.

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	758	0	*D
2	2.6	760	4.6	*D
3	4.6	759	5.6	*D
5	9.2	759	10.2	O—ON
18	20.9	757	19.9	*M
19	21.4	757	20.4	*M
21	22.3	758	22.3	*M
23	23.3	758	23.3	*D
25	22.6	758	22.6	*D
26	22.9	758	22.9	*E
30	23.9	757	22.9	*E

Table 9·7

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.03 g ferrous stearate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	760	0	✽M
3	1.2	760	1.2	✽M
9	3.6	761	2.6	○—○D
12	4.3	761	3.3	○—○N
24	4.6	759	5.6	✽M
46	4.8	759	5.8	○—○N
60	5.9	760	5.9	○M
72	5.9	760	5.9	●N
84	5.8	760	5.8	○M

Table 9·8

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.0486 g cobalt octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	758	0	✽M
3	2.1	760	4.1	✽M
9	4.5	760	6.5	○—○D
12	4.8	761	7.8	○—○N
24	6.0	761	9.0	✽M
36	6.4	760	8.4	○—○N
48	6.8	759	7.8	○M
60	6.9	760	8.9	●N
72	7.2	760	9.2	○M
84	7.2	760	9.2	●N

Table 9·9

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.51 g cobalt naphthenate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	745	0	✲M
$\frac{1}{2}$	14.8	745	14.8	✲M
3	14.8	743	16.8	✲M
5	14.9	743	16.9	○—○D
21	15.2	744	16.2	● M
27	15.2	744	16.2	●D
30	15.2	743	17.2	○ N
36	15.4	743	17.4	○N
48	15.4	743	17.4	○M

Table 1·1·1

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.50 g cobalt octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	738	0	✲M
18	16.1	738	16.1	○—○N
21	16.1	738	16.1	○—○N
24	20.1	742	16.1	○ M
43	30.5	742	25.5	○ M
46	30.5	742	25.5	○—○D
60	30.5	742	25.5	● N

Table 1.1.2

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.020 g ferrous salicylate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	761	0	✽M
3	0	761	0	✽M
9	0	760	1	○—○N
12	2.6	759	4.6	○—○N
24	3.0	759	5.0	✽M
36	6.2	760	5.2	○—○N
48	6.8	760	5.8	✽M
60	8.2	761	8.2	△N

Table 1.1.3

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.0315 g ferrous octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	760	0	✽M
3	1	760	1	✽M
12	2.6	760	2.6	○—○N
36	3.8	758	5.8	○—○N
48	4.2	758	2.2	△ N
60	4.6	758	2.6	○ M
72	4.8	758	2.8	● N
84	5.1	759	4.1	△ N

Table 1·1·4

Oxygen absorption of linoleic acid during autoxidation at 80^0C in the presence of 0.0493 g nickel octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	753	0	✿M
3	1.5	753	1.5	✿M
12	3.6	752	4.6	○—○N
36	4.3	749	7.3	✿M
48	4.8	749	7.8	●N
60	5.1	750	8.1	△M
72	6.1	751	8.1	○N

Table 1·1·5

Oxygen absorption of linoleic acid during autoxidation at 80^0C in the presence of 0.0613 g cobalt stearate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	761	0	✿M
3	3.1	761	3.1	✿M
12	3.6	764	6.6	○—○N
36	3.9	764	6.9	○—○N
48	4.2	761	4.2	△N
50	4.3	765	0.3	△M
72	4.3	764	1.3	●N
84	4.8	764	1.8	○N
96	4.8	764	1.8	○M

Table 1·1·6

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid (lead oleate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	759	0	O—ON
3	0.9	763	-3.1	O—ON
22	4.3	767	-3.7	O—OM
44	5.3	766	-1.7	O—OD
90	5.6	762	2.6	✻D
140	5.7	761	3.7	✻D
180	5.7	761	3.7	✻D

Table 1·1·7

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid (lead naphthenate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	763	0	✻D
3	0	763	0	✻D
18	0.2	757	6.2	✻M
20	0.3	757	6.3	O—ON
44	2.3	759	6.3	● D
60	3.0	760	6.0	O—OM
90	4.1	761	6.1	✻D
140	5.2	762	6.2	✻D
180	5.2	762	6.2	O—OD

Table 1·1·8

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid (nickel octoate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	730	0	✲M
3	0	730	0	✲D
4	0.2	733	-2.8	✲D
21	0.8	729	1.8	○M
36	1.1	728	3.1	○D
46	1.2	733	0.2	○—○D
60	1.4	732	-0.6	○—○M

Table 1·1·9

Oxygen absorption of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid (cobalt oleate).

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	731	0	✲M
2	0	730	1	✲D
3	0	730	1	✲D
4	0.3	733	-1.7	○D
21	0.9	731	0.9	○M
36	1.2	730	2.2	○—○N
46	1.4	733	0.6	○—○M
60	1.6	732	0.6	○—○M

Table 1·2·1

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.02 g ferrous salicylate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	761	0	△M
3	0	761	0	△M
9	0	760	1	○D
12	2.6	759	4.6	○N
24	3.0	759	5.0	○—○M
36	6.2	760	7.2	△N
48	6.8	760	7.8	●M

Table 1·2·2

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.0315 g ferrous octoate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	760	0	△M
3	1	760	1	△M
12	2.6	760	2.6	●N
36	3.8	758	5.8	●M
48	4.2	759	5.2	○N
60	4.6	759	5.6	○—○M
72	4.8	758	6.8	○—○N
84	5.1	759	6.1	△M

Table 1·2·3

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.0613 g cobalt stearate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	761	0	✻M
3	3.1	764	0.1	O—OD
12	3.6	764	0.6	O—ON
36	3.9	764	0.9	●N
48	4.2	761	4.2	✻M
60	4.3	765	8.3	○N
72	4.3	765	8.3	△M

Table 1·2·4

Oxygen absorption of linoleic acid during autoxidation at 80^{0}C in the presence of 0.03 g ferrous stearate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	760	0	✻M
3	1.2	760	1.2	✻M
9	3.6	761	2.6	✻E
12	4.3	761	3.3	O—ON
24	4.6	759	5.6	✻M
48	4.6	758	6.6	O—ON
60	4.6	758	6.6	✻M
72	4.6	758	6.6	●N

Table 1·2·5

Oxygen absorption of linoleic acid during autoxidation at 120^0C in the presence of 0.05% iron on the weight of acid (ferrocene).

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	756	0	● D
1/5	1	756	1	● D
1/2	1.1	756	1.1	● D
2	12.4	756	12.4	△ D
4	*			

* overflow of mercury

Table 1·2·6

Oxygen absorption of linoleic acid during autoxidation at 120^0C in the presence of 0.05% iron on the weight of acid (cobalt octoate).

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	756	0	● D
1/5	4.3	756	4.3	● D
1/2	10.1	756	10.1	● D
2	*			

* overflow of mercury

Table 1·2·7

Oxygen absorption of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, dipivaloylferrocene

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	751	0
1.00	4.2	751	4.2
1.50	9.7	752	9.7
2.00	11.5	752	10.5
3.75	15.3	750	16.3
5.00	15.3	751	15.3
23.00	15.3	750	16.3

Table 1·2·8

Oxygen absorption of linoleic acid during autoxidation at 60°C in the presence of equal proportions (0.05%) iron on the weight of acid (mono- and dipivaloylferrocene)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	765	0
3	1.6	765	1.6
5	2.0	765	2.0
23.5	6.0	765	6.0
27.0	6.0	765	6.0
31.0	6.0	765	6.0
35.0	6.0	765	6.0

Table 1·2·9

Oxygen absorption of linoleic acid during autoxidation at 120°C in the presence of equal amounts of iron (0.05%) on the weight of acid (dipavaloylferrocene (No O_2 was purged into flask))

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	765	0
1	0	765	0
3	0	765	0
21	0	762	3
30	0	761	4
45	0	757	8

Table 1·3·0

Oxygen absorption of linoleic acid during autoxidation at 120°C in the presence of 0.05% metal on the weight of acid, nickelocene

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	750	0
$\frac{1}{4}$	3.4	750	3.4
$\frac{1}{2}$	5.7	750	5.7
3	5.9	750	5.9
5	8.2	750	8.2
12	10.3	751	9.3
18	12.4	750	12.4
21	14.0	750	14.0

Table 1·3·1

Oxygen absorption of linoleic acid during autoxidation at 120^0C in the presence of 0.05% iron on the weight of acid, mono-dipivalylferrocene (O_2 was not purged in but air was present in the flask)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	765	0
1	0.8	765	0.8
3	1.0	764	2.0
21	3.6	764	4.6
24	4.0	763	5.0
30	4.0	761	7.0
45	4.0	757	12.0

Table 1·3·2

Oxygen absorption of linoleic acid during autoxidation at 120^0C in the presence of 0.05% iron on the weight of acid, monopivaloylyferrocen (O_2 was not purged in but air in the flask was not evacuated)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10
0	0	765	0
1	1	765	1.0
3	1.2	765	1.2
21	1.6	764	2.6
24	1.9	763	3.9
30	1.9	761	5.9
45	2.4	757	10.4

Table 1·3·3

Oxygen absorption of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, (ferrous salicylate)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	763	0	*D
½	1.9	763	1.9	*D
3	9.9	763	9.9	O—ON
3½	11.9	763	11.9	*D
5½	14.2	763	14.2	O—OE
10	*	763		O—OM

* overflow of mercury in the manometer

Table 1·3·4

Oxygen absorption of linoleic acid during autoxidation at 120°C in the presence of 0.05% metal on the weight of acid, lead naphthenate

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	763	0	*D
1½	5.0	763	5.0	*D
4	*4.9	763	4.9	*D
18	5.0	757	11.0	*M
20	5.0	756	12.0	O—ON

* overflow of mercury but the experiment was continued

Table 1·3·5

Oxygen absorption of linoleic acid during autoxidation at 120^0C in the presence of 0.05% iron on the weight of acid, Fe/Trilon A complex (H_2O solvent)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	750	0	*D
1	0.5	751	0.5	*D
1½	4.0	751	0.6	*D
4	10.2	752	8.2	●N
7	11.9	753	8.9	O—ON
10	10.4	754	14.4	O—ON
23	12.3	754	16.3	O—ON
30	13.6	754	9.6	▼D
96	13.9	752	11.9	▼D
100	14.2	752	12.2	O—OE

Table 1·3·6

Oxygen absorption of linoleic acid during autoxidation at 120^0C in the presence of 0.05% iron on the weight of acid (ferrocene dicarboxylic acid)

TIME (Hours)	ΔL (mm Hg) × 10	PRESSURE P (mm Hg)	ΔP (mm Hg) × 10	WEATHER CONDITIONS
0	0	750	0	*D
1	1.9	751	0.9	*D
1½	6.4	751	5.4	*D
4	14.4	752	12.4	O—ON

Table 1·3·7

Changes in Iodine value of linoleic acid during autoxidation at room temperature

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.0	0.1262	155
3	28.0	0.1262	155
6	28.0	0.1262	155
9	28.1	0.1262	153
12	28.2	0.1262	151
24	28.4	0.1262	147
30	28.6	0.1262	143
42	28.8	0.1262	139

$N = 0.2$

$T_2 = 35.7$ mls

Table 1·3·8

Changes in Iodine value of linoleic acid during autoxidation at 60^0C

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.0	0.1262	155
3	28.2	0.1262	151
6	28.3	0.1262	149
9	28.4	0.1262	147
15	28.6	0.1262	143
24	28.8	0.1262	139
30	29.1	0.1262	133
42	29.4	0.1262	127

$N = 0.2$

$T_2 = 35.7$ mls

Table 1·3·9 Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.25% iron on the weight of acid (Fe/Trilon A)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.00	0.1262	157
3	20.10	0.1262	155
6	20.13	0.1262	154
9	20.15	0.1262	154
12	20.17	0.1262	153
24	20.19	0.1262	153
36	20.21	0.1262	153
48	20.25	0.1262	152
60	20.27	0.1262	151
72	20.20	0.1262	153

T_2 = 27.3 mls

N = 0.2

Table 1·4·0 Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.25% iron on the weight of acid (monopivaloylferrocene).

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.20	0.1262	157
3	20.28	0.1262	155
6	20.27	0.1262	155
9	20.29	0.1262	155
12	20.31	0.1262	155
18	20.41	0.1262	153
24	20.45	0.1262	152
36	20.50	0.1262	151
48	20.55	0.1262	150
60	20.50	0.1262	151
72	20.57	0.1262	150

T_2 = 2.80 mls

N = 0.2

Table 1·4·1

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.25% iron on the weight of acid, dipivaloylferrocene

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.30	0.1262	155
3	20.30	0.1262	155
9	20.35	0.1262	154
15	20.42	0.1262	152
21	20.38	0.1262	153
36	20.45	0.1262	152
48	20.50	0.1262	151
60	20.48	0.1262	151
72	20.52	0.1262	151

T_2 = 28.0 mls

N = 0.2

Table 1·4·2

Changes in Iodine value of linoleic acid during autoxidation at 60^0C in the presence of 0.25% iron on the weight of acid, monopivaloylferrocene

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.20	0.1262	157
3	20.30	0.1262	155
9	20.38	0.1262	153
18	20.42	0.1262	152
24	20.48	0.1262	151
33	20.60	0.1262	149
42	20.70	0.1262	147
48	20.76	0.1262	146
60	20.81	0.1262	145
72	20.92	0.1262	142

T_2 = 28.0 mls

N = 0.2

Table 1·4·3

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.25% metal on the weight of acid, (cobalt octoate)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.16	0.1262	154
3	20.26	0.1262	152
6	20.32	0.1262	150
9	21.20	0.1262	133
12	21.54	0.1262	126
24	21.78	0.1262	121
48	21.88	0.1262	119
60	21.19	0.1262	113
72	21.35	0.1262	110

T_2 = 27.8 mls

N = 0.2

Table 1·4·4

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.25% iron on the weight of acid, (Fe/EDTA complex)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.92	0.1262	160
3	20.12	0.1262	156
6	20.14	0.1262	156
9	20.20	0.1262	155
12	20.19	0.1262	155
24	20.22	0.1262	154
36	20.29	0.1262	153
48	20.27	0.1262	153
60	20.30	0.1262	153
72	20.33	0.1262	152

T_2 = 27.9 mls

N = 0.2

Table 1·4·5

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.25% iron on the weight of acid, (ferrocene dicarboxylic acid)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.10	0.1262	157
3	20.15	0.1262	156
6	20.20	0.1262	155
9	20.22	0.1262	154
12	20.24	0.1262	154
24	20.27	0.1262	153
36	20.26	0.1262	153
48	20.30	0.1262	153
60	20.40	0.1262	151
72	20.43	0.1262	150

T_2 = 27.9 mls

N = 0.2

Table 1·4·6

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.25% iron on the weight of acid, (ferrocene)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.95	0.1262	156
3	20.00	0.1262	155
6	20.00	0.1262	155
9	20.06	0.1262	154
12	20.10	0.1262	153
24	20.15	0.1262	152
36	20.10	0.1262	153
48	20.15	0.1262	152
60	20.20	0.1262	151
72	20.20	0.1262	151

T_2 = 27.7 mls

N = 0.2

Table 1·4·7

Changes in Iodine value of linoleic acid during autoxidation at room temperature under O_2 in the presence of 0.25% metal on the weight of acid (cobalt stearate)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.95	0.1262	156
3	20.25	0.1262	150
6	20.35	0.1262	148
9	20.46	0.1262	146
12	20.54	0.1262	144
24	20.92	0.1262	136
36	21.23	0.1262	130
48	21.52	0.1262	124
60	21.65	0.1262	122
72	21.96	0.1262	115

T_2 = 27.7 mls

N = 0.2

Table 1·4·8

Changes in Iodine value of linoleic acid during autoxidation under O_2 in the presence of 0.25% iron on the weight of acid, (ferrous salicylate) 23°C

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.95	0.1262	158
3	19.95	0.1262	158
6	20.00	0.1262	157
9	20.05	0.1262	156
12	20.15	0.1262	154
24	20.20	0.1262	153
36	20.28	0.1262	151
48	20.30	0.1262	151
60	20.40	0.1262	149
72	20.47	0.1262	147

T_2 = 27.8 mls

N = 0.2

Table 1·4·9

Changes in Iodine value of linoleic acid during autoxidation under O_2 at room temperature in the presence of 0.25% iron on the weight of acid , ferrous stearate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.9	0.1262	155
3	19.9	0.1272	155
9	20.0	0.1262	153
12	20.1	0.1262	151
24	20.1	0.1262	157
42	20.2	0.1262	149
72	20.3	0.1262	147
76	20.4	0.1262	145

T_2 = 27.6 mls

N = 0.2

Table 1·5·0

Changes in Iodine value of linoleic acid during autoxidation under oxygen at room temperature with no additions.

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.90	0.1262	159
3	20.00	0.1262	157
6	20.20	0.1262	153
9	20.10	0.1262	155
12	20.20	0.1262	153
24	20.30	0.1262	157
36	20.35	0.1262	150
48	20.30	0.1262	151
60	20.40	0.1262	149
72	20.35	0.1262	150

T_2 = 27.8 mls

N = 0.2

Table 1·5·1

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid (ferrocene).

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.0	0.1262	155
3	28.0	0.1262	155
6	28.0	0.1262	155
9	28.1	0.1262	153
15	28.2	0.1262	151
24	28.3	0.1262	149
30	28.3	0.1262	149
42	28.3	0.1262	149

N = 0.2

T_2 = 35.7 mls

Table 1·5·2

Changes in Iodine value of linoleic acid during autoxidation at 60^{0}C in the presence of 0.05% iron on the weight of acid (ferrocene).

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.0	0.1262	155
3	28.1	0.1262	153
6	28.2	0.1262	151
9	28.4	0.1262	149
15	28.5	0.1262	145
24	28.6	0.1262	143
30	28.9	0.1262	137
42	29.1	0.1262	133

N = 0.2

T_2 = 35.7 mls

Table 1·5·3

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid. (ferrous stearate.)

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.1	0.1262	153
3	28.4	0.1262	149
6	28.7	0.1262	141
9	28.9	0.1262	137
15	29.3	0.1262	129
24	30.0	0.1262	115
30	30.2	0.1262	111
42	30.4	0.1262	107

N = 0.2

T_2 = 35.7 mls

Table 1·5·4

Changes in Iodine value of linoleic acid during autoxidation at 60^0C in the presence of 0.05% iron on the weight of acid (ferrous octoate.)

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.1	0.1262	153
3	28.6	0.1262	143
6	28.9	0.1262	137
9	29.1	0.1262	133
15	30.2	0.1262	111
24	30.4	0.1262	107
30	30.6	0.1262	103
42	30.5	0.1262	105

T_2 = 35.7 mls

N = 0.2

Table 1·5·5
Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid ferrous octoate.

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.0	0.1262	157
3	20.0	0.1262	157
6	20.1	0.1262	155
9	20.1	0.1262	155
15	20.3	0.1262	151
24	20.6	0.1262	149
36	20.9	0.1262	139
48	21.1	0.1262	135
60	21.3	0.1262	131

T_2 = 27.8 mls
N = 0.2

Table 1·5·6
Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% nickel on wt. of acid nickelocene.

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.3	0.1262	157
3	20.3	0.1262	157
6	20.3	0.1262	157
9	20.4	0.1262	155
12	20.6	0.1262	151
15	20.5	0.1262	153
24	20.7	0.1262	149
36	20.6	0.1262	151
48	20.6	0.1262	151
60	20.6	0.1262	151

T_2 = 28.1 mls

N = 0.2

Table 1·5·7

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid, Fe/EDTA (Methyl ethyl ketone solvent).

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.4	0.1262	157
3	21.6	0.1262	153
9	21.7	0.1262	151
15	21.7	0.1262	151
24	22.1	0.1262	143
36	22.8	0.1262	129
48	23.0	0.1262	125
60	23.5	0.1262	115

$N = 0.2$

$T_2 = 29.2$ mls

Table 1·5·8

Changes in Iodine value of linoleic acid during autoxidation at 60 C in the presence of 0.05% iron on the weight of acid, Fe/EDTA (methyl ethyl ketone solvent)

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.4	0.1262	157
3	21.8	0.1262	149
9	22.1	0.1272	143
15	22.7	0.1262	131
24	23.2	0.1262	121
36	23.6	0.1262	113
48	24.1	0.1262	103
60	24.8	0.1262	87

$N = 0.2$

$T_2 = 29.2$ mls

Table 1·5·9

Changes in Iodine value of linoleic acid during autoxidation at 60^{0}C temperature in the presence of 0.05% iron on the weight of acid, ferrous salicylate (methyl ethyl ketone solvent)

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	17.3	0.1262	155
3	17.8	0.1262	145
9	18.2	0.1262	137
15	18.8	0.1262	125
24	19.1	0.1262	119
36	19.8	0.1262	105
48	20.0	0.1262	101
60	20.0	0.1262	101

N = 0.2

T_2 = 25.0 mls

Table 1·6·0

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid, ferrous salicylate (methyl ethyl ketone solvent)

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	17.3	0.1262	155
3	17.6	0.1262	148
9	17.9	0.1262	143
15	18.0	0.1262	141
24	18.4	0.1262	133
36	18.6	0.1262	129
48	18.9	0.1262	123
60	19.0	0.1262	125

N = 0.2

T_2 = 25.0 mls

Table 1·6·1

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid, Dipivaloylferrocene

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	29.3	0.1262	155
3	29.3	0.1262	155
6	29.4	0.1262	153
9	29.2	0.1262	157
21	29.5	0.1262	151
36	29.6	0.1262	149
48	29.6	0.1262	149
60	29.8	0.1262	145

$N = 0.2$

$T_2 = 37.0$ mls

Table 1·6·2

Changes in Iodine value of linoleic acid during autoxidation at 60^0C in the presence of 0.05% iron on the weight of acid, Dipivaloylferrocene

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	29.3	0.1262	155
3	29.4	0.1262	153
6	29.4	0.1262	153
9	29.4	0.1262	153
15	29.6	0.1262	149
21	29.5	0.1262	151
36	29.8	0.1262	145
48	29.9	0.1262	143
60	30.2	0.1262	137

$N = 0.2$

$T_2 = 37.0$ mls

Table 1·6·3

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid, ferrous stearate

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.8	0.1262	165
3	20.1	0.1262	159
6	20.6	0.1262	149
9	20.9	0.1262	143
21	21.2	0.1262	137
28	21.1	0.1262	139
44	22.4	0.1262	113
50	22.8	0.1262	105
60	22.9	0.1262	103

T_2 = 28.0 mls

N = 0.2

Table 1·6·4

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% metal on the weight of acid, nickel octoate

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.0	0.1262	161
3	20.8	0.1262	145
6	21.6	0.1262	129
9	22.0	0.1262	121
15	22.3	0.1262	115
27	23.0	0.1262	101
44	22.5	0.1262	103
50	23.0	0.1262	101
60	22.9	0.1262	103

T_2 = 28.0 mls

N = 0.2

Table 1·6·5

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid, ferrocene dicarboxylic acid

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	23.6	0.1262	157
3	23.6	0.1262	157
6	23.9	0.1262	151
9	23.8	0.1262	153
15	24.2	0.1262	145
36	24.4	0.1262	141
48	24.9	0.1262	131
60	25.1	0.1262	127

N = 0.2

T_2 = 31.4 mls

Table 1·6·6

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid Fe/Trilon A complex (HCl solvent)

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.8	0.1262	161
3	21.95	0.1262	158
6	22.1	0.1262	155
15	22.6	0.1262	145
30	22.5	0.1262	139
44	23.0	0.1262	137
60	23.3	0.1262	131

N = 0.2

T_2 = 29.8 mls

Table 1·6·7

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% metal on the weight of acid. (cobalt oleate.)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.6	0.1262	159
3	21.3	0.1262	145
6	21.8	0.1262	135
9	22.3	0.1262	125
15	22.8	0.1262	115
24	23.1	0.1262	109
27	23.3	0.1262	105
44	24.0	0.1262	91
50	24.5	0.1262	81
60	25.0	0.1262	70

T_2 = 28.5 mls

N = 0.2

Table 1·6·8

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% metal on the weight of acid (lead naphthenate)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.6	0.1262	155
3	21.7	0.1262	153
6	21.8	0.1262	151
9	21.9	0.1262	149
15	22.2	0.1262	143
21	22.7	0.1262	133
27	22.8	0.1262	131
44	23.1	0.1262	125
50	23.4	0.1262	119
60	23.6	0.1262	115

T_2 = 29.3 mls

N = 0.2

Table 1·6·9

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid [dicyclopentadinyliron (Oil solvent)].

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	23.6	0.1262	155
3	23.6	0.1262	155
6	23.6	0.1262	155
9	23.6	0.1262	155
15	23.8	0.1262	151
20	23.2	0.1262	153
27	23.8	0.1262	151
44	23.9	0.1262	149
50	24.1	0.1262	145
60	24.2	0.1262	143

T_2 = 31.3 mls

N = 0.2

Table 1·7·0

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid [Fe/EDTA (HCl solvent)]

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.3	0.1262	157
3	21.4	0.1262	155
6	21.45	0.1262	154
9	21.4	0.1262	155
15	21.5	0.1262	153
21	21.55	0.1262	152
27	21.6	0.1262	151
44	21.75	0.1262	148
50	21.8	0.1262	147
60	21.9	0.1262	145

T_2 = 29.1 mls

N = 0.2

Table 1·7·1

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% metal on the weight of acid (cobalt Naphthenate).

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.5	0.1262	155
3	21.9	0.1262	147
6	22.1	0.1262	143
9	22.8	0.1262	129
15	23.1	0.1262	123
21	23.4	0.1262	117
27	23.7	0.1262	111
44	24.3	0.1262	99
50	24.7	0.1262	91
60	25.1	0.1262	83

T_2 = 29.2 mls

N = 0.2

Table 1·7·2

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% metal on the weight of acid (nickel stearate.)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.9	0.1262	155
3	20.2	0.1262	149
6	20.8	0.1262	137
9	21.2	0.1262	129
21	21.6	0.1262	121
44	22.0	0.1262	113
50	22.4	0.1262	107
60	22.9	0.1262	95

T_2 = 27.6 mls

N = 0.2

Table 1·7·3

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of equal amounts (0.05%) iron on the weights of acid, mono- and dipivaloylferrocenes

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.3	0.1262	157
3	22.2	0.1262	139
12	23.1	0.1262	121
24	22.2	0.1262	139
36	22.8	0.1262	127
48	22.2	0.1262	139
60	22.5	0.1262	133

N = 0.2

T_2 = 29.1 mls

Table 1·7·4

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of equal amounts (0.05%) iron on the weights of mono- and dipivaloylferrocenes

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.3	0.1262	157
3	23.7	0.1262	109
12	23.9	0.1262	105
24	24.0	0.1262	103
36	24.1	0.1262	101
48	24.0	0.1262	103
60	24.2	0.1262	99

N = 0.2

T_2 = 29.1 mls

Table 1·7·5

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.05% iron on the weight of acid (ferrocene dicarboxylic acid)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	23.7	0.1262	155
3	23.7	0.1262	155
6	23.8	0.1262	153
9	24.0	0.1262	149
15	24.3	0.1262	143
24	24.9	0.1262	131
30	25.0	0.1262	129
44	25.8	0.1262	113
60	26.2	0.1262	105

T_2 = 31.4 mls

N = 0.2

Table 1·7·6

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.05% iron on the weight of acid Fe/Trilon A (HCl solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.8	0.1262	157
3	21.9	0.1262	155
6	22.2	0.1262	149
9	22.8	0.1262	137
15	23.0	0.1262	133
24	23.4	0.1262	125
30	23.6	0.1262	121
44	24.0	0.1262	113
50	24.3	0.1262	107
60	24.4	0.1262	105

T_2 = 29.6 mls

N = 0.2

Table 1·7·7

Changes in Iodine value of linoleic acid during autoxidation at 60^{0}C temperature in the presence of 0.05% metal on the weight of acid (ferrous salicylate)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	16.9	0.1262	163
3	17.4	0.1262	153
6	17.9	0.1262	143
9	18.1	0.1262	139
15	18.5	0.1262	131
24	19.0	0.1262	121
36	19.6	0.1262	109
48	19.9	0.1262	103
60	20.1	0.1262	99

T_2 = 25.0mls

N = 0.2

Table 1·7·8

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% metal on the weight of acid (cobalt octoate)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	16.8	0.1262	166
3	17.9	0.1262	145
6	18.3	0.1262	137
9	18.9	0.1262	125
15	18.7	0.1262	129
24	19.8	0.1262	107
36	20.2	0.1262	99
44	21.6	0.1262	70
50	22.8	0.1262	48

T_2 = 25.1 mls

N = 0.2

Table 1·7·9

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid, Fe/Trilon A (methyl ethyl ketone solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	27.7	0.1262	157
3	27.9	0.1262	153
6	28.2	0.1262	147
9	28.1	0.1262	149
15	28.4	0.1262	143
24	28.8	0.1262	135
36	29.3	0.1262	125
48	29.8	0.1262	115
60	30.1	0.1262	107

T_2 = 35.5 mls

N = 0.2

Table 1·8·0

Changes in Iodine value of linoleic acid during autoxidation at 60^{0}C in the presence of 0.05% iron on the weight of acid, Fe/Trilon A (methyl ethyl ketone solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	27.7	0.1262	157
3	27.9	0.1262	153
6	28.2	0.1262	147
9	28.7	0.1262	137
15	28.8	0.1262	135
24	29.1	0.1262	129
36	29.6	0.1262	119
48	30.2	0.1262	107
60	30.8	0.1262	95

T_2 = 35.5 mls

N = 0.2

Table 1·8·1

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.05% on the weight of acid (cobalt naphthenate).

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.5	0.1262	155
3	22.0	0.1262	145
6	22.3	0.1262	139
9	22.9	0.1262	127
15	23.4	0.1262	117
21	23.6	0.1262	113
7	24.0	0.1262	105
44	24.5	0.1262	95
50	24.9	0.1262	87
60	25.4	0.1262	76

T_2 = 29.2 mls

N = 0.2

Table 1·8·2

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.05% iron on the weight of acid, nickel stearate.

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.9	0.1262	155
3	20.1	0.1262	151
6	20.6	0.1262	141
9	20.9	0.1262	135
15	21.5	0.1262	123
27	21.9	0.1262	115
44	22.3	0.1262	107
50	22.6	0.1262	101
60	23.1	0.1262	91

T_2 = 27.6 mls

N = 0.2

Table 1·8·3

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.05% iron on the weight of acid, dicyclopenladinyliron (oil solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	23.60	0.1262	155
3	23.60	0.1262	155
6	23.60	0.1262	155
9	23.70	0.1262	153
15	23.95	0.1262	148
20	24.20	0.1262	143
26	24.55	0.1262	136
44	25.30	0.1262	121
50	25.70	0.1262	113
60	25.60	0.1262	115

T_2 = 31.3 mls

N = 0.2

Table 1·8·4

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.05% iron on the weight of acid, Fe/EDTA (HCl solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.30	0.1262	157
3	21.40	0.1262	155
6	21.60	0.1262	151
9	21.90	0.1262	145
15	22.30	0.1262	137
20	22.40	0.1262	135
26	22.60	0.1262	131
44	23.30	0.1262	117
50	23.80	0.1262	107
60	24.00	0.1262	103

T_2 = 29.1 mls

N = 0.2

Table 1·8·5

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.05% iron on the weight of acid, (cobalt oleate) .

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.8	0.1262	155
3	21.6	0.1262	139
6	21.9	0.1262	133
9	22.5	0.1262	121
15	22.8	0.1262	115
21	23.3	0.1262	105
27	23.5	0.1262	101
44	24.3	0.1262	86
50	24.7	0.1262	75
60	24.8	0.1262	74

T_2 = 28.5 mls

N = 0.2

Table 1·8·6

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.05% iron on the weight of acid (lead naphthenate) .

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.6	0.1262	155
3	21.7	0.1262	153
6	21.7	0.1262	153
9	21.8	0.1262	151
15	21.9	0.1262	149
21	22.1	0.1262	129
27	22.4	0.1262	123
44	22.8	0.1262	115
50	23.1	0.1262	109
60	23.4	0.1262	103

T_2 = 29.3 mls

N = 0.2

Table 1·8·7

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.05% iron on the weight of acid (ferrous stearate) .

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.9	0.1262	163
3	20.3	0.1262	155
6	20.9	0.1262	143
9	21.3	0.1262	135
15	22.0	0.1262	121
21	22.3	0.1262	115
28	22.9	0.1262	103
44	22.8	0.1262	105
50	23.0	0.1262	101
60	22.9	0.1262	103

T_2 = 28.0 mls

N = 0.2

Table 1·8·8

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.05% iron on the weight of acid. (nickel octoate)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.0	0.1262	161
3	20.3	0.1262	155
6	20.6	0.1262	149
9	20.9	0.1262	143
21	21.2	0.1262	137
28	22.8	0.1262	105
44	23.0	0.1262	101
50	23.0	0.1262	101
60	22.9	0.1262	103

T_2 = 28.0 mls

N = 0.2

Table 1·8·9

Changes in Iodine value of linoleic acid during autoxidation at 60^0C with no additions

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.85	0.1262	158
3	20.00	0.1262	155
6	19.95	0.1262	155
9	20.13	0.1262	152
12	20.15	0.1262	152
24	20.23	0.1262	150
36	20.32	0.1262	148
48	20.53	0.1262	144
60	20.61	0.1262	143
72	20.73	0.1262	140

T_2 = 27.7 mls

N = 0.2

Table 1·9·0

Changes in Iodine value of linoleic acid during autoxidation at 60^0C in the presence of 0.25% iron on the weight of acid (ferrous stearate).

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.10	0.1262	155
3	20.11	0.1262	155
9	20.27	0.1262	151
15	20.30	0.1262	151
24	20.52	0.1262	146
36	20.64	0.1262	144
48	20.72	0.1262	142
60	21.00	0.1262	137
72	21.70	0.1262	134

T_2 = 27.8 mls

N = 0.2

Table 1·9·1

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.25% iron on the weight of acid (ferrous salicylate).

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.00	0.1262	157
3	20.30	0.1262	151
9	20.45	0.1262	148
18	20.58	0.1262	145
24	20.85	0.1262	140
36	21.10	0.1262	135
48	21.32	0.1262	130
60	21.56	0.1262	125
72	21.72	0.1262	122

T_2 = 27.8 mls

N = 0.2

Table 1·9·2

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.25% iron on the wéight of acid (cobalt stearate).

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.10	0.1262	155
3	20.18	0.1262	153
9	20.24	0.1262	152
15	20.43	0.1262	148
24	20.95	0.1262	138
36	21.35	0.1262	130
48	21.86	0.1262	119
60	21.78	0.1262	121
72	21.98	0.1262	117

T_2 = 27.8 mls

N = 0.2

Table 1·9·3

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.25% iron on the weight of acid (ferrocene dicarboxylic acid)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.00	0.1262	157
3	20.20	0.1262	153
9	20.30	0.1262	151
15	20.60	0.1262	145
21	20.58	0.1262	145
27	20.90	0.1262	139
33	20.84	0.1262	140
48	21.10	0.1262	135
60	21.35	0.1262	129
72	21.45	0.1262	129

T_2 = 27.8mls

N = 0.2

Table 1·9·4

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.25% iron on the weight of acid (ferrocene).

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.11	0.1262	155
3	20.15	0.1262	154
9	20.16	0.1262	154
15	20.45	0.1262	148
24	21.00	0.1262	137
30	21.20	0.1262	133
36	21.40	0.1262	129
48	21.35	0.1262	130
60	21.45	0.1262	128
72	21.95	0.1262	126

T_2 = 27.8 mls

N = 0.2

Table 1·9·5

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.25% iron on the weight of acid, (cobalt octoate).

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.10	0.1262	155
3	20.20	0.1262	153
9	20.40	0.1262	149
15	20.60	0.1262	145
21	21.00	0.1262	137
33	21.45	0.1262	128
42	21.80	0.1262	121
48	22.10	0.1262	115
60	22.84	0.1262	100
72	22.90	0.1262	99

T_2 = 27.8mls

N = 0.2

Table 1·9·6

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.25% iron on the weight of acid (Fe/EDTA complex).

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.14	0.1262	156
3	20.20	0.1262	155
9	20.25	0.1262	152
15	20.38	0.1262	149
21	20.36	0.1262	150
33	20.42	0.1262	148
42	20.40	0.1262	149
54	20.49	0.1262	147
60	20.54	0.1262	146
72	20.68	0.1262	143

T_2 = 27.85mls

N = 0.2

Table 1·9·7

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.25% iron on the weight of acid (dipivaloylferrocene).

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.35	0.1262	156
3	20.38	0.1262	155
9	20.42	0.1262	154
15	20.54	0.1262	152
21	20.60	0.1262	151
36	20.90	0.1262	148
48	21.10	0.1262	141
54	21.20	0.1262	139
60	21.30	0.1262	137
72	21.35	0.1262	136

T_2 = 28.1 mls

N = 0.2

Table 1·9·8

Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.25% iron on the weight of acid (Fe/Trilon A)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.00	0.1262	157
3	20.10	0.1262	155
6	20.16	0.1262	154
12	20.19	0.1262	153
18	20.30	0.1262	151
24	20.28	0.1262	151
36	20.38	0.1262	149
48	20.36	0.1262	150
60	20.46	0.1262	148
72	20.52	0.1262	146

T_2 = 27.8 mls

N = 0.2

Table 1·9·9

Changes in Iodine value of linoleic acid during autoxidation at 60°C temperature in the presence of 0.05% iron on the weight of acid (monopivaloylferrocene).

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.6	0.1262	155
3	29.0	0.1262	147
9	29.4	0.1262	139
15	29.8	0.1262	131
21	31.3	0.1262	101
36	31.35	0.1262	100
48	31.31	0.1262	100

N = 0.2

T_2 = 36.3 mls

Table 2·10

Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% iron on the weight of acid (monopivaloylferrocene)

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.6	0.1262	155
3	28.6	0.1262	155
9	28.7	0.1262	153
15	28.6	0.1262	155
21	28.7	0.1262	153
36	28.8	0.1262	151
48	28.8	0.1262	151

N = 0.2

T_2 = 36.3 mls

Table 2·20

Changes in Iodine value of linoleic acid during autoxidation at 80^{0}C with no additions

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.00	0.1262	155
3	28.56	0.1262	144
9	28.76	0.1262	140
15	29.00	0.1262	135
24	28.82	0.1262	138
36	29.00	0.1262	135
48	28.80	0.1262	139
60	28.96	0.1262	136
72	29.00	0.1262	135

T_2 = 35.7mls

N = 0.2

Table 2·30

Changes in Iodine value of linoleic acid during autoxidation at 80^{0}C in the presence of 0.25% iron on the weight of acid, ferrous stearate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.20	0.1262	157
3	20.50	0.1262	151
9	20.85	0.1262	144
15	20.92	0.1262	142
24	21.00	0.1262	141
36	21.42	0.1262	132
48	21.50	0.1262	131
60	21.48	0.1262	131
72	21.51	0.1262	131

T_2 = 28.0 mls

N = 0.2

Table 2·40

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.25% iron on the weight of acid, cobalt stearate.

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.10	0.1262	155
3	20.20	0.1262	153
9	20.40	0.1262	149
15	20.62	0.1262	144
24	20.90	0.1262	139
36	21.28	0.1262	131
48	21.24	0.1262	132
60	21.43	0.1262	128
70	21.61	0.1262	125

T_2 = 27.8 mls

N = 0.2

Table 2·50

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.25% iron on the weight of acid, ferrous salicylate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.25	0.1262	156
3	20.42	0.1262	152
9	20.60	0.1262	149
15	20.73	0.1262	146
24	20.96	0.1262	142
36	21.32	0.1262	134
48	21.48	0.1262	131
60	21.52	0.1262	130

T_2 = 28.0 mls

N = 0.2

Table 2·60

Changes in Iodine value of linoleic acid during autoxidation at 80^0C in the presence of 0.25% iron on the weight of acid, (ferrocene dicarboxylic acid)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.25	0.1262	156
3	20.64	0.1262	148
9	20.90	0.1262	143
18	21.38	0.1262	133
24	21.84	0.1262	124
36	21.96	0.1262	122
48	22.11	0.1262	118
60	22.32	0.1262	114
66	22.40	0.1262	113
72	22.32	0.1262	114

T_2 = 28.0 mls

N = 0.2

Table 2·70

Changes in Iodine value of linoleic acid during autoxidation at 80^0C in the presence of 0.25% iron on the weight of acid, (ferrocene) .

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.13	0.1262	158
3	20.36	0.1262	154
9	20.57	0.1262	149
18	20.86	0.1262	144
27	21.32	0.1262	134
36	21.65	0.1262	128
48	21.58	0.1262	129
60	21.71	0.1262	126
72	21.86	0.1262	123

T_2 = 28.0 mls

N = 0.2

Table 2·80

Changes in Iodine value of linoleic acid during autoxidation at 80^{0}C in the presence of 0.25% iron on the weight of acid, cobalt octoate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.30	0.1262	155
3	20.42	0.1262	152
9	20.83	0.1262	144
15	21.21	0.1262	137
24	21.82	0.1262	124
36	21.92	0.1262	122
48	22.20	0.1262	117
60	22.50	0.1262	111
70	22.78	0.1262	105

T_2 = 28.0 mls

N = 0.2

Table 2·90

Changes in Iodine value of linoleic acid during autoxidation at 80^{0}C in the presence of 0.25% iron on the weight of acid, Fe/EDTA

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.25	0.1262	156
3	20.44	0.1262	152
9	20.82	0.1262	144
15	20.98	0.1262	141
21	21.34	0.1262	134
33	21.96	0.1262	122
42	22.00	0.1262	121
48	22.32	0.1262	114
60	22.36	0.1262	113
70	22.40	0.1262	113

T_2 = 28.0 mls

N = 0.2

Table 2·1·0

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.25% iron on the weight of acid , dipivalylferrocene and monopivaloylferrocenes combined

TIME (Hours)	TITRE (mls)	SAMPLE WEIGHT (g)	IODINE VALUE
0	20.36	0.1262	156
3	20.45	0.1262	154
9	20.58	0.1262	151
18	20.92	0.1262	144
24	21.00	0.1262	143
36	21.22	0.1262	138
48	21.35	0.1262	136
60	21.45	0.1262	134
72	21.52	0.1262	132

$N = 0.2$

$T_2 = 28.10$ mls

Table 2·1·1

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.25% iron on the weight of acid (monopivaloylferrocene)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.30	0.1262	159
3	20.65	0.1262	152
9	20.83	0.1262	148
15	20.98	0.1262	145
21	21.31	0.1262	139
33	21.53	0.1262	134
39	21.92	0.1262	126
48	22.98	0.1262	125
60	22.10	0.1262	123
72	22.22	0.1262	120

T_2 = 28.2 mls

N = 0.2

Table 2·1·2

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.25% iron on the weight of acid Fe/Trilon A (methyl ethyl ketone solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.30	0.1262	155
3	20.40	0.1262	153
9	20.70	0.1262	147
15	20.92	0.1262	142
24	21.11	0.1262	130
36	22.21	0.1262	116
48	22.51	0.1262	110
60	22.80	0.1262	105
72	22.95	0.1262	102

T_2 = 28.00 mls

N = 0.2

Table 2·1·3

Changes in Iodine value of linoleic acid during autoxidation at 80 °C in the presence of equal amounts (0.05%) iron on the weights of acid, mono- and dipivaloylferrocenes

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.3	0.1262	157
3	21.3	0.1262	157
12	22.4	0.1262	135
24	23.6	0.1262	111
36	24.0	0.1262	103
48	25.3	0.1262	76
60	25.4	0.1262	74

T_2 = 29.1 mls

N = 0.2

Table 2·1·4

Changes in Iodine value of linoleic acid during autoxidation at 120 °C in the presence of equal amounts (0.05%) iron on the weights of acid, mono- and dipivaloylferrocenes

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.3	0.1262	157
3	24.0	0.1262	103
12	25.8	0.1262	66
24	28.6	0.1262	10
36	28.2	0.1262	18
48	28.6	0.1262	10
60	28.9	0.1262	4

T_2 = 29.1 mls

N = 0.2

Table 2·1·5

Changes in Iodine value of linoleic acid during autoxidation at 80^{0}C in the presence of (0.05% iron on the weight of acid, Fe/EDTA (methyl ethyl ketone as solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.4	0.1262	157
3	22.1	0.1262	143
15	23.1	0.1262	123
24	23.8	0.1262	109
36	24.0	0.1262	106
48	24.6	0.1262	93
60	24.5	0.1262	87

T_2 = 0.2 mls

N = 0.2

Table 2·1·6

Changes in Iodine value of linoleic acid during autoxidation at 120^{0}C in the presence of 0.05% iron on the weight of acid, Fe/EDTA (methyl ethyl ketone solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.5	0.1262	154
3	22.6	0.1262	133
9	23.0	0.1262	125
15	24.3	0.1262	99
24	25.4	0.1262	87
36	26.1	0.1262	75
48	26.8	0.1262	62
60		0.1262	48

T_2 = 29.2 mls

N = 0.2

Table 2·1·7

Changes in Iodine value of linoleic acid during autoxidation at 80^{0}C in the presence of 0.05% iron on the weight of acid, ferrous salicylate (methyl ethyl ketone)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	17.3	0.1262	155
3	18.1	0.1262	139
6	19.2	0.1262	117
9	19.8	0.1262	105
15	20.1	0.1262	99
24	20.8	0.1262	85
36	21.2	0.1262	76
48	21.6	0.1262	65
60	21.9	0.1262	62

T_2 = 25.0 mls

N = 0.2

Table 2·1·8

Changes in Iodine value of linoleic acid during autoxidation at 120^{0}C in the presence of 0.05% iron on the weight of acid, ferrous salicylate (methyl ethyl ketone solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	17.3	0.1262	155
3	18.8	0.1262	125
6	19.8	0.1262	105
9	20.3	0.1262	95
15	21.0	0.1262	81
24	21.8	0.1262	64
36	22.0	0.1262	60
48	22.9	0.1262	42
60	23.1	0.1262	38

T_2 = 25.0 mls

N = 0.2

Table 2 1·9

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid, Fe/Trilon A (methyl ethyl ketone)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	27.7	0.1262	157
3	28.1	0.1262	149
6	28.4	0.1262	143
9	28.9	0.1262	133
15	29.3	0.1262	125
24	29.8	0.1262	115
36	30.2	0.1262	107
48	30.8	0.1262	95
60	31.1	0.1262	89

T_2 = mls

N = 0.2

Table 2·2·0

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, Fe/Trilon A (methyl ethyl ketone solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	27.7	0.1262	157
3	28.5	0.1262	141
9	29.3	0.1262	125
15	30.0	0.1262	111
24	30.4	0.1262	103
36	31.0	0.1262	91
48	31.8	0.1262	74
60	32.0	0.1262	70

T_2 = mls

N = 0.2

Table 2·2·1

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid (ferrocene).

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.0	0.1262	155
3	28.4	0.1262	149
6	28.8	0.1262	139
9	29.1	0.1262	133
15	29.6	0.1262	123
24	29.9	0.1262	117
30	30.1	0.1262	113
42	30.4	0.1262	107

T_2 = 35.7 mls

N = 0.2

Table 2·2·2

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid (ferrocene)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.0	0.1262	155
3	28.9	0.1262	137
6	29.3	0.1262	129
9	29.8	0.1262	119
15	30.2	0.1262	111
24	30.8	0.1262	99
30	31.1	0.1262	93
42	31.53	0.1262	84

T_2 = 35.7 mls

N = 0.2

Table 2·2·3

Changes in Iodine value of linoleic acid during autoxidation at 80°C.

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.0	0.1262	155
3	28.6	0.1262	143
6	28.5	0.1262	149
9	28.8	0.1262	139
15	29.0	0.1262	135
24	29.4	0.1262	127
30	29.8	0.1262	119
42	30.2	0.1262	111

N = 0.2

T_2 = 35.7 mls

Table 2·2·4

Changes in Iodine value of linoleic acid during autoxidation at 120°C

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.0	0.1262	155
3	28.8	0.1262	139
6	29.1	0.1262	133
9	29.6	0.1262	123
15	29.9	0.1262	117
24	30.2	0.1262	111
30	30.6	0.1262	103
42	30.9	0.1262	97

N = 0.2

M = 0.1262 gr

T_2 = 35.7 mls

Table 2·2·5

Changes in Iodine value of linoleic acid during autoxidation at 80^0C in the presence of 0.05% iron on the weight of acid mono-pivaloylferrocene

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.6	0.1262	155
3	29.6	0.1262	135
9	30.4	0.1262	119
15	31.3	0.1262	101
21	32.0	0.1262	87
36	33.0	0.1262	66
48	34.1	0.1262	44

T_2 = 36.3 mls

N = 0.2

Table 2·2·6

Changes in Iodine value of linoleic acid during autoxidation at 120^0C in the presence of 0.05% iron on the weight of acid mono-pivaloylferrocene

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.6	0.1262	155
3	29.9	0.1262	129
9	31.4	0.1262	99
15	32.2	0.1262	83
21	33.0	0.1262	66
36	34.0	0.1262	46
48	34.8	0.1262	30

Table 2·2·7

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid, Dipivaloylferrocene

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	29.3	0.1262	155
3	29.9	0.1262	143
6	30.2	0.1262	137
9	30.6	0.1262	129
15	31.0	0.1262	121
21	31.8	0.1262	105
36	32.3	0.1262	95
48	33.1	0.1262	78

T_2 = 37.0 mls

N = 0.2

Table 2·2·8

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid Dipivaloylferrocene

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	29.3	0.1262	155
3	30.1	0.1262	139
6	30.7	0.1262	127
9	31.1	0.1262	119
15	32.0	0.1262	101
21	32.4	0.1262	93
36	33.8	0.1262	64
48	34.6	0.1262	48

Table 2·2·9

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid, ferrous octoate

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.0	0.1262	155
3	28.9	0.1262	139
6	29.1	0.1262	133
9	30.3	0.1262	109
15	31.1	0.1262	93
24	31.8	0.1262	78
30	32.2	0.1262	70
42	33.0	0.1262	54

T_2 = 35.7 mls

N = 0.2

Table 2·3·0

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, ferrous octoate

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.0	0.1262	155
3	29.1	0.1262	133
6	29.8	0.1262	119
9	30.9	0.1262	97
15	31.4	0.1262	87
24	32.0	0.1262	74
30	32.8	0.1262	58
42	33.2	0.1262	50

T_2 = 35.7 mls

N = 0.2

Table 2·3·1

Changes in Iodine value of linoleic acid during autoxidation at 80^0C in the presence of 0.05% iron on the weight of acid, ferrous stearate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.90	0.1262	163
3	20.70	0.1262	147
6	21.10	0.1262	139
9	21.90	0.1262	123
21	22.80	0.1262	105
28	23.10	0.1262	99
44	23.90	0.1262	83
50	24.20	0.1262	75
60	24.38	0.1262	73

T_2 = 28.0 mls

N = 0.2

Table 2·3·2

Changes in Iodine value of linoleic acid during autoxidation at 80^0C in the presence of 0.05% metal on the weight of acid, nickel octoate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.00	0.1262	161
3	20.60	0.1262	149
6	20.80	0.1262	145
9	21.60	0.1262	129
21	22.30	0.1262	115
28	23.30	0.1262	95
44	23.50	0.1262	91
50	23.60	0.1262	88
60	23.82	0.1262	84

T_2 = 28.0 mls

N = 0.2

Table 3·3·3

Changes in Iodine value of linoleic acid during autoxidation at 80^{0}C in the presence of 0.05% metal on the weight of acid, cobalt oleate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.8	0.1262	155
3	21.2	0.1262	147
6	21.4	0.1262	143
9	21.9	0.1262	133
15	22.1	0.1262	129
21	22.8	0.1262	115
27	23.0	0.1262	111
44	23.8	0.1262	95
60	24.0	0.1262	91

T_2 = 28.5mls

N = 0.2

Table 3·3·4

Changes in Iodine value of linoleic acid during autoxidation at 80^{0}C in the presence of 0.05% metal on the weight of acid, lead naphthenate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.60	0.1262	155
3	21.65	0.1262	154
6	21.70	0.1262	153
9	21.75	0.1262	152
15	21.80	0.1262	151
21	22.00	0.1262	147
27	22.20	0.1262	143
44	22.50	0.1262	137
50	22.81	0.1262	131
60	22.90	0.1262	129

T_2 = 29.3 mls

N = 0.2

Table 3·3·5

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid, ferrous salicylate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	18.30	0.1262	159
3	18.30	0.1262	149
6	19.20	0.1262	141
9	19.80	0.1262	129
16	20.20	0.1262	121
24	20.50	0.1262	115
36	21.60	0.1262	93
48	22.00	0.1262	85
60	22.45	0.1262	78

T_2 = 26.2 mls

N = 0.2

Table 3·3·6

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.05% metal on the weight of acid, cobalt octoate.

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	17.40	0.1262	155
3	18.30	0.1262	137
6	18.30	0.1262	129
9	19.20	0.1262	119
15	19.80	0.1262	107
27	20.60	0.1262	91
44	21.80	0.1262	66
50	22.10	0.1262	60
60	22.40	0.1262	54

T_2 = 25.1 mls

N = 0.2

Table 3·3·7

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid, ferrocene dicarboxylic acid

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	23.2	0.1262	155
3	23.2	0.1262	155
6	23.9	0.1262	151
9	24.2	0.1262	145
15	24.6	0.1262	137
24	25.1	0.1262	127
30	25.6	0.1262	117
44	26.1	0.1262	107
60	26.4	0.1262	94

T_2 = 31.4 mls

N = 0.2

Table 3·3·8

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid, Fe/Trilon A (HCl solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.80	0.1262	155
3	21.95	0.1262	152
6	22.30	0.1262	145
9	22.60	0.1262	139
15	22.90	0.1262	133
26	23.40	0.1262	123
44	24.20	0.1262	107
50	24.60	0.1262	99
60	24.70	0.1262	95

T_2 = 29.5 mls

N = 0.2

Table 3·3·9

Changes in Iodine value of linoleic acid during autoxidation at 80^{0}C in the presence of 0.05% metal on the weight of acid, nickelocene

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.4	0.1262	157
3	20.6	0.1262	153
6	20.5	0.1262	155
9	20.7	0.1262	151
15	21.0	0.1262	149
26	21.3	0.1262	139
36	21.9	0.1262	127
44	22.2	0.1262	121
50	22.8	0.1262	109
60	22.9	0.1262	107

T_2 = 28.2 mls

N = 0.2

Table 3·4·0

Changes in Iodine value of linoleic acid during autoxidation at 80^{0}C in the presence of 0.05% metal on the weight of acid, ferrous octoate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.10	0.1262	159
3	20.40	0.1262	153
6	20.90	0.1262	143
9	21.30	0.1262	135
15	21.20	0.1262	137
27	21.40	0.1262	133
44	21.60	0.1262	128
50	21.65	0.1262	128
60	21.71	0.1262	127

T_2 = 28.0 mls

N = 0.2

Table 3·4·1

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid, iron dicyclopentadinyl (oil solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	23.6	0.1262	159
3	23.9	0.1262	153
6	24.3	0.1262	149
9	24.8	0.1262	135
15	25.1	0.1262	129
20	25.6	0.1262	119
26	26.1	0.1262	109
44	27.2	0.1262	87
50	27.8	0.1262	74
60	28.2	0.1262	63

T_2 = 31.5 mls

N = 0.2

Table 3·4·2

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.05% iron on the weight of acid, cobalt naphthenate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.5	0.1262	155
3	22.3	0.1262	139
6	22.7	0.1262	131
9	23.0	0.1262	125
15	23.8	0.1262	109
21	24.0	0.1262	105
27	24.4	0.1262	97
44	24.8	0.1262	89
50	25.1	0.1262	83
60	25.4	0.1262	76

T_2 = 29.2 mls

N = 0.2

Table 3·4·3

Changes in Iodine value of linoleic acid during autoxidation at 60^{0}C in the presence of 0.05% iron on the weight of acid, ferrous octoate

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.1	0.1262	155
3	20.6	0.1262	151
9	21.0	0.1262	137
15	21.7	0.1262	123
24	21.9	0.1262	119
36	22.1	0.1262	115
48	22.5	0.1262	107
60	22.9	0.1262	102

T_2 = 27.8 mls

N = 0.2

Table 3·4·4

Changes in Iodine value of linoleic acid during autoxidation at 60^{0}C in the presence of 0.05% metal on the weight of acid, nickelocene

TIME (Hours)	TITRE (T_1) ml	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.2	0.1262	157
3	20.2	0.1262	157
6	20.4	0.1262	153
9	20.7	0.1262	147
15	20.7	0.1262	147
24	20.9	0.1262	143
36	21.2	0.1262	137
48	21.8	0.1262	125
60	22.0	0.1262	121

T_2 = 28.0 mls

N = 0.2

Table 3·4·5

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, ferrous stearate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.9	0.1262	165
3	20.8	0.1262	147
6	21.3	0.1262	137
9	22.1	0.1262	121
21	22.6	0.1262	111
28	22.8	0.1262	107
44	22.9	0.1262	105
50	23.0	0.1262	103
60	23.1	0.1262	101

T_2 = 28.1 mls

N = 0.2

Table 3·4·6

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% metal on the weight of acid, nickel octoate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.2	0.1262	157
3	20.9	0.1262	143
6	21.4	0.1262	133
9	22.3	0.1262	115
15	22.6	0.1262	109
21	23.0	0.1262	101
28	23.0	0.1262	101
44	23.1	0.1262	101
50	23.0	0.1262	101
60	22.9	0.1262	103

T_2 = 28.0 mls

N = 0.2

Table 3·4·7

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% metal on the weight of acid, cobalt naphthenate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.5	0.1262	155
3	22.6	0.1262	133
6	23.1	0.1262	123
9	23.9	0.1262	107
15	24.1	0.1262	103
24	24.0	0.1262	104
44	24.2	0.1262	101
50	24.3	0.1262	99
60	24.2	0.1262	101

T_2 = 29.2 mls

N = 0.2

Table 3·4·8

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% metal on the weight of acid, co^{++} octoate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	19.9	0.1262	155
3	20.0	0.1262	153
6	20.1	0.1262	151
9	20.2	0.1262	149
15	20.8	0.1262	137
24	21.9	0.1262	115
44	22.5	0.1262	103
50	22.6	0.1262	101
60	22.6	0.1262	101

T_2 = 27.6 mls

N = 0.2

Table 3·4·9

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% metal on the weight of acid, cobalt oleate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.8	0.1262	155
3	21.0	0.1262	151
6	21.3	0.1262	145
9	21.7	0.1262	137
15	22.0	0.1262	131
21	22.5	0.1262	121
27	22.9	0.1262	113
44	23.4	0.1262	103
60	23.5	0.1262	93

T_2 = 28.5 mls

N = 0.2

Tdble 3·5·0

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% metal on the weight of acid, lead naphthenate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.60	0.1262	155
3	21.65	0.1262	154
6	21.70	0.1262	153
9	21.70	0.1262	153
15	21.75	0.1262	152
21	21.80	0.1262	151
27	21.95	0.1262	148
44	22.00	0.1262	147
52	22.60	0.1262	135
60	22.90	0.1262	129

T_2 = 29.3 mls

N = 0.2

Table 3·5·1

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, bicyclopentadinyliron

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	23.7	0.1262	155
3	24.0	0.1262	149
6	24.6	0.1262	137
9	25.0	0.1262	129
15	25.3	0.1262	123
20	25.6	0.1262	117
26	26.8	0.1262	93
44	27.6	0.1262	77
50	28.0	0.1262	68
60	28.6	0.1262	56

T_2 = 31.4 mls

N = 0.2

Table 3·5·2

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, Fe/Trilon A (oil solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.9	0.1262	163
3	21.4	0.1262	153
6	21.9	0.1262	143
9	22.1	0.1262	139
15	22.5	0.1262	131
30	22.8	0.1262	125
44	23.3	0.1262	115
50	23.7	0.1262	107
60	24.1	0.1262	99

T_2 = 29.0 mls

N = 0.2

Table 3·5·3

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, ferrous salicylate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	18.4	0.1262	157
3	19.0	0.1262	145
6	19.8	0.1262	129
9	20.2	0.1262	121
15	20.9	0.1262	107
24	21.6	0.1262	93
36	22.4	0.1262	77
48	23.3	0.1262	58
60	23.8	0.1262	48

T_2 = 26.2 mls

N = 0.2

Table 3·5·4

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% metal on the weight of acid, cobalt octoate.

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	17.4	0.1262	155
3	19.0	0.1262	123
6	20.7	0.1262	89
9	21.0	0.1262	83
15	21.8	0.1262	66
27	22.4	0.1262	54
44	23.8	0.1262	26
50	24.0	0.1262	22
60	24.4	0.1262	14

T_2 = 25.1 mls

N = 0.2

Table 3·5·5

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% metal on the weight of acid; nickelocene

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.5	0.1262	157
3	20.8	0.1262	151
6	21.0	0.1262	147
9	21.5	0.1262	137
15	21.85	0.1262	130
20	22.1	0.1262	125
26	22.5	0.1262	117
36	23.2	0.1262	103
44	22.8	0.1262	111
50	23.4	0.1262	99
60	23.8	0.1262	91

T_2 = 28.3 mls

N = 0.2

Table 3·5·6

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, ferrous octoate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.2	0.1262	157
3	20.3	0.1262	155
6	20.6	0.1262	149
9	21.4	0.1262	133
15	21.8	0.1262	125
20	22.0	0.1262	121
30	22.4	0.1262	113
44	22.8	0.1262	105
50	23.0	0.1262	101
60	23.4	0.1262	93

T_2 = 28.0 mls

N = 0.2

Table 3·5·7

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, ferrocene dicarboxylic acid

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	23.7	0.1262	155
3	24.0	0.1262	149
6	24.6	0.1262	137
9	25.0	0.1262	129
15	25.2	0.1262	125
24	25.8	0.1262	113
30	26.0	0.1262	109
44	26.6	0.1262	97
60	26.8	0.1262	93

T_2 = 31.4 mls

N = 0.2

Table 3·5·8

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.05% iron on the weight of acid, Fe/EDTA (HCl solvent)

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	21.2	0.1262	157
3	21.6	0.1262	149
6	22.0	0.1262	141
9	22.5	0.1262	131
15	22.9	0.1262	123
24	23.1	0.1262	119
30	23.6	0.1262	109
44	23.9	0.1262	103
50	24.2	0.1262	97
60	24.3	0.1262	95

T_2 = 29.0 mls

N = 0.2

Table 3·59

Changes in Iodine value of linoleic acid during autoxidation at 120^{0}C in the presence of 0.25% iron on the weight of acid, cobalt octoate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.30	0.1272	155
3	20.96	0.1262	142
9	21.36	0.1262	134
15	21.86	0.1262	124
21	22.00	0.1262	121
45	22.20	0.1262	117
60	22.30	0.1262	115
72	22.40	0.1262	113

T_2 = 28.0 mls

N = 0.2

Table 3·6·0

Changes in Iodine value of linoleic acid during autoxidation at 120^{0}C in the presence of 0.25% iron on the weight of acid, Fe/EDTA

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.25	0.1262	158
3	21.22	0.1262	138
9	21.42	0.1262	134
15	21.98	0.1262	123
24	21.72	0.1262	128
33	21.93	0.1262	124
42	22.11	0.1262	120
51	22.24	0.1262	118
60	22.50	0.1262	113
72	22.86	0.1262	105

T_2 = 28.1 mls

N = 0.2

Table 3·6·1

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.25% iron on the weight of acid, ferrocene dicarboxylic acid.

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.30	0.1262	155
3	20.82	0.1262	144
9	21.00	0.1262	141
18	21.48	0.1262	131
24	21.86	0.1262	123
36	22.11	0.1262	118
46	22.21	0.1262	116
60	22.23	0.1262	116
72	22.38	0.1262	113

T_2 = 28.0 mls
N = 0.2

Table 3·6·2

Changes in Iodine value of linoleic acid during autoxidation at 120 C in the presence of 0.25% iron on the weight of acid, ferrocene

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.42	0.1262	156
3	20.93	0.1262	146
9	21.36	0.1262	138
18	21.41	0.1262	137
21	21.92	0.1262	126
27	22.13	0.1262	122
36	22.60	0.1262	113
48	23.00	0.1262	105
60	23.12	0.1262	102
72	23.32	0.1262	98

T_2 = 28.2 mls
N = 0.2

Table 3·6·3

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.25% iron on the weight of acid , dipivaloylferrocene.

TIME (Hours)	TITRE (mls)	SAMPLE WEIGHT (g)	IODINE VALUE
0	20.41	0.1262	157
3	21.00	0.1262	145
9	21.62	0.1262	132
15	22.21	0.1262	120
24	22.86	0.1262	107
36	23.12	0.1262	102
48	24.11	0.1262	82
60	24.30	0.1262	78
72	24.86	0.1262	67

$N = 0.2$

$T_2 = 28.2$ mls

Table 3·6·4

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.25% iron on the weight of acid, monopivaloylferrocene

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.32	0.1262	156
3	20.86	0.1262	146
9	21.45	0.1262	134
15	22.00	0.1262	123
24	22.48	0.1262	113
36	22.69	0.1262	109
48	22.59	0.1262	111
60	22.95	0.1262	104
72	23.11	0.1262	100

T_2 = 28.1 mls

N = 0.2

Table 3·6·5

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.25% iron on the weight of acid, Fe/Trilon A

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.42	0.1262	156
3	20.69	0.1262	151
9	21.00	0.1262	145
18	22.00	0.1262	125
21	21.96	0.1262	125
36	22.13	0.1262	122
48	22.51	0.1262	110
60	22.80	0.1262	106
72	22.71	0.1262	106

T_2 = 28.2 mls

N = 0.2

Table 3·6·6

Changes in Iodine value of linoleic acid during autoxidation at 120°C with no additions

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.00	0.1262	155
3	28.62	0.1262	142
9	28.60	0.1262	142
15	29.00	0.1262	135
24	29.50	0.1262	125
36	29.80	0.1262	119
48	29.75	0.1262	120
60	29.62	0.1262	122
72	29.75	0.1262	120

T_2 = 35.7mls

N = 0.2

Table 3·6·7

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.25% iron on the weight of acid, ferrous stearate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.30	0.1262	155
3	21.00	0.1262	141
9	21.20	0.1262	137
15	21.50	0.1262	131
24	21.68	0.1262	129
36	22.32	0.1262	114
48	22.42	0.1262	112
60	22.51	0.1262	110
72	22.61	0.1262	108

T_2 = 28.0 mls

N = 0.2

Table 3·6·6

Changes in Iodine value of linoleic acid during autoxidation at 120°C with no additions

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	28.00	0.1262	155
3	28.62	0.1262	142
9	28.60	0.1262	142
15	29.00	0.1262	135
24	29.50	0.1262	125
36	29.80	0.1262	119
48	29.75	0.1262	120
60	29.62	0.1262	122
72	29.75	0.1262	120

T_2 = 35.7mls

N = 0.2

Table 3·6·7

Changes in Iodine value of linoleic acid during autoxidation at 120°C in the presence of 0.25% iron on the weight of acid, ferrous stearate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.30	0.1262	155
3	21.00	0.1262	141
9	21.20	0.1262	137
15	21.50	0.1262	131
24	21.68	0.1262	129
36	22.32	0.1262	114
48	22.42	0.1262	112
60	22.51	0.1262	110
72	22.61	0.1262	108

T_2 = 28.0 mls

N = 0.2

Table 3·6·8

Changes in Iodine value of linoleic acid during autoxidation at 120^{0}C in the presence of 0.25% iron on the weight of acid, cobalt stearate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.30	0.1262	155
3	21.11	0.1262	139
9	21.60	0.1262	129
15	21.70	0.1262	125
21	22.34	0.1262	114
27	22.43	0.1262	112
36	22.69	0.1262	107
48	23.00	0.1262	101
60	23.36	0.1262	93
72	23.48	0.1262	91

T_2 = 28.0 mls

N = 0.2

Table 3·6·9

Changes in Iodine value of linoleic acid during autoxidation at 120 C in the presence of 0.25% iron on the weight of acid, ferrous salicylate

TIME (Hours)	TITRE (T_1) mls	SAMPLE WEIGHT (M) gr	IODINE VALUE
0	20.25	0.1262	156
3	20.73	0.1262	146
9	21.23	0.1262	136
15	21.86	0.1262	124
18	21.92	0.1262	122
24	22.26	0.1262	115
36	22.33	0.1262	114
48	22.43	0.1262	112
60	22.62	0.1262	108
72	22.73	0.1262	106

T_2 = 28.0 mls

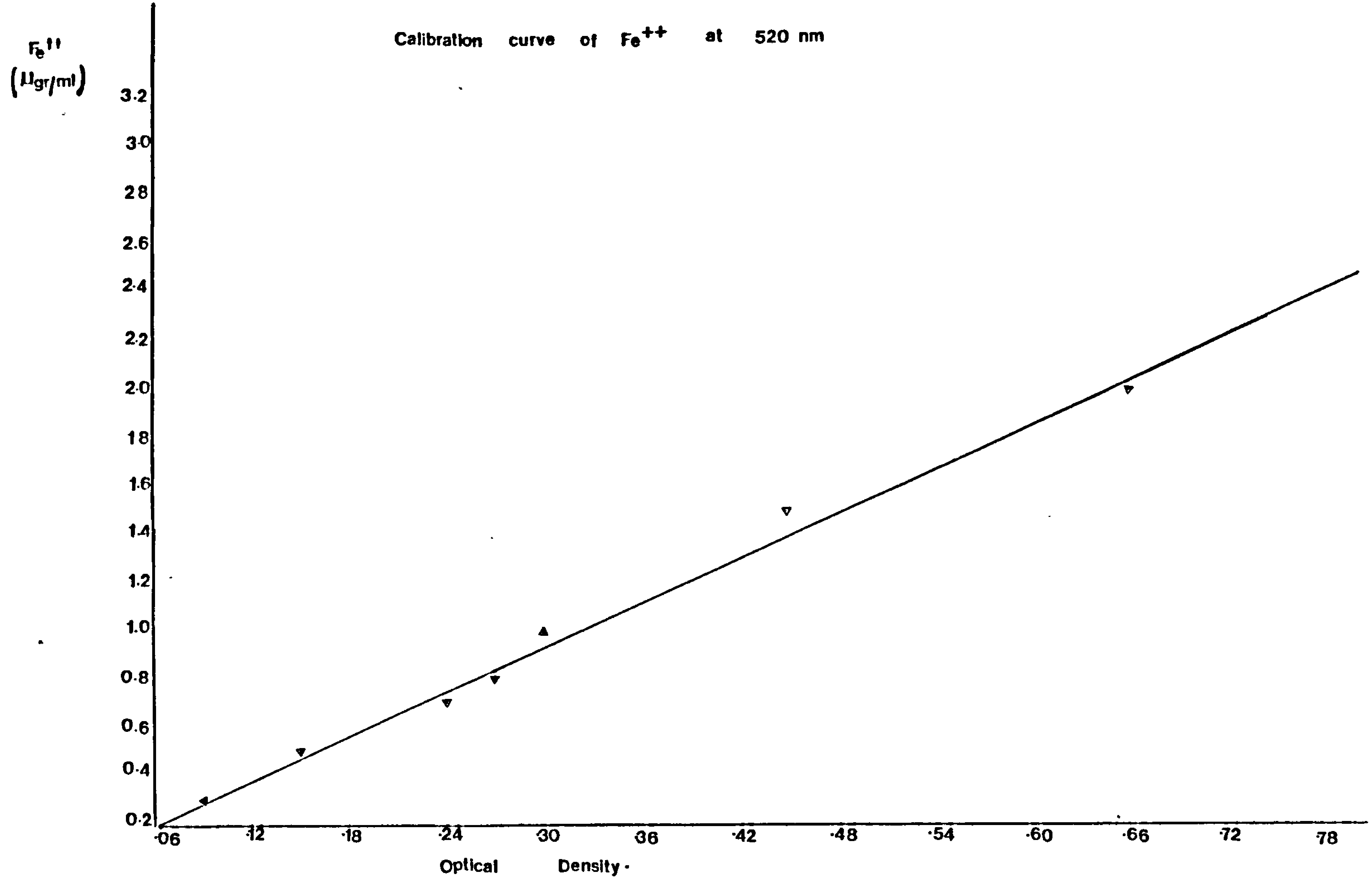
N = 0.2

Table 3·7·0

Determination of Fe^{+++} in aqueous solutions

(Standardisation of $FeCl_2$ solution) l = 520 nm

Fe^{+++} Ugr/ml	Optical Density
0.200	0.06
0.300	0.09
0.500	0.15
0.700	0.23
0.800	0.25
1.000	0.30
1.500	0.45
2.000	0.65
3.000	0.92



Calibration curve of Fe^{++} at 520 nm

Table 3·7·1

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% iron on the weight of acid, ferrous octoate.

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	15	0.490	0.145	52
3	25	0.240	0.070	43
6	25	0.442	0.12	79
24	25	0.200	0.060	36
47	25	0.442	0.120	79
53.3	25	0.430	0.950	57
70	25		0.110	76

Table 3·7·2

Changes in peroxide value of linoleic acid during autoxidation at 60°C in the presence of oxygen and 0.05% iron on the weight of acid, ferrous octoate.

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	15	0.490	1.450	52	0
3	40	1.170	0.360	333	*
6	35	0.410	0.105	102	50
24	25	0.510	0.155	91	39
47	30	0.442	0.120	94	42
53.3	25	0.500	0.150	89	37
70	35	0.485	0.145	121	69

* point omitted on graph

Table 3·7·3

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% iron on the weight of acid, ferrous stearate

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.450	0.125	80
3	35	0.286	0.085	71
6	35	0.474	0.135	118
24	35	0.200	0.060	50
47	30	0.260	0.080	55
53.3	25	0.450	0.125	80
70	35	0.498	0.147	124

Table 3·7·4

Changes in peroxide value of linoleic acid during autoxidation at 60°C in the presence of oxygen and 0.05% iron on the weight of acid, ferrous stearate

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.450	0.125	80
3	25	0.430	0.115	76
6	35	0.454	0.125	113
24	30	0.400	0.100	85
47	25	0.566	0.190	101
53.3	25	0.562	0.180	100
70	25	0.521	0.160	96

x = 50 mls
c = 0.26gr

Table 3·7·5

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% metal on the weight of acid, Fe/EDTA complex.

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.883	0.285	156	0
3	25	1.498	0.470	266	100
6	25	0.620	0.210	110	-
22	35	0.750	0.239	186	30
25	25	1.104	0.350	196	40
28	25	1.720	0.550	306	150
48	25	0.583	0.293	317	161
68	30	0.980	0.285	210	50

Table 3·7·6

Changes in peroxide value of linoleic acid during autoxidation at 60°C in the presence of oxygen and 0.05% on the weight of acid Fe/EDTA complex.

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV	
0	25	0.883	0.285	156	0	
3	25	1.580	0.500	281	125	
6	25	0.898	0.275	160	4	
22	25	1.410	0.418	251	95	
25	25	1.860	0.610	331	175	
28	50	2.000	0.650	711	555	Samples were analysed after several hours
46	50	1.720	0.550	611	455	
65	50	2.000	0.650	711	555	

Table 3·7·7

Changes in peroxide value of linoleic acid during autoxidation at 80°C in the presence of oxygen and 0.05% iron the weight of acid, Fe/EDTA complex.

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.883	0.285	156	0
3	25	1.350	0.425	240	84
6	25	0.720	0.225	128	*
9	25	1.340	0.419	238	82
25	25	2.260	0.740	401	245
46	25	2.260	0.740	401	245
65	25	2.260	0.740	401	245

Table 3·7·8

Changes in peroxide value of linoleic acid during autoxidation at 120°C in the presence of oxygen and 0.05% iron on the weight of acid, Fe/EDTA complex

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.883	0.285	156	0
3	30	1.370	0.435	292	136
6	30	1.150	0.351	245	89
22	30	1.850	0.590	394	238
25	40	1.011	0.321	287	131
46	35	1.530	0.485	381	225
65	35	1.630	0.520	406	250

Table 3·7·9

Changes in peroxide value of linoleic acid during autoxidation at 80°C in the presence of oxygen and 0.05% iron on the weight of acid, ferrous stearate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.450	0.125	80
3	25	0.232	0.080	41
6	35	0.481	0.140	120
24	25	0.232	0.080	41
47	25	0.462	0.130	82
53.33	25	0.464	0.132	83
70	25	0.472	0.136	84

Table 3·8·0

Changes in peroxide value of linoleic acid during autoxidation at 120°C in the presence of oxygen and 0.05% iron on the weight of acid, ferrous stearate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.425	0.125	80	0
3	35	0.432	0.116	108	28
6	35	0.440	0.117	109	29
24	35	0.450	0.118	112	32
47	35	0.470	0.119	117	37
53.3	35	0.632	0.210	157	77
70	35	0.698	0.220	174	94

Table 3·8·1

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% iron on the weight of acid, ferrocene dicarboxylic acid

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	10	2.580	0.800	183
3	10	0.568	0.180	40
5	20	1.370	0.430	195
21	20	1.440	0.451	204
26	25	0.993	0.291	176
44	25	1.095	0.323	195
68	25	1.350	0.420	240
72	25	1.022	0.311	182

Table 3·8·2

Changes in peroxide value of linoleic acid during autoxidation at 80^{0}C in the presence of oxygen and 0.05% iron on the weight of acid, ferrocene dicarboxylic acid

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	10	2.580	0.800	183	0
3	10	1.330	0.415	95	-
5	10	1.980	0.610	141	-
21	25	1.460	0.460	259	76
26	25	2.970	0.910	528	345
44	25	2.810	0.868	499	316
68	45	1.710	0.545	547	364
72	45	2.000	0.615	640	457

Table 3·8·3

Changes in peroxide value of linoleic acid during autoxidation at 60^{0}C in the presence of oxygen and 0.05% iron on the weight of acid . ferrocene dicarboxylic acid

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	10	2.580	0.800	183	0
3	20	2.070	0.670	294	111
5	30	1.230	0.380	262	79
21	25	2.580	0.800	458	275
26	25	1.200	0.371	213	30
44	25	0.804	0.258	143	*
68	25	1.720	0.550	306	123
72	25	1.820	0.620	324	141

Table 3·8·4

Changes in peroxide value of linoleic acid during autoxidation at 120^{0}C in the pr-sence of oxygen and 0.05% iron on the weight of acid . ferrocene dicarboxylic acid

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	10	2.580	0.800	183	0
3	10	1.580	0.500	112	-
5	25	1.498	0.468	266	83
21	25	1.500	0.486	266	83
26	25	1.630	0.524	290	107
44	25	1.820	0.544	323	140
68	30	1.830	0.584	390	207
72	30	1.850	0.590	395	212

Table 3·8·5

Changes in peroxide value of linoleic acid during autoxidation at 80°C in the presence of oxygen and 0.05% iron on the weight of acid monopivaloylferrocene

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	35	0.200	0.100	50	0
3	35	0.740	0.235	184	134
19	35	0.600	0.196	149	99
25	35	1.395	0.385	347	297
46	35	1.420	0.410	353	303
60	35	1.595	0.420	397	347

Table 3·8·5

Changes in peroxide value of linoleic acid during autoxidation at 120°C in the presence of oxygen and 0.05% iron on the weight of acid monopivaloylferrocene

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	35	0.200	0.100	50	0
3	35	0.395	0.195	98	48
19	35	0.800	0.250	199	149
25	35	0.201	0.051	5o	*
46	35	0.695	0.221	173	123
60	35	1.100	0.320	274	224

Table 3·8·6

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% iron on the weight of acid dipivaloylferrocene

x = 50 ml
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.220	0.110	39	0
3	15	0.440	0.130	47	8
19	35	0.200	0.060	50	11
25	25	0.460	0.165	82	43
46	30	0.440	0.126	94	55
60	35	0.350	0.134	87	48

Table 3·8·7

Changes in peroxide value of linoleic acid during autoxidation at 60°C in the presence of oxygen and 0.05% iron on the weight of acid dipaloylferrocene

x = 50 ml
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.220	0.110	39	0
3	30	0.200	0.105	43	4
19	35	3.040	0.930	756	717
25	25	1.130	0.380	201	162
46	35	1.200	0.370	299	260
60	35	1.320	0.410	328	289

Table 3·8·8

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and equal weights (0.05%) mono- and dipivaloylferrocene

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	35	0.300	0.09	75	0
3	30	0.480	0.14	102	27
19	25	0.248	0.08	44	-
25	25	0.502	0.15	89	14
46	30	0.462	0.13	99	24
60	30	0.480	0.14	102	27

Table 3·8·9

Changes in peroxide value of linoleic acid during autoxidation at 60°C in the presence of oxygen and equal weights of metal (0.05%) mono- and dipivaloylferrocene

x = 50 mls
c = 0.126 gr.

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	35	0.300	0.09	75	0
3	25	0.542	0.17	96	21
19	35	1.100	0.35	274	199
25	25	2.000	0.65	355	280
46	30	1.880	0.61	400	325
60	30	1.520	0.48	324	249

Table 3·9·0

Changes in peroxide value of linoleic acid during autoxidation at 80^{0}C in the presence of oxygen and equal weights of metal (0.05%) mono- and dipivaloylferrocene

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	35	0.300	0.090	75	0
3	35	0.424	0.115	106	31
19	35	0.582	0.190	145	70
46	25	0.620	0.182	110	35
60	35	0.655	2.000	163	88

Table 3·9·1

Changes in peroxide value of linoleic acid during autoxidation at 120 C in the presence of oxygen and equal weights (0.05%) metal mono- and dipivaloylferrocene

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	35	0.300	0.09	75	0
3	35	0.630	0.21	157	82
19	35	0.931	0.29	232	157
25	25	1.000	0.30	178	103
46	25	0.720	0.23	128	53
60	30	0.850	0.28	181	106

Table 3·9·2

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% iron on the weight of acid monopivaloylferrocene

x = 50 mls

TIME (Hours)	C (gr)	D (ml)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	0.126	35	0.200	0.100	50	0
3	0.126	35	0.527	0.175	131	81
19	0.126	35	0.240	0.110	60	10*
25	0.126	25	0.840	0.260	149	99
46	0.126	40	0.560	0.190	159	109
60	0.126	40	0.580	0.196	165	115

Table 3·9·3

Changes in peroxide value of linoleic acid during autoxidation at 60°C in the presence of oxygen and 0.05% iron on the weight of acid monopivaloylferrocene

x = 50 mls

TIME (Hours)	C (gr)	D (ml)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	0.126	35	0.200	0.100	50	0
3	0.126	25	0.780	0.245	139	89
19	0.126	25	1.090	0.325	194	144
25	0.126	25	1.500	0.430	267	217
46	0.126	40	2.000	0.550	569	519
60	0.126	40	2.500	0.580	711	661

Table 3·9·4

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% metal on the weight of acid, nickel octoate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.252	0.080	45
3	25	0.200	0.060	36
6	35	0.252	0.080	63
23	35	0.240	0.070	60
27	35	0.300	0.090	75
46	25	1.332	0.410	237
52	35	1.230	0.375	306

Table 3·9·5

Changes in peroxide value of linoleic acid during autoxidation at 60°C in the presence of oxygen and 0.05% metal on the weight of acid, nickel octoate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.252	0.080	45
3	25	0.200	0.060	36
6	25	0.323	0.100	57
23	25	0.442	0.120	79
27	40	0.200	0.060	57
47	40	0.194	0.500	55
52	25	1.340	0.440	238

Table 3·9·6

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% metal on the weight of compound Fe/Trilon A complex

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	1.200	0.370	213
3	25	2.110	0.695	375
6	25	1.150	0.360	204
22	25	1.000	0.300	178
25	25	1.720	0.550	306
46	35	1.010	0.310	251
65	35	1.050	0.321	261

Table 3·9·7

Changes in peroxide value of linoleic acid during autoxidation at 60°C in the presence of oxygen and 0.05% metal on the weight of compound Fe/Trilon A

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	1.200	0.370	213
3	20	1.870	0.600	266
6	25	1.150	0.360	204
22	25	1.520	0.480	213
25	30	1.530	0.482	326
28	30	3.030	0.930	646
46	30	2.000	0.650	426
65	30	2.770	0.850	591

Table 3·9·8

Changes in peroxide value of linoleic acid during autoxidation at 80^{0}C in the presence of oxygen and 0.05% iron on the weight of acid ferrous salicylate

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	35	0.330	0.100	82
3	25	1.230	0.380	219
6	45	0.200	0.06	64
22	25	0.500	0.150	124
28	25	0.460	0.130	89
48	35	0.425	0.115	106
51	45	0.300	0.090	96
71.5	45	0.220	0.075	70

Table 3·9·9

Changes in peroxide value of linoleic acid during autoxidation at 120^{0}C in the presence of oxygen and 0.05% iron on the weight of acid ferrous salicylate

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	35	0.330	0.100	82
3	10	1.170	0.360	83
22	35	0.263	0.080	65
28	45	0.200	0.060	64
48	45	0.460	0.130	147
51	45	0.315	0.095	101
71.2	55	0.230	0.078	90

Table 4·0·0

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% iron on the weight of acid ferrous salicylate

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	35	0.330	0.100	82
3	45	0.263	0.080	84
6	45	0.200	0.060	64
22	35	0.263	0.080	66
28	35	0.343	0.115	85
48	35	0.422	0.110	105
51	55	0.315	0.095	123
71.5	35	0.294	0.085	73

Table 4·1·0

Changes in peroxide value of linoleic acid during autoxidation at 60^{0}C in the presence of O_2 and 0.05% iron on the weight of acid, ferrous salicylate

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	35	0.330	0.100	82
3	25	0.330	0.100	82
6	40	0.200	0.055	57
22	25	0.452	0.125	80
28	35	0.430	0.112	106
48	35	0.440	0.140	109
51	35	0.410	0.104	102
71.5	35	0.420	0.111	105

Table 4·1·1

Changes in peroxide value of linoleic acid during autoxidation at 80^0C in the presence of oxygen and 0.05% iron on the weight of acid, - (ferrous octoate)

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	15	0.490	0.145	52
3	30	0.450	0.125	96
6	25	0.300	0.090	53
24	25	0.240	0.070	43
47	25	0.569	0.186	101
53.33	30	0.300	0.090	54
70	35	0.318	0.095	79

Table 4·1·2

Changes in peroxide value of linoleic acid during autoxidation at 120^0C in the presence of oxygen and 0.05% iron on the weight of acid, - (ferrous octoate)

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	15	0.490	0.145	52
3	25	0.562	0.180	100
6	35	0.400	0.102	100
24	30	0.212	0.065	45
47	30	0.481	0.140	103
53.33	30	0.450	0.125	100
70	30	0.300	0.090	64

Table 4·1·3

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% metal on the weight of acid ferrocene

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.420	0.120	75
3	25	0.428	0.125	76
6	45	0.200	0.060	57
22	35	0.312	0.095	78
28	45	0.263	0.080	84
48	45	0.232	0.110	74
51	35	0.503	0.150	125
71.5	35	0.467	0.135	116

Table 4·1·4

Changes in peroxide value of linoleic acid during autoxidation at 60^{0}C in the presence of oxygen and 0.05% metal on the weight of acid, cobalt octoate

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.420	0.120	75
3	25	0.525	0.174	93
6	35	0.260	0.080	65
22	35	0.263	0.083	65
28	45	0.230	0.100	74
48	45	0.503	0.150	161
51	45	0.405	0.105	130
71.5	45	0.230	0.100	74

Table 4·1·5

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% metal on the weight of acid (nickelocene)

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.442	0.120	75
3	10	1.200	0.350	85
6	30	0.461	0.130	93
24	45	0.212	0.065	68
47	40	0.518	0.158	110
53.33	35	0.312	0.095	78
70	50	0.200	0.060	71

Table 4·1·6

Changes in peroxide value of linoleic acid during autoxidation at 60°C in the presence of oxygen and 0.05% metal on the weight of acid (nickelocene)

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.442	0.120	79	0
3	10	1.200	0.350	85	6
6	25	0.531	0.165	94	*15
24	35	0.542	0.170	135	56
47	25	0.750	0.238	133	54
53.33	30	0.561	0.180	120	41
70	35	0.568	0.185	141	62

Table 4·1·7

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% metal on the weight of acid - cobalt stearate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.240	0.075	43
3	25	0.247	0.080	44
6	25	0.247	0.080	44
23	25	0.301	0.091	54
27	30	1.480	0.468	263
47	50	2.000	0.650	711
52	55	1.520	0.480	594

Bath overheated

Table 4·1·8

Changes in peroxide value of linoleic acid during autoxidation at 60 C in the presence of oxygen and 0.05% metal on the weight of acid · cobalt stearate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.240	0.075	43	0
3	25	0.310	0.093	55	12
6	25	0.320	0.098	57	14
27	30	0.625	0.200	133	90
47	25	1.230	0.340	219	176
52	35	1.590	0.525	396	353

Table 4·1·9

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% metal on the weight of acid, nickel stearate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.300	0.090	53
3	15	0.260	0.080	28
6	15	0.200	0.060	21
23	25	0.195	0.050	35
27	25	0.500	0.150	89
47	25	1.048	0.310	186
52	55	0.804	0.260	313

Table 4·2·0

Changes in peroxide value of linoleic acid during autoxidation at 60°C in the presence of oxygen and 0.05% metal on the weight of acid, nickel stearate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.300	0.090	53	0
6	25	0.644	0.195	114	61
23	25	0.481	0.125	86	33
27	25	1.220	0.295	217	164
47	25	3.040	0.960	540	487
52	35	2.230	0.710	396	343

Table 4·2·1

Changes in peroxide value of linoleic acid during autoxidation at 80 C in the presence of oxygen and 0.05% metal on the weight of acid, cobalt stearate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.240	0.075	43	0
3	25	0.200	0.060	36	
6	25	0.300	0.090	53	10
23	25	0.322	0.100	57	14
27	25	0.463	0.130	82	39
47	25	1.520	0.480	270	227 *
52	25	1.320	0.420	235	152

Table 4·2·2

Changes in peroxide value of linoleic acid during autoxidation at 120°C in the presence of oxygen and 0.05% metal on the weight of acid, cobalt stearate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.240	0.075	43
3	25	0.200	0.060	36
27	25	0.530	0.160	94
47	25	0.690	0.220	123
52	25	1.290	0.400	229

Table 4·2·3

Changes in peroxide value of linoleic acid during autoxidation at 80°C in the presence of oxygen and 0.05% metal on the weight of acid, nickelocene

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.442	0.120	79	0
3	25	0.430	0.110	76	0
6	45	0.300	0.090	96	17
24	35	0.410	0.104	102	23
47	35	0.623	0.197	111	32
53.33	30	0.460	0.130	98	-
70	35	0.440	0.120	109	30

Table 4·2·4

Changes in peroxide value of linoleic acid during autoxidation at 120°C in the presence of oxygen and 0.05% metal on the weight of acid, nickelocene

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.442	0.120	79
3	25	0.481	0.140	86
6	35	0.312	0.095	78
24	25	0.208	0.070	37
47	25	0.521	0.160	93
53.3	25	0.323	0.100	57
70	25	0.403	0.105	72

Table 4·2·5

Changes in peroxide value of linoleic acid during autoxidation at 80°C in the presence of oxygen and 0.05% metal on the weight of acid, nickel stearate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.300	0.090	53	0
3	35	0.230	0.080	41	-
6	25	0.501	0.155	89	36
23	25	0.223	0.070	40	-
27	25	0.524	0.160	93	40
47	25	1.580	0.500	281	228
52	35	1.280	0.400	318	265

Table 4·2·6

Changes in peroxide value of linoleic acid during autoxidation at 120°C in the presence of oxygen and 0.05% metal on the weight of acid, nickel stearate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.
0	25	0.300	0.090	53
6	25	0.200	0.060	36
27	25	0.432	0.130	77
47	25	0.129	0.401	23
52	35	0.110	0.310	27

Table 4·2·7

Changes in peroxide value of linoleic acid during autoxidation at 80°C in the presence of oxygen and 0.05% metal on the weight of acid, nickel octoate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.252	0.080	45	0
6	25	0.444	0.125	79	34
27	25	0.563	0.185	100	55
47	25	1.580	0.500	281	236
52	25	1.310	0.440	233	188

Table 4·2·8

Changes in peroxide value of linoleic acid during autoxidation at 120°C in the presence of oxygen and 0.05% metal on the weight of acid; nickel octoate

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	0.252	0.080	45	0
6	35	0.200	0.060	50	5
27	35	0.543	0.160	135	90
47	25	1.220	0.365	217	172
52	45	1.120	0.340	358	313

Table 4·2·9

Changes in peroxide value of linoleic acid during autoxidation at 80^{0}C in the presence of oxygen and 0.05% iron on the weight of acid, ferrocene dicyclopentadiene

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	10	1.000	0.300	71	0
3	10	2.370	0.775	168	97
5	20	1.420	0.451	202	131
21	30	1.060	0.320	225	155
26	35	0.698	0.220	174	103
44	25	0.631	0.200	112	41
68	25	0.720	0.230	128	57
72	25	-	-	-	

* solution on cooling turned colourless

Table 4·3·0

Changes in peroxid value of linoleic acid during autoxidation at 120^{0}C in the presence of oxygen and 0.05% iron on the weight of acid, ferrocene dicyclopentadiene (HCl solvent)

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	10	1.100	0.300	71	0
3	10	1.104	0.350	79	8
21	25	0.800	0.250	142	71
26	25	0.631	0.200	112	41
44	25	0.498	0.148	88	17
68	25	1.300	0.410	231	160
72	25	1.380	0.430	245	174

Table 4·3·1

Changes in peroxide value of linoleic acid during autoxidation at 80^{0}C in the presence of oxygen and 0.05% iron on the weight of acid, dipivaloylferrocene

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	35	0.200	0.100	50	0
3	35	0.480	0.140	119	69
19	25	1.080	0.320	192	142
25	25	1.170	0.360	208	158
46	40	0.502	0.150	143	93
60	40	1.060	0.320	301	251

Table 4·3·2

Changes in peroxide value of linoleic acid during autoxidation at 120^{0}C in the presence of oxygen and 0.05% iron on the weight of acid, dipivaloylferrocene

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV	
0	35	0.200	0.100	50	0	
3	35	0.561	0.180	140	90	
19	35	0.862	0.270	214	164	
25	35	0.421	0.110	105	55	*
46	35	0.648	0.210	115	65	*
60	35	1.060	0.320	264	214	

Table 4·3·3

Changes in peroxide value of linoleic acid during autoxidation at room temperature in the presence of oxygen and 0.05% iron on the weight of acid, ferrocene dicyclopentadient

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	10	1.000	0.300	71	0
3	10	0.698	0.220	50	-
5	20	1.170	0.331	166	95
21	25	0.520	0.158	92	21
26	25	0.492	0.138	84	13
44	25	0.832	0.280	148	77
68	25	1.250	0.394	222	151

Table 4·3·4

Changes in peroxide value of linoleic acid during autoxidation at 120^{0}C in the presence of oxygen and 0.05% iron on the weight of acid, ferrocene dicyclopentadiene

x = 50 mls
c = 0.126 gr

TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	10	1.000	0.300	71	0
3	10	1.500	0.475	107	36
5	10	1.430	0.450	102	31
21	25	2.000	0.650	355	284
26	25	1.500	0.475	267	196 *
44	25	1.720	0.552	306	235
68	25	3.040	0.931	540	469
72	25	1.720	0.552	306	239 *

Table 4·3·5

Changes in peroxide value of linoleic acid during autoxidation at 80^{0}C in the presence of oxygen and 0.05% metal on the weight of acid,- Fe/Trilon A

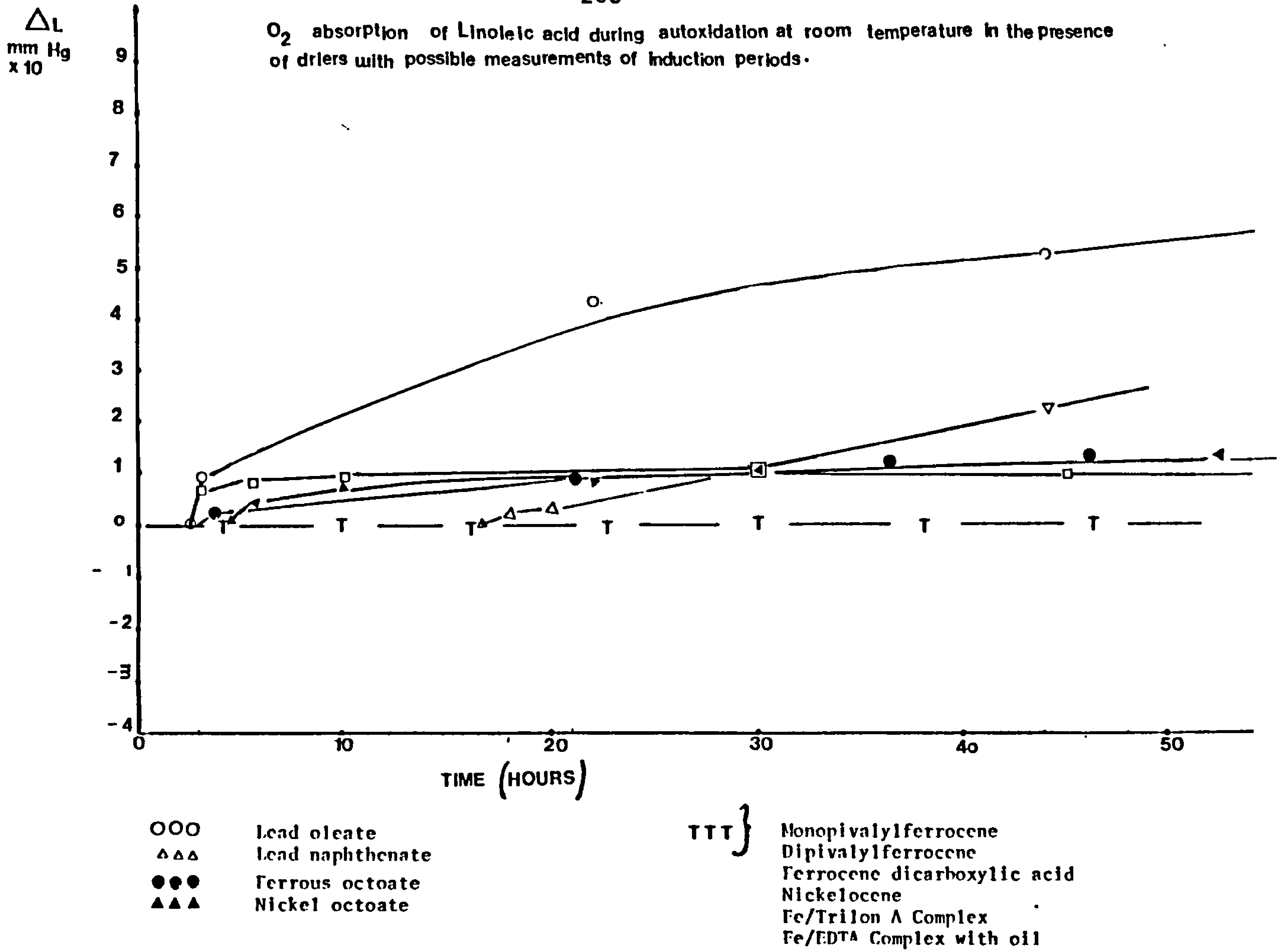
TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	1.200	0.370	213	0
3	25	1.750	0.560	311	98
6	40	0.840	0.260	239	26
22	35	1.350	0.418	323	110
25	25	2.970	0.900	528	315
28	30	2.770	0.850	591	378
46	40	1.450	0.450	412	199
65	40	1.680	0.540	478	265

Table 4·3·6

Changes in peroxide value of linoleic acid during autoxidation at 120^{0}C in the presence of oxygen and 0.05% metal on the weight of acid, Fe/Trilon A complex

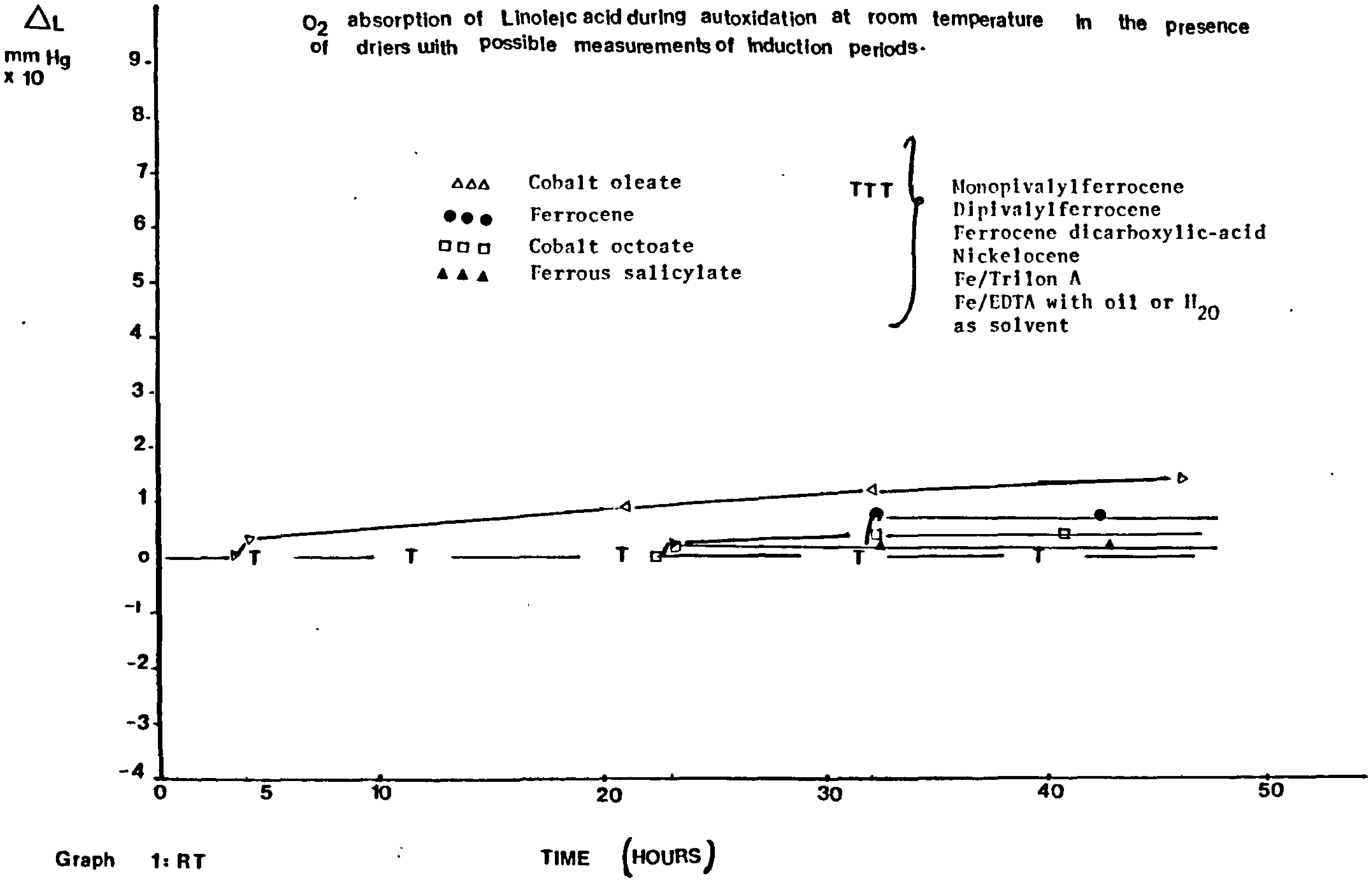
TIME (Hours)	D (mls)	Fe^{+++} (Ugr/ml)	O.D.	P.V.	ΔPV
0	25	1.200	0.370	213	0
3	25	1.230	0.375	219	6
6	35	1.010	0.305	251	38
22	40	1.230	0.375	350	137
25	40	1.220	0.340	347	134
46	40	1.750	0.530	498	285
65	40	1.580	0.500	449	236

Graph 2 : RT

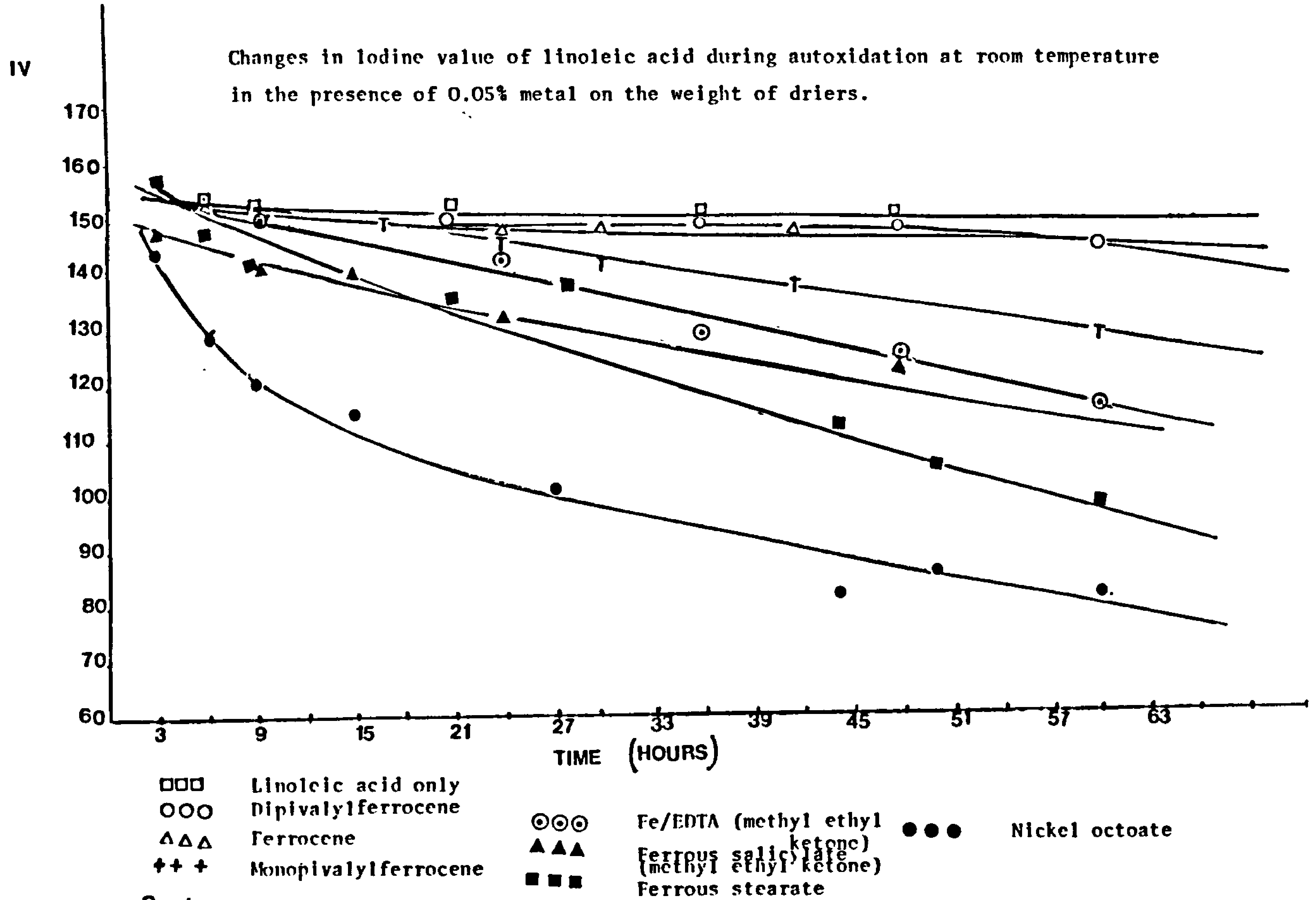


O_2 absorption of Linoleic acid during autoxidation at room temperature in the presence of driers with possible measurements of induction periods.

O_2 absorption of Linoleic acid during autoxidation at room temperature in the presence of driers with possible measurements of induction periods.



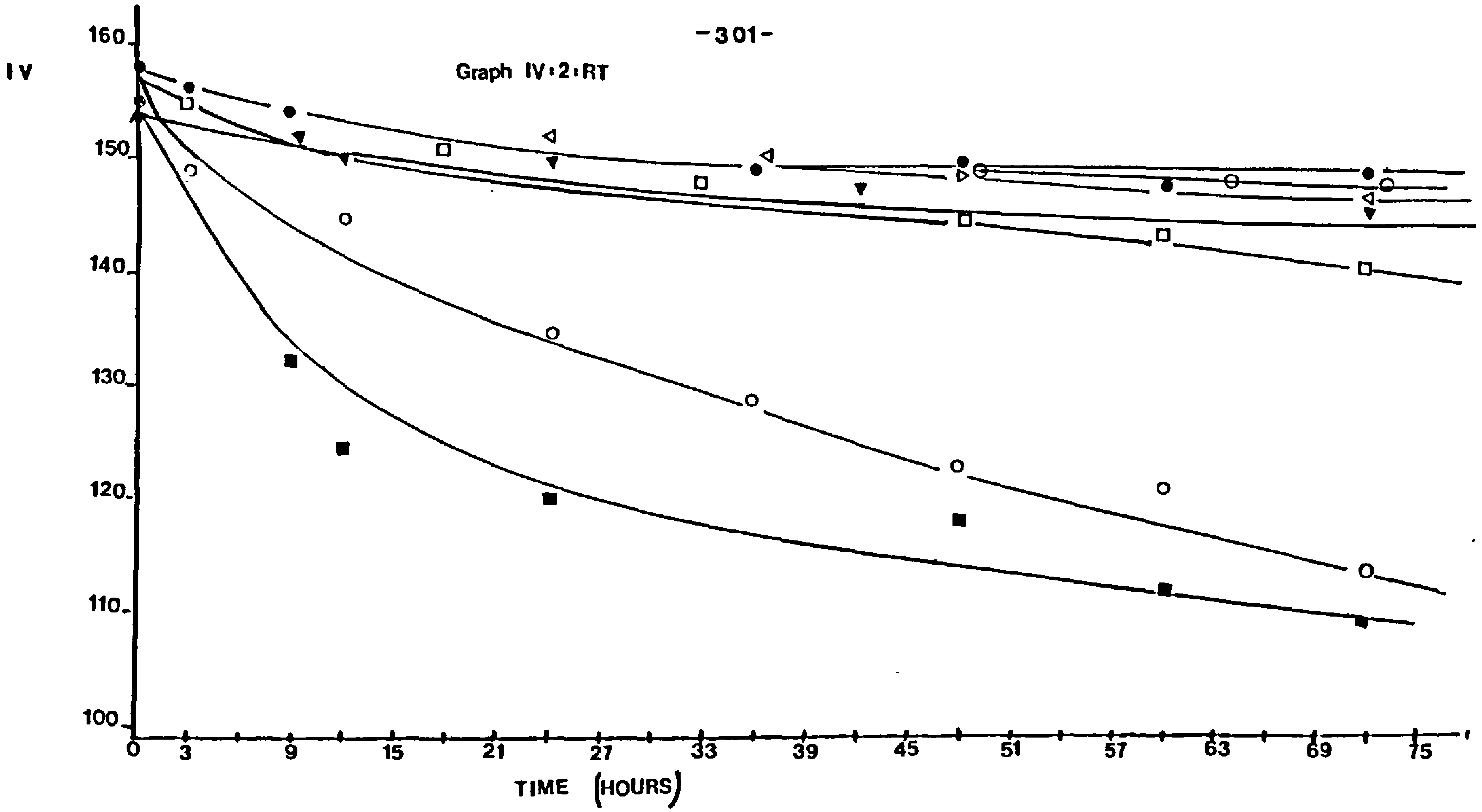
Graph 1: RT



Changes in Iodine value of linoleic acid during autoxidation at room temperature in the presence of 0.05% metal on the weight of driers.

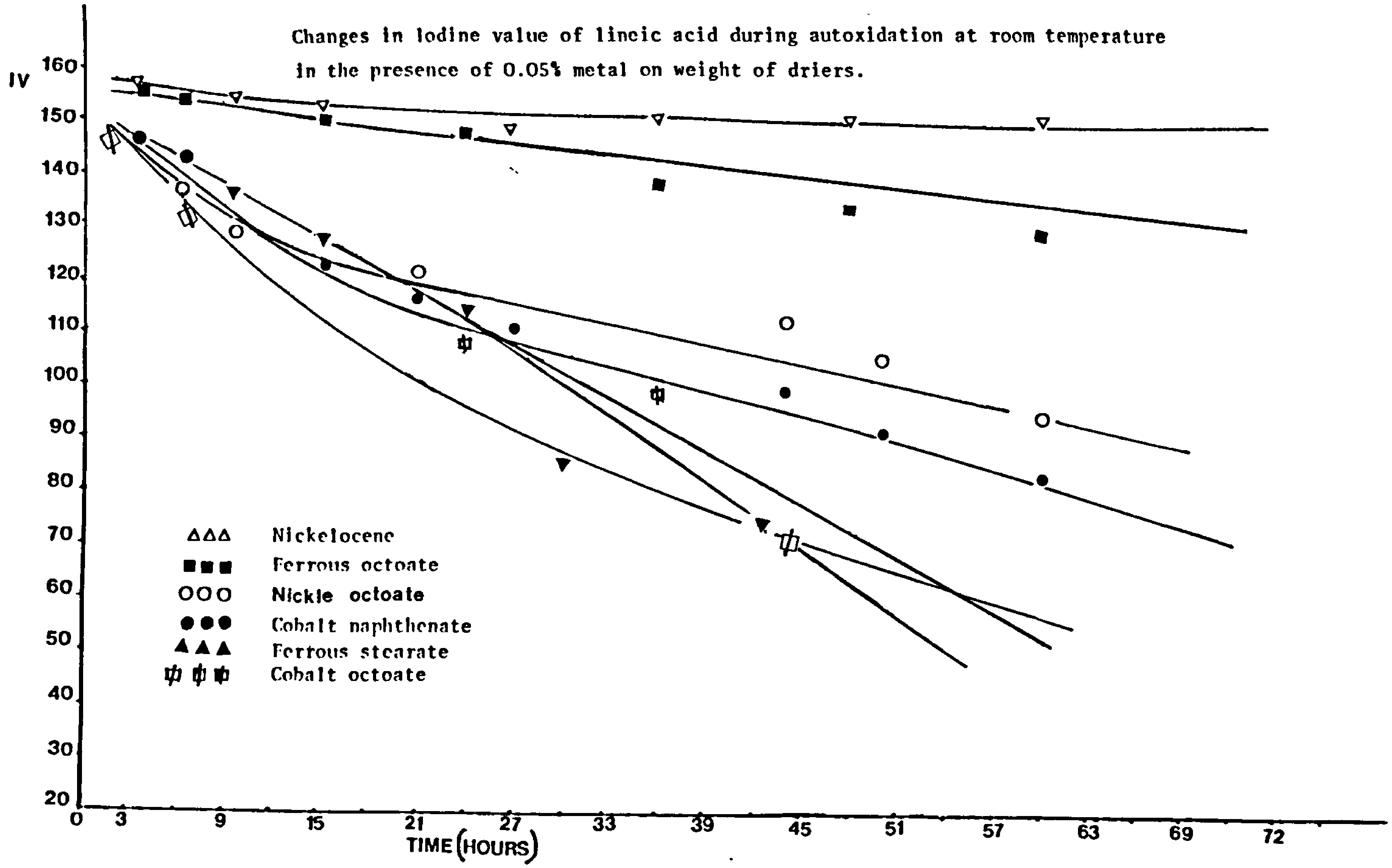
Graph IV:1:RT

Graph IV:2:RT



CATALYTIC EFFICIENCY OF SOME DRIERS [0·25% METAL] AT ROOM TEMPERATURE·

▲▲▲ Ferrous stearate
●●● Linoleic acid only
▽△▽ Ferrous salicylate
○○○ Ferrocene dicarboxylic acid
□□□ Cobalt octoate
○○○ Monopivalylferrocene
■■■ Cobalt stearate

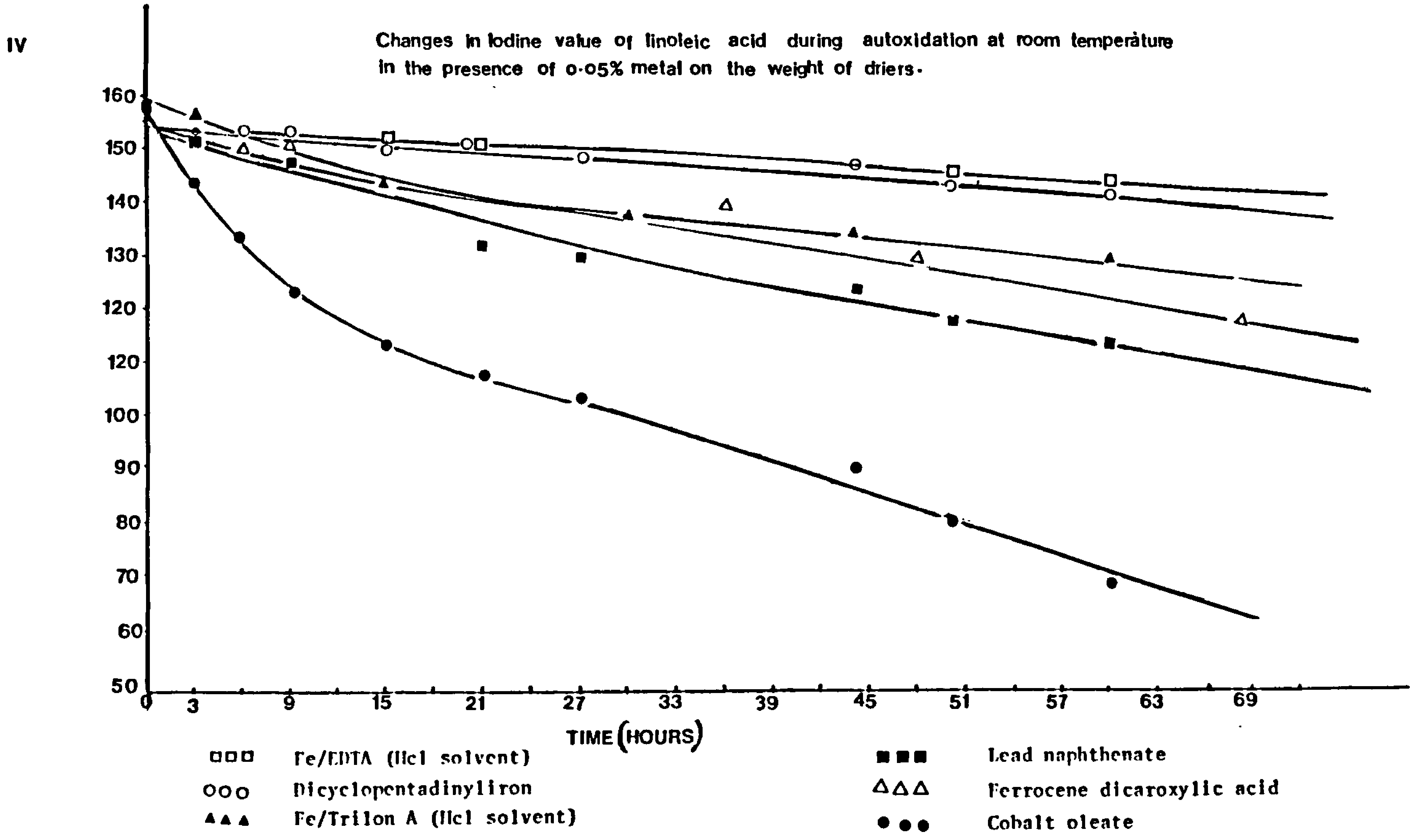


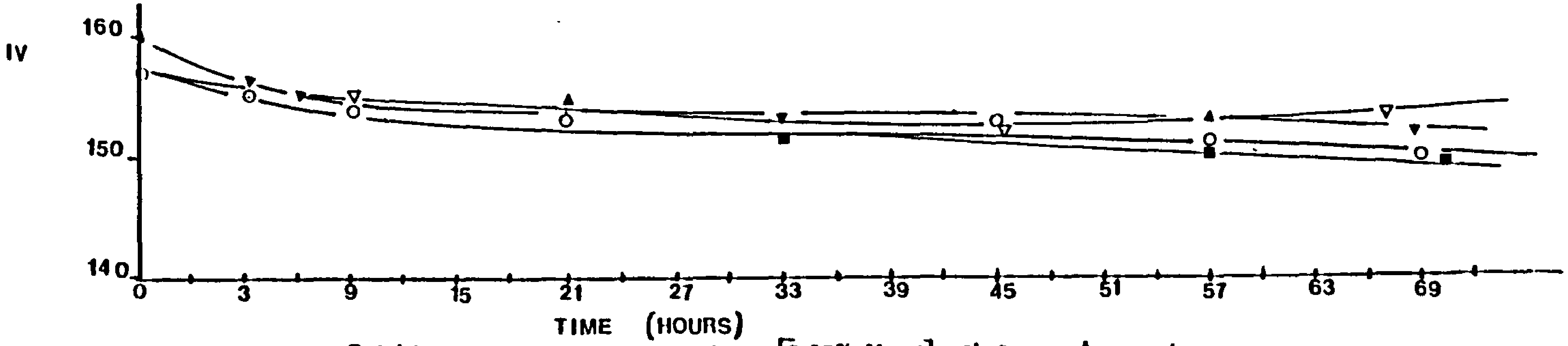
Changes in iodine value of lineic acid during autoxidation at room temperature in the presence of 0.05% metal on weight of driers.

Graph IV:3 ,RT

Graph IV: 4 :RT

Changes in iodine value of linoleic acid during autoxidation at room temperature in the presence of 0·05% metal on the weight of driers.





Catalytic efficiency of some driers [0·25% Metal] at room temperature·

△△△ Fe/Trilon A Complex

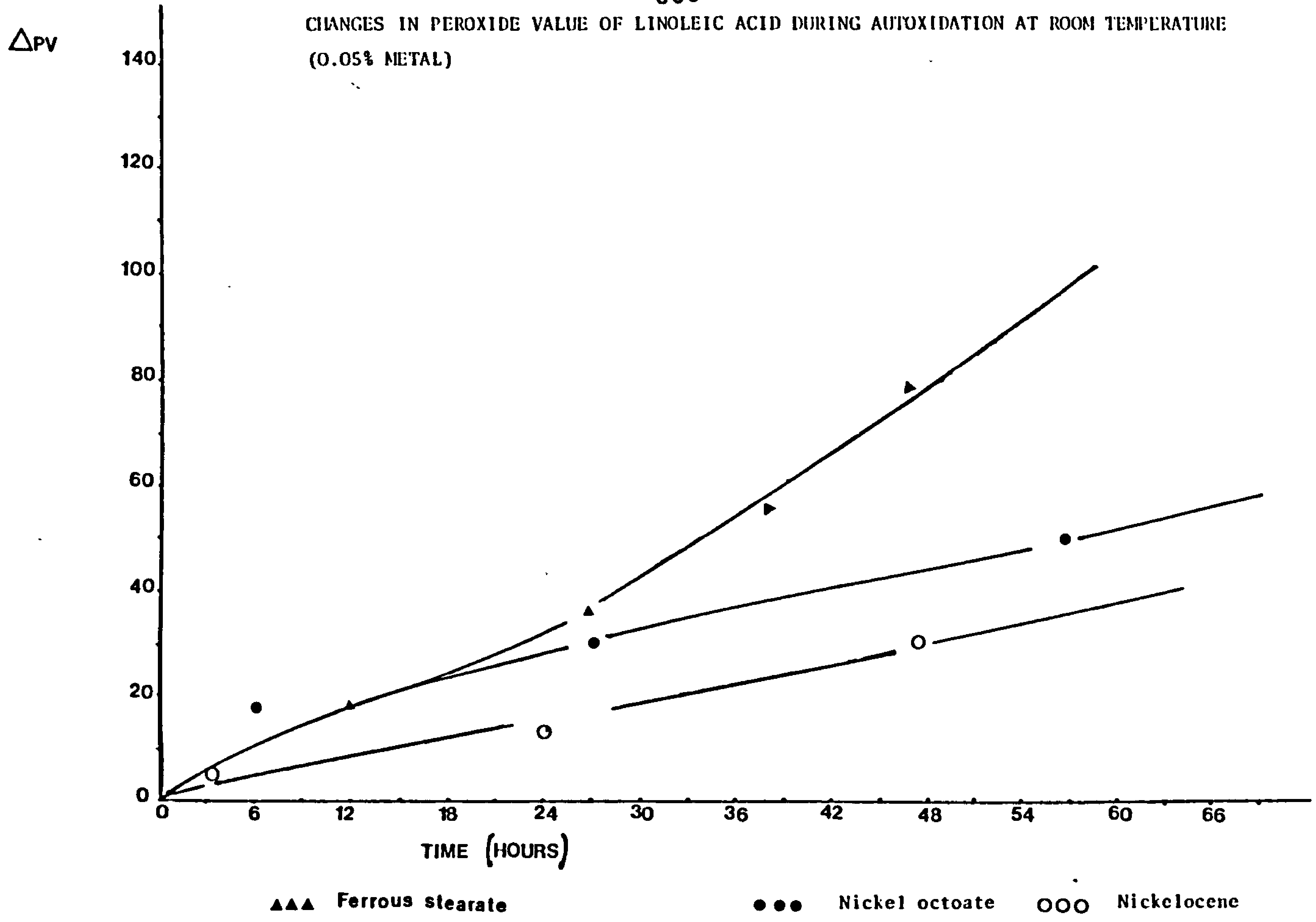
▲▲▲ Fe/EDTA Complex

○○○ Ferrocene dicarboxylic acid and ferrocene respectively

■■■ Dipivalyferrocene

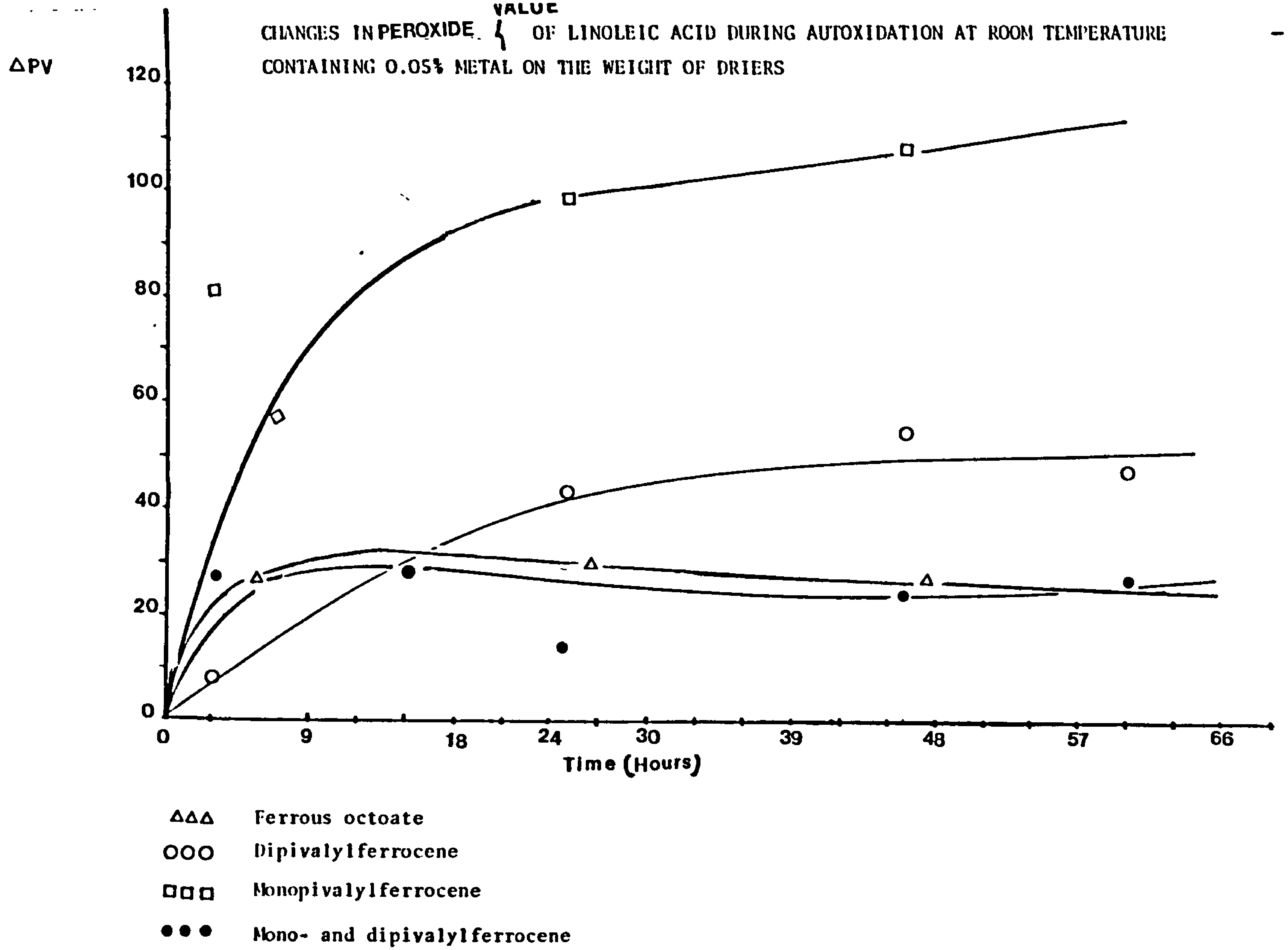
Graph IV·5·RT·

CHANGES IN PEROXIDE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT ROOM TEMPERATURE
(0.05% METAL)



Graph PV:1.RT

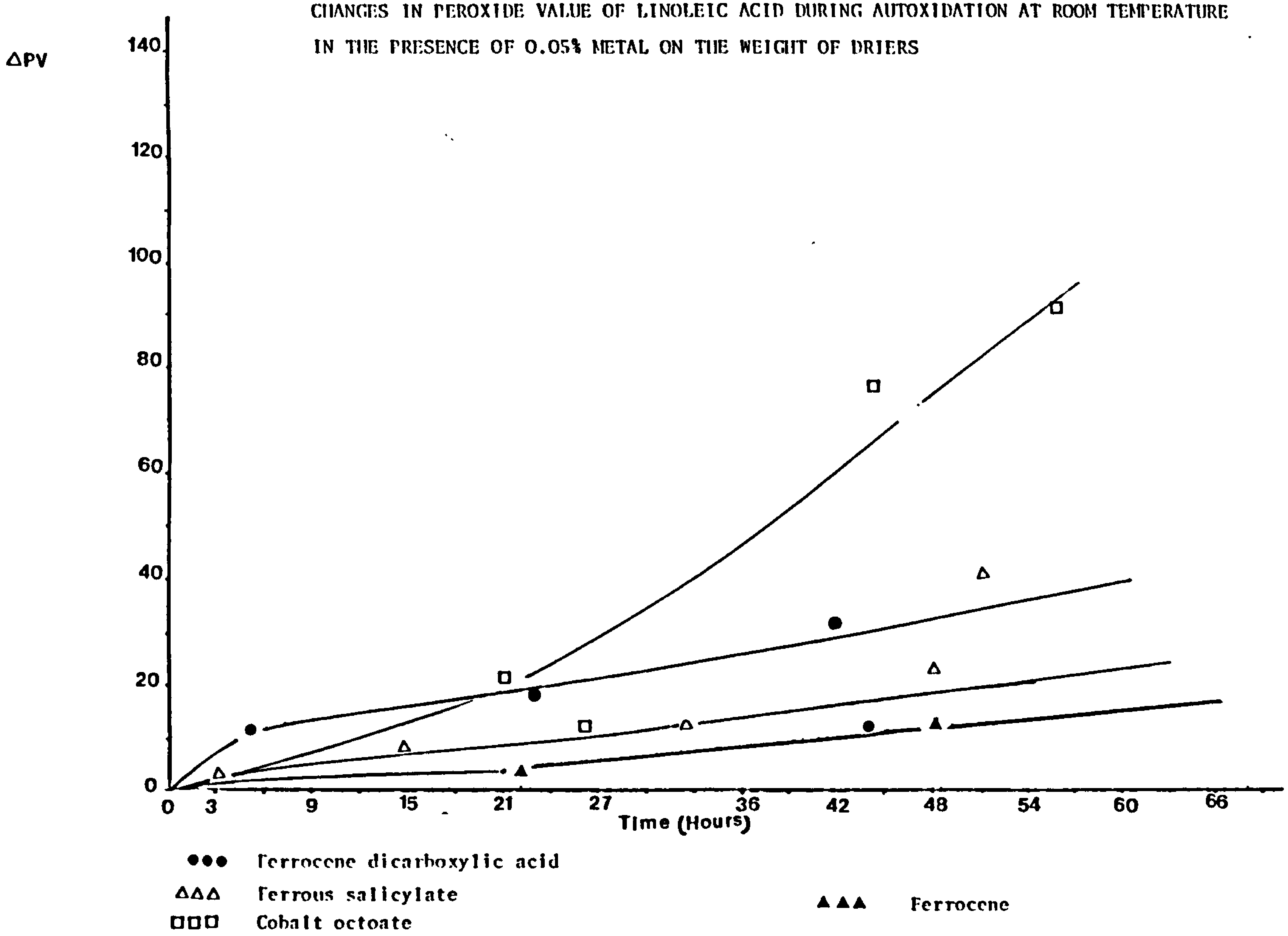
CHANGES IN PEROXIDE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT ROOM TEMPERATURE CONTAINING 0.05% METAL ON THE WEIGHT OF DRIERS



Graph PV:2:RT

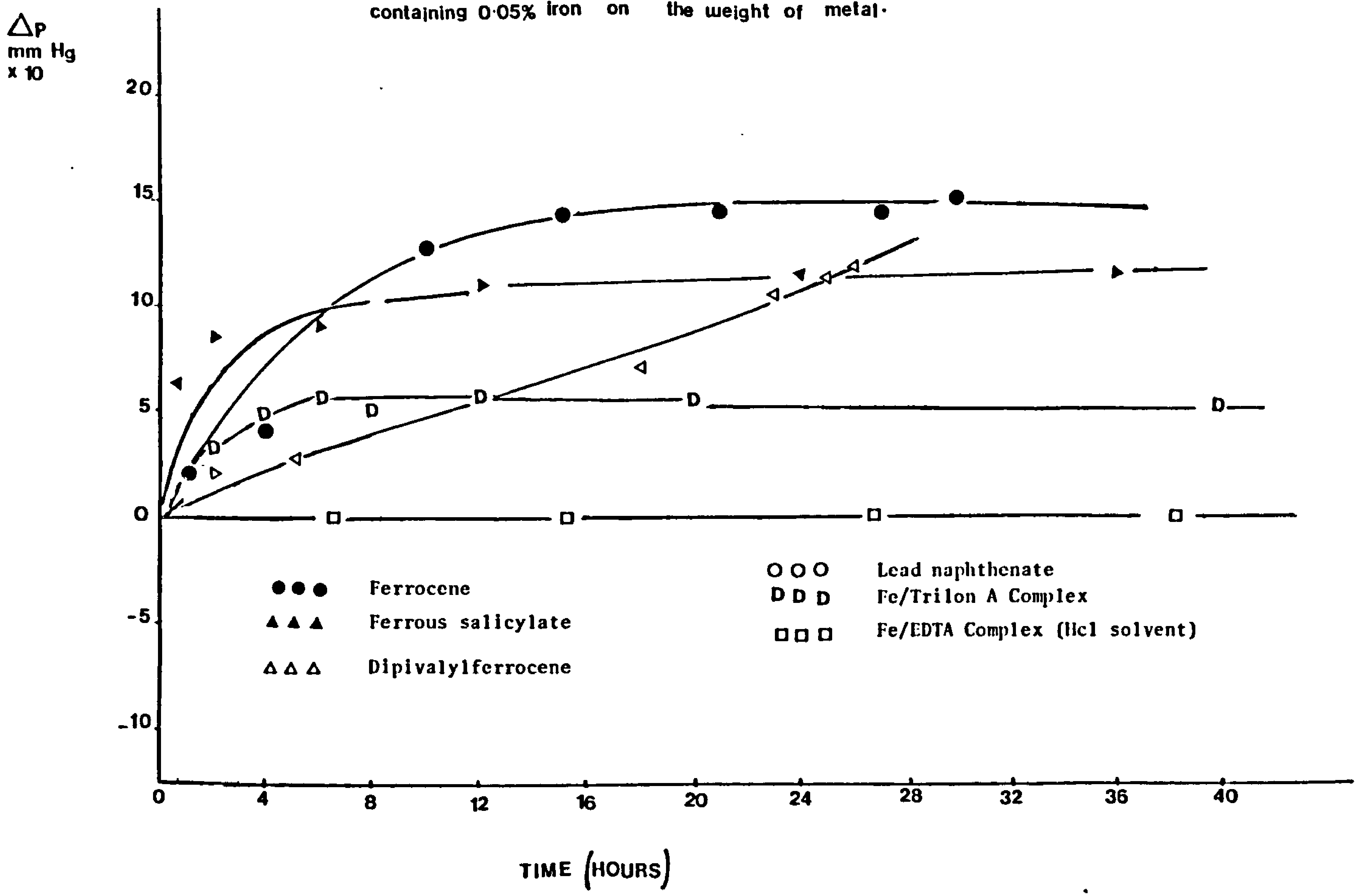
Graph PV:3:RT

CHANGES IN PEROXIDE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT ROOM TEMPERATURE IN THE PRESENCE OF 0.05% METAL ON THE WEIGHT OF DRIERS

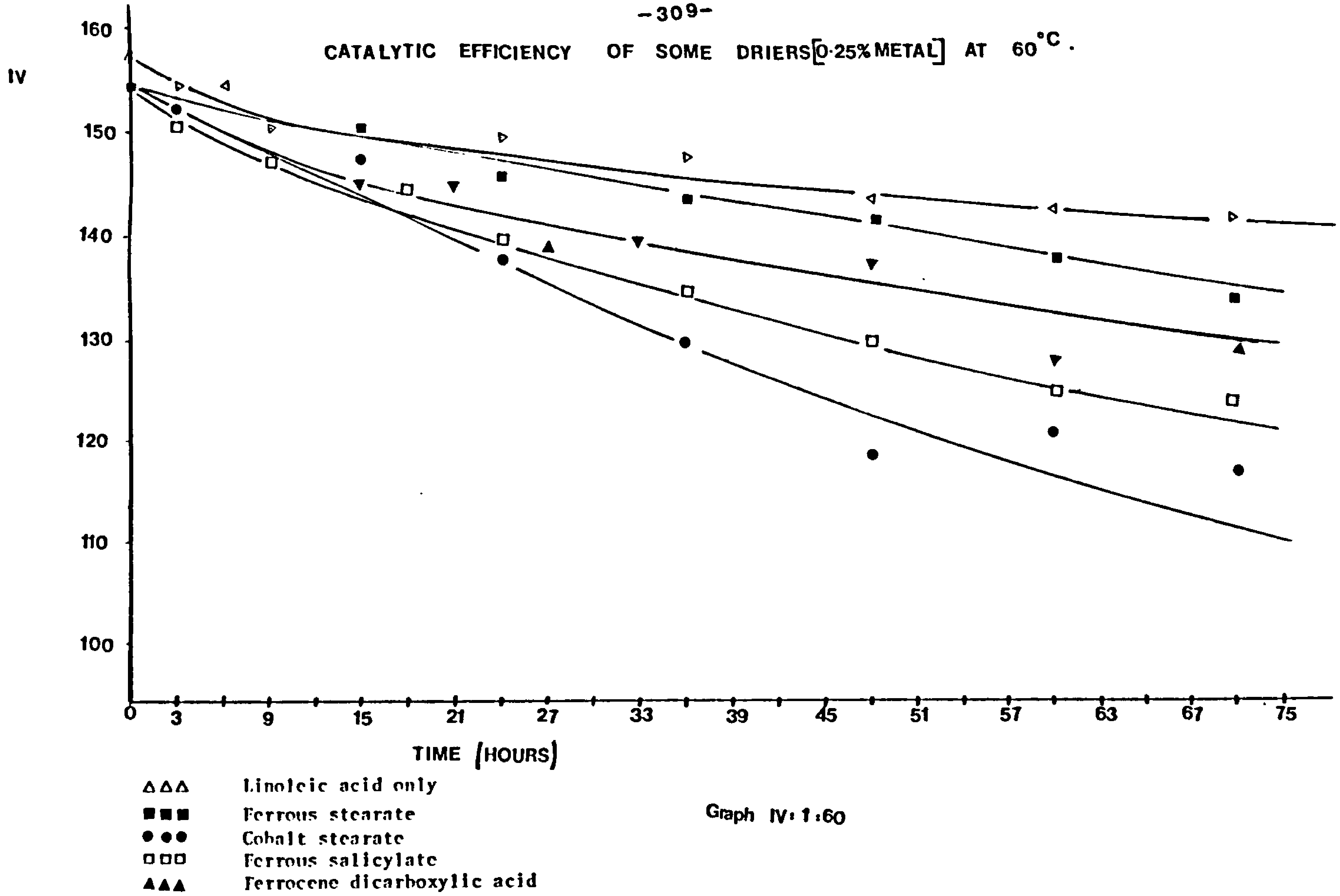


Graph 2 · 60

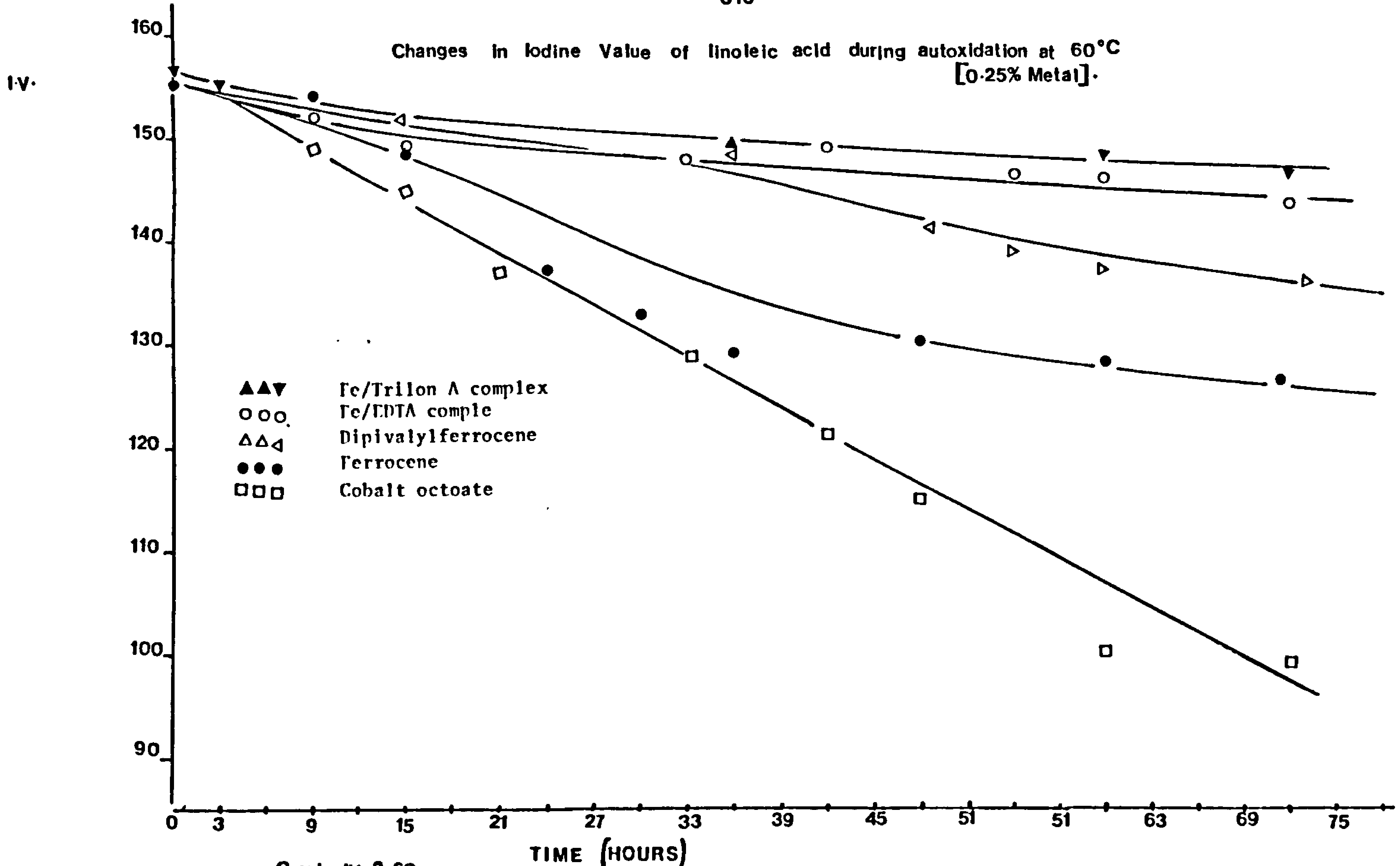
O_2 absorption of linoleic acid during autoxidation at 60°C containing 0·05% iron on the weight of metal·



CATALYTIC EFFICIENCY OF SOME DRIERS[0·25% METAL] AT 60°C.



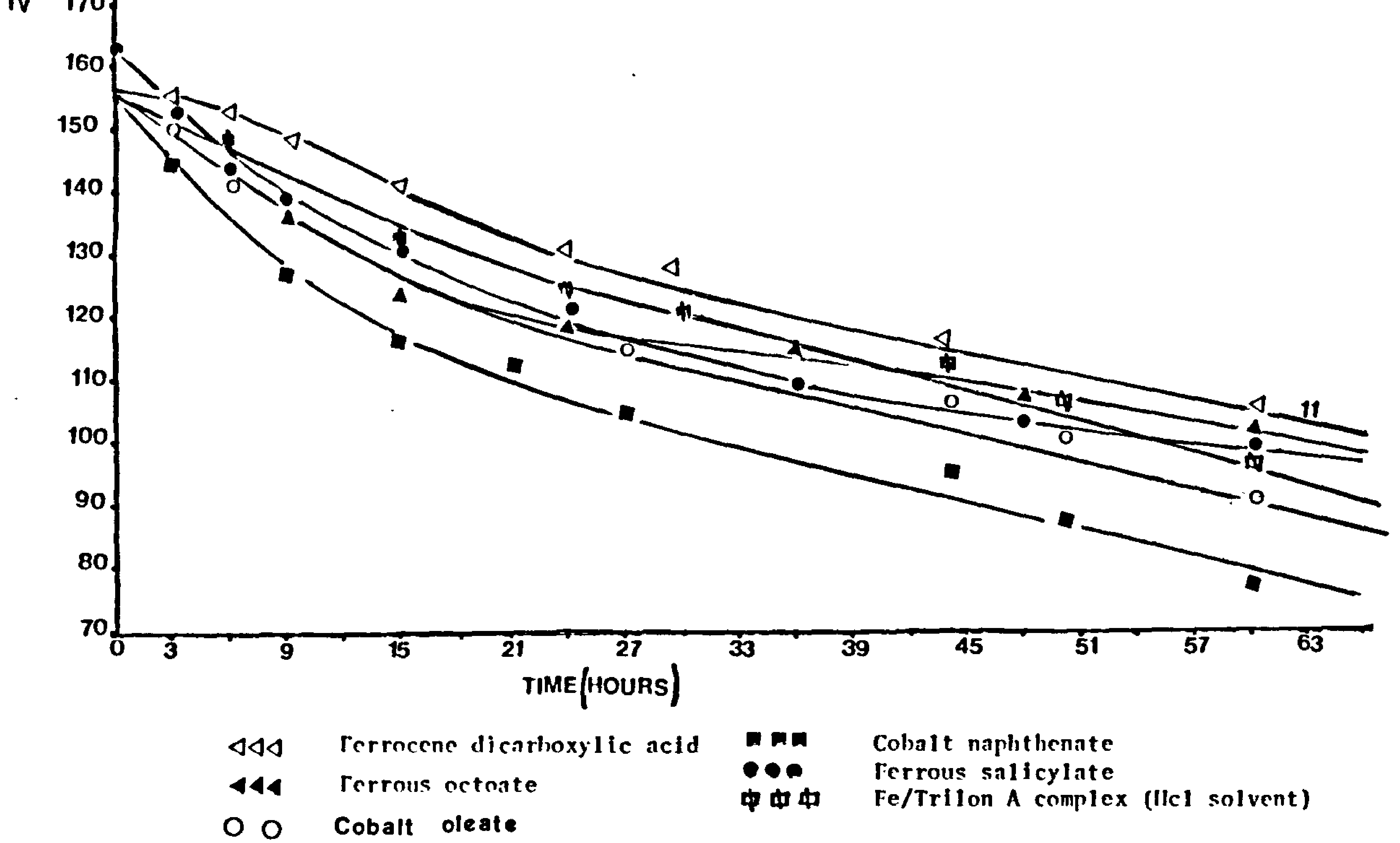
Graph IV:1:60



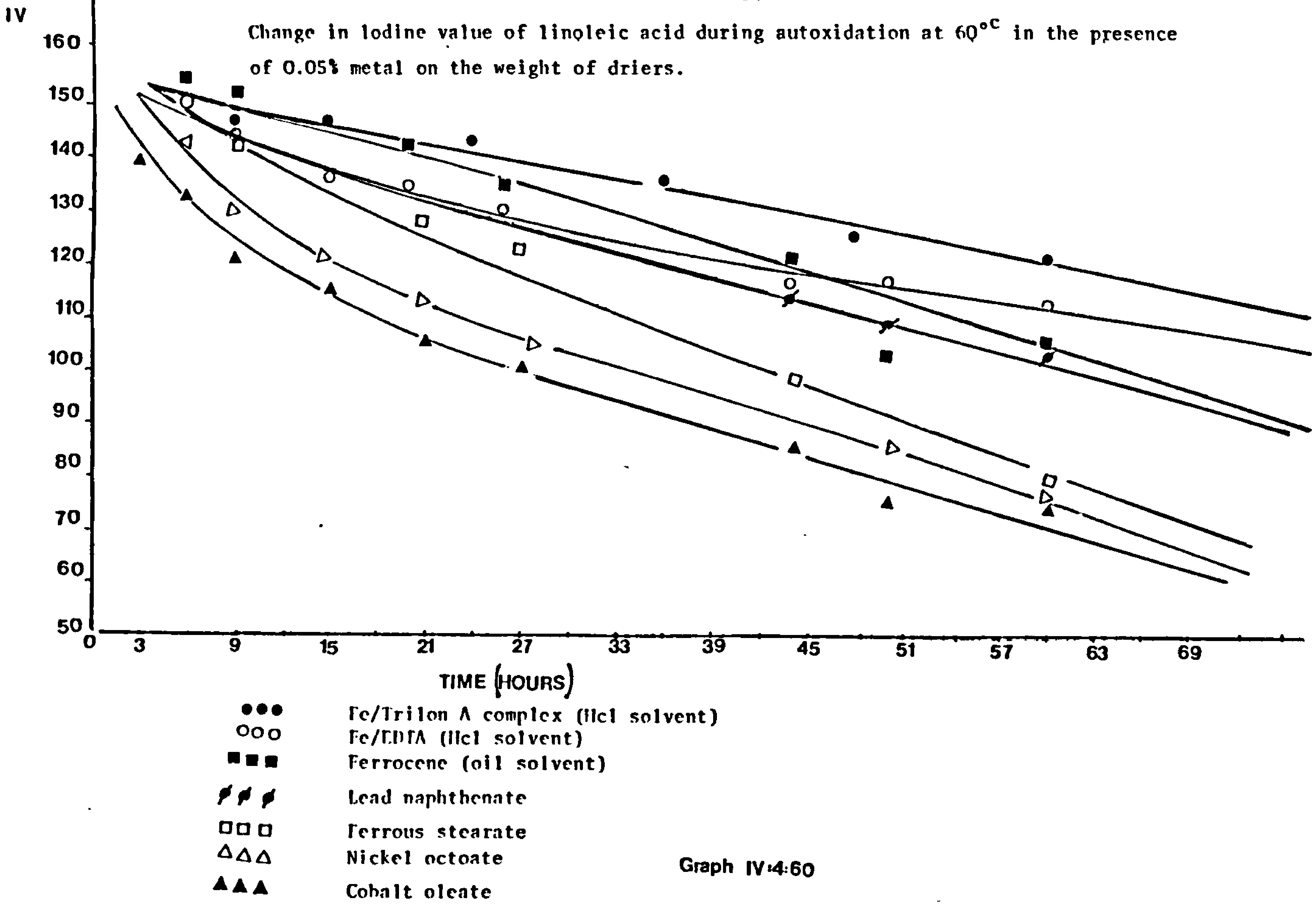
Changes in Iodine Value of linoleic acid during autoxidation at 60°C [0·25% Metal].

Graph IV:2:60

CHANGES IN IODINE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT 60°C IN THE PRESENCE OF 0.05% METAL ON THE WEIGHT OF DRIERS.

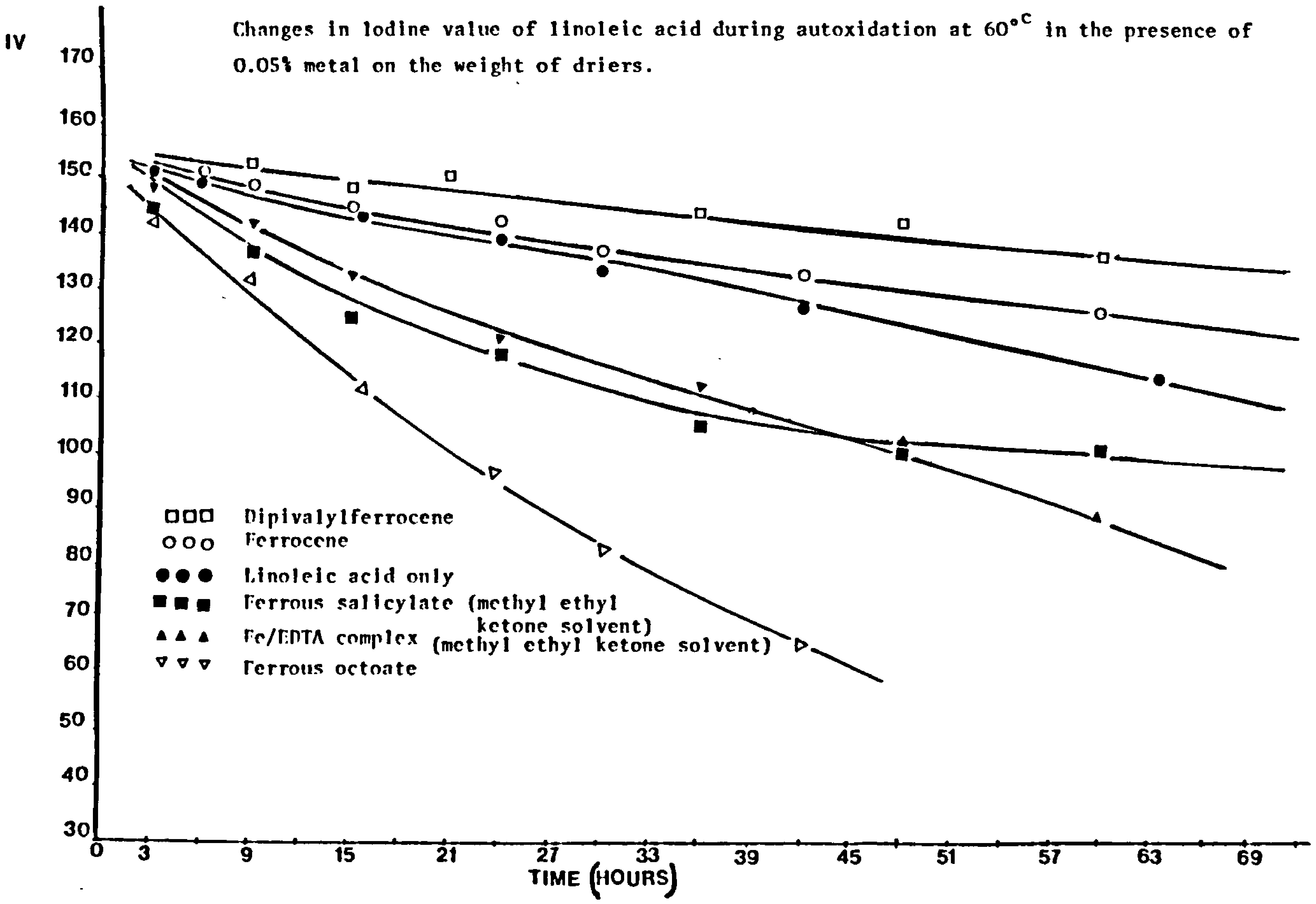


Graph IV:3 :60

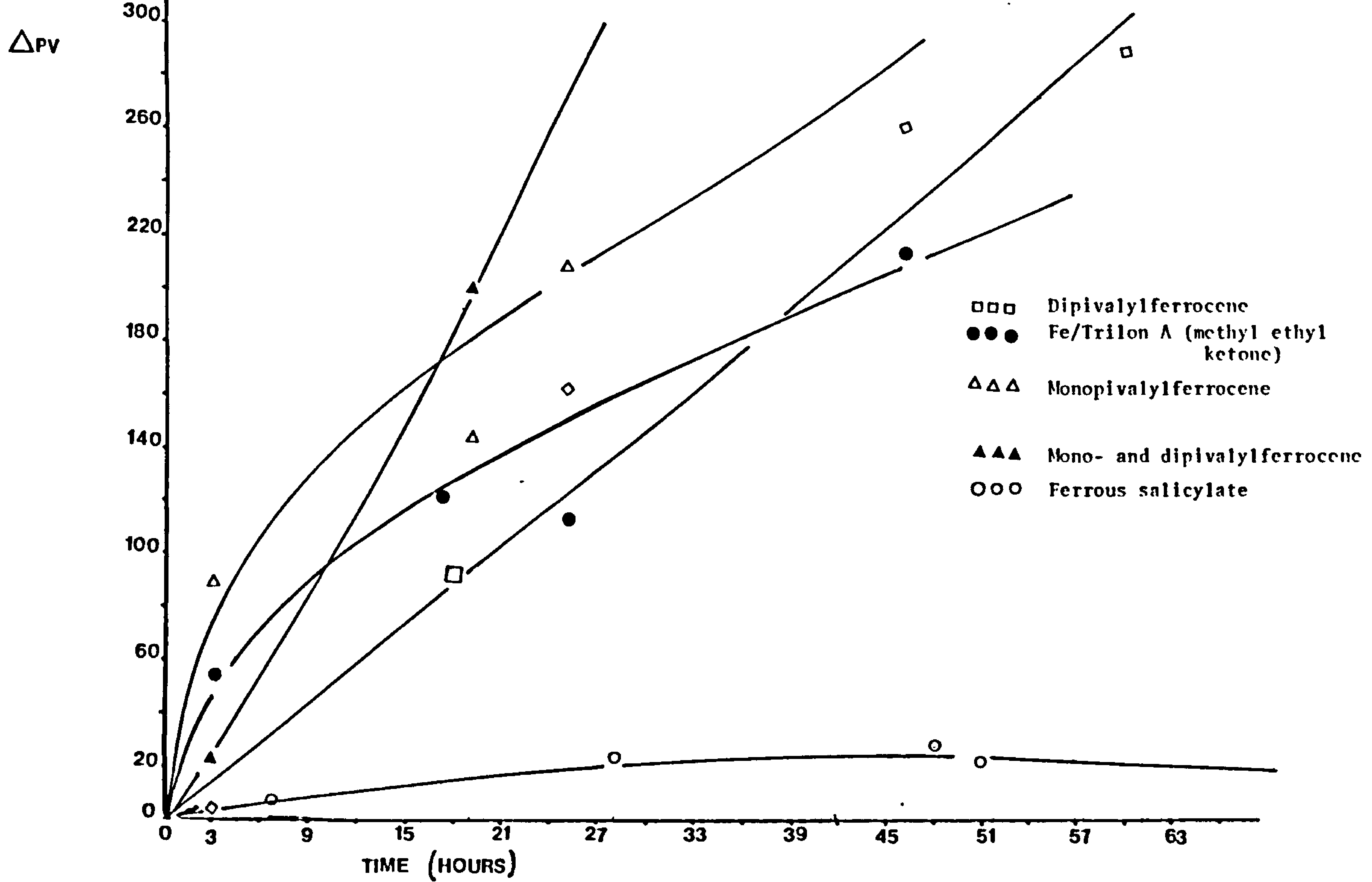

Change in iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.05% metal on the weight of driers.

Graph IV:4:60

Graph IV:5:60



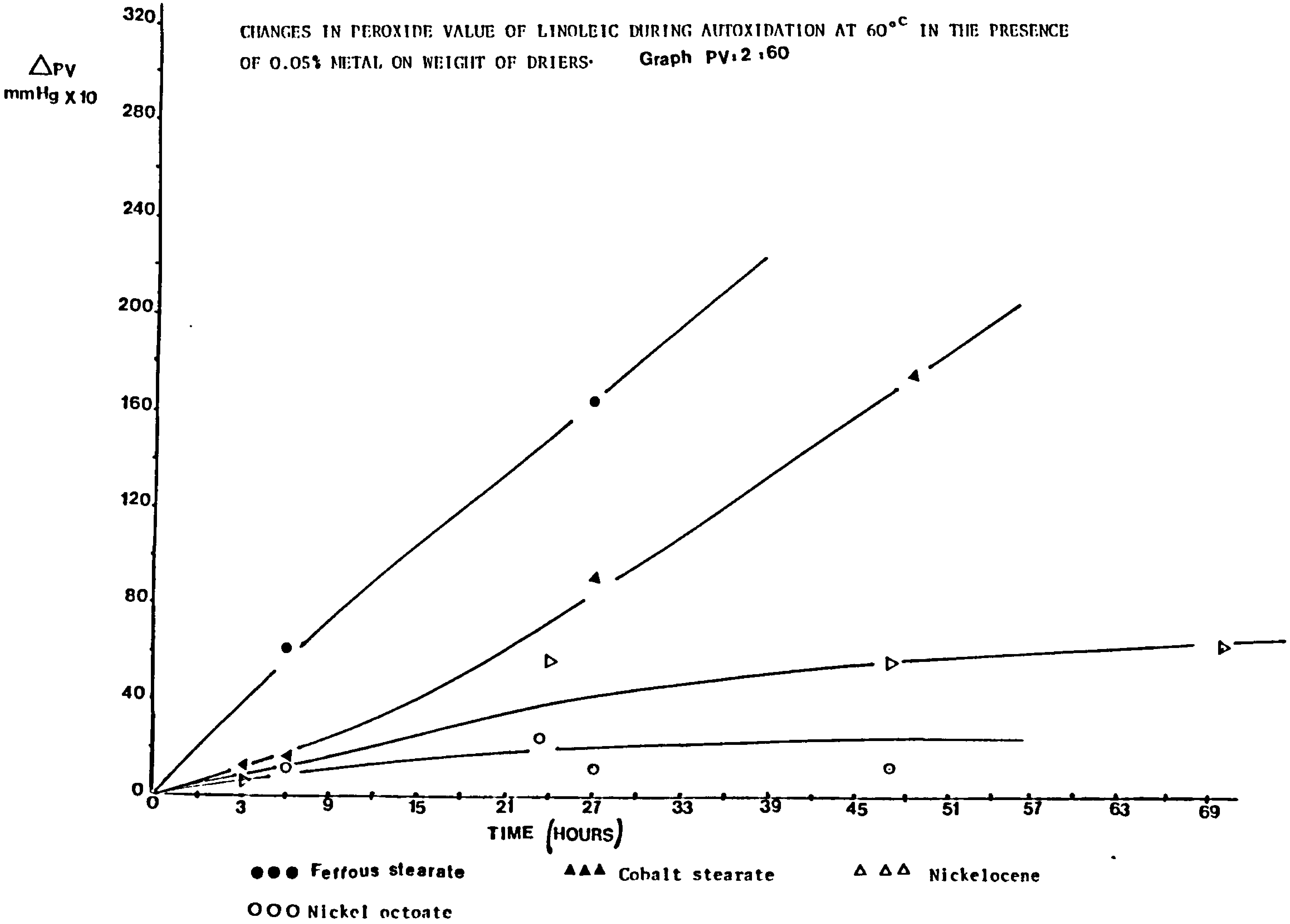
Changes in Iodine value of linoleic acid during autoxidation at 60°C in the presence of 0.05% metal on the weight of driers.



CHANGES IN IODINE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT 60°C IN THE PRESENCE OF 0.05% METAL

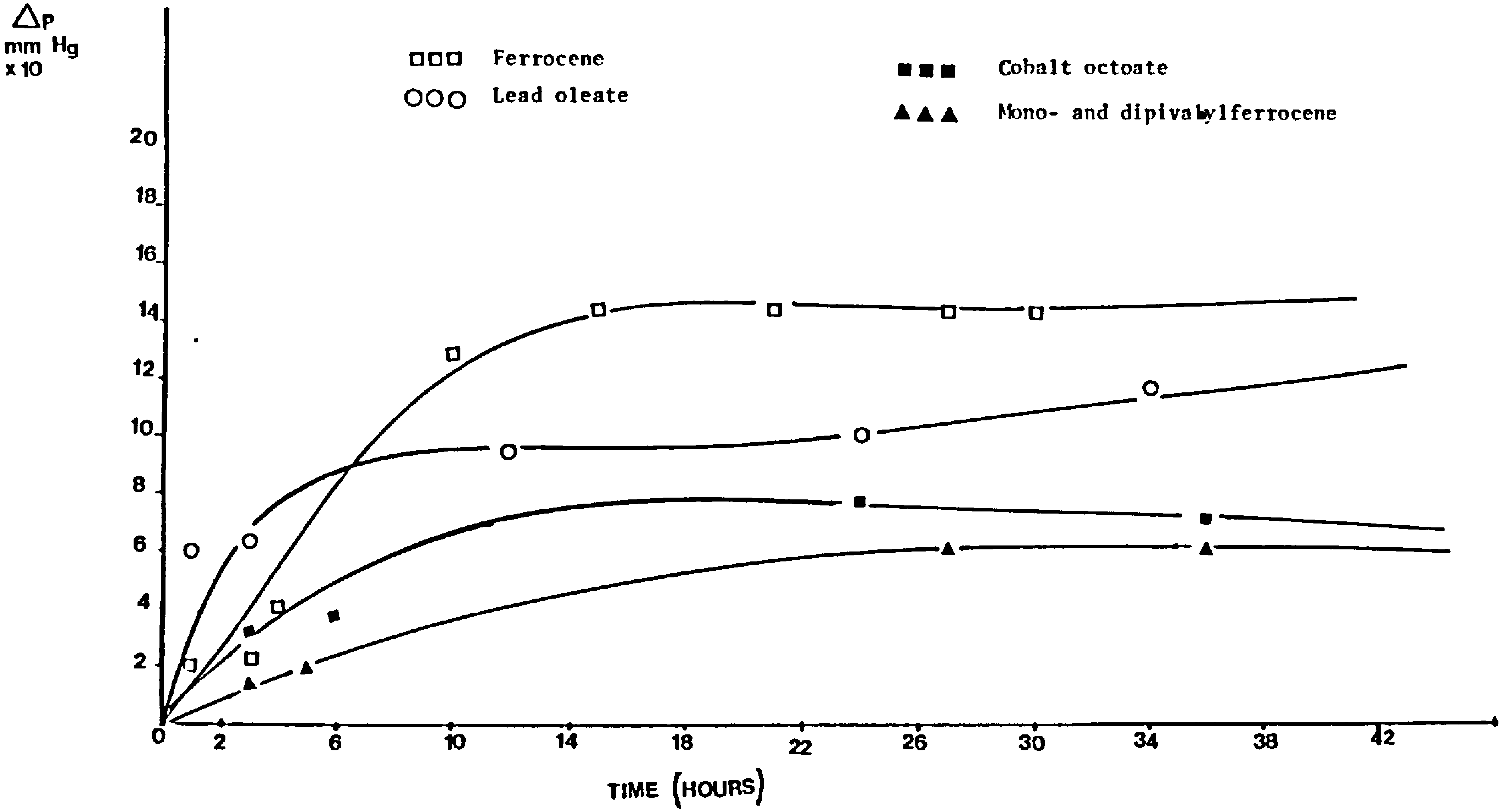
Graph PV·1.60

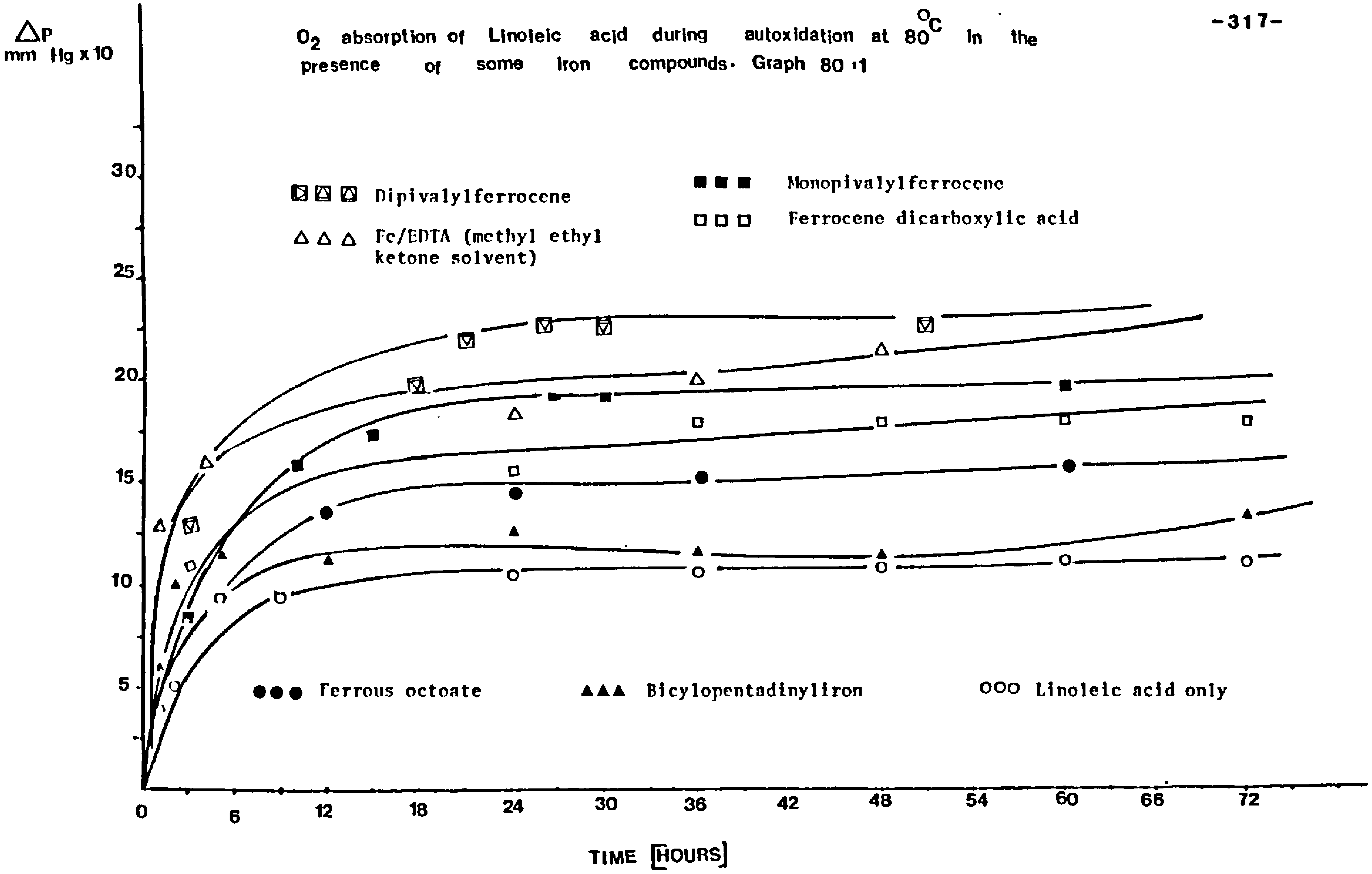
CHANGES IN PEROXIDE VALUE OF LINOLEIC DURING AUTOXIDATION AT 60°C IN THE PRESENCE OF 0.05% METAL ON WEIGHT OF DRIERS. Graph PV:2 :60



Graph 1·60

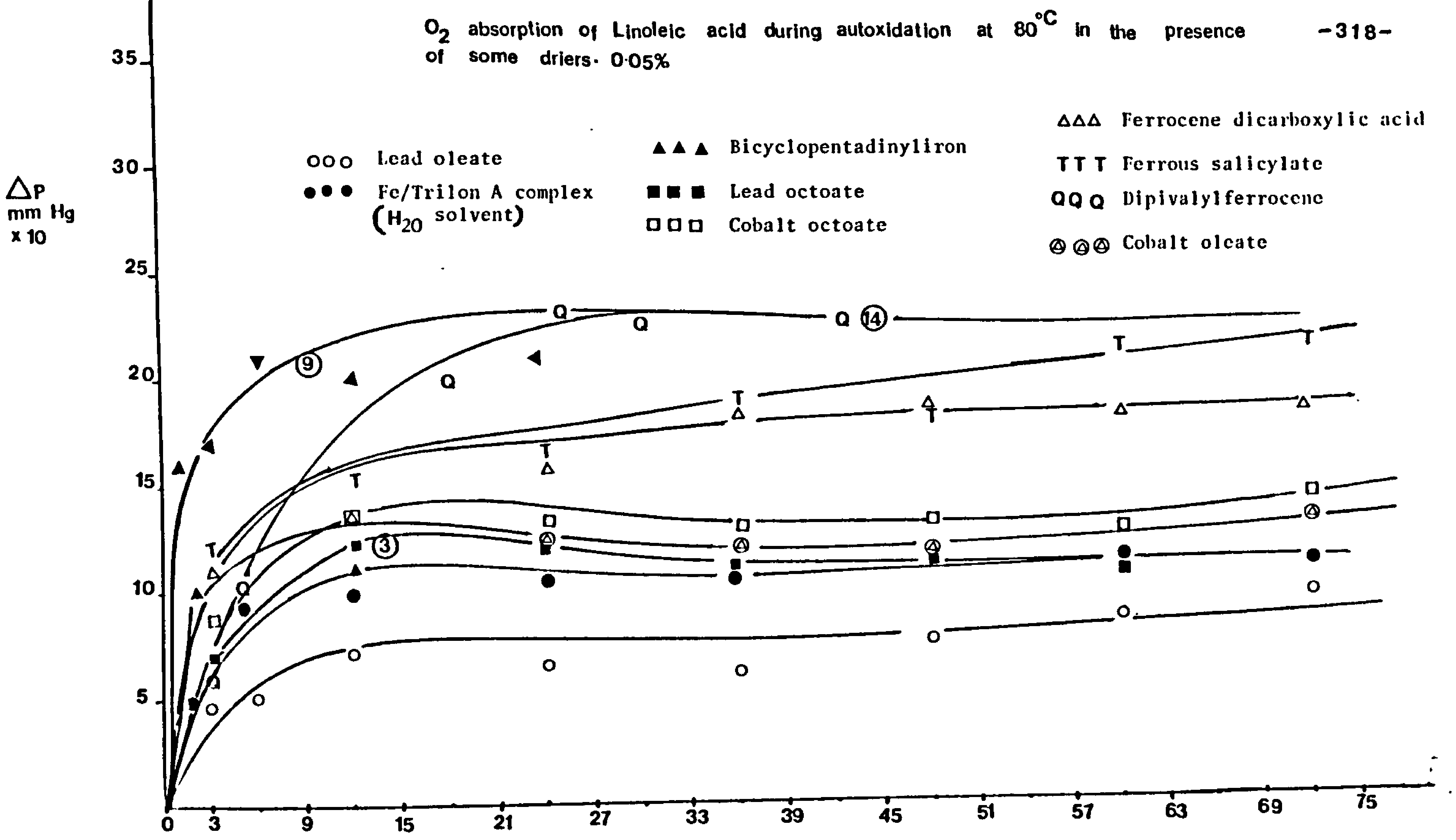
O_2 absorption of linoleic acid during autoxidation at 60°C in the presence of some driers. [0·05% metal on weight of driers].





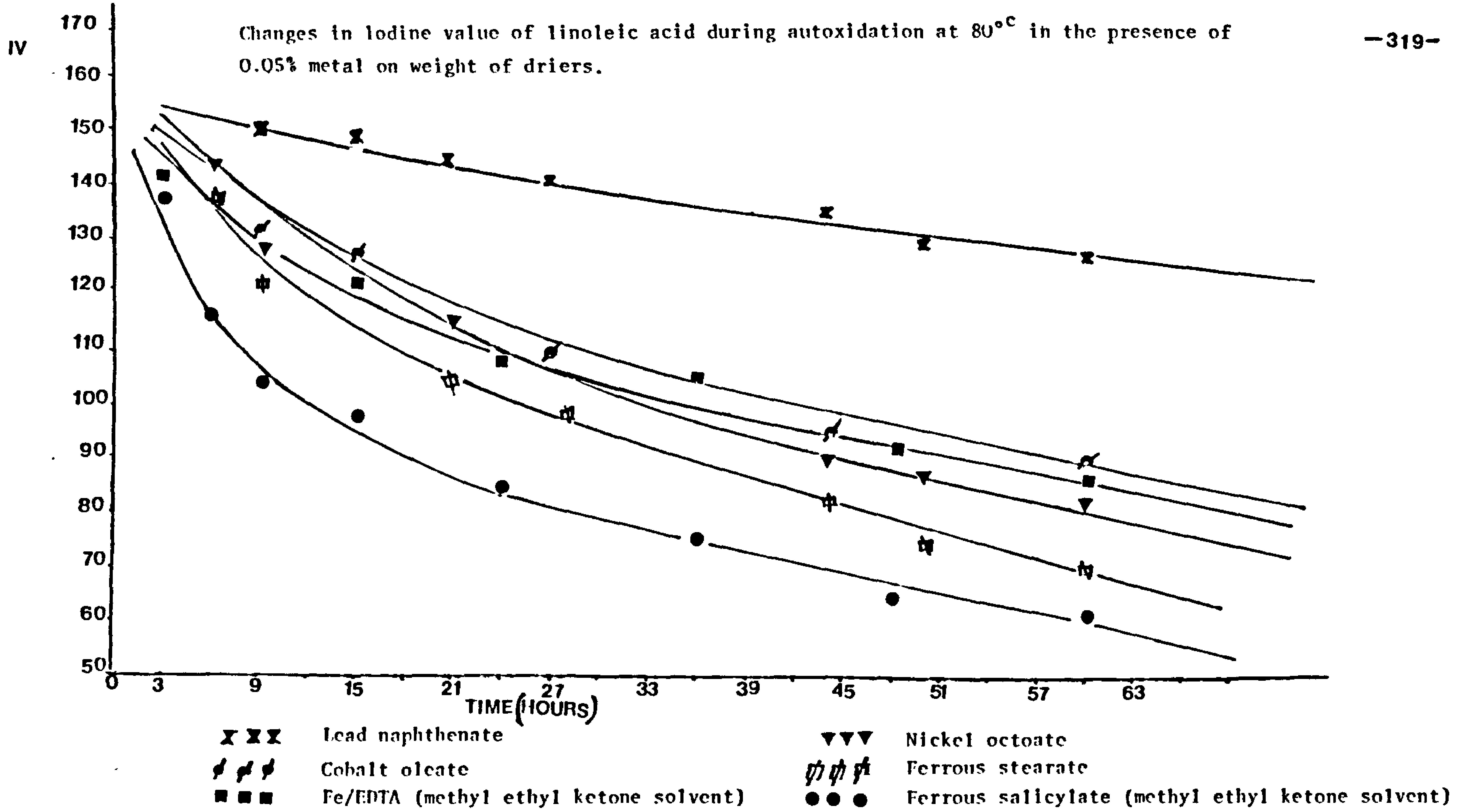
O_2 absorption of Linoleic acid during autoxidation at 80°C in the presence of some iron compounds. Graph 80·1

O_2 absorption of Linoleic acid during autoxidation at 80°C in the presence of some driers· 0·05%



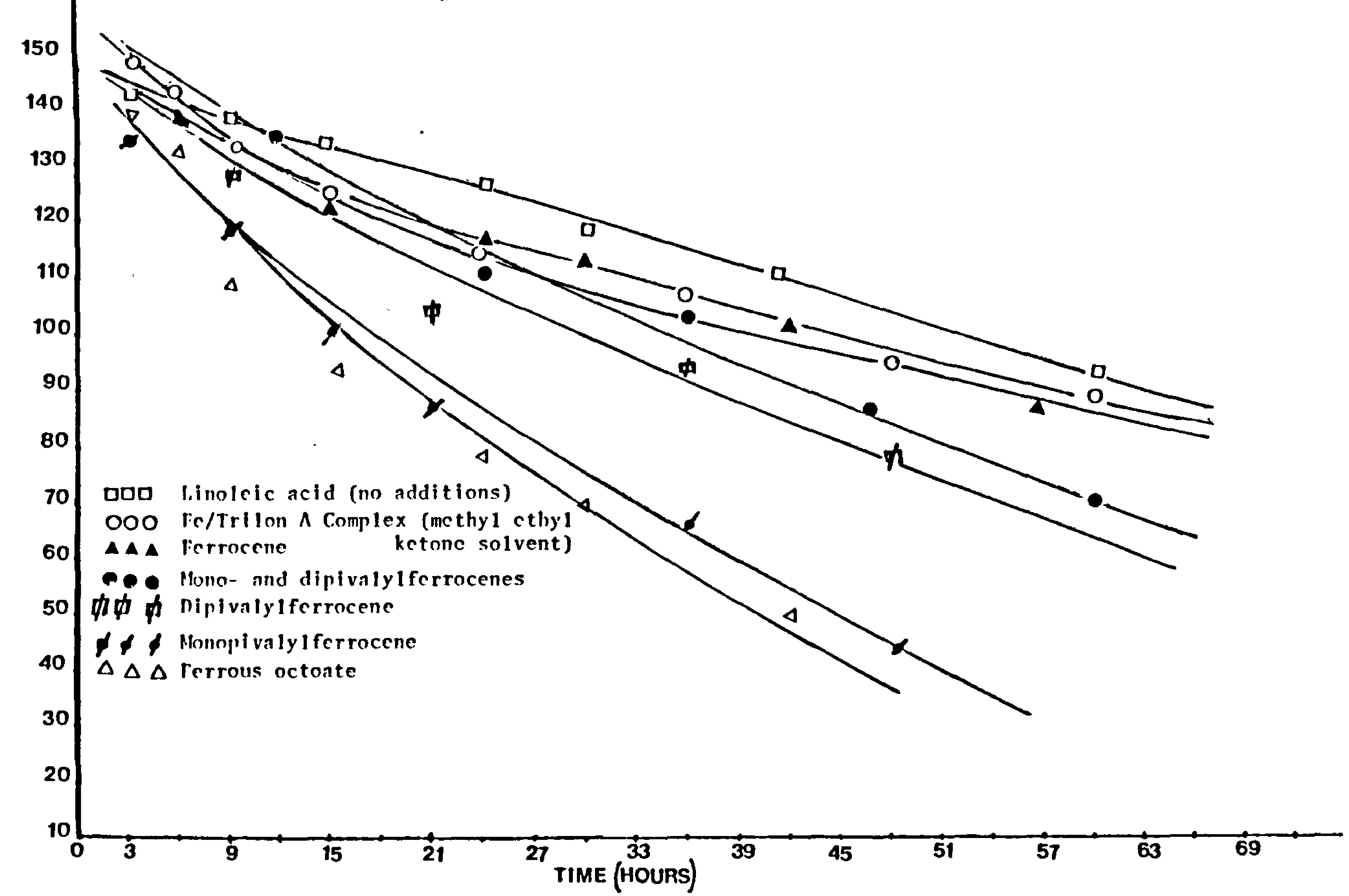
Graph 80·2

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.05% metal on weight of driers.



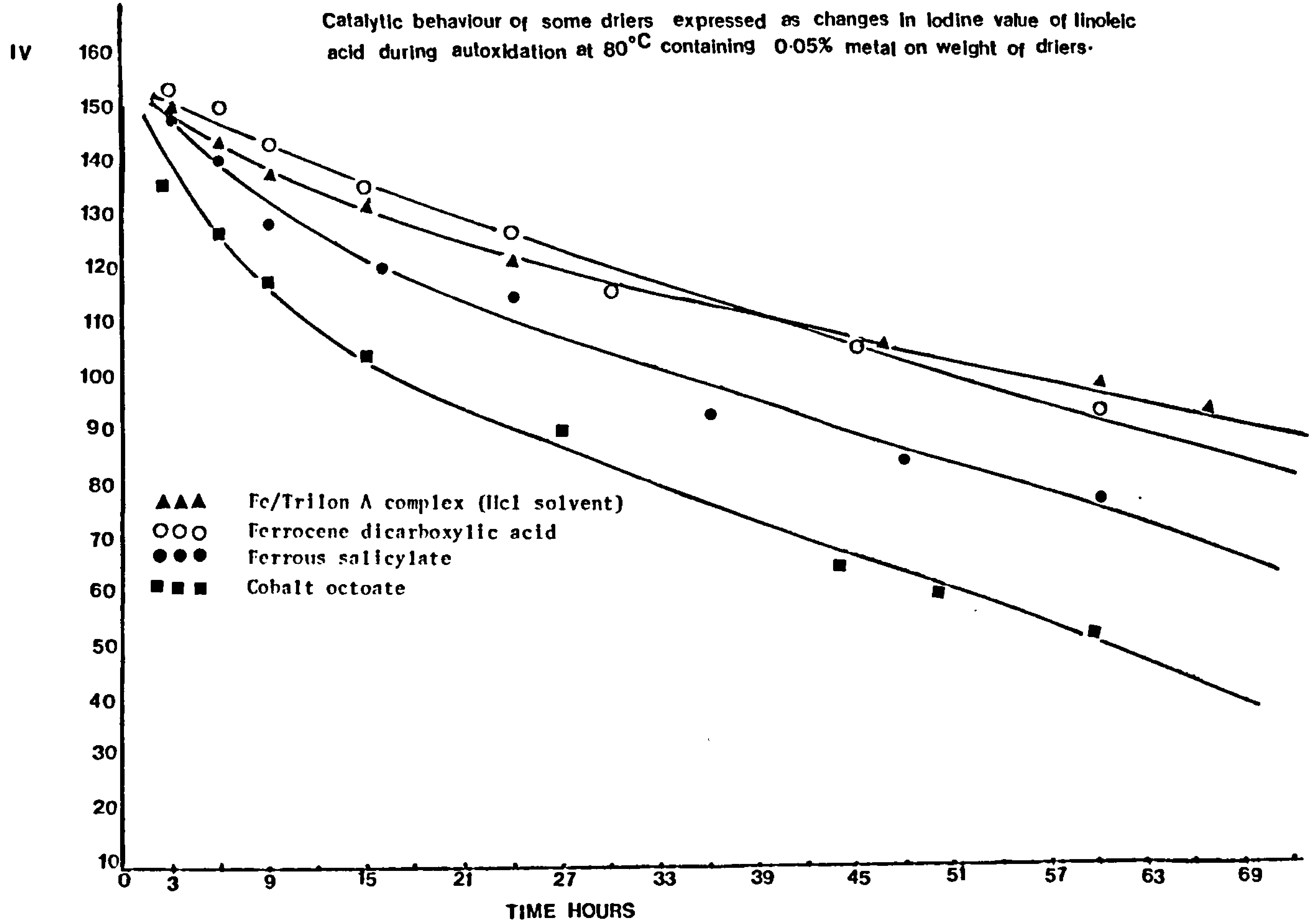
Graph IV:1:80

Changes in Iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.05% metal on weight of driers.

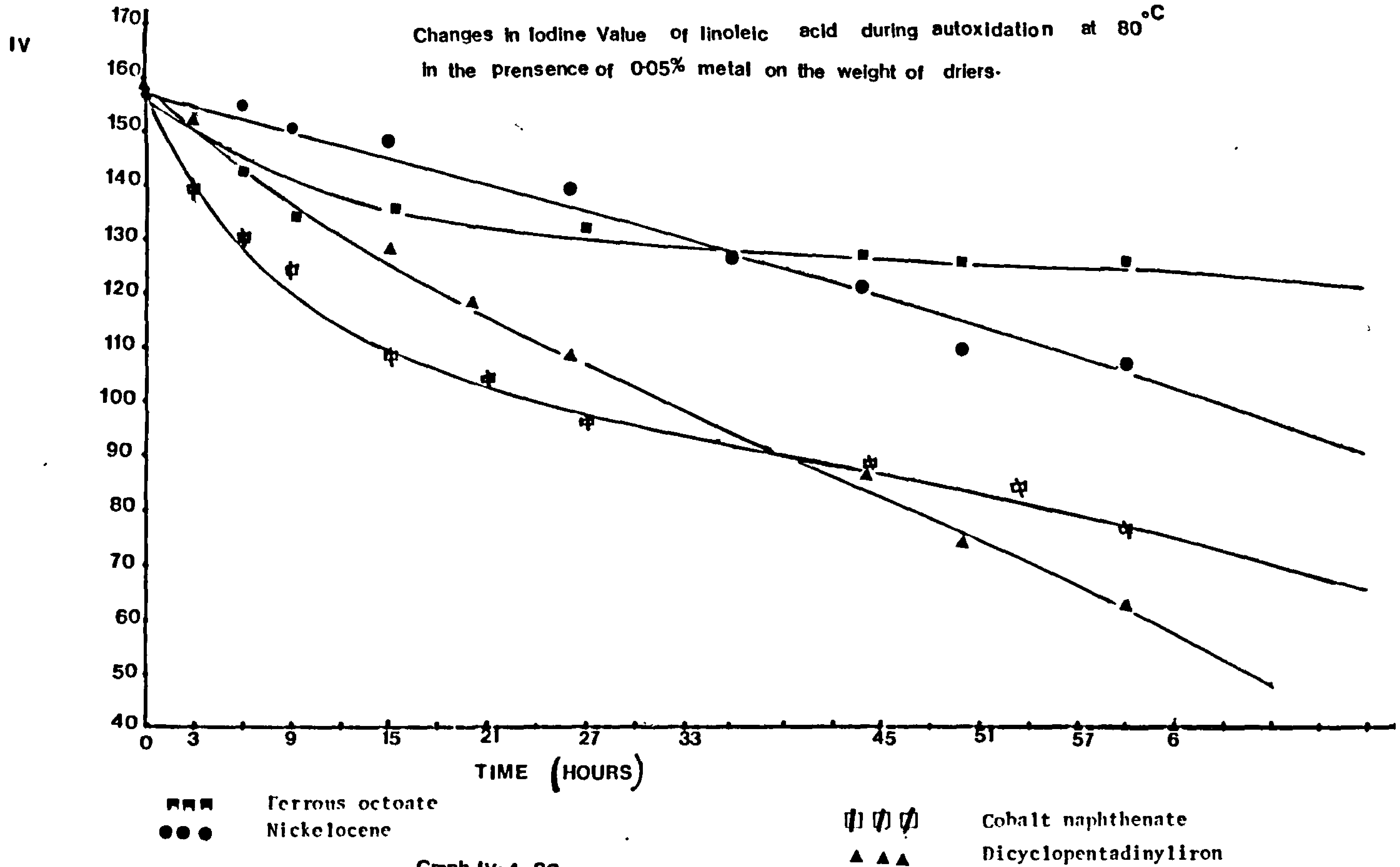


Graph IV:2 :80

Catalytic behaviour of some driers expressed as changes in iodine value of linoleic acid during autoxidation at 80°C containing 0·05% metal on weight of driers·

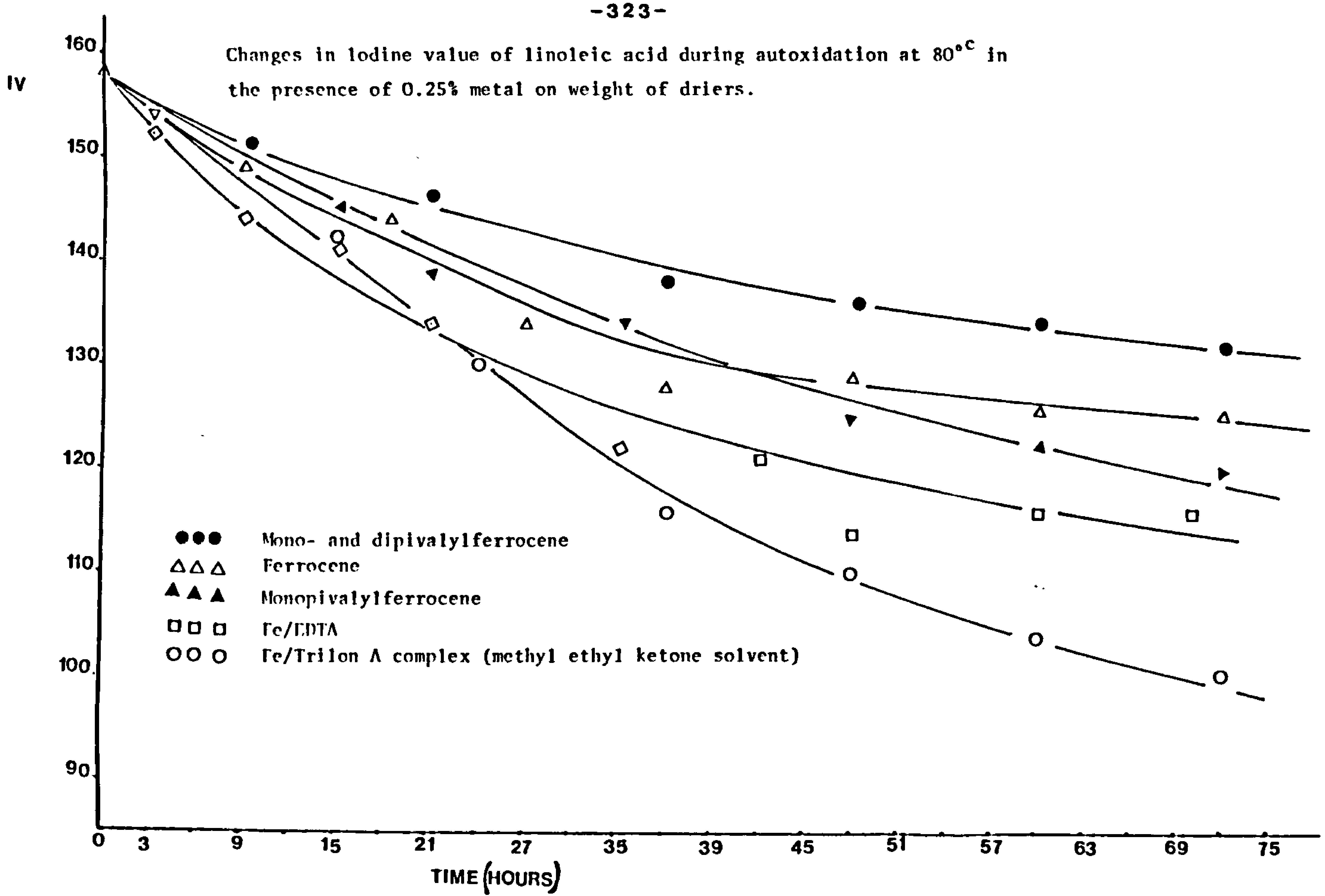


Graph IV:3:80



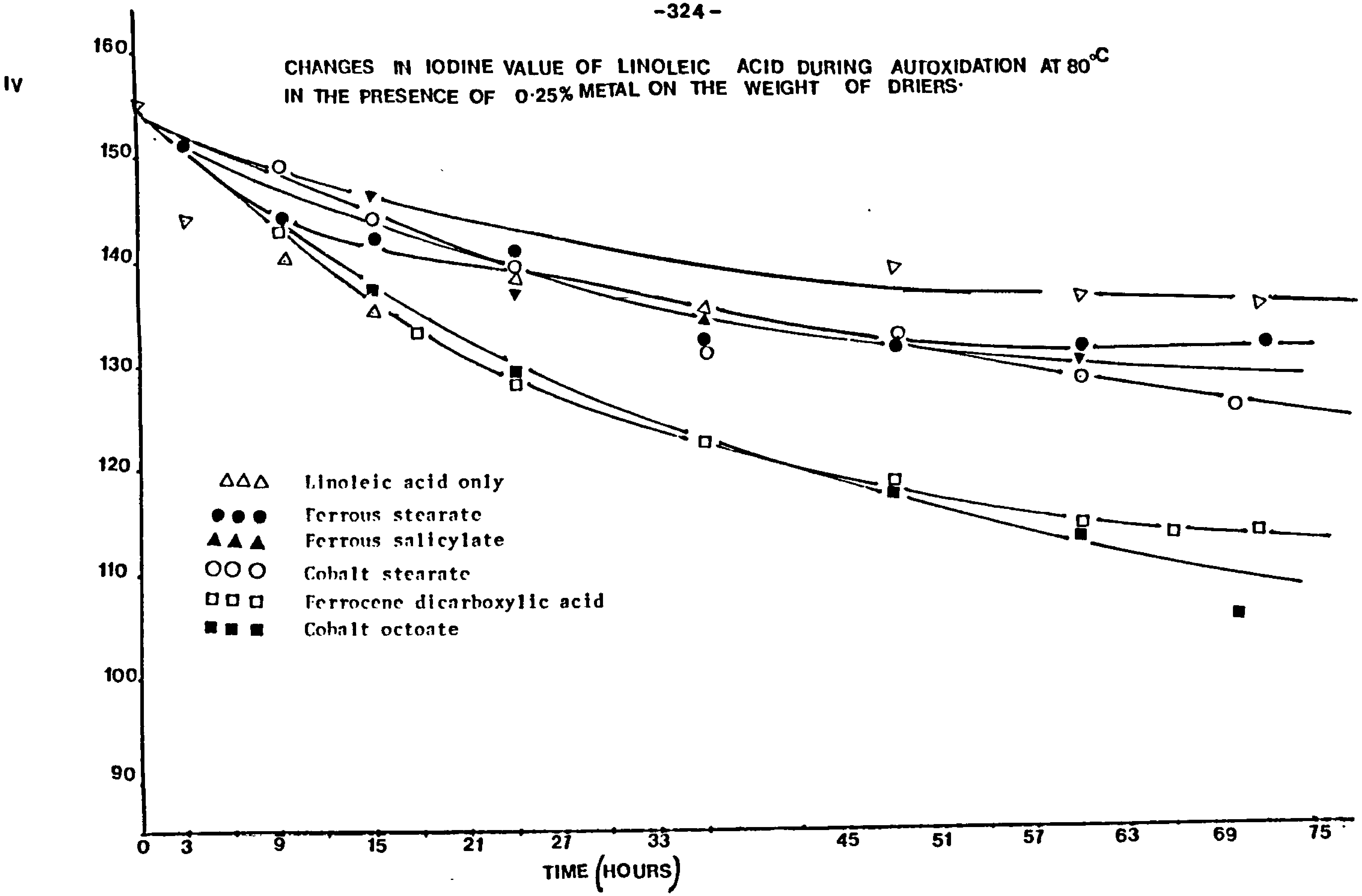
Changes in Iodine Value of linoleic acid during autoxidation at 80°C in the prensence of 0·05% metal on the weight of driers·

Graph IV·4·80



Changes in iodine value of linoleic acid during autoxidation at 80°C in the presence of 0.25% metal on weight of driers.

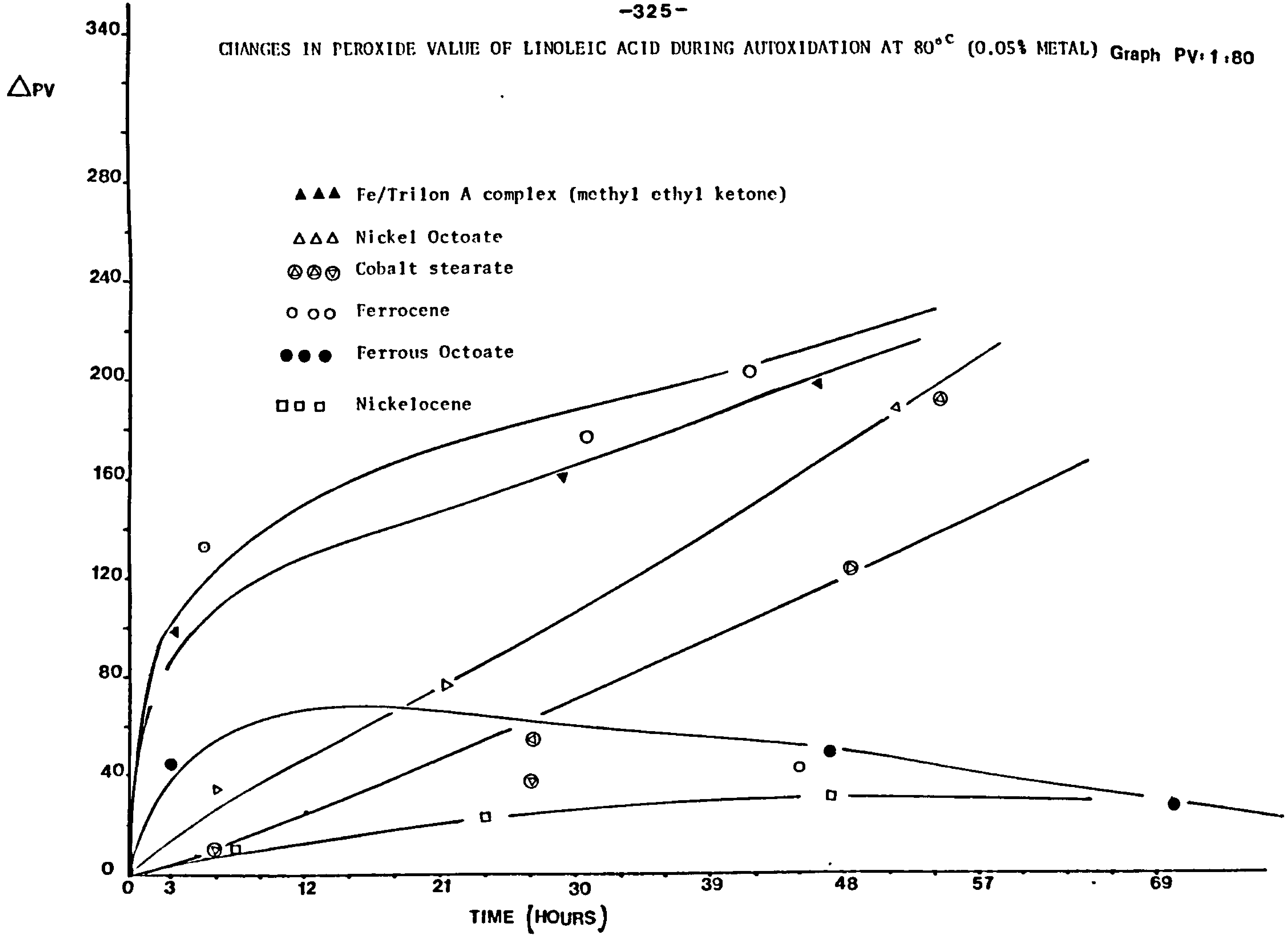
Graph IV:5:80

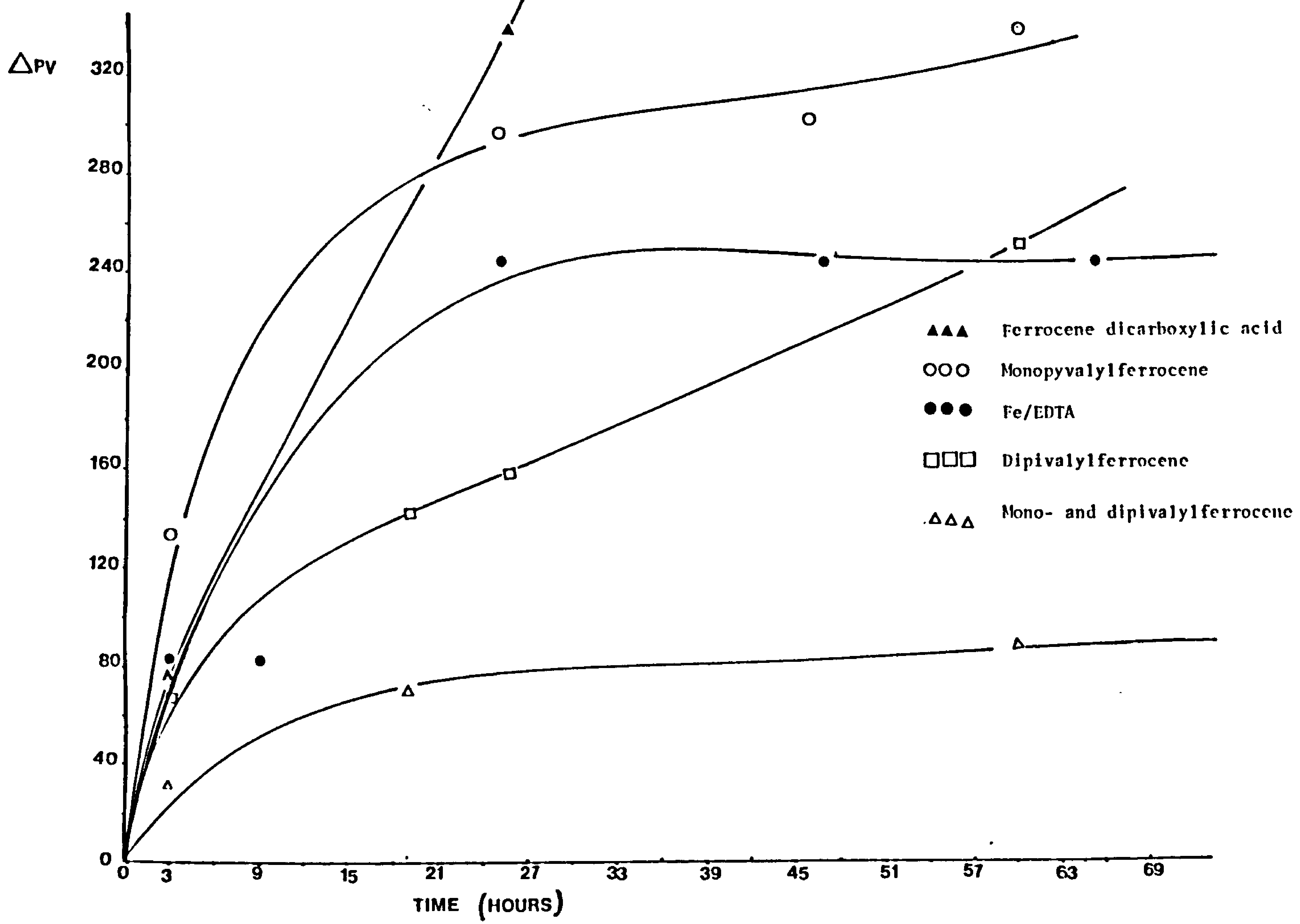


CHANGES IN IODINE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT 80°C IN THE PRESENCE OF 0·25% METAL ON THE WEIGHT OF DRIERS·

Graph IV·6 ·80

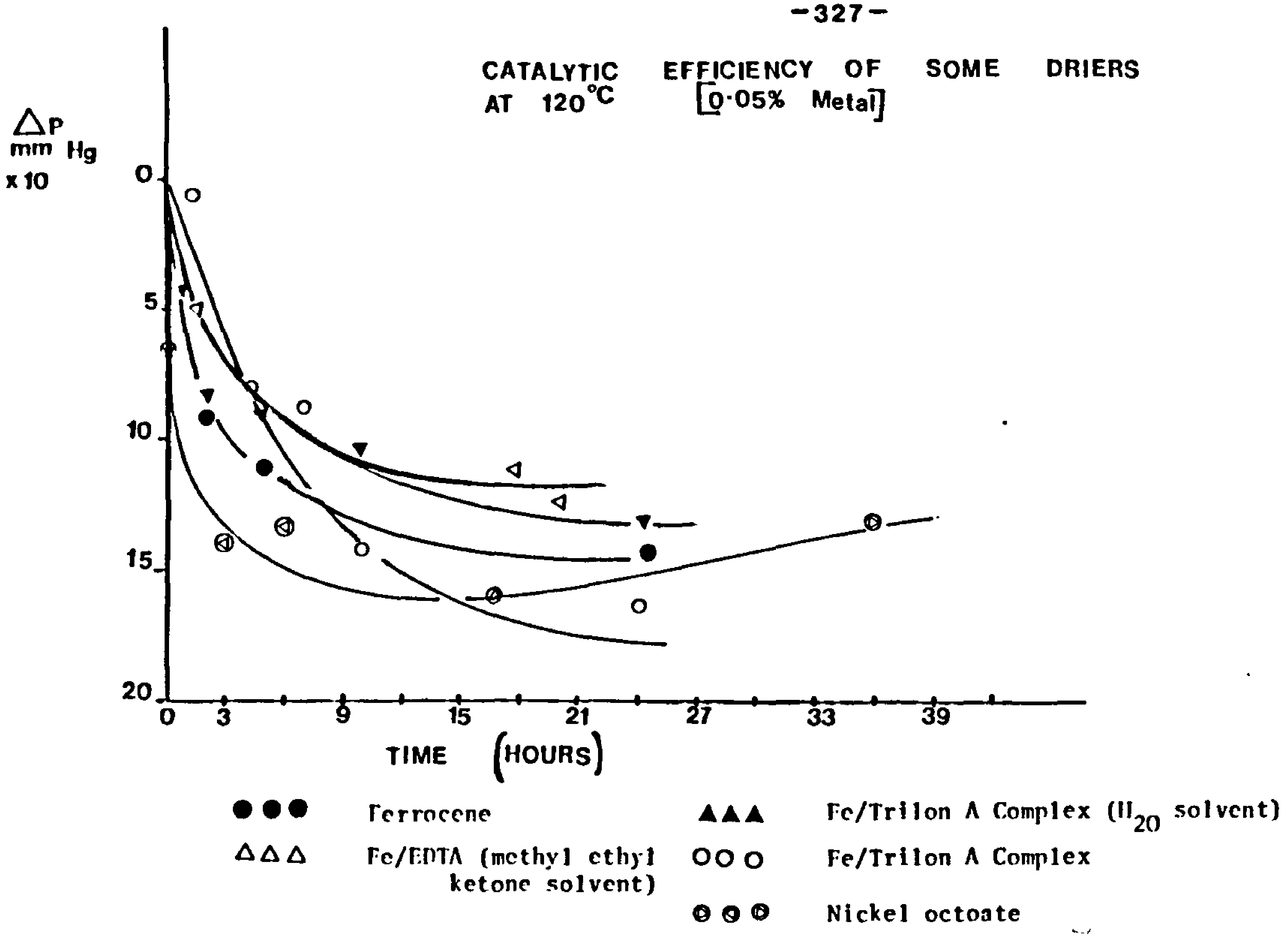
CHANGES IN PEROXIDE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT 80°C (0.05% METAL) Graph PV: 1:80



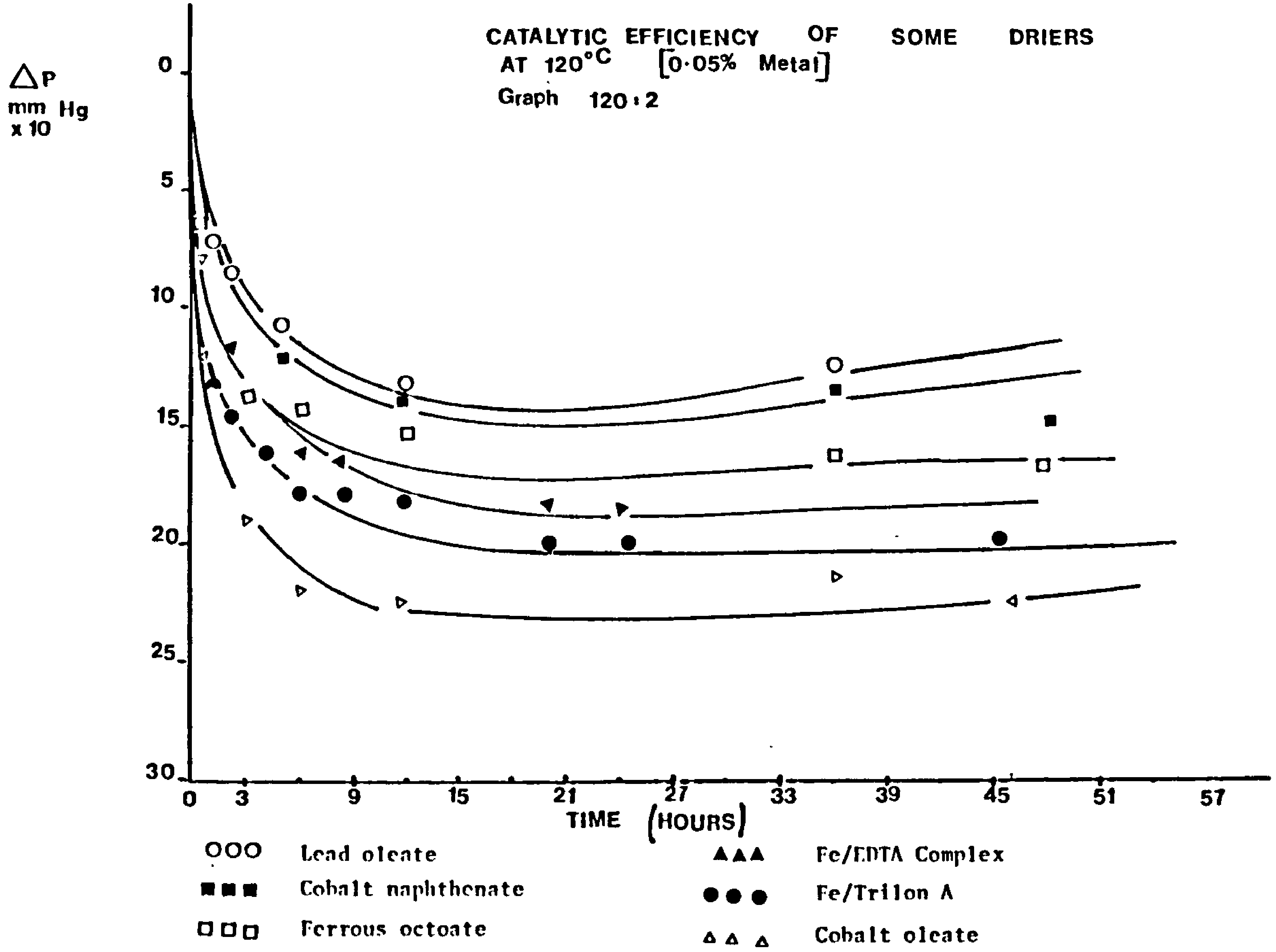


CHANGES IN PEROXIDE VALUE OF LINOLEIC ACID AT 80°C (0.05% METAL) Graph PV:2:80

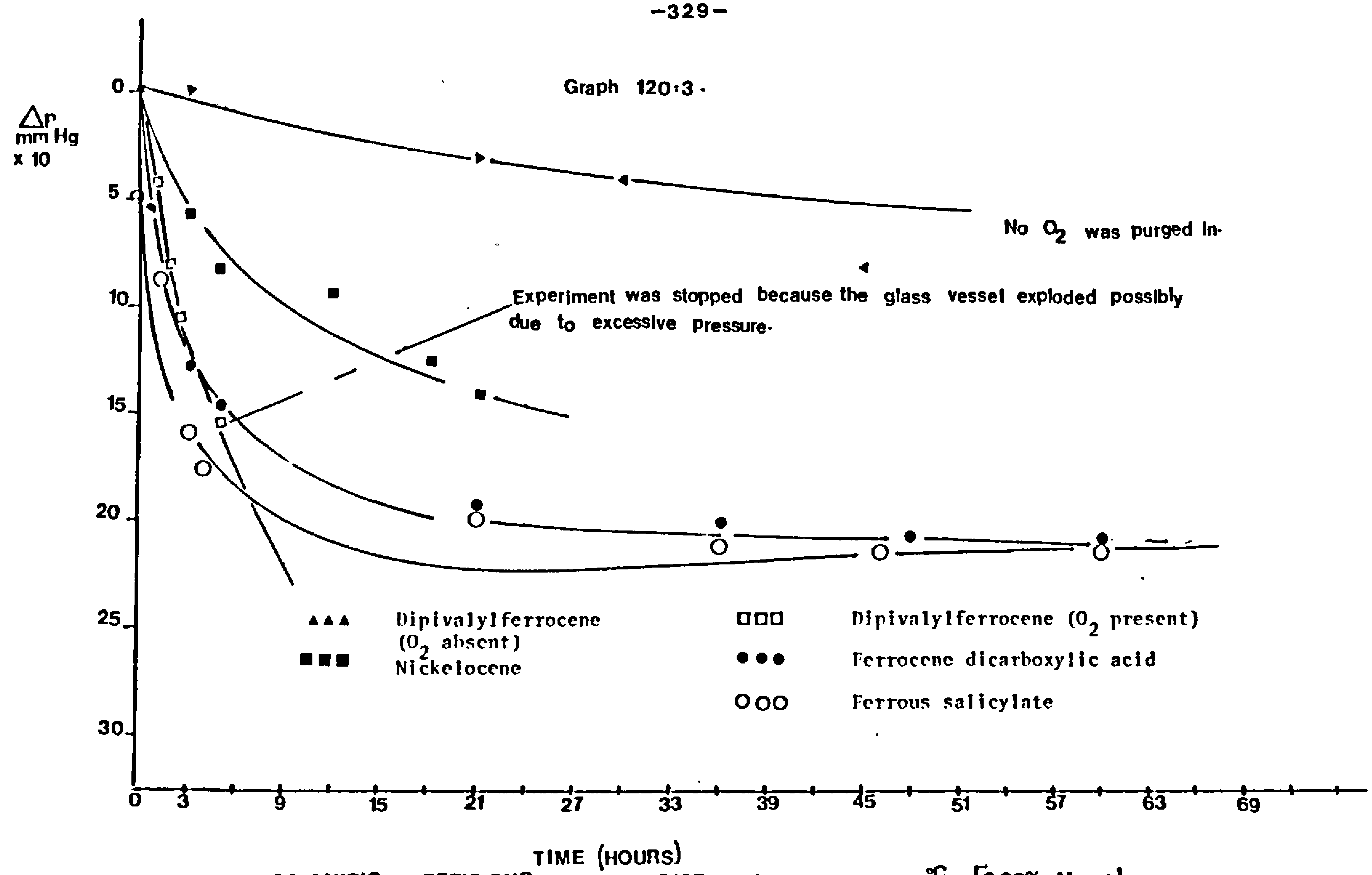
CATALYTIC EFFICIENCY OF SOME DRIERS
AT 120°C [0·05% Metal]



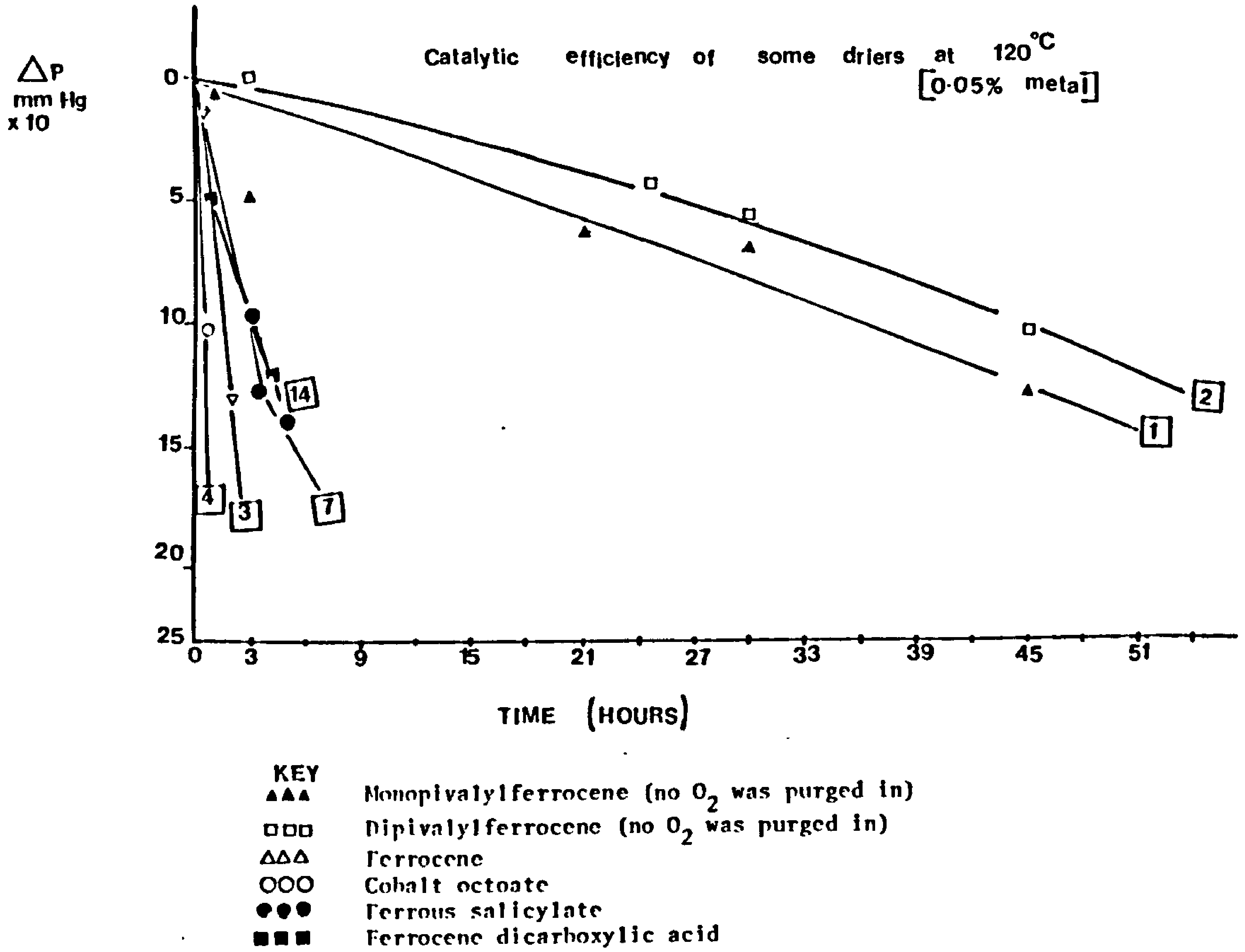
Graph 120·1



CATALYTIC EFFICIENCY OF SOME DRIERS
AT 120°C [0·05% Metal]
Graph 120 : 2

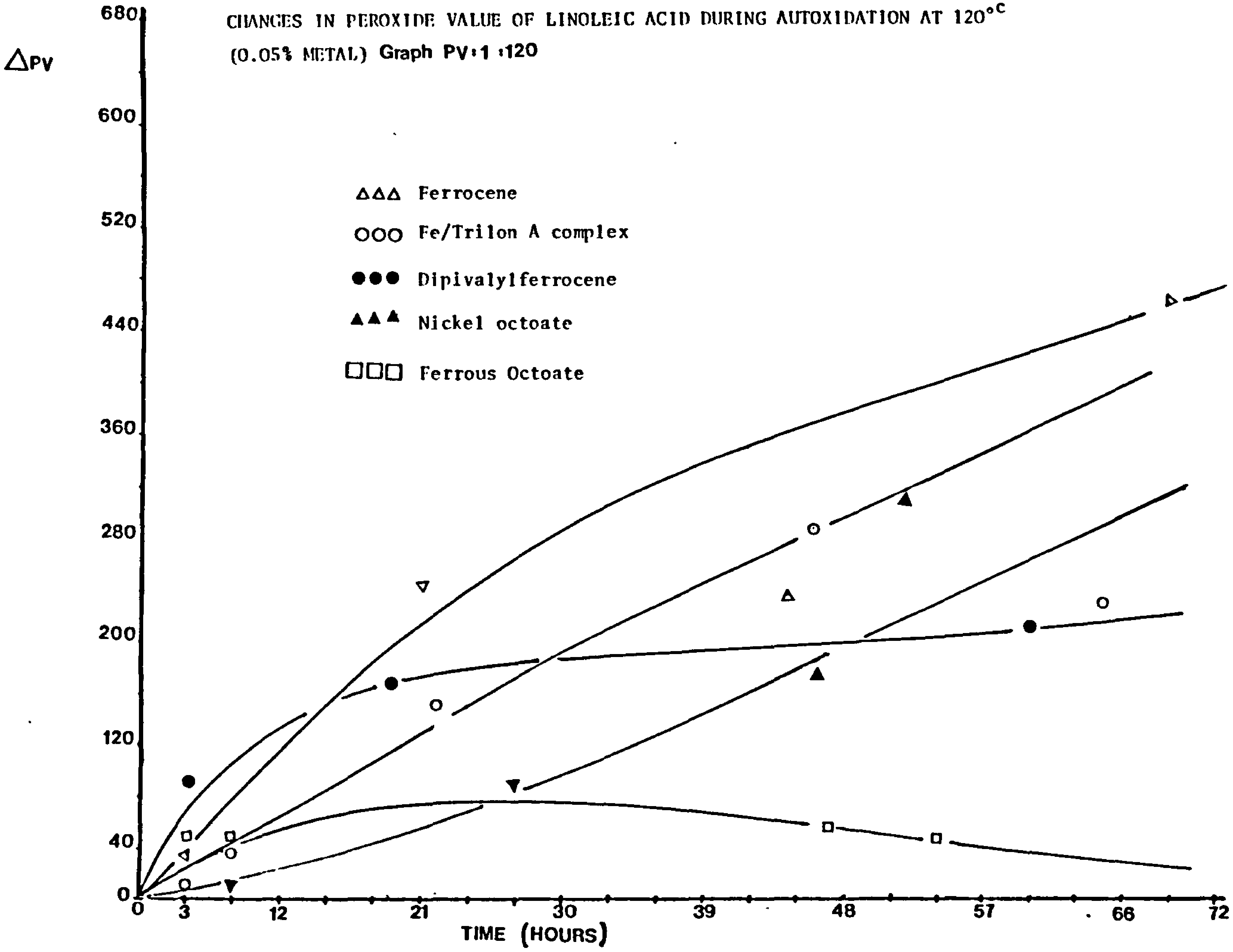


CATALYTIC EFFICIENCY OF SOME DRIERS AT 120°C [0·05% Metal].



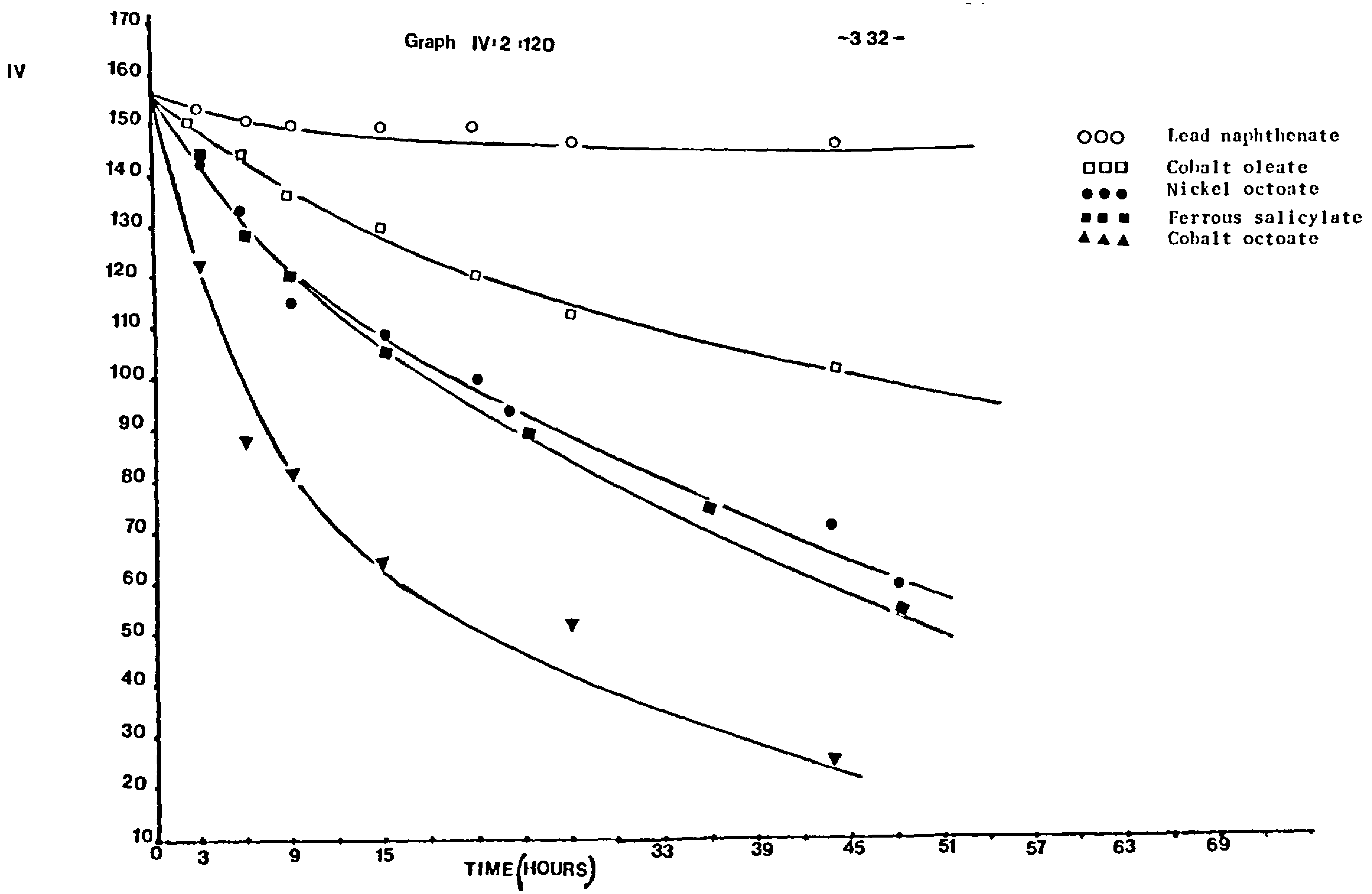
Graph 120 :4

3,4,7 & 14 were interrupted by overflow of Hg at manometer ends.



CHANGES IN PEROXIDE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT 120°C
(0.05% METAL) Graph PV:1 :120

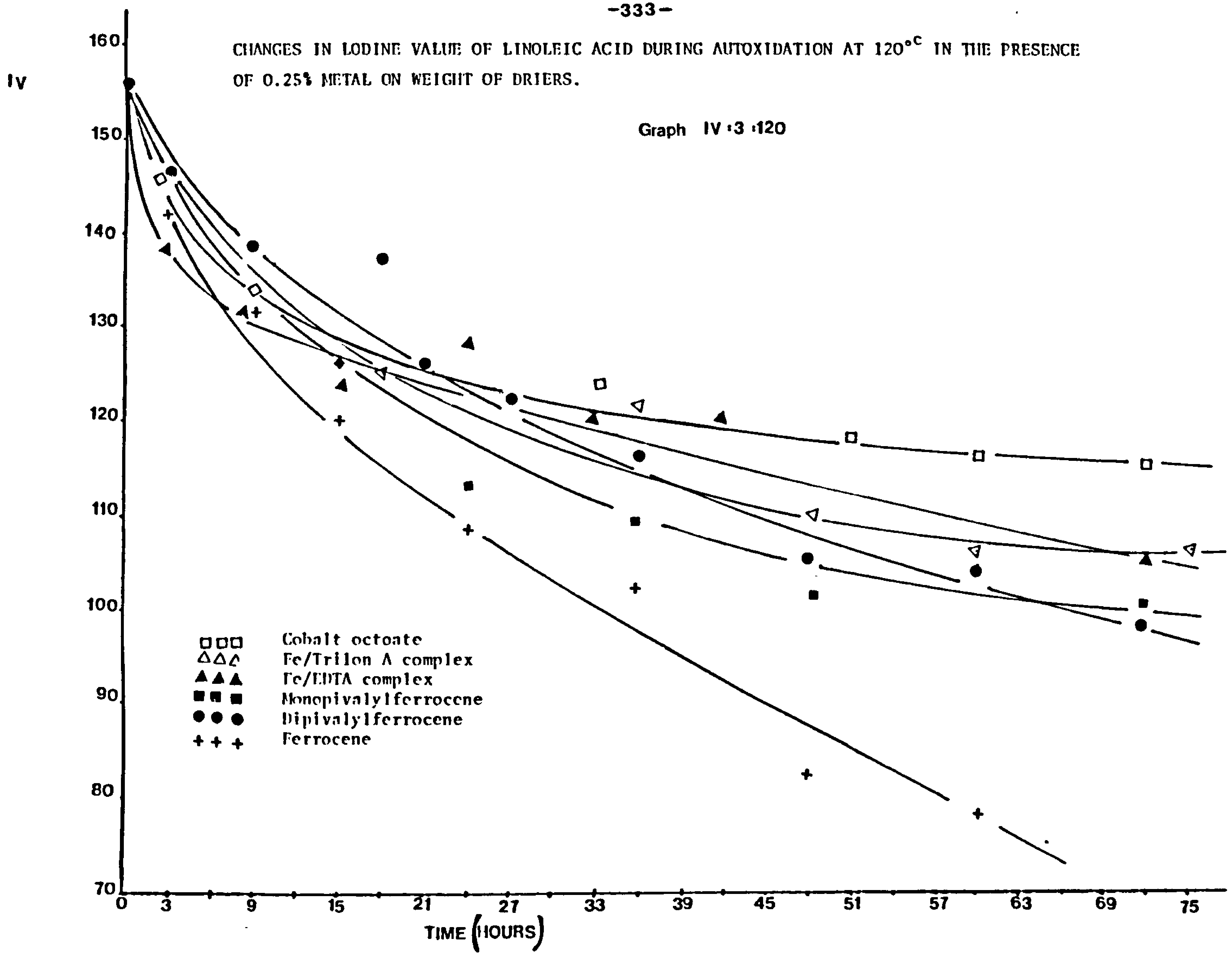
Graph IV:2 :120



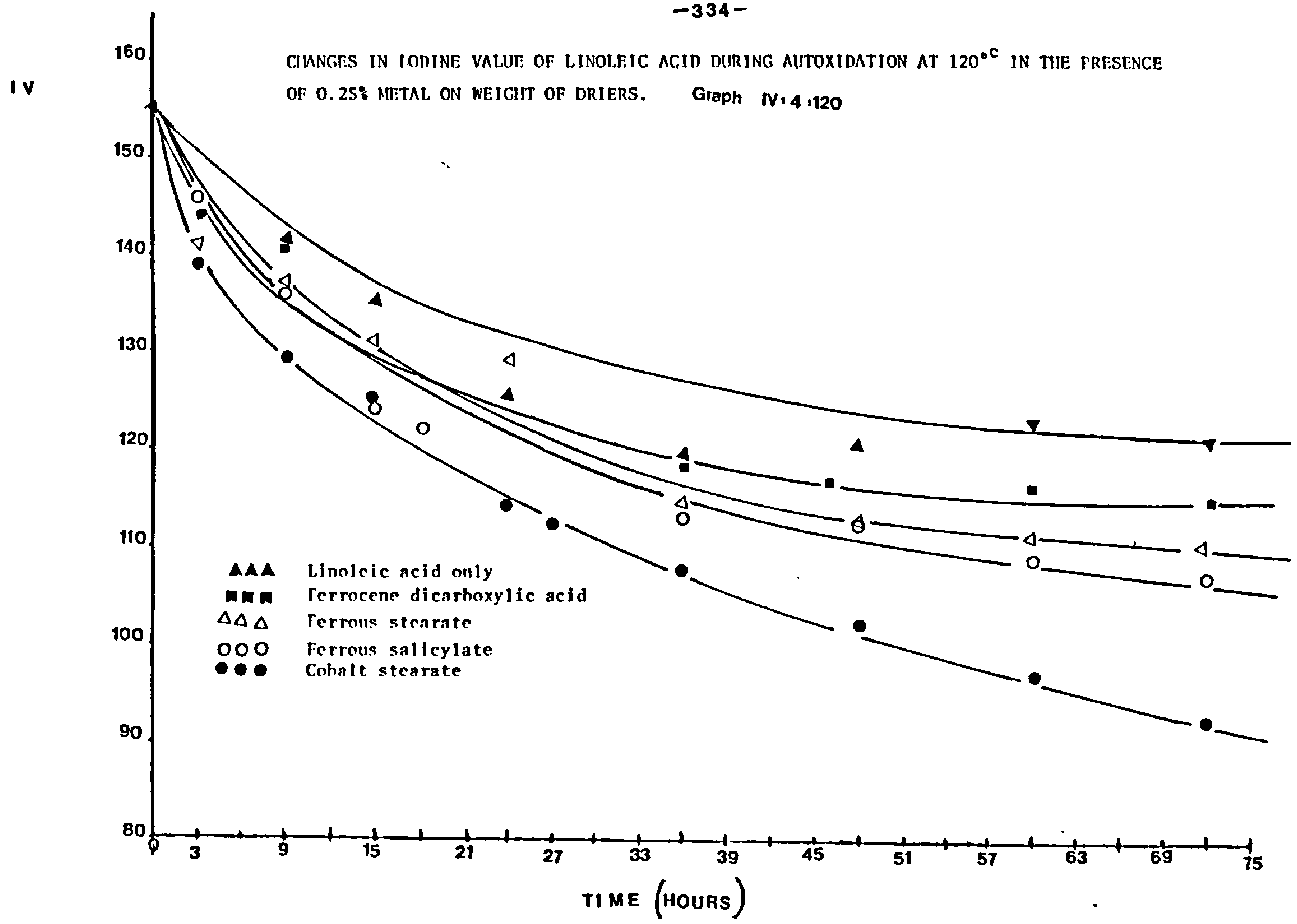
Catalytic performance of some driers 0·05% metal on the weight of driers at 120°C.

CHANGES IN IODINE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT 120°C IN THE PRESENCE OF 0.25% METAL ON WEIGHT OF DRIERS.

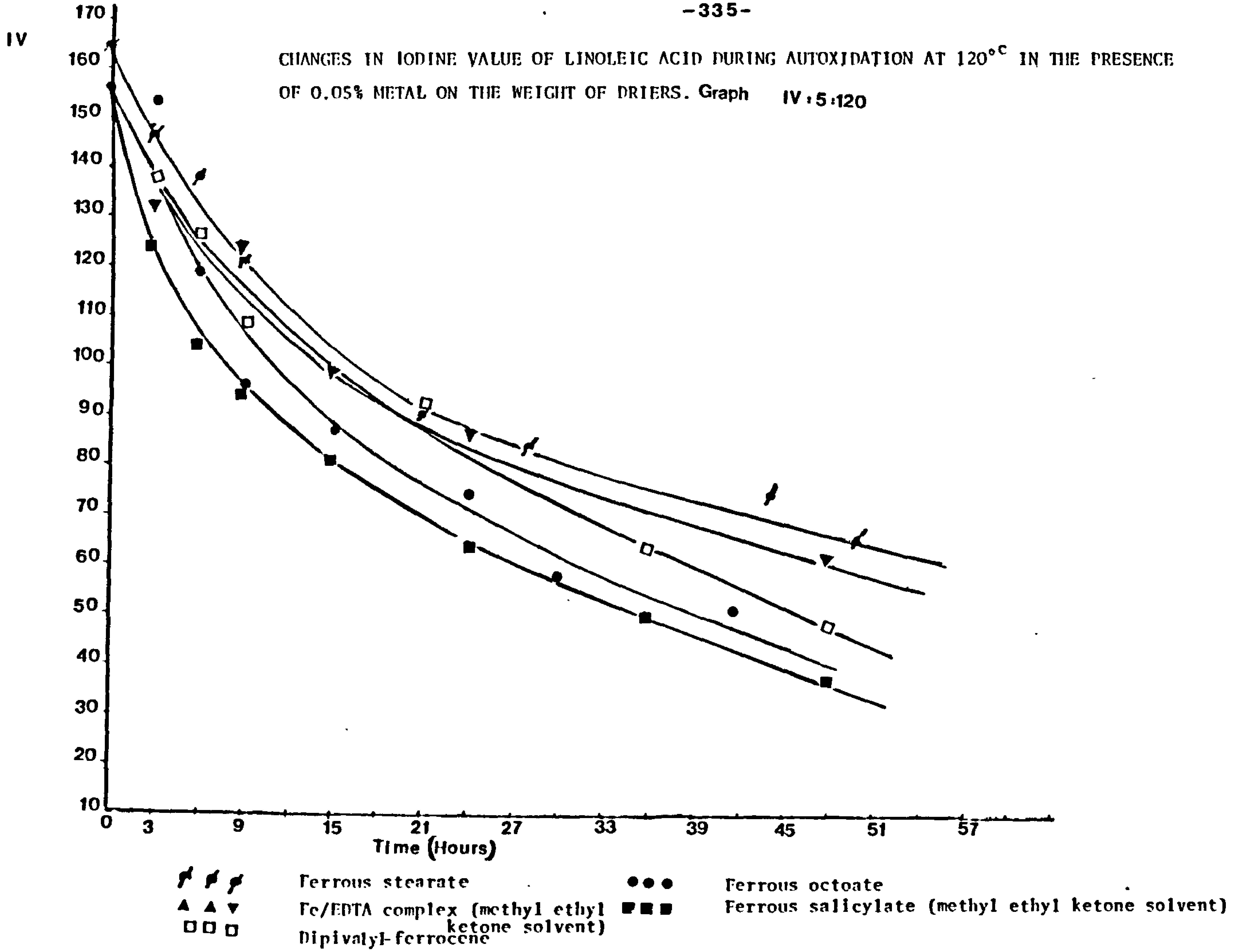
Graph IV:3:120



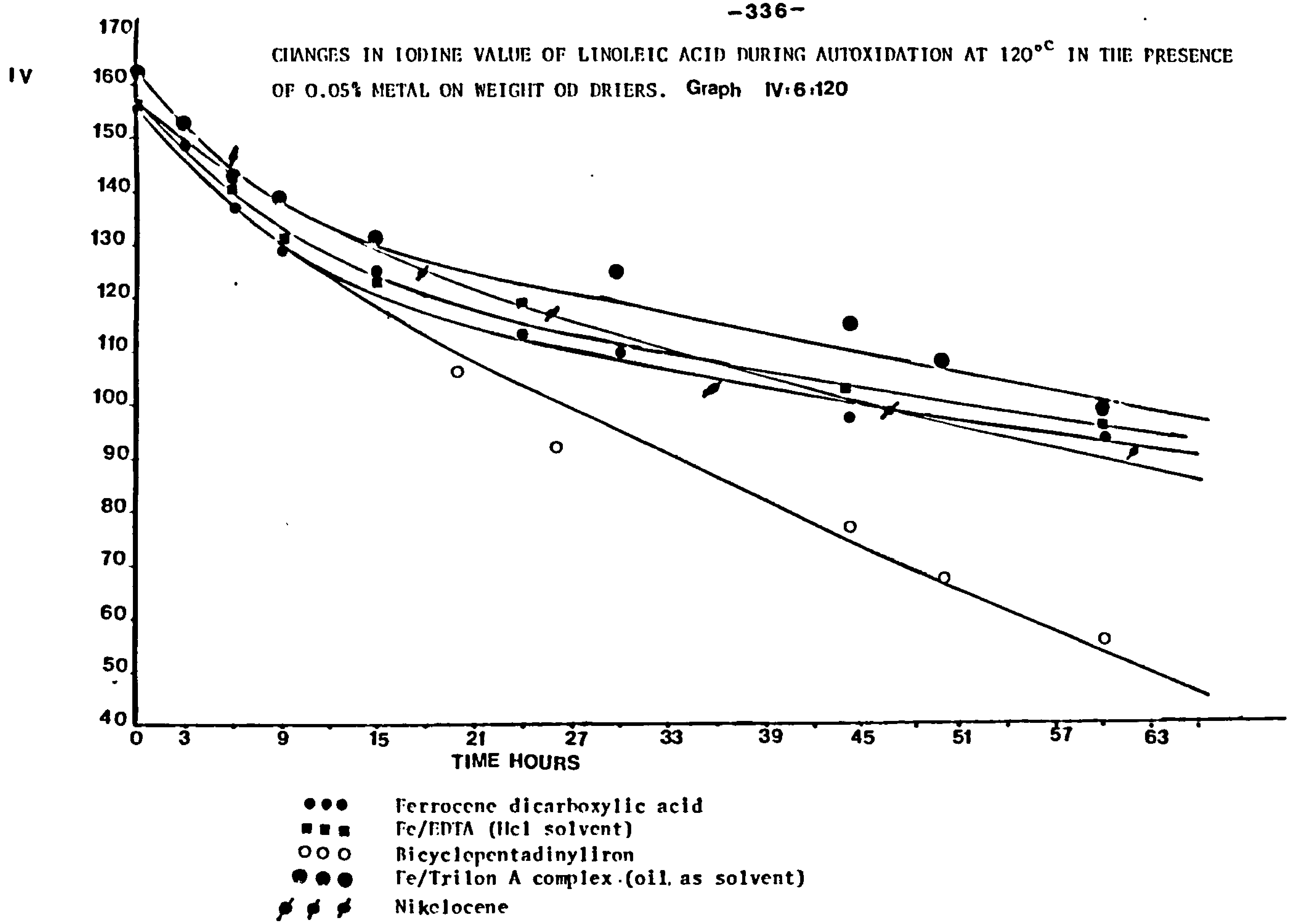
CHANGES IN IODINE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT 120°C IN THE PRESENCE OF 0.25% METAL ON WEIGHT OF DRIERS. Graph IV·4·120



CHANGES IN IODINE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT 120°C IN THE PRESENCE OF 0.05% METAL ON THE WEIGHT OF DRIERS. Graph IV:5:120

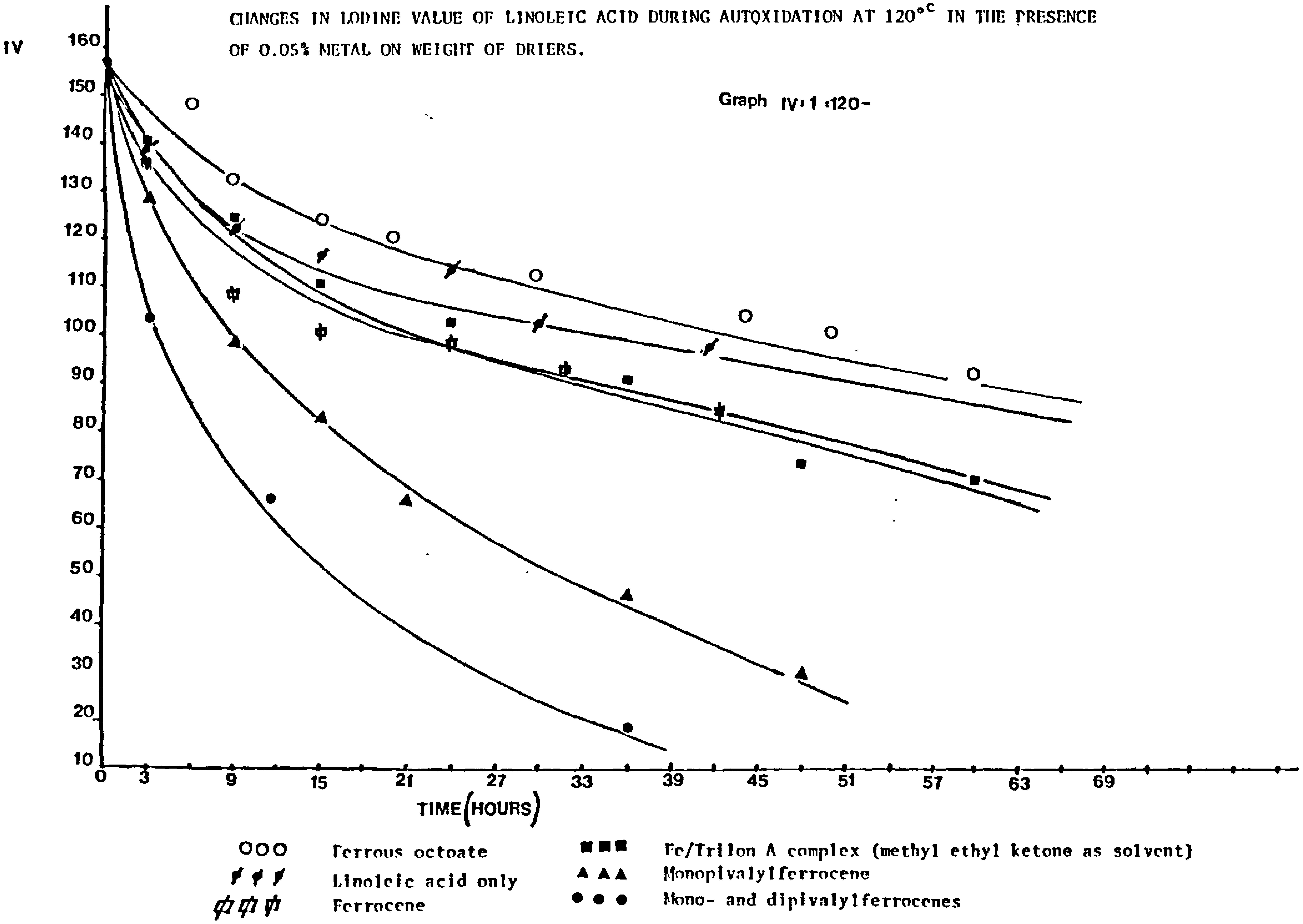


CHANGES IN IODINE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT 120°C IN THE PRESENCE OF 0.05% METAL ON WEIGHT OD DRIERS. Graph IV:6:120



CHANGES IN IODINE VALUE OF LINOLEIC ACID DURING AUTOXIDATION AT 120°C IN THE PRESENCE OF 0.05% METAL ON WEIGHT OF DRIERS.

Graph IV:1:120-



CHAPTER 7

DISCUSSION AND CONCLUSIONS

The scope of this work was to provide an assessment of the catalytic efficiency of some iron co-ordination compounds compared with the more conventional driers at low and elevated temperatures.

The aim was to investigate the use of iron co-ordination compounds as stoving (high temperature) catalysts for oil-based coatings.

As mentioned earlier (p.105); the industrialization of the painting process raised the demand for a shortening of the time required for drying and improved high temperature characteristics of coated surfaces. These important industrial requirements have been achieved in two ways:

(i) By the development of finishes which dry spontaneously in much shorter times than the conventional oil paints, and

(ii) By the development of finishes whose rate of drying is either dependent on or is greatly accelerated by the provision of energy such as heat. Stoving catalysts are those that operate at high reaction temperatures during drying processes.

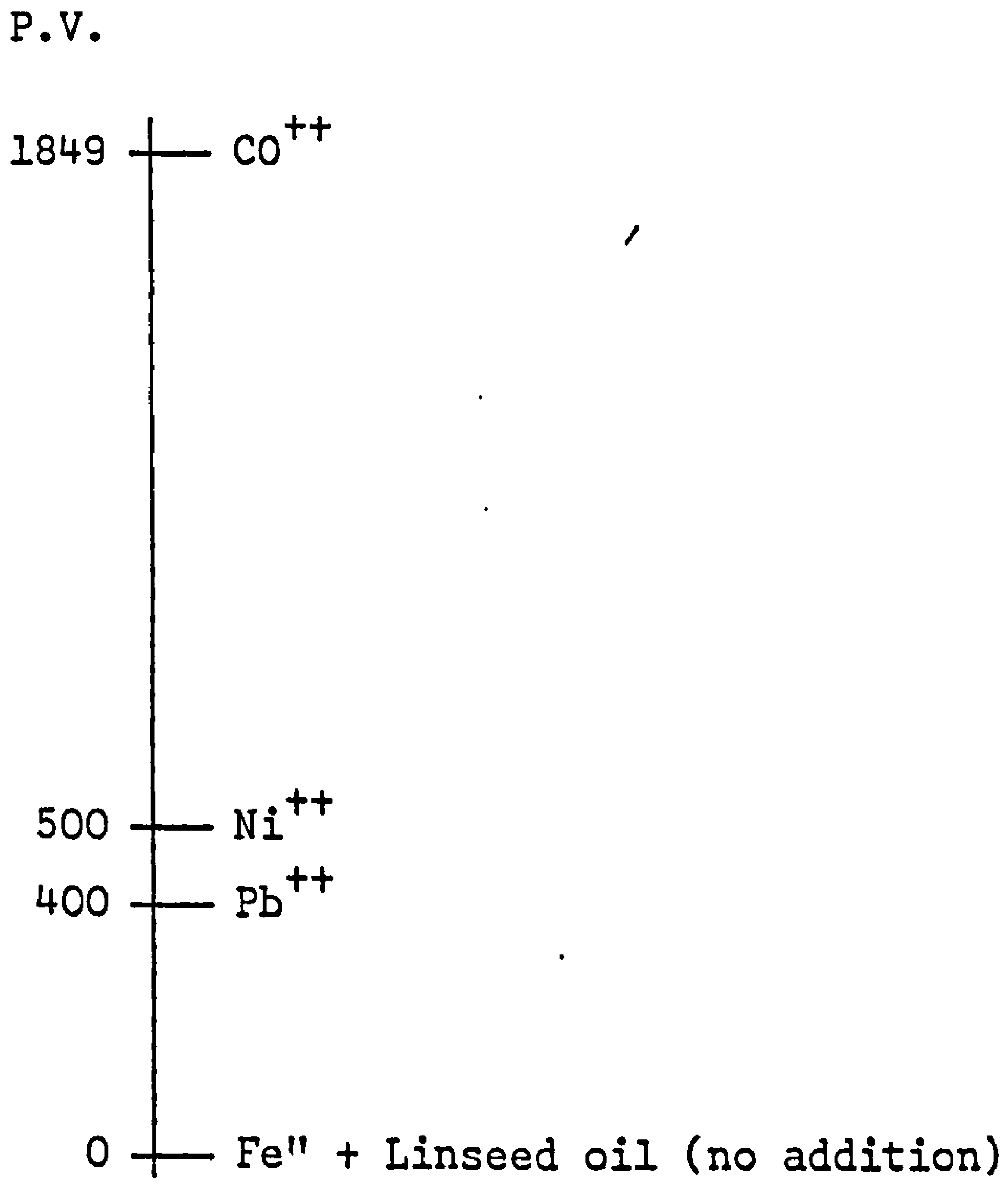
The need for temperature activated catalysts is linked with mass production techniques, introducing economies in drying costs; time; space and less wastage of coating materials. Stoved objects can be subjected to uses where room temperature coated objects cannot be employed.

The decision to investigate iron co-ordination compounds as possible stoving catalysts has arisen from the results of work carried out in this department.

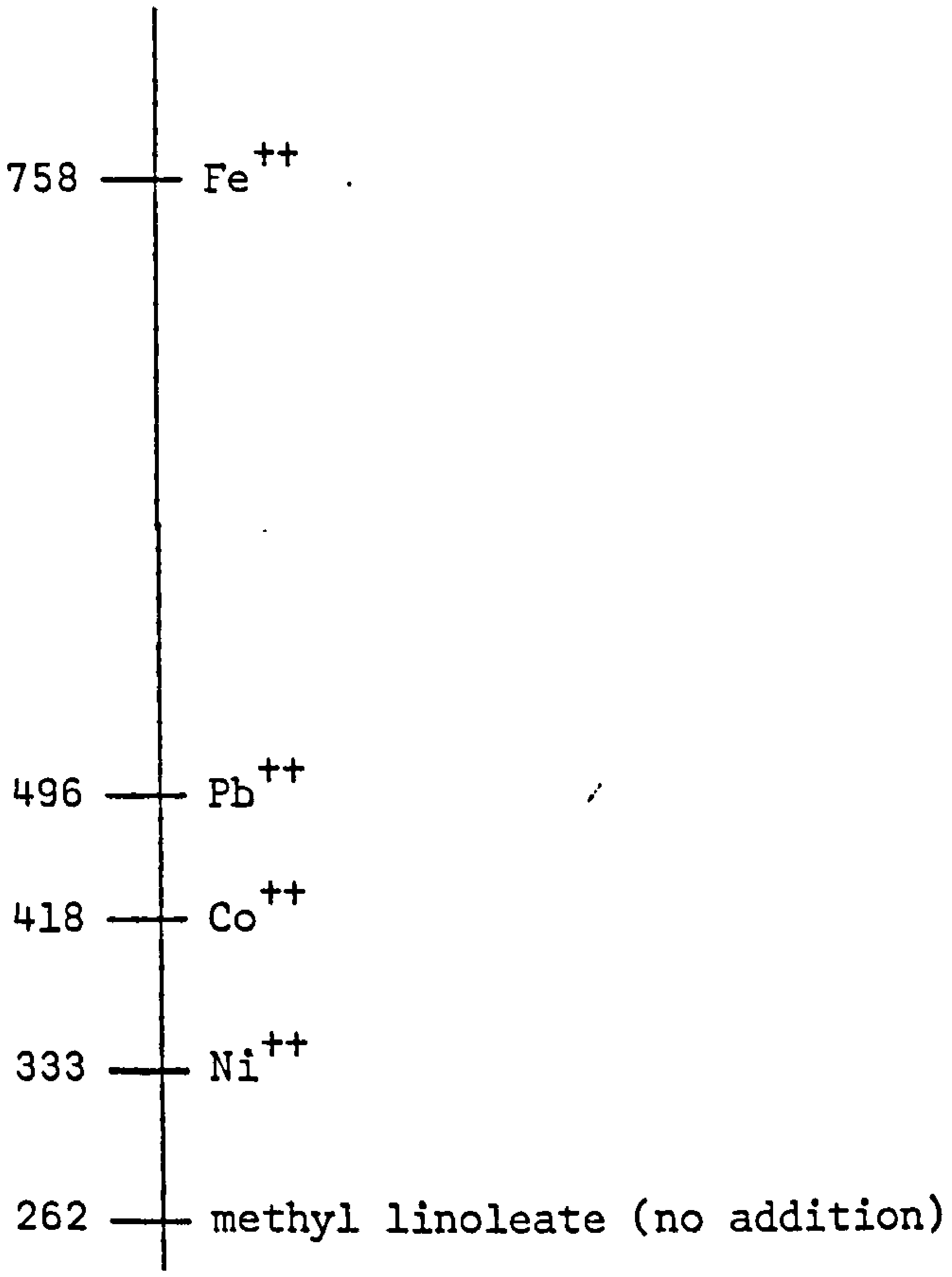
Arghande(248) studied the autoxidation of methyl linoleate catalysed by various metal stearates. He observed that iron stearate behaved differently from the other metal salts. A summary of Arghande's findings is as follows:

(i) Peroxide value after 33 days of autoxidation in the presence of linseed oil and 0.01% metal stearates is as shown below.

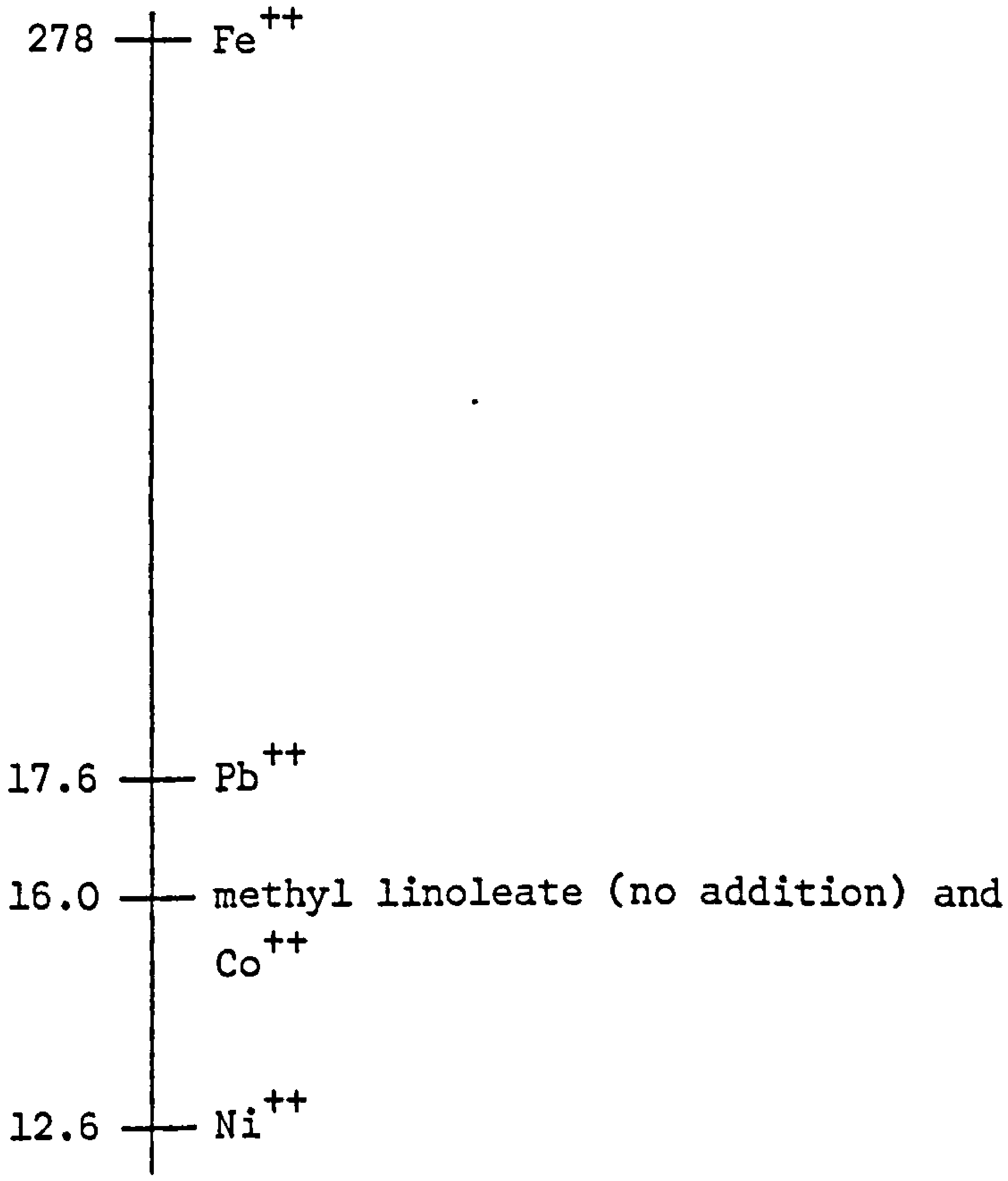
(i)



(ii) Changes in molecular weight after 33 days of autoxidation are as shown below.



(iii) Observed viscosity changes after 33 days of autoxidation (centipoises) are as shown below.



(iv) Volatile products (mainly aldehydes and ketones) were quantitatively estimated. The ratios of total volatile products released after 33 days by autoxidised methyl linoleate in the presence of metal stearates are as follows.

(1) Fe^{++} (1.2 mls)
(2) CO^{++} (0.7 mls)
(3) Ni^{++} (0.4 mls)
(4) Pb^{++} (0.2 mls)
(5) Methyl linoleate (no addition) (< 0.1 mls)

Prompted by the findings of Arghande, further work was done by Sanda(11) who observed that at low concentrations and low temperatures, ferrous stearate was as reactive as other conventional driers. Other observations made by Sanda are as follows:

(i) Peroxides inhibit iron catalysis during autoxidation and such effect is shown particularly at high iron concentrations.

(ii) Peroxides are more rapidly destroyed in iron catalysed autoxidation particularly at high iron concentrations.

(iii) Metal deactivation affects the kinetic behaviour of iron catalysed autoxidation. The effect of metal deactivation is significant at low iron concentrations.

Metal deactivation at low concentrations and severe peroxide decomposition at high metal concentrations are apparently the main causes of the anomalous behaviour shown by iron stearate observed by Sanda.

It has been known that iron compounds are more active at higher temperatures(249) so that the next area of investigation was an examination of 'blocked' iron compounds as possible stoving catalysts in autoxidative systems. Typically compounds such as Ferrocene; Fe/EDTA; Fe/Trilon A complex; Ferrocene dicarboxylic acid; Ferrous salicylate; monopivaloylferrocene and dipivaloylferrocene etc. have been studied in this work.

Ferrocene, the parent compound in this work has earlier been discussed (Chapter 4). Ferrocene is an orange crystalline solid with a camphor-like odour. It has a melting point of 173-174°C and resists pyrolysis at 400°C. Ferrocene is insoluble in water, sparingly soluble in benzene, ether and petroleum ether. It evolves toxic products on decomposition and heating. It has moderate fire risk.

Ferrocene has been used as additive for fuel oils to improve efficiency of combustion and eliminate smoke; as anti-knock agent, and as a catalyst in the manufacture of coatings for missiles and satellites, in the production of ultraviolet absorbers, in high temperature lubricant and intermediate for high temperature polymer manufacture(250).

Other features of ferrocene have been discussed (pp.113-118).

BLOCKED CATALYSTS AT LOW AND HIGH TEMPERATURE REACTIONS

(i) AT LOW TEMPERATURES: The reactivity of a blocked catalyst at low temperatures is negligible. Additionally, in such compounds as ferrocene, the metal is zerovalent iron firmly held by the two cyclopentadienyl rings (p.113). At room temperatures, the ferrocene is catalytically inert in autoxidative systems.

(ii) AT STOVING TEMPERATURES: The action of a blocked catalyst at stoving temperatures should involve a breakdown of the metal ions from the ligand and probable subsequent change in the oxidation state of the metal.

e.g. $\mathrm{Fe} \longrightarrow \mathrm{Fe}^{++} \longrightarrow \mathrm{Fe}^{+++}$

$\mathrm{Fe\ complex} \longrightarrow \mathrm{Fe}^{++} \longrightarrow \mathrm{Fe}^{+++}$

These reactions are reversible at temperatures below stoving.

1.1 ECONOMIC ASPECTS OF BLOCKED CATALYSTS

(i) RAW MATERIAL SAVINGS The function of stoving catalysts is of considerable importance to the industrial paint technologist whose aim it is to maximise profits through effective utility of his raw materials. For instance, the stove enamelling of items often requires the preparation of a large volume of paint solution for dipping the objects e.g. refrigerators; coolers, cars, etc. which without the existence of blocked catalysts might become useless shortly after use (air-dried paints would rapidly become tacky and viscous on exposure to air).

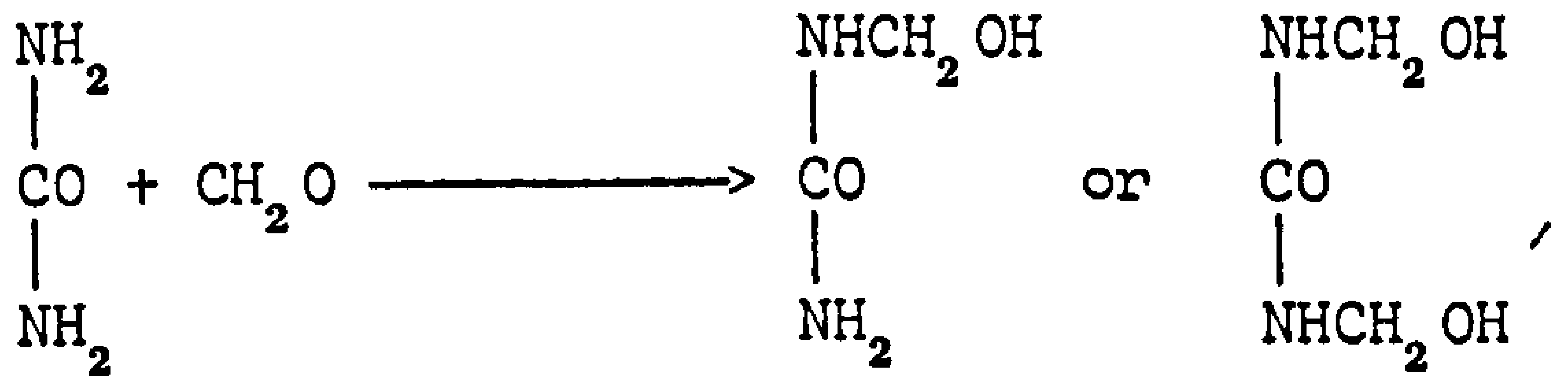
TIME: Time is of considerable significance in industrial processes. Stoving processes come to completion within minutes. This gives rise to rapid throughput of the coated materials.

SPACE: Since stoving processes come to completion so rapidly, there are considerable savings in floor space. This is because instead of an object to be painted and allowed to dry in three to six hours, it dries within minutes when subjected to stoving processes. Additionally, on cooling, the paint films are immediately hard enough for retailing, whereas conventional paints may take several days to become thoroughly through-hardened.

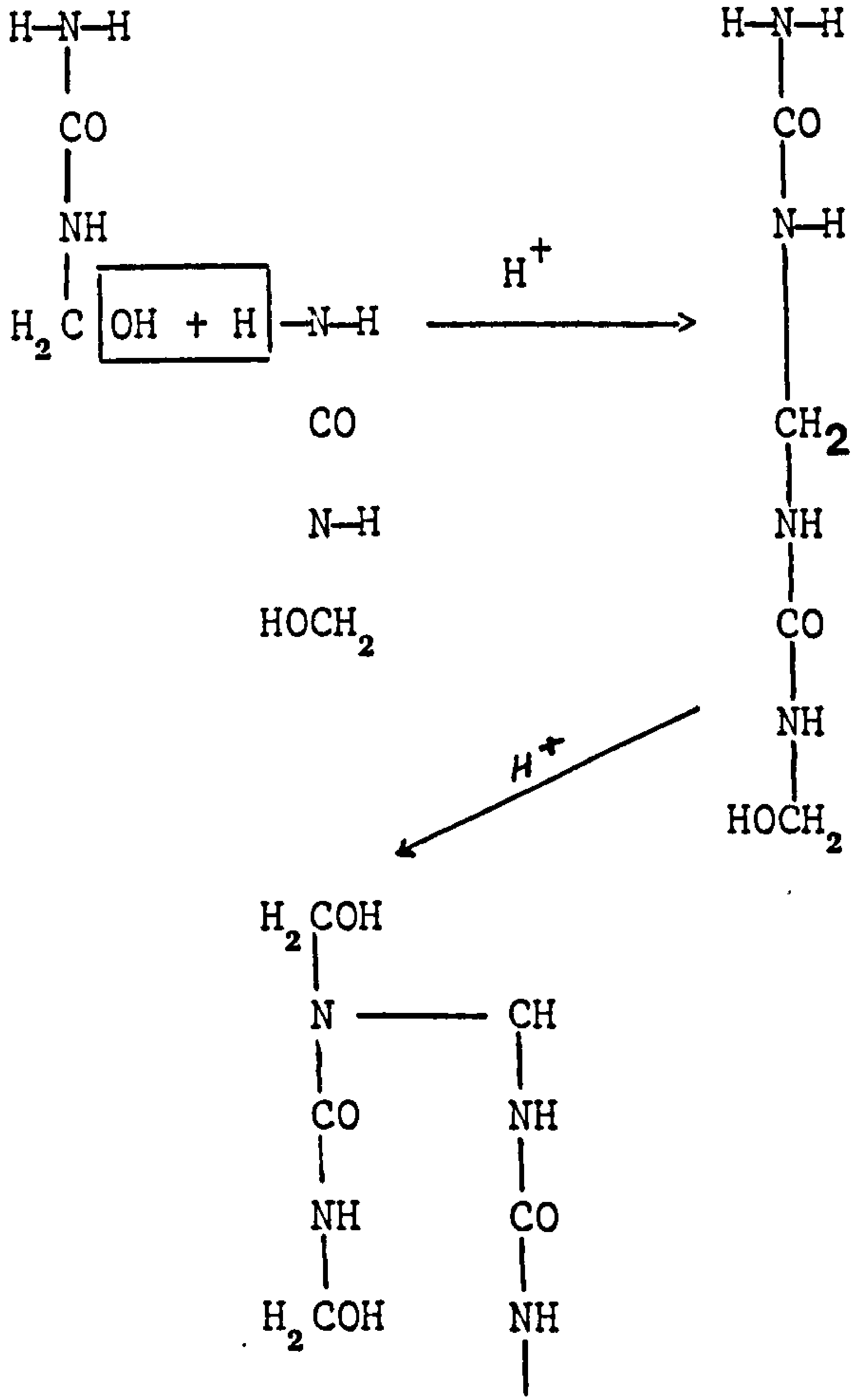
1.2 SOME APPLICATIONS OF HIGH TEMPERATURE CATALYSTS

Blocked catalysts have been employed variously in many industrial manufacturing processes e.g. use is made of urea-formaldehyde resin as anti-crease resistant finish in textile garments.

Under neutral or slightly alkaline conditions, urea and formaldehyde condense to give either mono-or di-methyol urea according to the molecular proportions of the reagents.

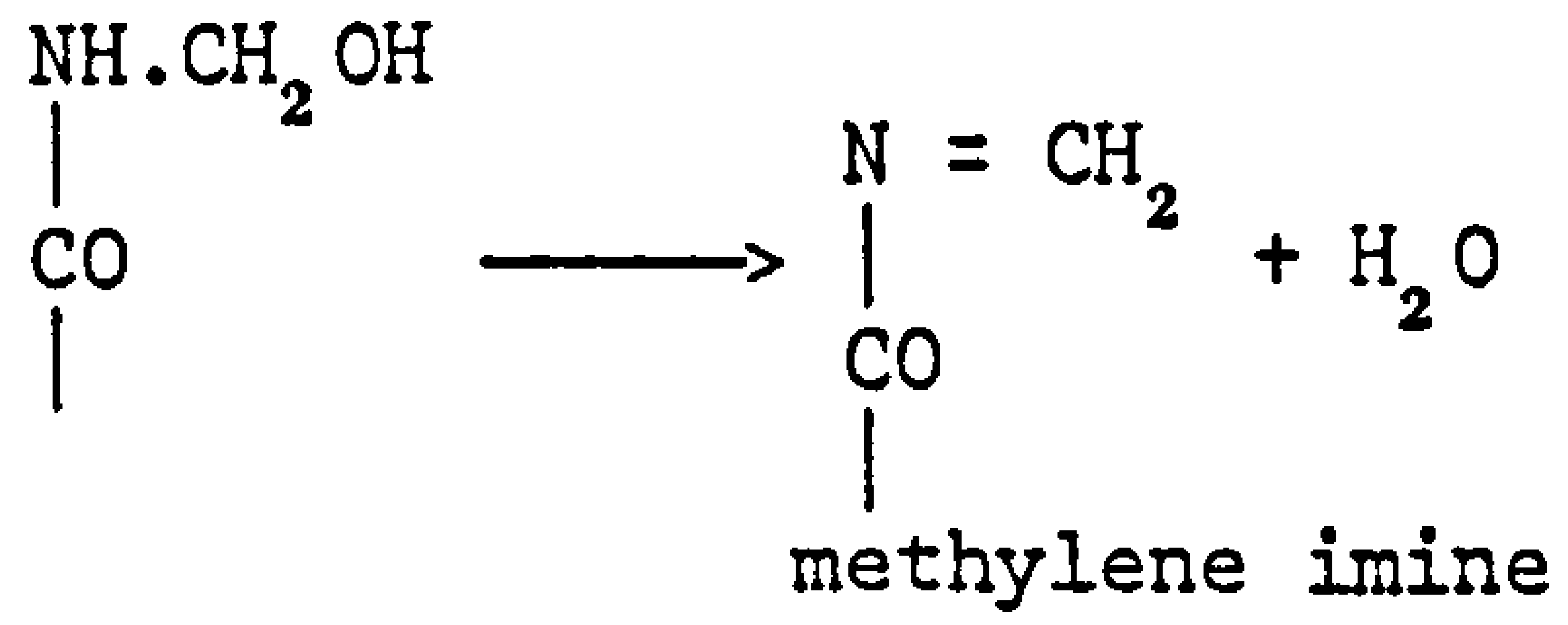


When formaldehyde and urea, or the methylol ureas are heated with acid catalysts, polymers are produced. The polymers are either linear or branched, the latter being of great importance in surface coatings.



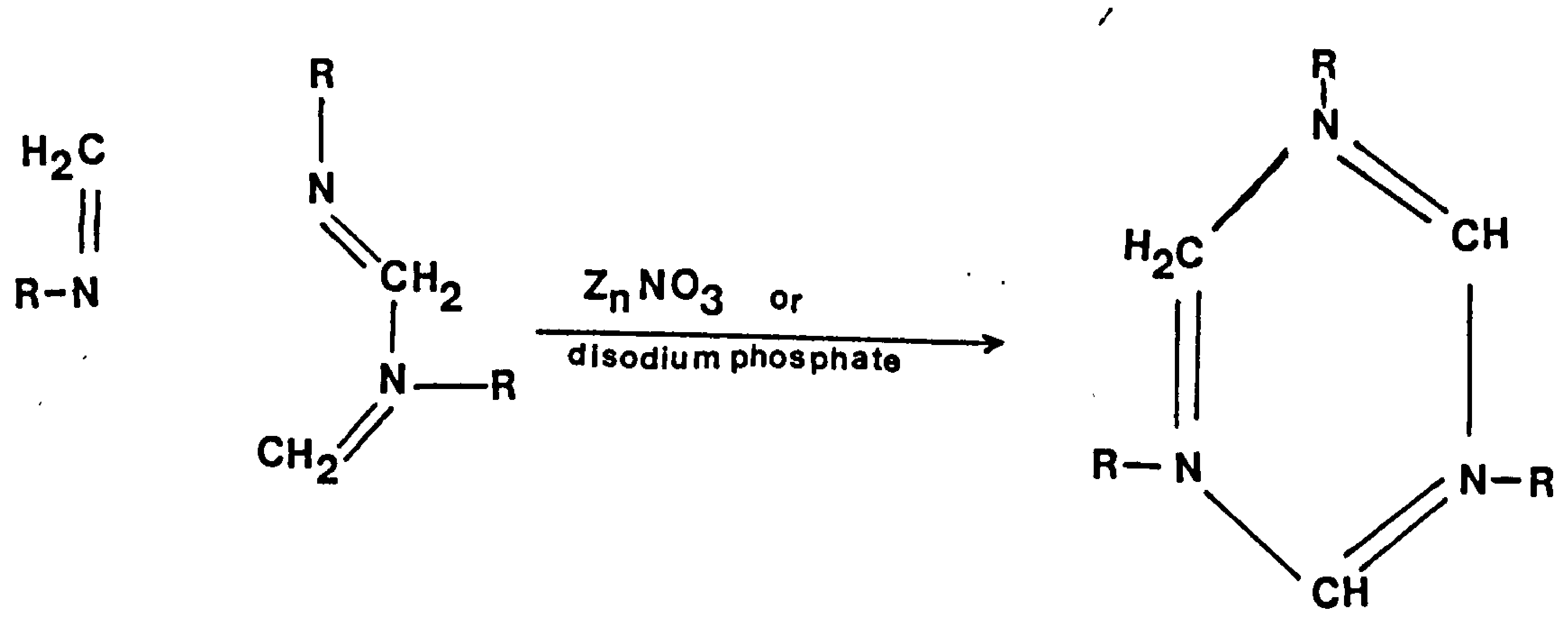
Branched polymer

It has been suggested that loss of water does not occur between molecules but that the first reaction is the loss of water to produce a methylene imine(251).

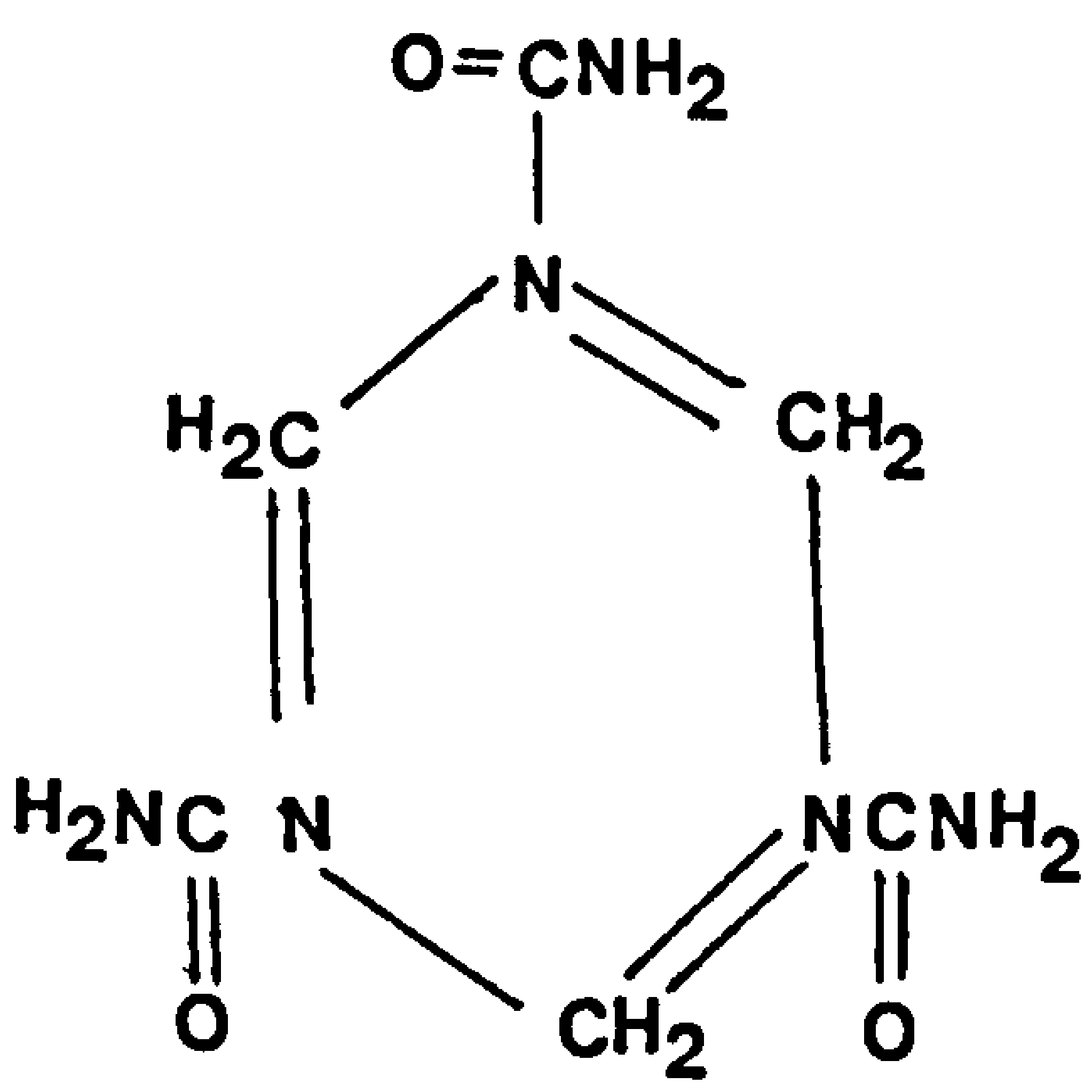


$$\begin{array}{l} NH.CH_2OH \\ | \\ CO \\ | \end{array} \longrightarrow \begin{array}{l} N = CH_2 \\ | \\ CO \\ | \end{array} + H_2O$$

The methylene imines produced from primary amines and formaldehyde undergo spontaneous trimerisation.



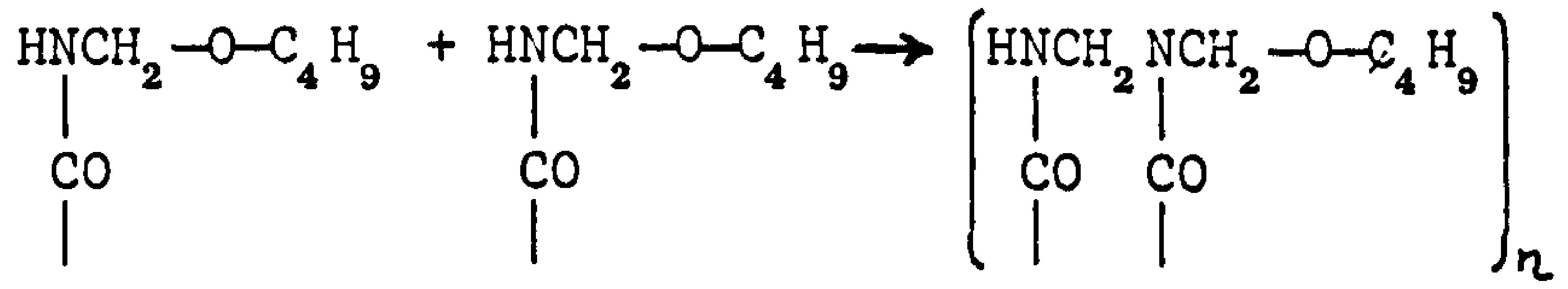
With methylene ureas, the structure produced is



Products of varying methylol content can be prepared with subsequent formation of polymers with varying complexity.

Melamine resins are often preferred to urea resins for stoving, as the original solutions show a greater compatibility with hydrocarbon solvents, are more rapidly cured on stoving, and the films produced are more resistant to the effects of light and heat and attack by chemicals.

On stoving butylated melamine resins, butanol is lost and polymerisation occurs as shown below in the presence of a catalyst.

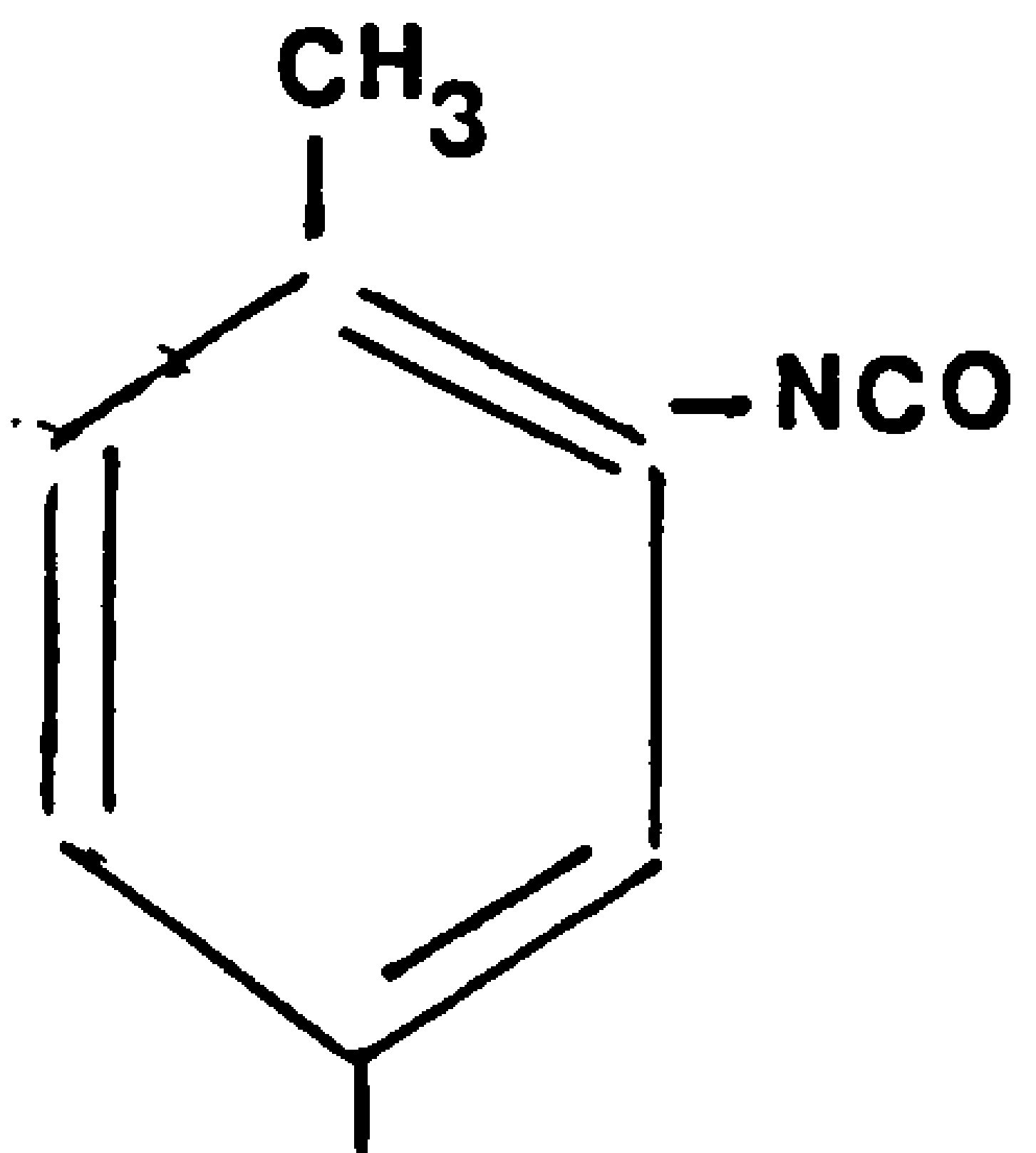


$$\underset{\underset{|}{\text{CO}}}{\underset{|}{\text{HN}}}\text{CH}_2\text{—O—C}_4\text{H}_9 + \underset{\underset{|}{\text{CO}}}{\underset{|}{\text{HN}}}\text{CH}_2\text{—O—C}_4\text{H}_9 \rightarrow \left[\underset{\underset{|}{\text{CO}}}{\underset{|}{\text{HN}}}\text{CH}_2\underset{\underset{|}{\text{CO}}}{\underset{|}{\text{N}}}\text{CH}_2\text{—O—C}_4\text{H}_9\right]_n$$

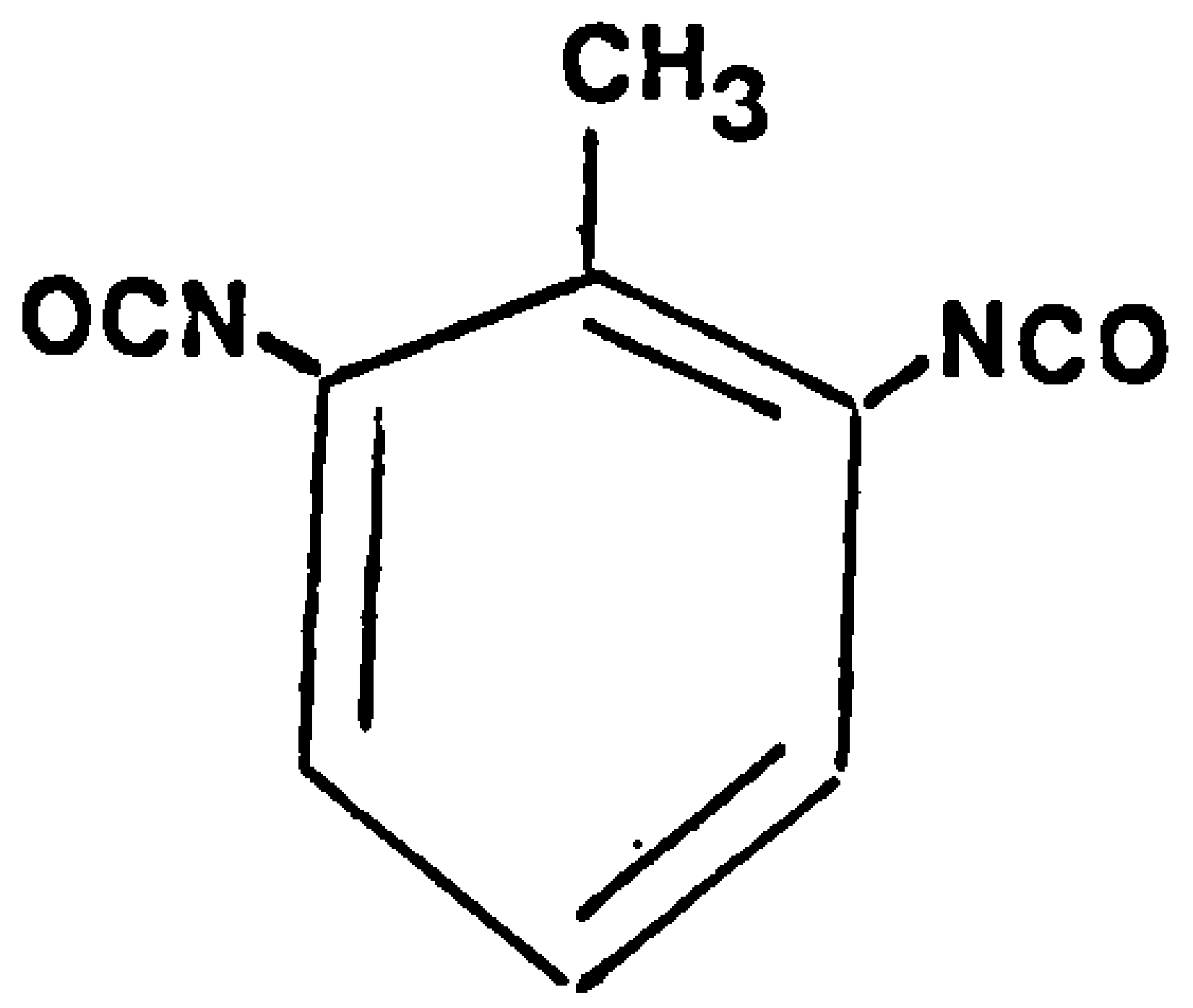
Some polyurethane resins (stoving or heat curing systems) can be produced from blocked adducts in stoving enamels. Polyurethane resins are polymers containing the urethane grouping $-\overset{\text{H}}{\overset{|}{\text{N}}}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{O}-$; with the main polymer backbone. They are formed by the reaction of isocyanates R—NCO— with hydroxyl compounds.

Polyurethanes prepared for surface coatings are derived from di-isocyanates which form linear polymers upon reaction with diols (aliphatic glycols) and cross-linked or network polymers when reacted with polyols (e.g. polyesters, polyethers and some vegetable oils as well as water). The most commonly used isocyanate is toluene di-isocyanate (TDI) which exists in two forms:

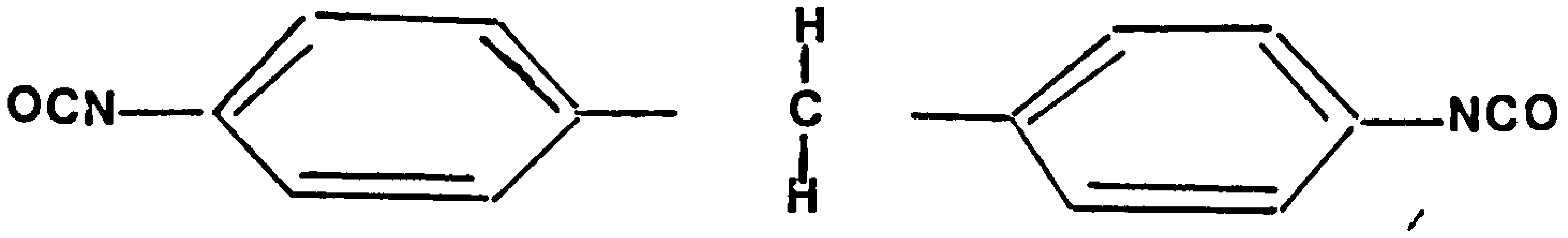
(i) 2, 4 isomer



(ii) 2, 6 isomer

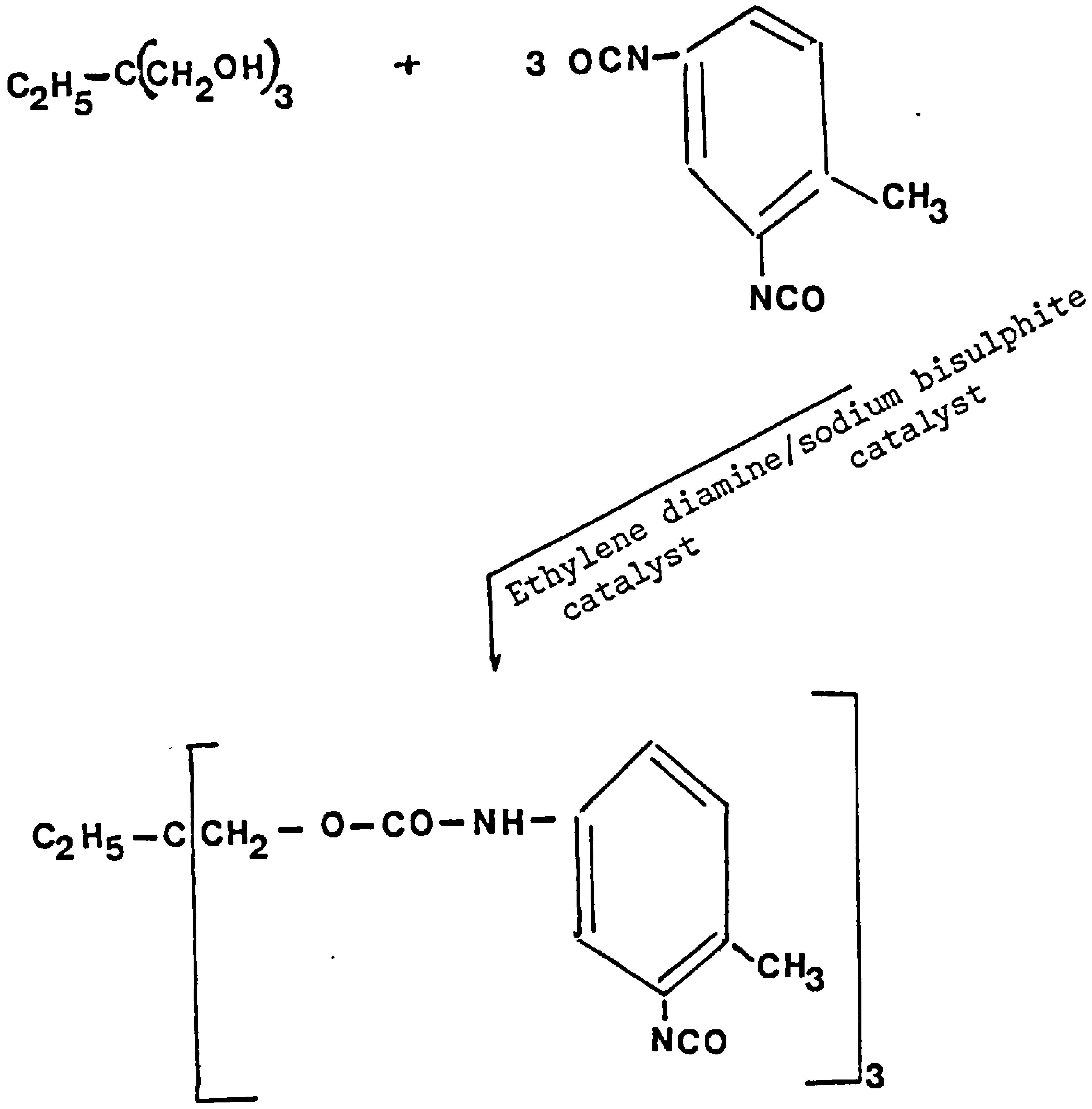


Other isocyanates of importance in the coating industry are diphenylmethane di-isocyanate (MDI)

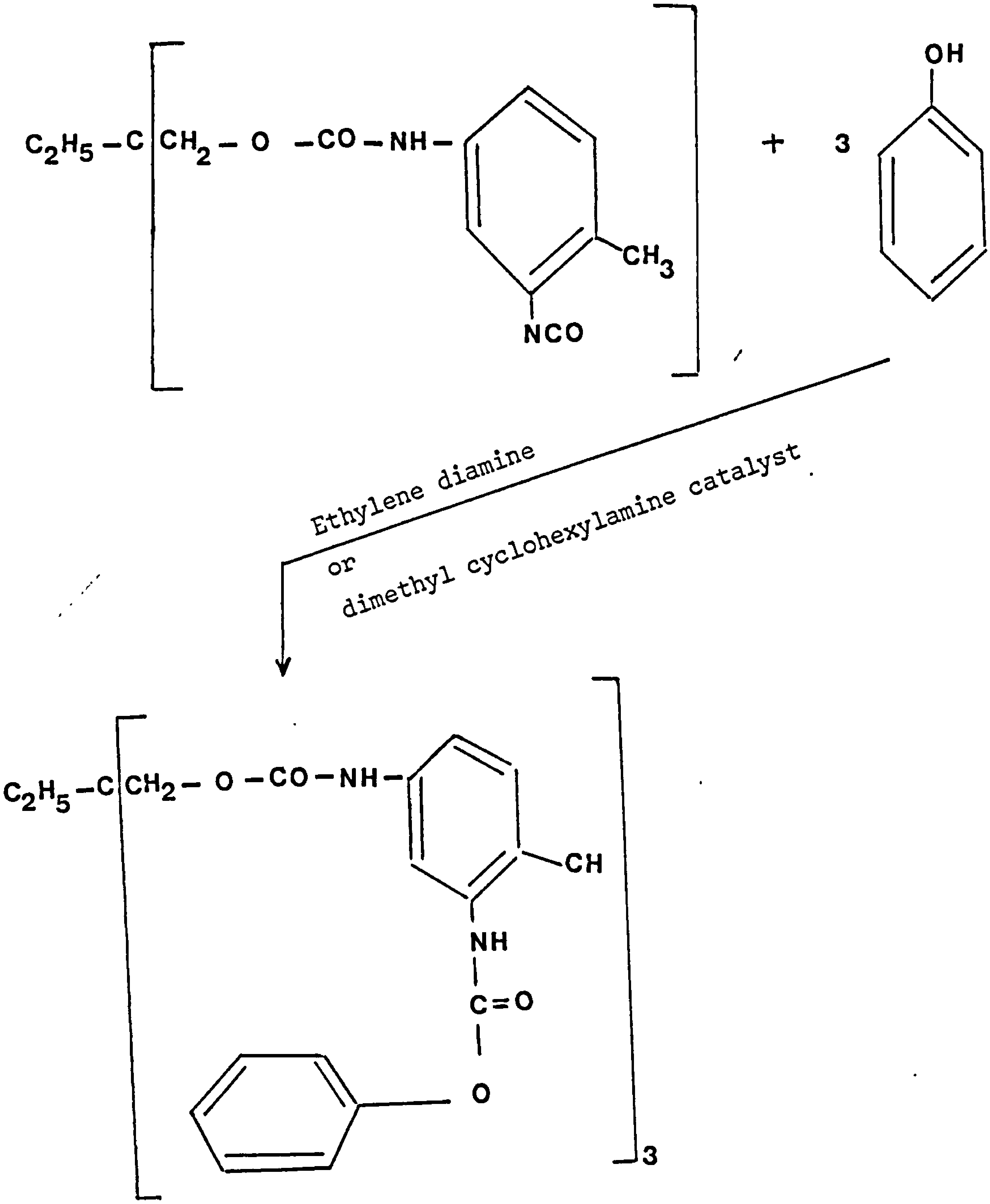


and hexamethylene di-isocyanate (HDI) OCN – $(CH_2)_6$ – NCO.

Typically excess toluene di-isocyanate (TDI) is reacted with a polyol such as trimethylol propane to form a urethane containing free isocyanate groups.



The free isocyanate groups may then be reacted with a phenol to form a thermally labile adduct.



When these blocked adducts are subjected to heat, typically 150°C, the free isocyanate groups are regenerated and cross-linking occurs with added hydroxy compounds present in binder formulation. Coating systems based on blocked adducts have the great advantage of stability during storage whilst the highly cross-linked polyurethane films exhibit excellent chemical and abrasion resistance.

Other high temperature catalysts employed in crease-resist and showerproof treatments of textile garments include tartaric acid; octadecycloxymethylpyridinium chloride; dihydrogen phosphate and stearamidomethylpyridinium chloride(252).

SILICONE RESINS

The use of oil-soluble organometallic catalysts such as zinc-2-ethylbenzeoate or tin naphthenate, zirconium oxychloride; and tertraethyl-O-titanate in the curing of silicone-based resins has been reported(252).

TECHNIQUES EMPLOYED

The comparative catalytic efficiency of the iron compounds was monitored through measurements of oxygen absorption and changes in iodine and peroxide values of cis 9, cis 12 octadecadienoic acid.

Reactions were carried out at room temperatures, 60°C, 80°C and 120°C.

Although stoving processes normally come into completion in a few minutes, the time scale was extended for up to 60 hours for practical purposes by using deliberately inefficient systems and temperatures below normal stoving levels (e.g. 150°C).

1.3 EXPERIMENTAL FINDINGS

OXYGEN ABSORPTION OF 9, 12 OCTADICDINOIC ACID IN THE PRESENCE OF CATALYSTS

(i) The Induction Period and Room Temperature Reactions

The measurement of induction period for all the driers employed in this work reveals that at room temperatures, the iron complexes have longer induction periods than the conventional driers (Graphs 1:RT; and 2:RT). The rate of oxygen absorption by uncatalysed 9, 12-octadecadienoic acid is very slow and at any temperature the absorption is a function of catalyst concentration in most cases.

The overall autoxidation rate at any temperature is a function of catalyst concentration. It is therefore expected that as well as simple temperature dependent increases in all cases in the rate of oxygen absorption, reactions catalysed by the inclusion of complexes may be expecially temperature sensitive, since the stability of complexes falls with increase in temperature. Since the stability constant of a complex is temperature dependent, as the temperature rises, the complexes break down increasingly releasing catalytic metal ions in amounts which determine their efficiency.

Measurements of induction periods for the various reaction systems agree with the postulations of Riche[191] who said that autoxidation of non-conjugated drying and semi-drying oils was due to attack by molecular oxygen at activated methylene groups to form hydroperoxides. The slow reaction rates at room temperature (Graphs 1:RT and 2:RT and Graphs lV:lRT - lV:5RT) increased with time due to removal of inhibitors from the system. Once complete removal has been affected, the reaction rate increases in the same pattern with all systems in which reaction parameters are identical. Additionally, in catalysed systems, where the catalyst is a metal ion, as is the case with much of this work, the oxidation state is often a critical factor in the initial catalytic activity of the system. The rates of reaction for each drier can be determined from the gradients of the oxygen up-take curves, which at room temperatures are least with the iron complexes compared with the conventional driers.

It has been observed that with the heavy metal salt-catalysed oxidation of aldehydes, the onset of oxygen absorption corresponded with a change of valency state of the metal(238). With a soluble cobalt salt catalyst, commencement of a reaction coincided with the change from the pink cobaltous to the green cobaltic trivalent state. Kagan and Lubarsky(239) observed similar results using manganous salts. Hence again, the onset of oxidation, after a well-defined induction period, corresponded with the formation of manganic ion, a reaction observed by a vivid colour change.

Incomplete transformation of cobalt catalyst to the higher valance state has been observed during the oxidation of some unsaturated hydrocarbons in acetic acid(239). Incomplete oxidation reactions must therefore affect the valence state of a metal catalyst and the overall rate of the reaction.

(ii) Catalyst Concentration

The results from this work on 0.25% iron and 0.05% iron on the weight of 9, 12-octadecadienoic acid reveal that a categoric statement cannot be made with reference to the catalyst concentration and reactivity. This is because a proportional increase in reactivity was observed with increased concentration of some catalysts on one hand, whilst with other iron compounds a less than proportional increase in rate of reaction was observed with increased catalyst concentration (Graph lV:2RT).

Catalyst efficiency may therefore be dependent on the experimental conditions. Peroxides are readily produced (at least in small amounts) even in uncatalysed autoxidation and they are possibly the agents causing the observed valency change of the metal catalysts.

$$M^{++} + ROOH \longrightarrow M^{+++} + RO^{\cdot} + OH^{-}$$

Oxidations catalysed by lead and cobalt salts have shorter induction periods compared with iron compounds confirming their use as room temperature catalysts (Graphs 1:RT and 2:RT).

(iii) Major Requirement of a Stoving Catalyst

For a compound to be employed as a stoving catalyst, one of its most important properties must be its ability to be non-reactive at room and preferably at moderate temperatures, but to be capable of showing maximum reactivity at about 150°C. This requirement is of course in addition to other properties expected of driers in general (see p.70). Stoving catalysts should therefore have very long induction periods at room or moderate temperatures which however should shorten or disappear at stoving temperatures. At low temperatures, stoving catalysts should show a low rate of reaction after the induction period. At stoving temperatures however, maximum catalytic activity should be shown as soon as the induction period is over if indeed such a period exists at all.

With reference to Graphs 1:RT and 2:RT, all the iron compounds except ferrocene and ferrous salicylate had lengthy induction periods at room temperatures. The most likely explanation for the different behaviour in the two groups of iron compounds is that the antioxidants in the system are more rapidly destroyed by ferrocene and ferrous salicylate than those based on the other iron compounds. It is believed that antioxidants are destroyed during the induction period. The following iron compounds showed no measurable rate of oxygen absorption at room temperatures: monopivaloyl ferrocene; dipivaloyl ferrocene; ferrocene dicarboxylic acid; Fe/EDTA and Fe/Trilon A complexes. The long induction periods associated with most of the iron compounds listed above are in line with the requirements of stoving catalysts at low temperatures. Ferrocene and ferrous salicylate appear at first sight to be less potentially useful than stoving catalysts because of their short induction periods. However, work at elevated temperatures shows the suitability of both compounds as stoving catalysts, since the other parameter of importance at room temperature is the rate of oxygen up-take of catalysed systems.

The reactions occurring during the induction period are not fully understood. It is probable that antioxidants are destroyed after which all definite chemical reactions of the main unsaturated components of the system occur.

Bolland and Gee(47) reported a finite rate of oxidation at the start of any reaction. Bateman et al.(48) suggested that the initial rate of oxidation approximated zero. Various samples of methyl linoleate when subjected to pure oxygen at atmospheric pressure (40^{0}C) gave irreproducible induction periods of up to 8 hours. Similar observations were made in this work as can be seen from the graphical representation of results at room temperatures (Graphs 1:RT and 2:RT). The induction period obtained for each of the compounds was far in excess of the 8 hours reported by Bateman et al.(48) There are two possible causes:

(i) There might be some differences in the purity of the 9, 12-octadecadienoic acid employed in this work and that employed by Bateman et al.(48)

(ii) There are bound to be differences in the existing experimental conditions in this work compared with those of Bateman et al.

Highly purified 9, 12-octadecadienoic acid has a long induction period with no measurable oxidation rate for several hours at room temperatures(85). Chain reactions may be initiated by some non-peroxidic free radicals or by stray radiation. Parallel chain reactions are initiated by radicals formed by decomposition of hydroperoxides(85).

The actual cause of the initial reaction in this work may include all of the above influences since all were present viz. stray radiation; heat and metal driers. The major autoxidative path must be via peroxide free-radicals. No form of initiators were introduced in the reaction vessels at the start of the experiments. The long induction periods observed at room temperatures when some iron compounds were present are co-incidentally one of the requirements of a stoving catalyst.

(iv) Conventional Room Temperature Driers

The behaviour of the conventional room temperature driers is in line with well established facts notably the short induction periods and high reactivities. These driers exert maximum reactivity at room and moderate reaction temperatures.

(v) Comparative Rates of Oxygen Absorption at Room Temperatures

The rate at which oxygen was absorbed by cis 9, cis 12-octadecadienoic acid catalysed by the various metal salts is as shown in Graphs 1:RT and 2:RT.

The cobalt and lead salts gave the shortest induction periods and the highest rates of reaction compared with the other driers.

Among the three iron compounds that showed low rates of oxygen absorption viz. ferrocene; ferrous salicylate and ferrous octoate, ferrocene had the longest induction period (31 hours); Ferrous salicylate (24 hours) and ferrous octoate (3 hours). All three catalysts gave much lower rates of oxygen up-take than the lead and cobalt salts.

The following iron compounds showed negligible rates of oxygen up-take up to 60 hours: Monopivaloyl ferrocene; dipivaloyl ferrocene; Fe/EDTA; Fe/Trilon A and ferrocene dicarboxylic acid.

Ferrocene and nickelocene each with zerovalent metal co-ordinated by two cyclopentadienyl rings should behave identically under the same experimental conditions. The observed differences in behaviour cannot be explained at present.

The order of reactivity for the iron compounds (complexes and non-complexes) is not clearly defined at this stage.

3.0 OXYGEN ABSORPTION OF CIS 9, CIS 12-OCTADECADIENOIC ACID AT 60^{0}C AND 80^{0}C

Induction periods were not observed at 60^{0}C, 80^{0}C and 120^{0}C. Autoxidation rates are temperature dependent, so the induction periods are likely to be shortened or even disappear with rise in temperature.

Reaction rates at 60^{0}C are higher than those at room temperature. Similarly, rates at 80^{0}C are higher than those at 60^{0}C.

Much higher rates of reaction were observed among some iron compounds and some conventional room temperature driers as the temperature was raised from 60^{0}C to 80^{0}C (see Generalized observation at 80^{0}C).

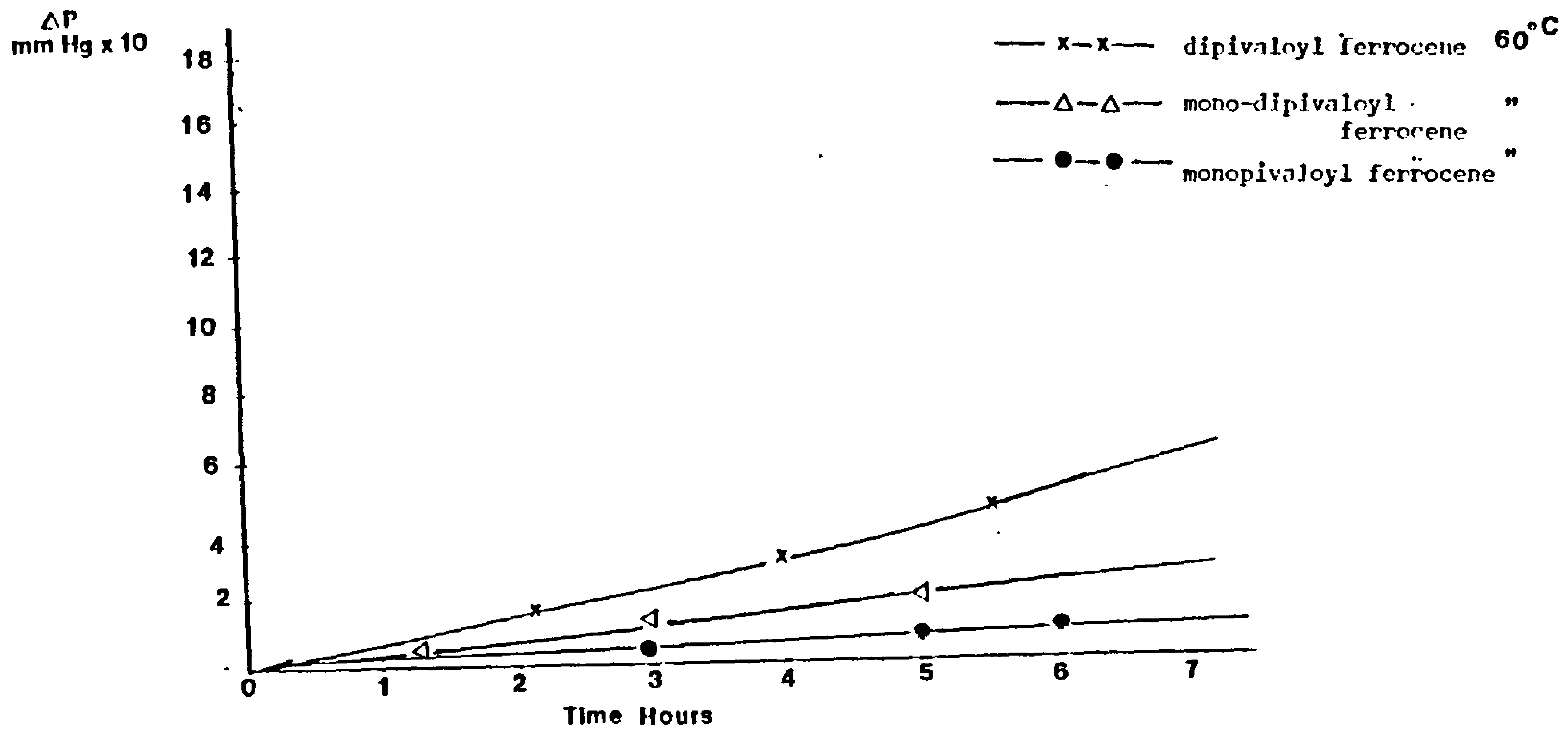
Increases in rates with rise in temperature have been observed by Strang and Wibaut(240) on saturated hydrocarbons in the liquid phase. With unsaturated hydrocarbons, the point of initial attack on the molecules whether by oxygen or a free radical is determined by the condition of minimum energy expenditure which in turn is related to the strength of the bond ruptured and the stability of the free radical formed. It follows that at 60^{0}C, the minimum energy required to break a bond and the stability of the radicals formed would be less than those at room temperature. These parameters were not investigated but serve to explain why the reaction rates at room temperatures are lower than those at 60^{0}C and otherhigher temperatures.

Walsh(241) working on the oxidation of straight chain and branched chain paraffins in the gaseous phase observed that many features of the low temperature combustions of fuels can be explained in terms of the initial formation and reaction of hydroperoxides. Walsh attributed the contributions arising from each drier to be dependent on its catalytic efficiency.

equil absorption

In Graph 1:60, the ferrocene systems showed higher initial rates of oxygen absorption than other catalysed systems. This is unexpected since the ferrocene systems are not expected to be very reactive at

No mutual interaction at O – 60°C



moderate temperatures due to their high stability constants (Fe^{2+} = $logk^{14.33}$; Fe^{3+} = $logk^{25.1}$; logk = 10.34).(253)

Next in the series is lead oleate followed by cobalt octoate and mono-dipivaloyl ferrocene (50/50) mixture. Systems catalysed by mono-pivaloylferrocene gave higher rates of maximum oxygen absorption than those catalysed by dipivaloyl ferrocenes.

(i) Synergism and No Mutual Interaction

The autoxidative behaviour of monopivaloyl ferrocene (Table 4.5) and dipivaloyl ferrocene (Table 4.6) at 60°C compared with their joint reactivity at the same temperature (Table 1.2.8) indicates no mutual interaction.

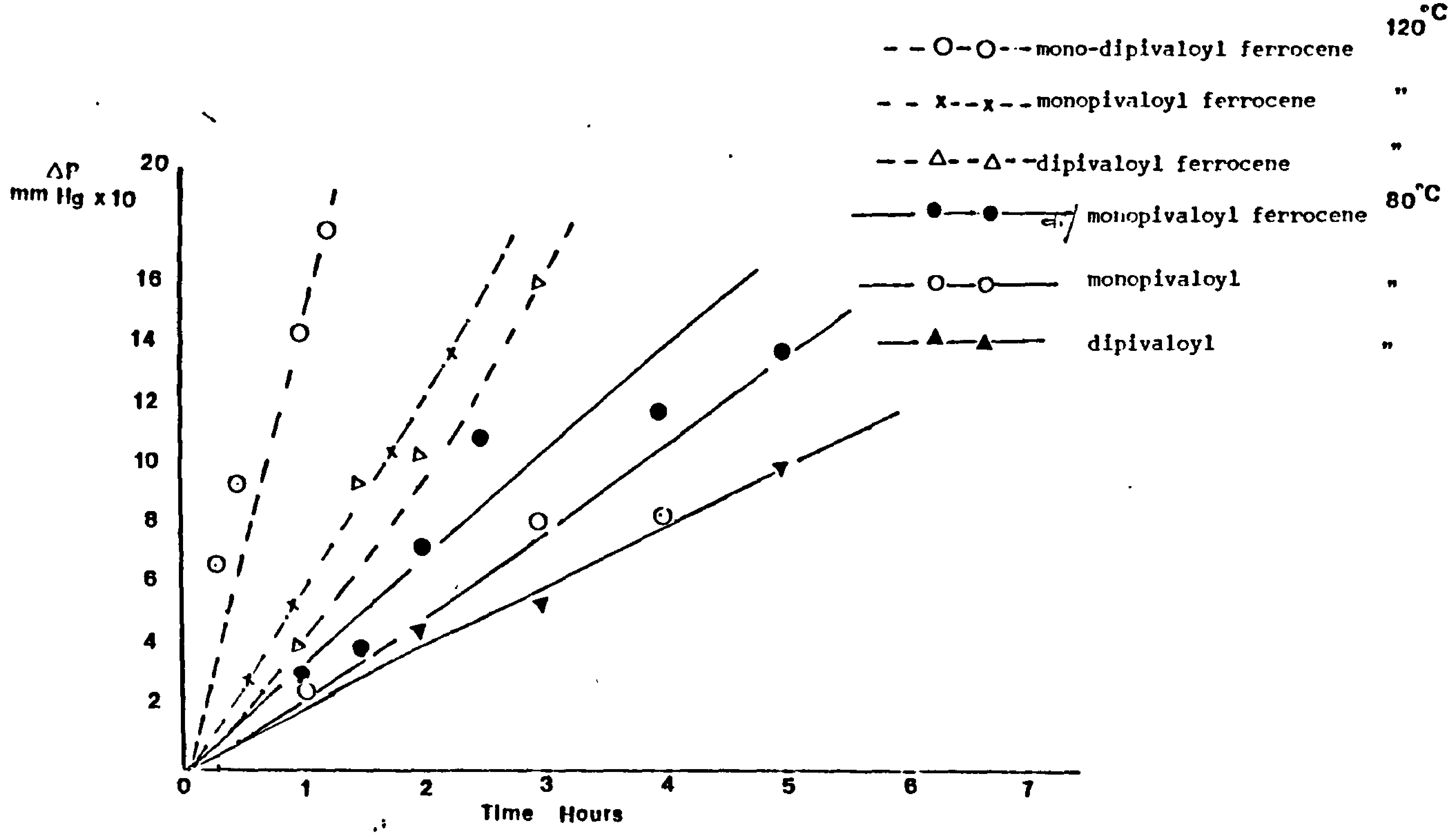
A synergistic effect was however observed at 80°C and 120°C (P 359). The rate of oxygen absorption at 120°C was still increasing at the end of the experiment.

(ii) Effect of Pure Oxygen

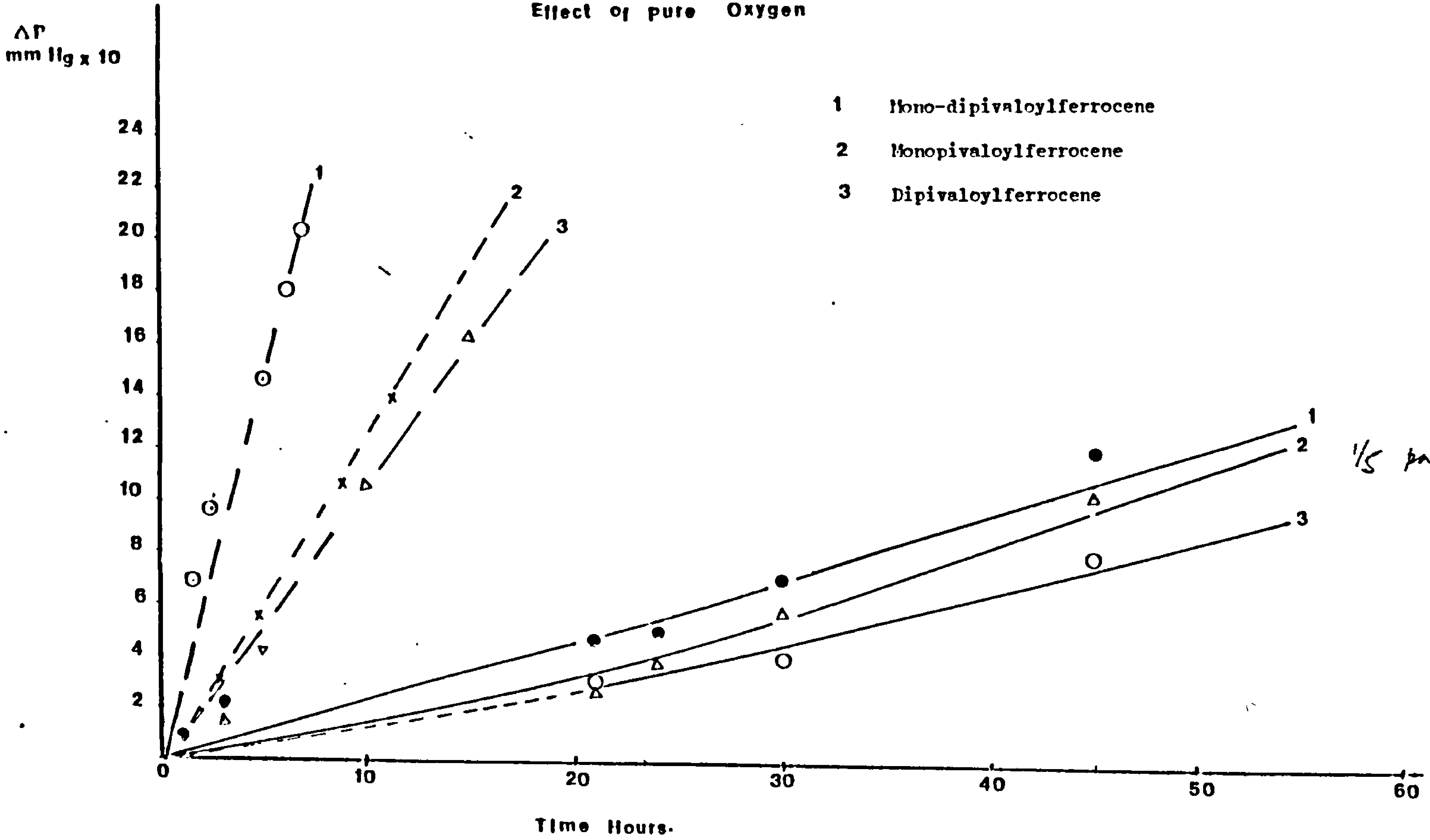
Tables 1.2.9, 1.3.1 and 1.3.2 show the effect of a reduced partial pressure of oxygen on the rate of autoxidation reaction when air was present in the reaction vessel compared with Tables 1·3·3; 1·3·4 ; 1·3·6 when pure oxygen (at a partial pressure five times higher) gave rise to increased reaction rates. Rates of oxygen up-take should vary in some way with the oxygen partial pressure if the reaction rates are a function of oxygen pressure. The effect of pure oxygen on the rate of autoxidation at high temperatures is illustrated graphically on page 360. It can therefore be said that autoxidation rates are influenced by the partial pressure of oxygen.

Bolland(91) observed that the rate of oxidation of ethyl linoleate at 40°C varied with oxygen pressure up to a limit. At a pressure that approximated the partial pressure of oxygen, the rate became independent of pressure i.e. the rate equation below is applicable at pressures below that limit.

Synergism at 80 – 120°C



Effect of pure Oxygen



1/5 partial pressure.

All reactions were carried out at 120°C.

$$-\frac{d[O_2]}{dt} = \frac{Km[O_2]}{[O_2] - Kn[FA]}$$

where

O_2 = oxygen pressure

Km, Kn = constants

FA = fatty acid concentration e.g. 9, 12-octadecadienoic acid

The results from this work (notably the extent of oxidation when air was present in the vessel and when pure oxygen was present) show that Bolland's rate equation applies even at partial pressures as high as one atmosphere. It can be seen (P 360) that autoxidation reactions in the presence of pure oxygen are faster by about the factor of the available pressure of oxygen at high temperatures. This result is in contrast to the findings of Bolland(91) who said that the rate of oxidation was independent of oxygen pressure at a partial pressure approximately that found in air at low temperatures.

With pure oxygen in the reaction vessel, the rate equation may be written as

$$\frac{d[O_2]}{dt} \propto \frac{d[P]}{dt}$$

Bolland's rate equation involving many of the factors i.e. hydroperoxide concentration inclusive is as follows:

$$-\frac{d[O_2]}{dt} = Km\frac{[FOOH][FA][O_2]}{[O_2] - Kn[FA]} + f\{[O_2][FA]\}$$

FOOH = hydroperoxide concentration. The second term $f\{[O_2][FA]\}$, an undefined function is considered negligible being comparatively small compared with the first except at very low hydroperoxide concentrations.

Applying the complex rate equation to this work to include changes in iodine values, we have

$$-\frac{d[O_2]}{dt} = Km\,\frac{[FOOH][\mathrm{lV}_{in} - \mathrm{lV}_t][O_2]}{[O_2] - Kn[\mathrm{lV}_{in} - \mathrm{lV}_t]}$$

Representing $[O_2]$ as partial pressure [P] we have

$$\frac{d[O_2]}{dt} = Km\,\frac{[FOOH][\mathrm{lV}_{in} - V_t][P]}{[P] - Kn[\mathrm{lV}_{in} - \mathrm{lV}_t]}$$

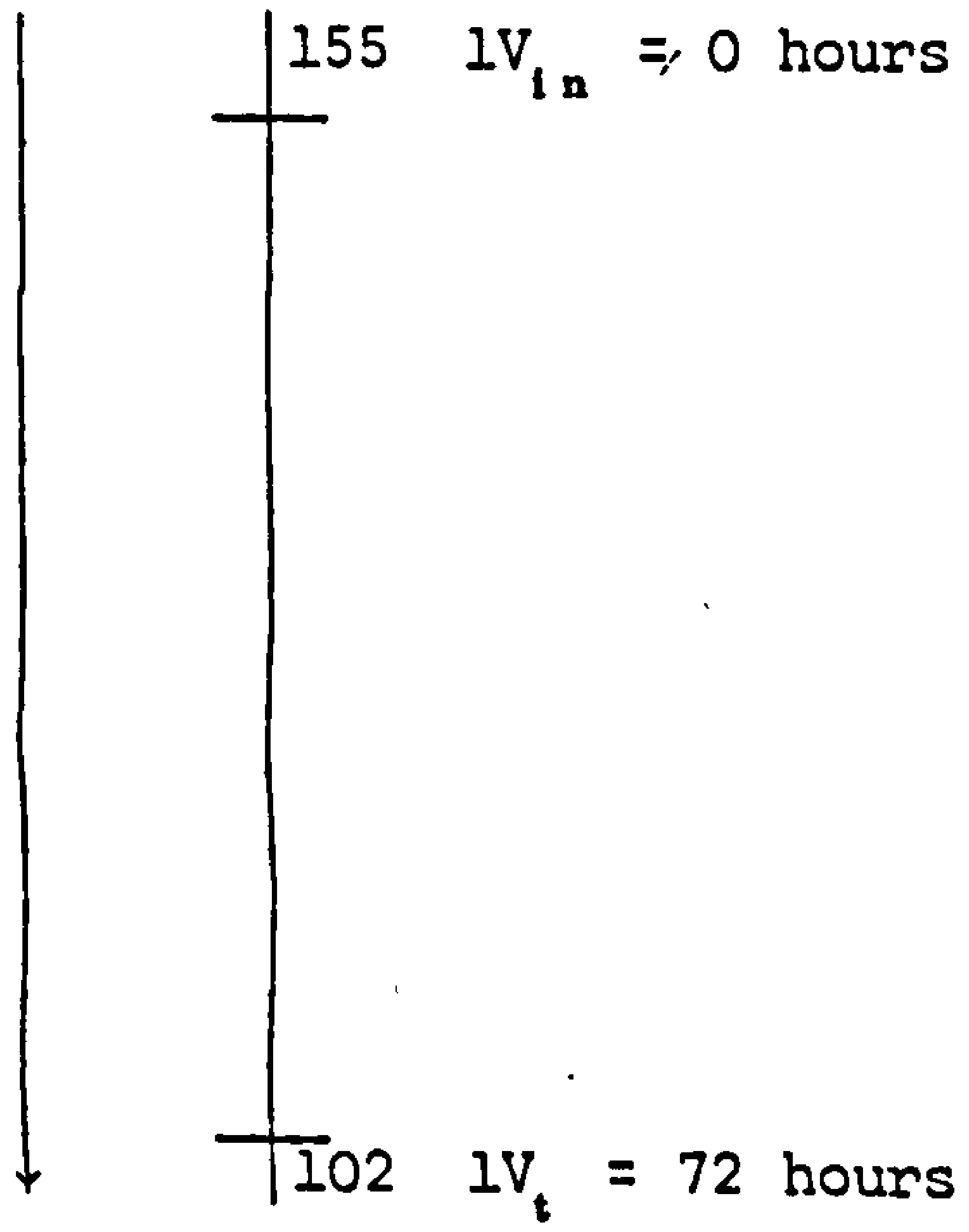
where lV_{in}, lV_t are the initial iodine values and iodine values at time t respectively.

Using values of l.V. changes from Table 2.1.2 we have

1 atmosphere = 101325 $N.m^{-2}$

= 1 kilobar

= 760 mm Hg



Representing partial pressure as one atmosphere (pure oxygen in flask) and substituting the value $(\mathrm{lV}_{in} - \mathrm{lV}_t)$ in the complex rate equation we have

$$\frac{d[O_2]}{dt} = Km\,\frac{[FOOH][\mathrm{lV}_{in} - \mathrm{lV}_t][P]}{[P] - Kn[\mathrm{lV}_{in} - \mathrm{lV}_t]}$$

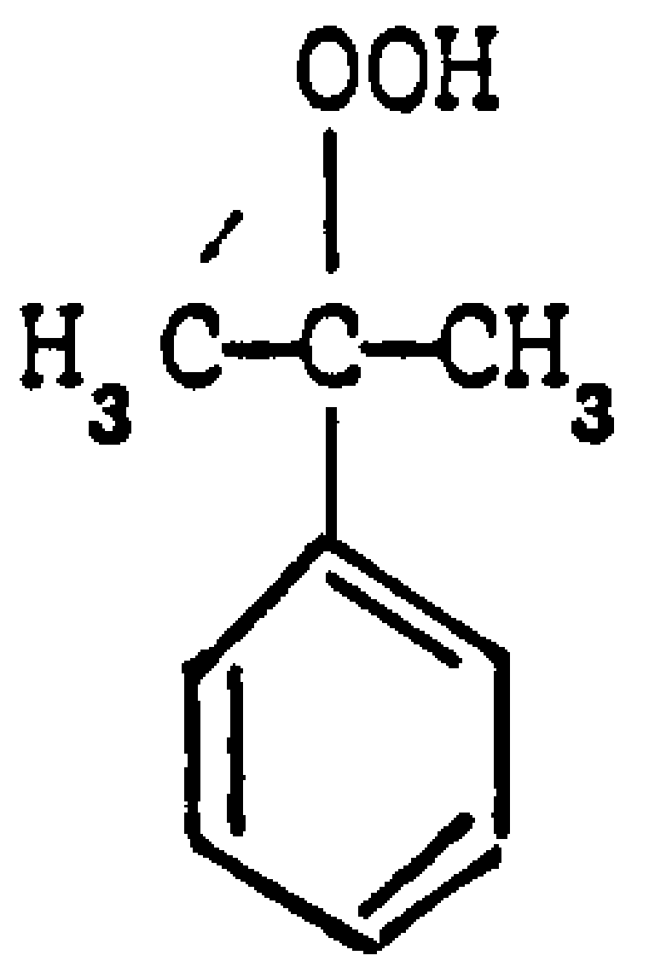
i.e. after 72 hours,

$$\frac{d[O_2]}{dt} = Km\,\frac{[FOOH][155 - 102][760]}{[760] - Kn[155 - 102]}$$

(iii) Prooxidant and Antioxidant Effects

The ability of some metallic soaps to promote or hinder oxidation of petroleum oils appears to be a function of temperature(165). An antioxidant effect is observed at low temperatures, whilst at high temperatures, a prooxidant effect is dominant.

Antioxidant effect was not observed in this work although, Tanaka, Kobayashi and Furihata(166) have reported that under certain conditions, a prooxidant may have antioxidant properties.

The reaction of cumene or hydroperoxide  or its derivatives with ferrous salts have been studied at low concentrations. The rate of ferrous ion disappearance in the presence of oxygen and alkoxy radicals was found to be second order at the initial stages but of a different order at later stages. This was explained by assuming that the alkoxy radicals were capable of forming hydroperoxides which reacted further with ferrous ions.

The differences in the reactivities between Fe/EDTA and Fe/NTA complexes are due to the differences in the amount of ferrous iron produced with rise in temperature assuming the thermal stability of the complexes is dependent on their stability constants at room temperatures.

Table 4·3·7 gives the stability constants of EDTA and NTA complexes with iron.

Table 4·3·7

STABILITY CONSTANTS OF SOME IRON COMPOUNDS			
CATION	EDTA	NTA	TEMPERATURE
Fe^{++}	$10^{14.33}$	$10^{8.33}$	293k
Fe^{3+}	$10^{25.1}$	-	293K

Values of stability constant at other temperatures are not available at the time of writing but the rate of oxidation at any temperature is an inverse function of the stability constants of the complexes.

Table 4·3·8

COMPARATIVE CATALYTIC ACTIVITY OF THE IRON COMPOUNDS

OXYGEN ABSORPTION

METAL DRIER	OXYGEN ABSORPTION			IODINE VALUE			PEROXIDE VALUE		
	R.T.	60°C	80°C	R.T.	60°C	80°C	R.T.	60°C	80°C
Ferrocene	0	2	4	1	2	3	1	3	5
Monopivaloyl Ferrocene	0	3	5	1	2	5	1	3	5
Dipivaloyl Ferrocene	0	3	5	1	3	5	1	3	5
Ferrocene Dicarboxylic Acid	0	2	4	1	2	3	1	4	3
Fe/EDTA Complex	0	1	4	1	2	4	1	2	5
Fe/NTA Complex	0	2	5	1	2	6	1	3	6
Ferrous Salicylate	1	4	5	1	2	4	1	3	4
Ferrous Stearate	3	4	4	4	3	3	2	-	4
Ferrous Octoate	3	4	4	4	3	3	3	4	4
Mono-Dipivaloyl Ferrocene	4	4	2	2	4	5	5	5	6

0 = No measurable oxygen up-take.

R.T. = Room Temperature.

The higher the figure, the more active are the driers at the reaction temperatures.

4.0 IODINE VALUES

Iodine values decrease in line with e.g. rates of oxygen up-take and peroxide values. The same observation was made in this work (Tables 1.3.7; 1.3.8, etc.). The model vehicle employed in this work, notably cis 9, cis 12-octadecadienoic acid manufactured by BDH Chemicals Ltd., had an average iodine value specification of 155. The results of the iodine values determined experimentally at t = 0 ranged from a value of 162 - 40 . The difference between the iodine value quoted by the supplier and the experimentally determined values could be due to the following:

(a) The interaction of atmospheric oxygen on the samples during handling as reported by Lea(259).

(b) Error introduced during sampling using very small samples of materials of varying viscosity.

The rate of change in iodine value is a function of the catalytic efficiency of the metal incorporated with the 9, 12-octadecadienoic acid.

(i) Iodine Values at Room Temperature

At room and moderate temperatures, cobalt and other driers showed the most rapid drop in iodine values (Tables 1.4.3; 1.4.7; 1.7.7; 1.9.5; 1.8.5). At room temperatures, the iron compounds showed very minimal drops generally in agreement with the results obtained during oxygen absorption experiments at the same temperature.

Increase in concentration of the drier did not accelerate the catalytic reactivity of the driers remarkably. This observation is confirmed by the results on 0.25% metal on weight of driers compared with those of 0.05% iron on the weight of acid at room temperature. Graphs on page 367 are extracts from work carried out by Moulton, Beal and Griffin(242) on soybean oil containing small amounts of nickel catalysts. The pattern of changes recorded is similar to that obtained from plots of iodine values determined from this work (Graphs on P367) Swern(243) and Paterson(244) also worked on nickel catalysts containing traces of copper and observed similar effects. It is believed that Paterson's catalysts could have performed better had the copper chromite been activated(245). There is no indication of temperature in the above literature(243),(244) which implies that the experiments were carried out at room temperature. In this work however, activation of the metal was achieved by increasing the temperature with subsequent improved catalytic performance in most cases. Beal, Moulton and Griffin(242) have observed that increasing the concentration of the metal catalyst did not correspond with improved catalytic efficincy in most cases (Tables 6.0; 5.9; 6.1; 6.2 are some results in agreement with the above reported literature).

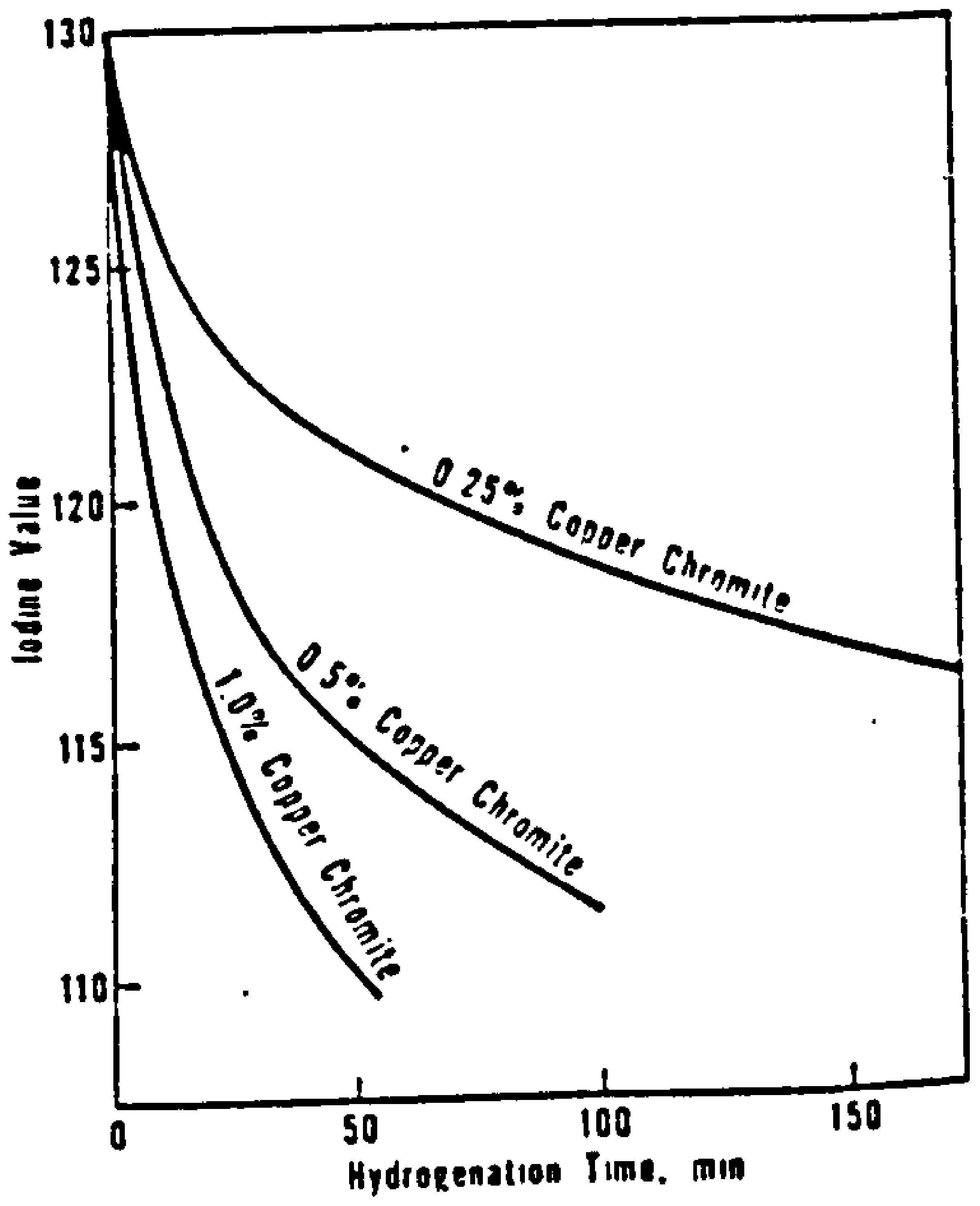
(ii) Iodine Values at 60°C

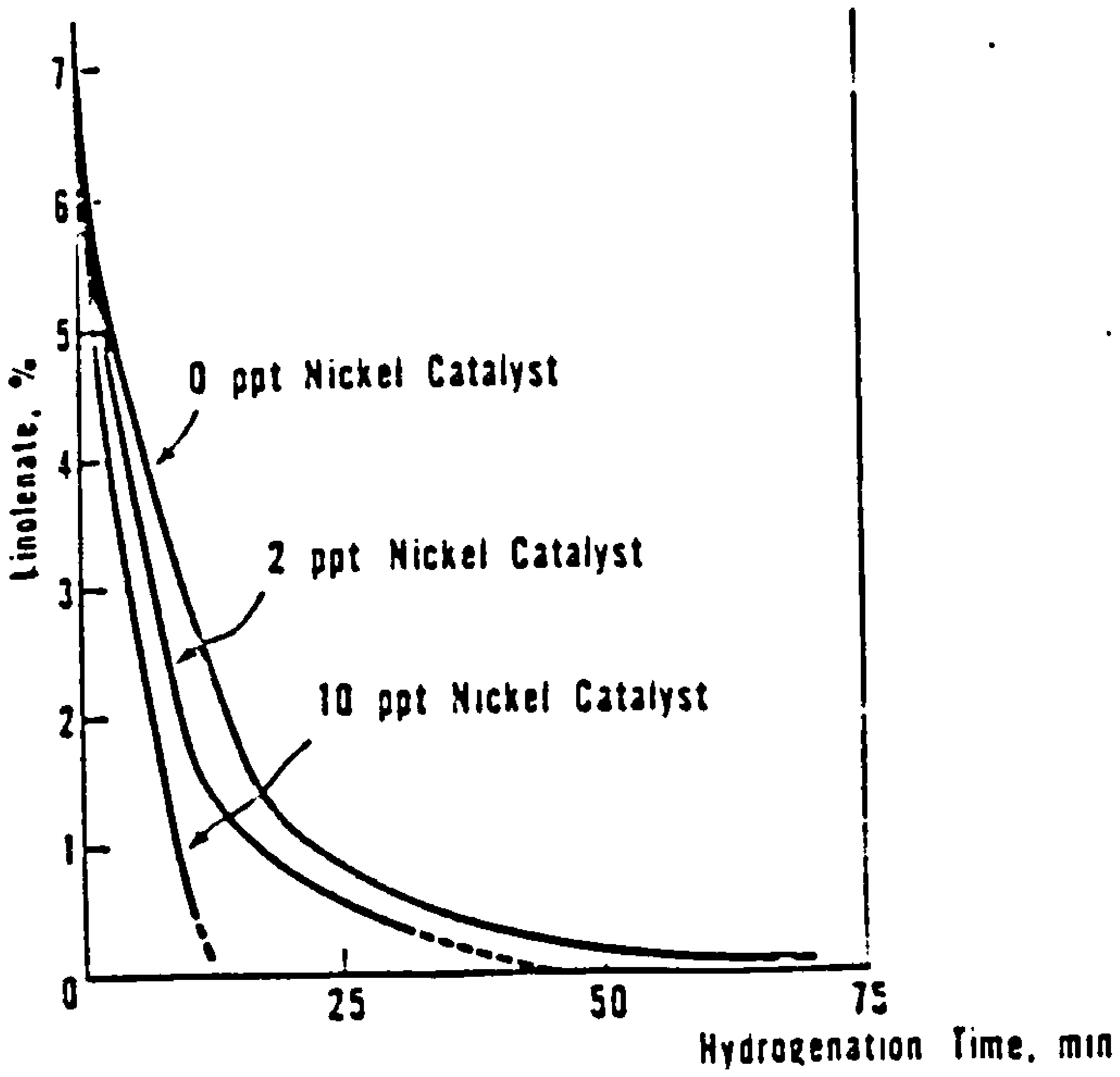
As in the case of oxygen absorption experiments, iodine value changes at 60 C are much faster than those at room temperature. This observation is more apparent with the conventional room temperature driers. With the iron compounds, most did not show considerable changes in iodine values over the period of the experiment, unlike the systems containing cobalt and lead (Tables 1.4.5; 1.4.6; 1.4.8).

(iii) Iodine Values at 80°C

At 80°C, the low temperature driers (cobalt and lead) showed comparative decrease in iodine value changes presumably due to deactivation compared with the iron compounds. The iron compounds became slightly more reactive than at 60°C. Most prominent among them are ferrous salicylate, monopivaloyl ferrocene, dipivaloyl ferrocene and ferrous octoate and ferrous stearate. The very good performance of ferrous stearate at this temperature is in agreement with the findings of Arghandeh[248] and the results obtained by Orr and Williams(172).

The observation further extends on the findings of Sanda(11) who reported that at low temperatures, ferrous stearate in low concentrations is comparably as active as other room temperature driers.





5.0 OXYGEN ABSORPTION OF CIS 9, CIS 12-OCTADECADIENOIC ACID AT 120°C

Absorption rates at 120°C are higher than those at 60°C and 80°C for the iron compounds. During severe conditions of autoxidation (120°C and above), the rate of reaction can no longer be equated with the rate of hydroperoxide formation(48),(144). One possible explanation is that at such reaction temperatures, loss of unsaturation may not be entirely caused by free-radical reactions initiated by radicals from the breakdown of peroxides. The reactions of conjugated and non-conjugated oils at high temperatures have been discussed (p.23) and it is likely that the widely accepted view of an addition-substitution reaction at a methylene group adjacent to the ehtylene group may have occurred at these temperatures. The result of high temperature treatment of non-conjugated oils e.g. 9, 12-octadecadienoic acid is that it becomes conjugated (modified). The effect of iron compounds at high temperatures is to catalyse the conjugation of the unsaturated oil.

(i) At 120°C the iron compounds showed faster drop in iodine values within a given time span than the non-ferrous compounds (Tables 2.1.3; 2.1.4). The catalytic performance of iron compounds was found to vary with the organic moiety, the solvent employed and the oxidation state of the iron.

The ferrocene-based compounds which showed low rates of maximum oxygen absorption at 60°C and 80°C, gave much higher rates at 120°C (Graphs 2.60; 120:1).

Table 4·3·8 gives a comparative assessment of the metal salts in terms of maximum oxygen absorption; changes in iodine value and peroxide values at the various reaction temperatures.

Tobolsky(144); Bauman and Maron(145) studied the autoxidation of ethyl linoleate and polybutadiene respectively. The result of the oxygen absorption experiments in this work bears some resemblance to those obtained by Tobolsky and Maron. They(144),(145) believe that the rate of oxidation is diffusion controlled and the extent of oxidation depends inversely on the thickness of the paint or oil film. Diffusion control must have been important at high temperatures (120°C) during oxygen up-take. This is because cis 9, cis 12-octadecadienoic acid became more viscous as it polymerized and oxygen up-take fell "rapidly" after 60 hours.

(i) Temperature Effect on Electron Mobility

A reaction mechanism involving the donation of electrons by the iron to form an unstable complex of the type below is said to be responsible for the increased catalytic activity of iron complexes

$$R\,O\,\overset{H}{O}\ :\ Fe^{++}$$

The above complex dissociates immediately to $RO_0 + .\overset{H}{O} : Fe^{++}$. The reaction involves the transfer of an electron to the O—O linkage from the Fe^{++}. The above reaction occurs more readily when the activation energy of the system is decreased by the presence of electron releasing groups in R. The presence of excess electron density on the O—O linkage causes more rapid dissociation and hence more rapid overall reaction rate assuming this dissociation as the rate controlling factor(172). The reactions of Fe/EDTA or Fe/NTA or Fe^{++} salicylate at room and 120°C may be explained by this mechanism. With dissociation as the controlling factor, the iron compounds were generally inert at room temperatures but very reactive at 120°C when large amounts of ferrous ions were available to co-ordinate with hydroperoxide.

(ii) Effect of Organic Radicals

It has been reported that organic radicals are extremely reactive towards oxygen(254),(255). The above view supports an earlier observation notably that the reactivity of an iron compound is affected by the type of ligand with which it is chelated and hence the supply of free iron ions under the given conditions.

Peroxides of low and high stabilities have been reported(256) and the presence of a specific type would determine the reactivity of the iron complex.

Kolthoff and Medallia(257) have shown that quantitatively and qualitatively, the reaction of ferrous compounds with peroxides is markedly different in the presence of oxygen than in its absence. This may explain the different order of activity among some driers when the partial pressure of oxygen was varied by using air as opposed to those reactions carried out in the presence of pure oxygen.

The most important point at this stage is not to determine the exact reaction mechanism but to assess the performance of the iron compounds at high temperatures.

The results show that all the iron compounds examined were extremely reactive at 120^{0}C under the existing experimental conditions. There are however, differences in the reactivities of the iron compounds arising from the ligand or ion with which the iron is associated. Typically ferrous salicylate, monopivaloyl ferrocene and dipivaloyl ferrocenes reacted violently after showing very high initial rates of oxygen absorption.

The order of reactivity for both the conventional and the iron-based compounds at low and elevated temperatures is given on the Tables at the end of the discussions.

At stoving temperatures, some of the conventional driers such as cobalt and lead salts showed initial rates of oxygen absorption comparable with the iron compounds, but the former showed reduced reactivity compared with room temperature results. Based on this observation, it can be said that iron compounds have potentials as stoving catalysts when chelated with a suitable organic compound.

6.0 PEROXIDE VALUES

In general, peroxide values increase with the extent of oxidation. The results from this work show that maximum peroxide value increases with rise in temperature. Peroxide levels also decrease eventually.

At high temperatures (120°C) somewhat variable results were obtained with some metals (Tables 3.9.8; 4.1.1; 4.2.5).

A number of factors may be responsible for the variations. The instability of hydroperoxide solutions in the presence of ions has earlier been mentioned (p.140). Hill's technique is noted for improved accuracy of analysis of hydroperoxide solutions but the interference of atmospheric oxygen at the moment of contact with the reagent and the fat peroxide(258) coupled with the various possible ways iron compounds can react with oxygen (see oxygen absorption, p.351) may explain the variable results. Peroxide values increase more rapidly in the presence of oxygen particularly at high temperatures in the case of iron compounds (Tables 3.8.2; 3.8.4).

At room and moderate temperatures, the conventional room temperature driers gave the highest rates of peroxidation.

Iron compounds showed minimal levels of peroxide values at room temperatures but with slight increases at moderate temperatures.

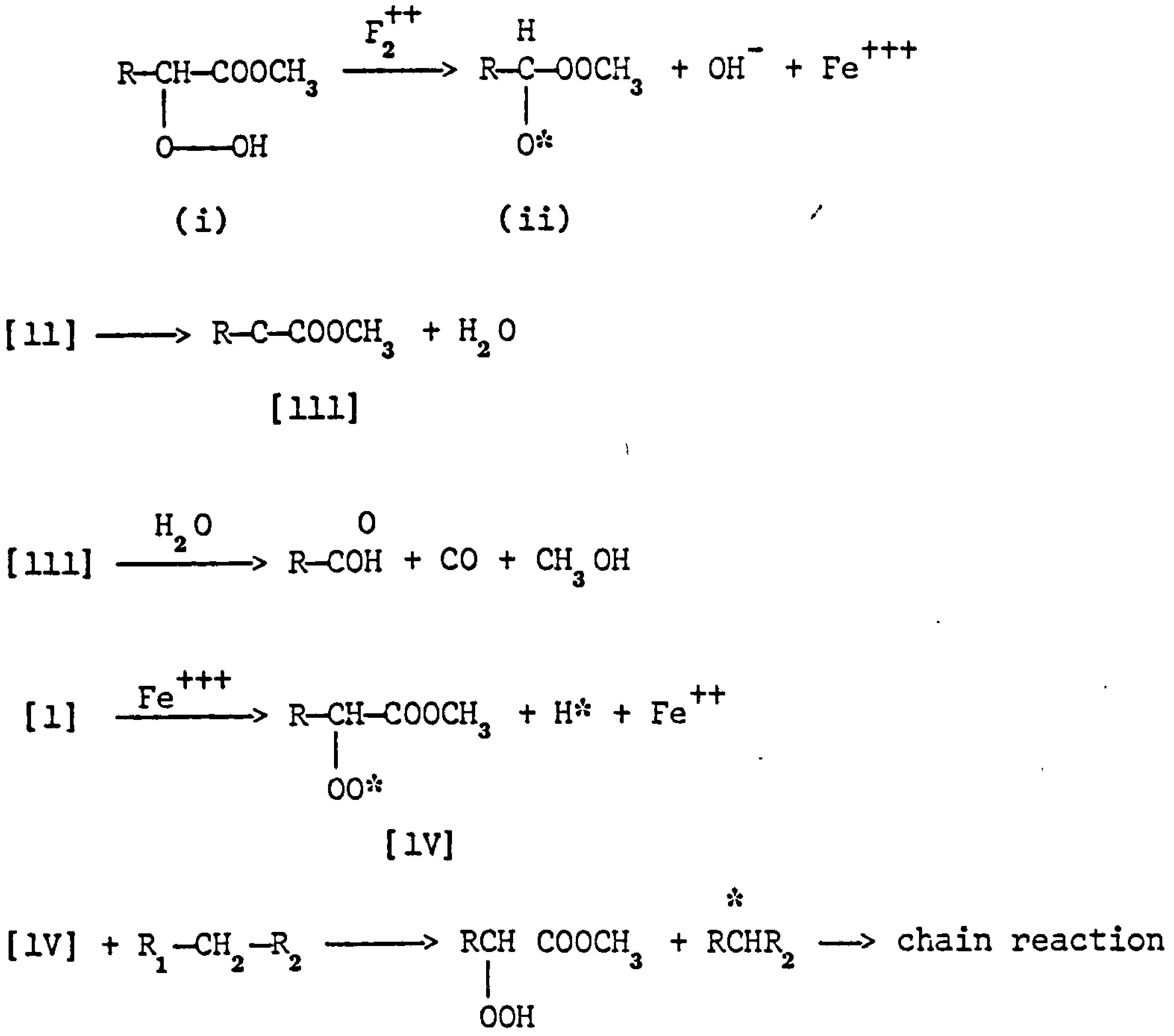
The reactivities of iron compounds at the double bonds of an unsaturated hydrocarbon probably are similar to the reactions of cobalt ions with unsaturated hydrocarbons e.g.

$$RCH = CH_2 + Co^{+++} \longrightarrow R\overset{*}{C}H - CH_2 + Co^{++}$$

With iron compounds, such reactions occur readily at elevated temperatures. The attack by the metal catalyst at the double bonds of an unsaturated hydrocarbon is due to interactions with the metal at the start of polymerisation reaction. Thus with iron compounds, the reaction is

$$RCH = CH_2 + Fe^{+++} \longrightarrow R\overset{*}{C}H - CH_2 + Fe^{++} \text{ (248)}$$

The autoxidation of 9, 12-octadecadienoic acid with different metal ions, shows different trends of autoxidation depending on the prevailing experimental conditions. The rapid reaction of iron compounds at high temperatures could be attributed to the formation of α-hydroperoxides as reported by Argandeh(248) and in the case of iron ions, the speculated reaction is as follows:



$$\underset{\text{(i)}}{R{-}\underset{\substack{|\\ O{-}{-}OH}}{CH}{-}COOCH_3} \xrightarrow{F_2^{++}} \underset{\text{(ii)}}{R{-}\overset{H}{\underset{\substack{|\\ O^*}}{C}}{-}OOCH_3} + OH^- + Fe^{+++}$$

$$[11] \longrightarrow \underset{[111]}{R{-}C{-}COOCH_3} + H_2O$$

$$[111] \xrightarrow{H_2O} R{-}\overset{O}{C}OH + CO + CH_3OH$$

OR

$$[1] \xrightarrow{Fe^{+++}} \underset{[1V]}{R{-}\underset{\substack{|\\ OO^*}}{CH}{-}COOCH_3} + H^* + Fe^{++}$$

$$[1V] + R_1{-}CH_2{-}R_2 \longrightarrow \underset{\substack{|\\ OOH}}{RCH}\ COOCH_3 + R\overset{*}{C}HR_2 \longrightarrow \text{chain reaction}$$

The reaction [111] $\xrightarrow{H_2O}$ $R\overset{O}{C}OH + CO + CH_3OH$ explains the production of the largest increase in carboxylic acids in iron compounds(248). More complex hydroperoxides including α-hydroperoxides are some possibilities

$$ROOH \xrightarrow{K_2} RO^* + \overset{*}{O}H \quad \text{or}$$
$$ROO^* + H^*$$

Thus high rates of peroxide formation give high rates of oxygen up-take. The decomposition of hydroperoxides by iron compounds at high temperatures must have been very close to 100% (Tables 4.3.4 ; 4.3.6)

This explains the accelerated rate of peroxidation, polymerisation and subsequent formation of by-products of secondary reactions at high temperatures in the presence of iron ions(248).

According to Sanda(11) the lower valence state of any metal is not a very active catalyst but the anomalous behaviour of ferrous stearate showed that it is iron (11) which influenced greatly the autoxidation reaction. Sanda(11) found that ferrous ion disappeared by a second order reaction

i.e. $$-\frac{d[Fe^{++}]}{dt} = K[Fe^{++}][ROOH]$$

If the lower valence state of iron is not active, then

$$-\frac{d[Fe^{++}]}{dt} \doteq 0 \qquad (a)$$

or $$[Fe^{++}][ROOH] \doteq 0 \qquad (b)$$

If the concentration of the iron used is high e.g. 0.25%, equation (b) is true when [ROOH] = ϕ where ϕ is a small value. This is possible only during induction period or during severe hydroperoxide decomposition such as those reactions at 120°C.

There is no clear distinction between the catalytic performance of chelated iron compounds and non-chelated compounds at high temperatures, though slight differences in reactivity may arise from differences in stability constants or ionisation constants of the complexes used.

The following charts give comparative assessment of the various driers employed in this work at the different reaction temperatures shown.

SUMMARY

The scope of this work was to provide a comparative assessment of catalytic efficiency in the series zerovalent iron compounds, other chelated ionised iron compounds, iron salts and similar conventional driers.

The research work was aimed at investigating the use of iron compounds as stoving catalysts.

The need for stoving catalysts in industrial processes was discussed.

The reactivities of blocked catalysts at room and elevated temperatures were examined. Some applications of high temperature catalysts were outlined.

Oxygen absorption of cis 9, cis 12-octadecadienoic acid in the presence of driers was discussed at room temperatures, 60°C, 80°C and 120°C.

Induction periods were measured at room temperatures; at 60°C and above, they were negligible.

The effect of catalyst concentration on the rate of reaction was discussed.

Properties of a good stoving catalyst were outlined to determine which of the iron compounds behaved in line with the established requirements.

Monopivaloyl ferrocene and dipivaloyl ferrocenes showed no mutual interaction at room temperatures and 60°C when equal amounts (1 : 1) were reacted under the same experimental conditions. At 80°C and 120°C, a synergistic effect was observed.

Zerovalent iron compounds became more reactive at elevated temperatures. Conventional metal salt driers especially cobalt and lead salts became less reactive at elevated temperatures.

Peroxide values increased with the extent of oxidation up to a maximum and remained constant with time.

Zerovalent iron compounds gave the highest rates of peroxidation at 120°C.

Typically zerovalent iron compounds such as ferrocene, monopivaloyl ferrocene and dipivaloyl ferrocenes, and a few other Fe^{++} compounds such as ferrous salicylate, Fe/NTA and Fe/EDTA complexes can be employed as stoving catalysts.

CONCLUSIONS

Iron compounds have increased catalytic efficiency at high temperatures.

The reactivity of iron co-ordination compounds is greatly incluenced by the organic moiety with which the iron is chelated.

At near stoving temperatures (120°C) reactions either catalysed by ferrous salicylate or mono- or dipivaloyl ferrocenes were very vigorous during oxygen up-take experiments. These compounds caused very high rates of oxygen absorption at the start of reaction.

The results from this work show that iron compounds can be employed as stoving catalysts in autoxidative paint systems. However, differences exist in the reactivities of the iron compounds arising probably from variations in their stability constants or ionisation.

Ferrous compounds such as the octoates and stearates were reactive at room temperatures with slight increases at elevated temperatures.

Iron complexes e.g. Fe/NTA; and Fe/EDTA were inactive at room temperatures but very reactive at elevated temperatures.

Ferrous salicylate caused low reactions at room temperatures which however increased much faster at elevated temperatures.

Zerovalent iron compounds were catalytically inert at room temperatures. These compounds however, catalysed much faster reactions at elevated temperatures.

Equal amounts (1 : 1) of mono- and dipivaloyl ferrocenes showed no mutual interactions at low temperatures. At high temperatures however, a synergistic effect was observed.

Increased metal content did not give proportional increase in catalytic reactivity by iron compounds in most cases.

Ethylenediamine tetra-acetic acid (EDTA) has been employed as a deactivating agent in some polymerisation reactions but the catalytic behaviour (120^0C) of chelated iron compounds indicates that a temperature dependent catalytic effect based on the deactivation (removal of metal ions from the system) is possible and that such a variation in the properties of chelated complexes makes it possible to behave as a stoving catalyst.

Many organic oxidation processes are catalytically promoted. Thus catalysis by metal ions play important roles in the control of selective and/or partial oxidation of alkanes, olefins and aromatic hydrocarbons to useful products.

Table 4·3·9

Maximum oxygen up-take of cis 9, cis 12-octadecadienoic acid at 60°C

Graph Number	Driers in order of maximum oxygen up-take
1:60	Ferrocene > lead oleate > cobalt octoate > mono-dipivaloyl ferrocene
2:60	Ferrocene > ferrous salicylate > dipivaloyl ferrocene > lead naphthenate > Fe/Trilon A > Fe/EDTA

Table 4·4·0

Maximum oxygen up-take of cis 9, cis 12-octadecadienoic acid at 80°C

Graph Number	Driers in order of maximum oxygen up-take
80:1	Dipivaloyl ferrocene > Fe/EDTA > monopivaloyl ferrocene > ferrocene dicarboxylic acid > ferrous octoate > linoleic acid only
80:2	Ferrocene = dipivaloyl ferrocene > ferrous salicylate > ferrocene dicarboxylic acid > lead oleate > Fe/NTA (H_2O solvent)

Table 4·4·1

Maximum oxygen up-take of cis 9, cis 12-octadecadienoic acid at 120°C

Graph Number	Driers in order of maximum O_2 up-take
120:1	Fe/NTA (methyl ethyl ketone solvent) > ferrocene > nickel octoate > Fe/NTA (H_2O solvent) > Fe/EDTA (H_2O solvent)
120:2	Cobalt oleate > Fe/NTA (acid medium) > Fe/EDTA (acid medium) > ferrous octoate > cobalt naphthenate > lead oleate
120:3	Dipivaloyl ferrocene > ferrous salicylate > ferrocene > dicarboxylic acid > dipivaloyl ferrocene (1/5 partial pressure of atmosphere)
120:4	Cobalt octoate > ferrocene > ferrous salicylate > ferrocene dicarboxylic acid > monopivaloyl ferrocene* > dipivaloyl ferrocene* * 1/5 partial pressure of atmosphere

Table 4·4·2

Comparative Maximum Oxygen Absorption of 9, 12-octadecadienoic Acid in the Presence of Driers

METAL DRIERS	ROOM TEMPERATURE	60^{o}C	80^{o}C	120^{o}C
Monopivaloyl Ferrocene	0	3	5	6
Dipivaloyl Ferrocene	0	2	4	5
Ferrocene	0	3	4	5
Ferrocene Dicarboxylic Acid	0	2	3	4
Nickelocene	0	2	3	3
Fe/EDTA Complex	0	2	4	4
Fe/NTA Complex	0	3	5	5
Cobalt Octoate	6	6	5	4
Cobalt Naphthenate	6	6	5	5
Ferrous Salicylate	2	3	3	6
Ferrous Stearate	2	3	3	4
Lead Oleate	4	4	3	3
Lead Octoate	4	4	3	4
Nickel Octoate	3	3	3	3
Mono-Dipivaloyl Ferrocene	4	4	3	2

0 = No measurable oxygen up-take.

The higher the figures, the more active is the metal salt at the reaction temperatures.

Table 4·4·3
Comparative changes in iodine value of cis 9, cis 12 octadecadienoic acid at 60^{0}C

Graph Number	Driers in order of highest drop in iodine values
1V:1:60	Cobalt stearate > ferrous salicylate > ferrocene dicarboxylic acid > ferrous stearate > cis 9, cis 12 octadecadienoic acid only
1V:2:60	Cobalt octoate > ferrocene > dipivaloyl ferrocene > Fe/EDTA > Fe/NTA
1V:3:60	Cobalt naphthenate > cobalt oleate > ferrous salicylate > ferrous octoate > Fe/Trilon A > ferrocene dicarboxylic acid
1V:4:60	Cobalt oleate > nickel octoate > ferrous stearate > lead naphthenate > ferrocene > Fe/EDTA* > Fe/NTA* * acid medium
1V:5:60	Ferrous octoate > ferrous salicylate > Fe/EDTA > cis 9, cis 12 octadecadienoic acid only > ferrocene > dipivaloyl ferrocene

Table 4·4·4

Comparative changes in iodine values of cis 9, cis 12 octadecadienoic acid at 80^{0}C

Graph Specification Number	Driers in order of highest drop in iodine value
1V:1:80	Ferrous salicylate > ferrous stearate > nickel octoate > Fe/EDTA > cobalt oleate > lead naphthenate
1V:2:80	Ferrous octoate > monopivaloyl ferrocene > dipivaloyl ferrocene > mono-dipivaloyl ferrocene > ferrocene > Fe/EDTA > 9, 12-octadecadienoic acid
1V:3:80	Cobalt octoate > ferrous salicylate > ferrocene dicarboxylic acid > Fe/Trilon A (acid medium)
1V:4:80	Cobalt naphthenate > ferrocene > ferrous octoate > nickelocene
1V:5:80	Fe/Trilon A (methyl ethyl ketone solvent) > Fe/EDTA > monopivaloyl ferrocene > ferrocene > mono-dipivaloyl ferrocene
1V:6:80	Ferrocene dicarboxylic acid > cobalt octoate > cobalt stearate > ferrous salicylate > ferrous stearate > linoleic acid

Table 4·4·5

Comparative changes in iodine value of 9, 12-octadecadienoic acid at 120^{0}C

Graph Specification Number	Driers in order of highest drop in iodine value
1V:1:120	Mono- and dipivaloyl ferrocene > mono-pivaloyl ferrocene > ferrocene > Fe/Trilon A > linoleic acid > Fe^{++} octoate
1V:2:120	Cobalt octoate > ferrous salicylate > nickel octoate > cobalt oleate > lead naphthenate
1V:3:120	Ferrocene > monopivaloyl ferrocene > dipivaloyl ferrocene > Fe/EDTA > Fe/Trilon A > nickel octoate
1V:4:120	Cobalt stearate > ferrous salicylate > ferrous stearate > ferrocene dicarboxylic acid > linoleic acid
1V:5:120	Ferrous salicylate > ferrous octoate > dipivaloyl ferrocene > Fe/EDTA > ferrous stearate
1V:6:120	Ferrocene nickelocene Fe/Trilon A Fe/EDTA > ferrocene dicarboxylic acid

Table 4 4 6
Comparative Changes in Iodine Value of 9, 12-Octadecadienoic Acid in the Presence of Metal Salts

METAL DRIER	ROOM TEMPERATURE	60°C	80°C	120°C
Ferrocene	1	2	3	5
Monopivaloyl Ferrocene	1	2	5	7
Dipivaloyl Ferrocene	1	3	5	7
Ferrocene Dicarboxylic Acid	1	2	3	3
Fe/EDTA Complex	1	2	4	5
Fe/NTA Complex	1	2	6	8
Ferrous Salicylate	1	2	4	6
Ferrous Stearate	4	3	3	3
Ferrous Octoate	4	3	3	3
Nickelocene	1	-	2	3
Cobalt Octoate	7	7	4	4
Cobalt Naphthenate	7	7	3	3
Nickel Octoate	2	3	2	2
Mono-Dipivaloyl Ferrocene	2	4	5	5

The higher the figures, the more active is the metal salt at the reaction temperature.

Table 4 4 7
Comparative increases in peroxidation of 9, 12-octadecadienoic acid at 60°C

Graph Specification Number	Driers in order of maximum increase in peroxide value
PV:1:60	Mono- and dipivaloyl ferrocene > monopivaloyl ferrocene > dipivaloyl ferrocene > Fe/EDTA > ferrous salicylate
PV:2:60	Ferrous stearate > cobalt stearate > nickelocene > nickel octoate

Table
Comparative increases in peroxidation of 9, 12-octadecadienoic acid at 80°C

Graph Specification Number	Driers in order of maximum increase in peroxide value
PV:1:80	Ferrocene > Fe/Trilon A > nickel octoate > cobalt octoate > ferrous octoate > nickelocene
PV:2:80	Monopivaloyl ferrocene > ferrocene dicarboxylic acid > Fe/EDTA > dipivaloyl ferrocene > mono-dipivaloyl ferrocene

Table 4·4·8

Comparative Changes in Peroxide Value of 9, 12-Octadecatdienoic acid at the Reaction Temperatures

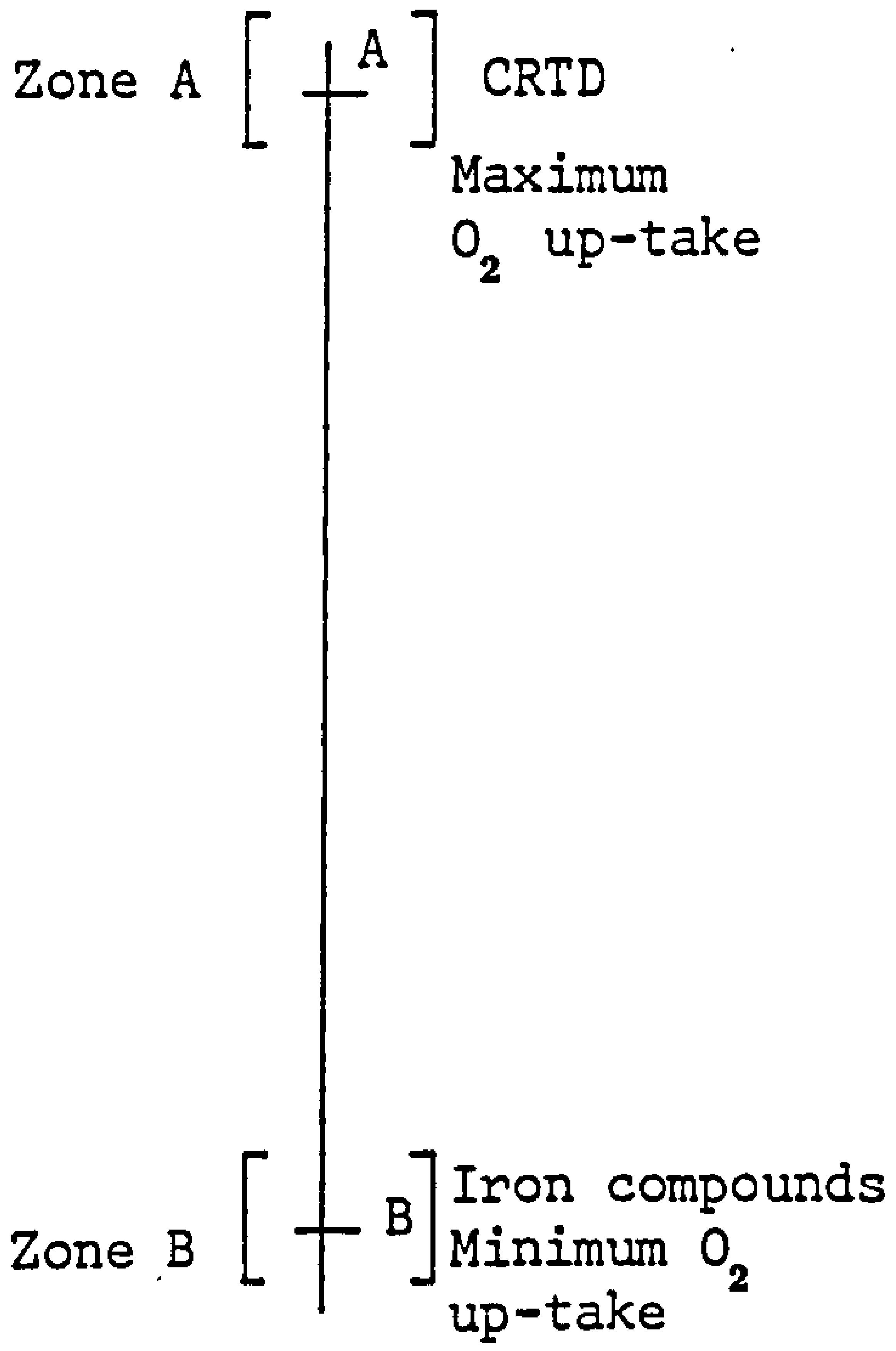
METAL DRIER	ROOM TEMPERATURE	60°C	80°C	120°C
Fe^{++} Octoate	5	3	4	4
Fe^{++} Salicylate	2	3	4	5
Fe^{++} Stearate	2	-	3	4
Monopivaloyl ferrocene	1	3	5	5
Dipivaloyl ferrocene	1	3	5	5
Mono- and dipivaloyl ferrocene	5	5	6	5
Nickelocene	1	-	4	3
Ferrocene	1	4	5	6
Fe^{0} Dicarboxylic Acid	1	4	3	3
Cobalt Octoate	6	5	3	2
Co^{++} Oleate	5	6	3	2
Fe/EDTA Complex	1	2	5	6
Fe/Trilon A Complex	1	2	6	7

The higher the figure, the better the performance of the drier at the reaction temperatures.

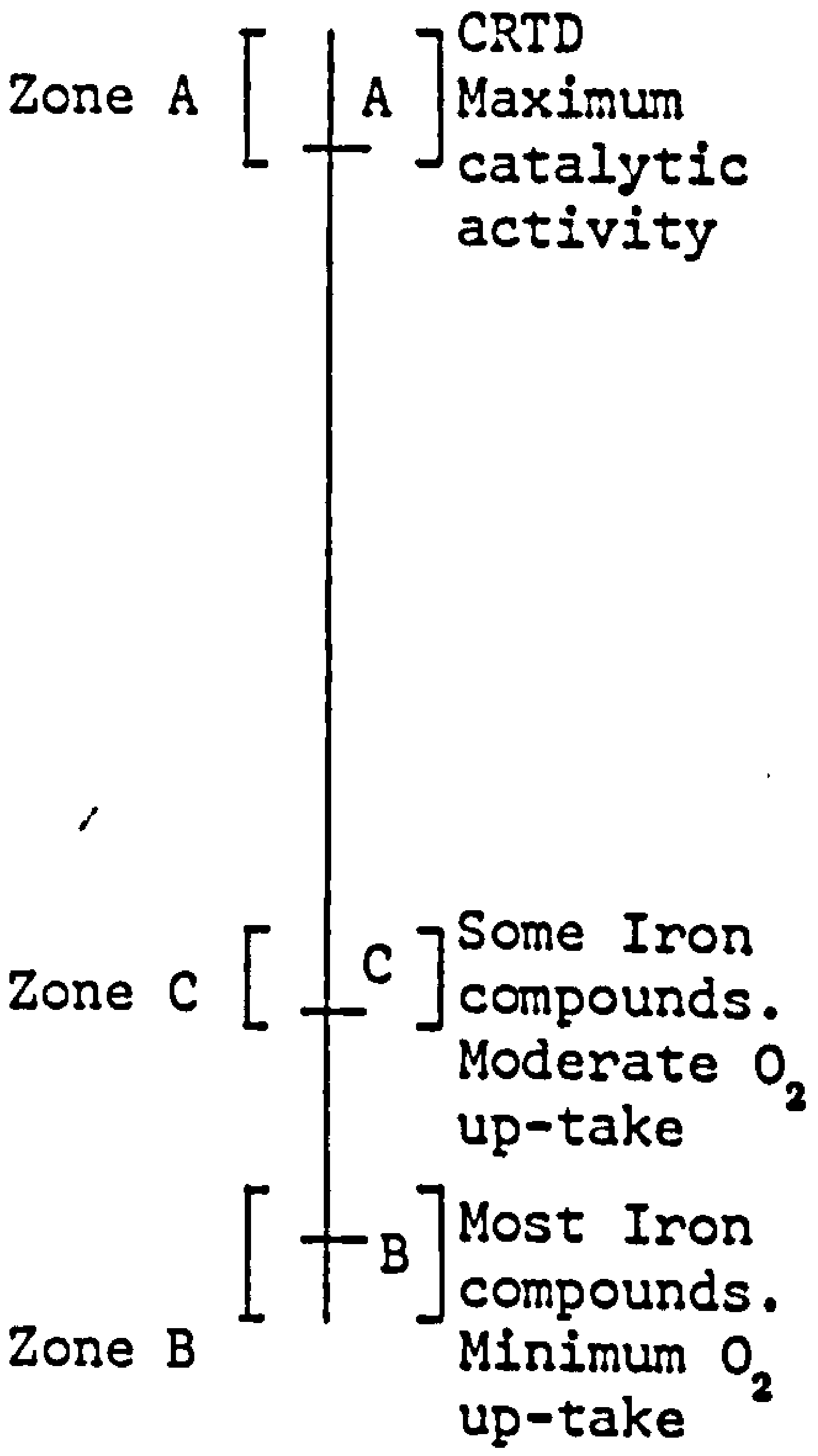
OXYGEN ABSORPTION

t_1 = 0 hours; t_2 = 60 hours

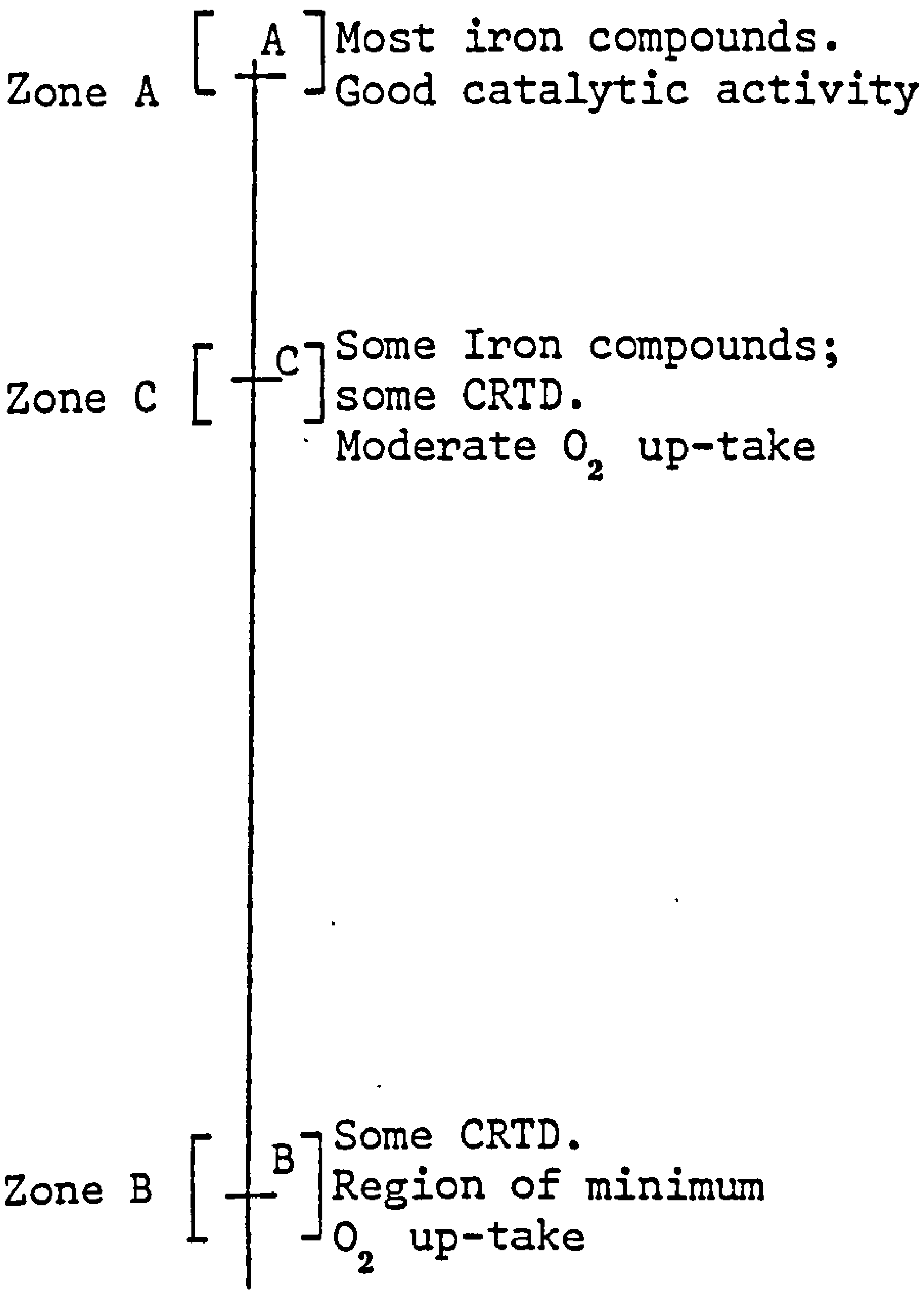
ROOM TEMPERATURE



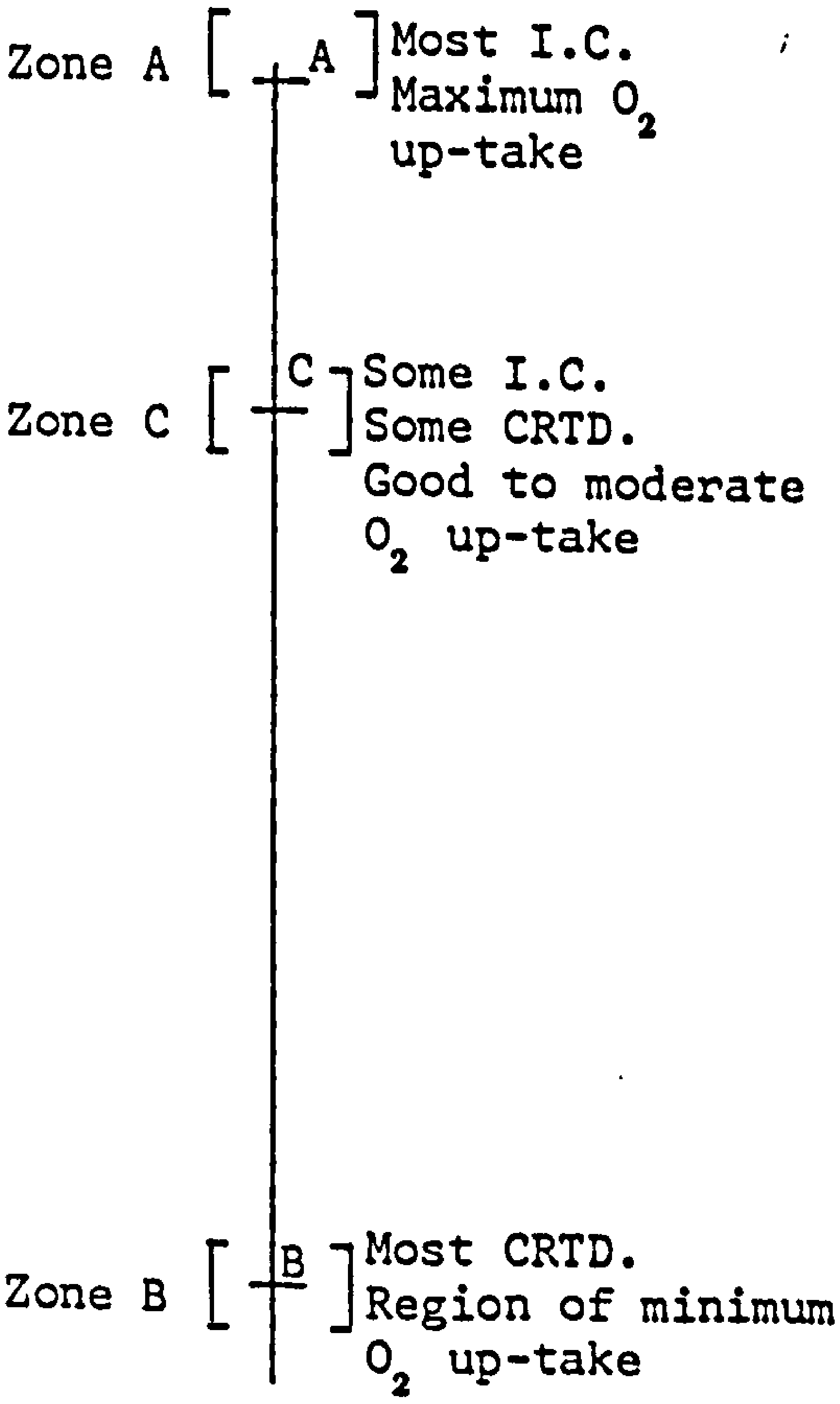
60° C



80° C

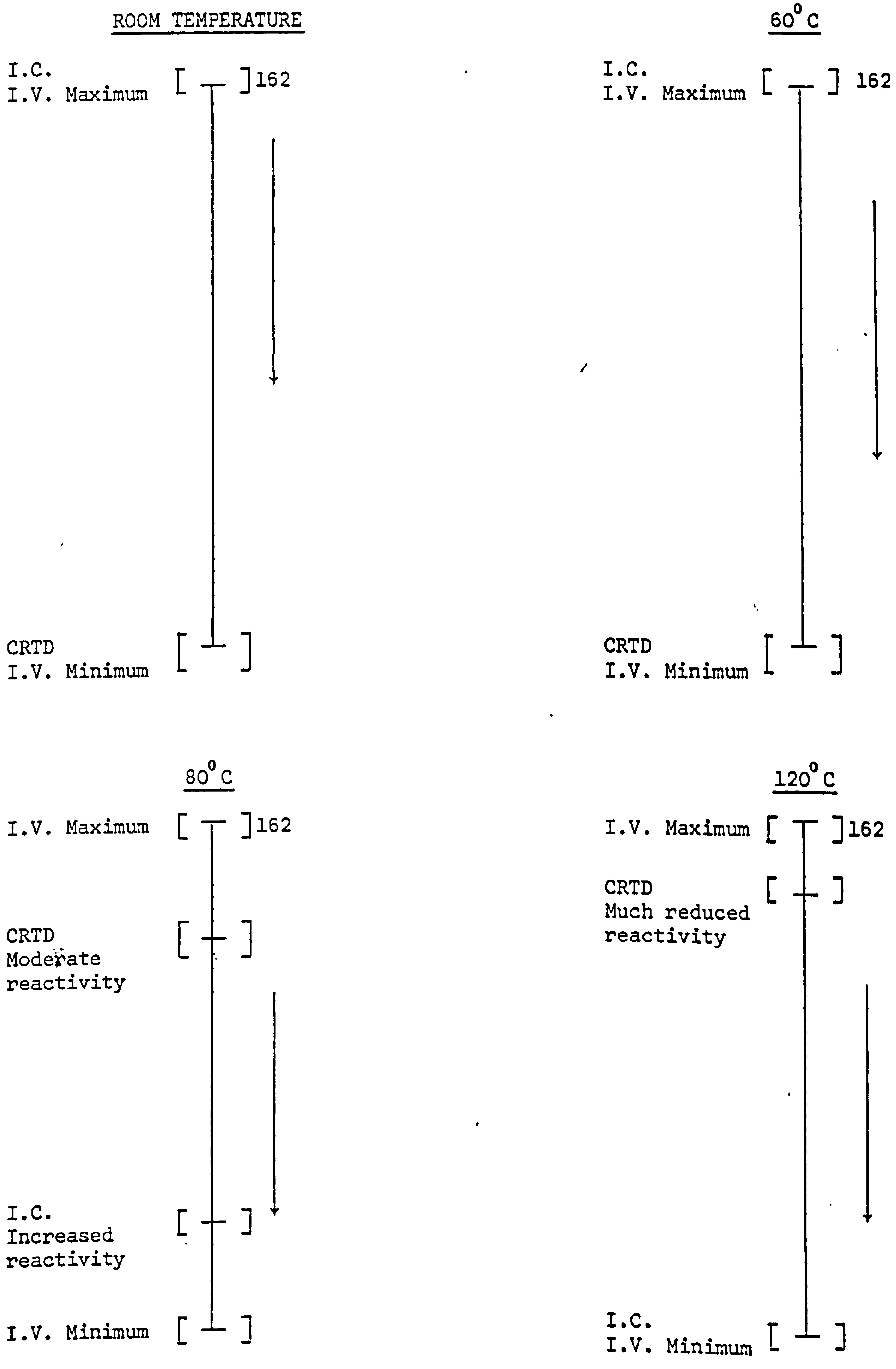


120° C

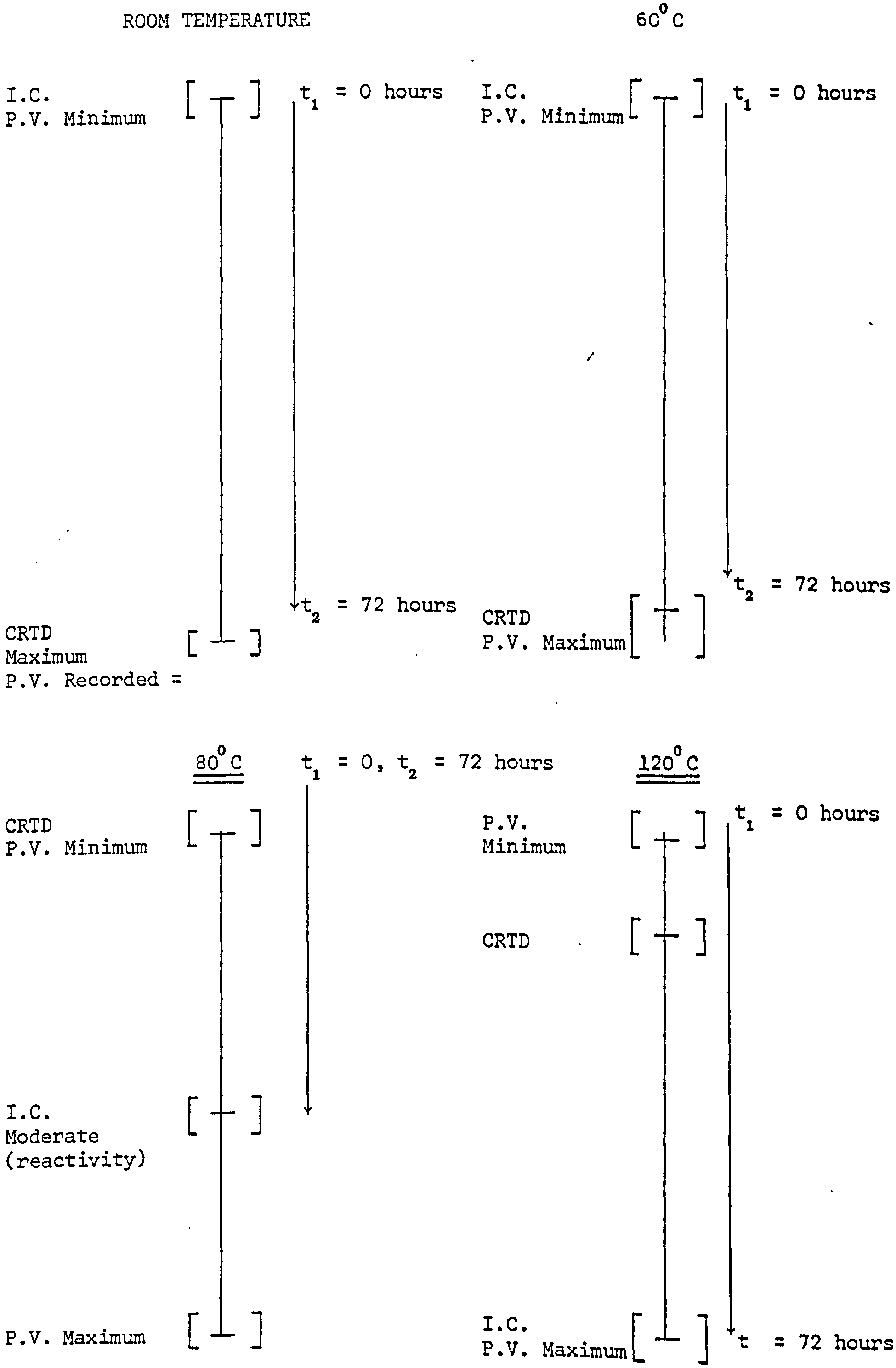


IODINE VALUES

t = 60 - 72 hours

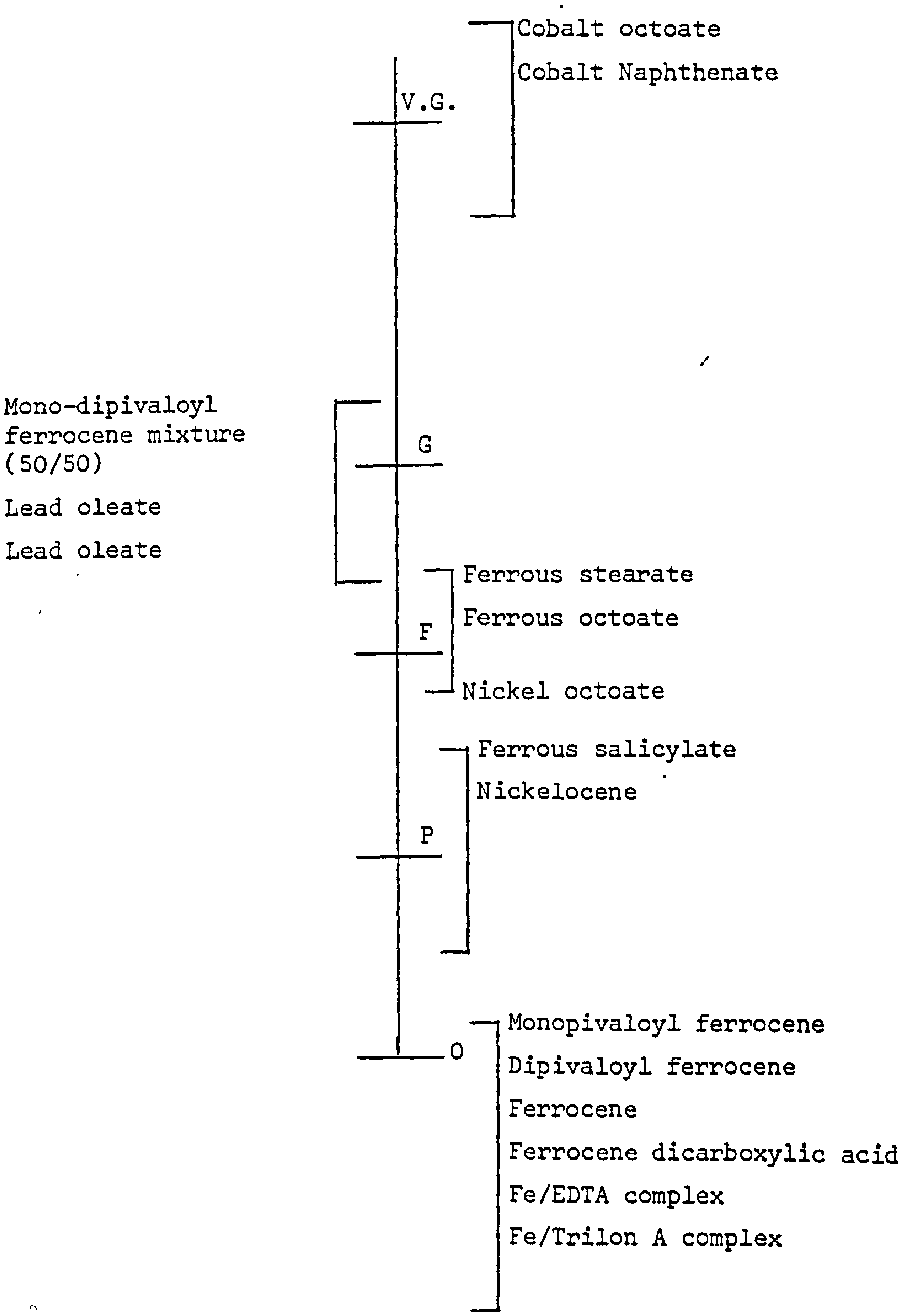


PEROXIDE VALUES



(i.ii) SUMMARY CHARTS

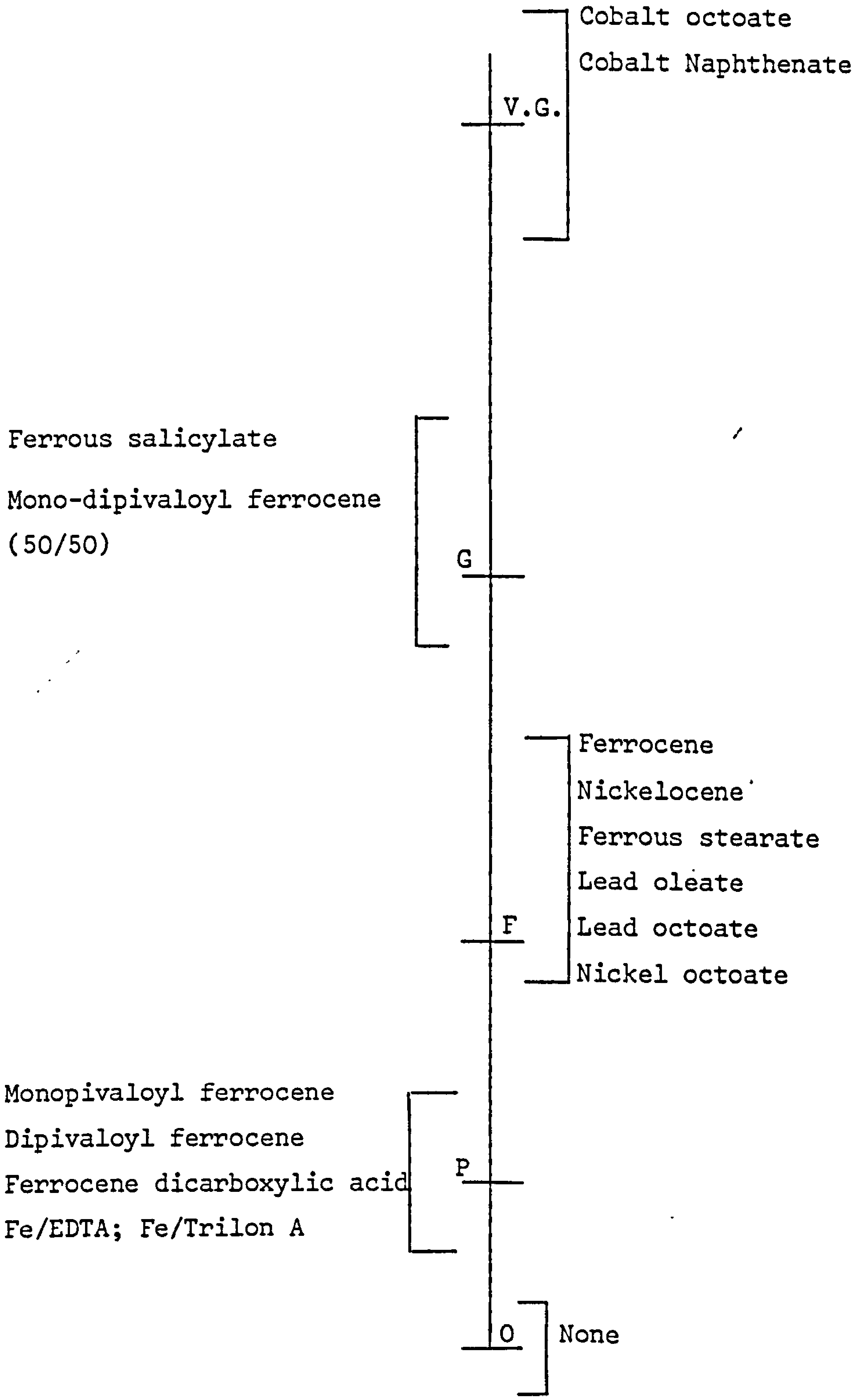
Oxygen absorption at room temperature



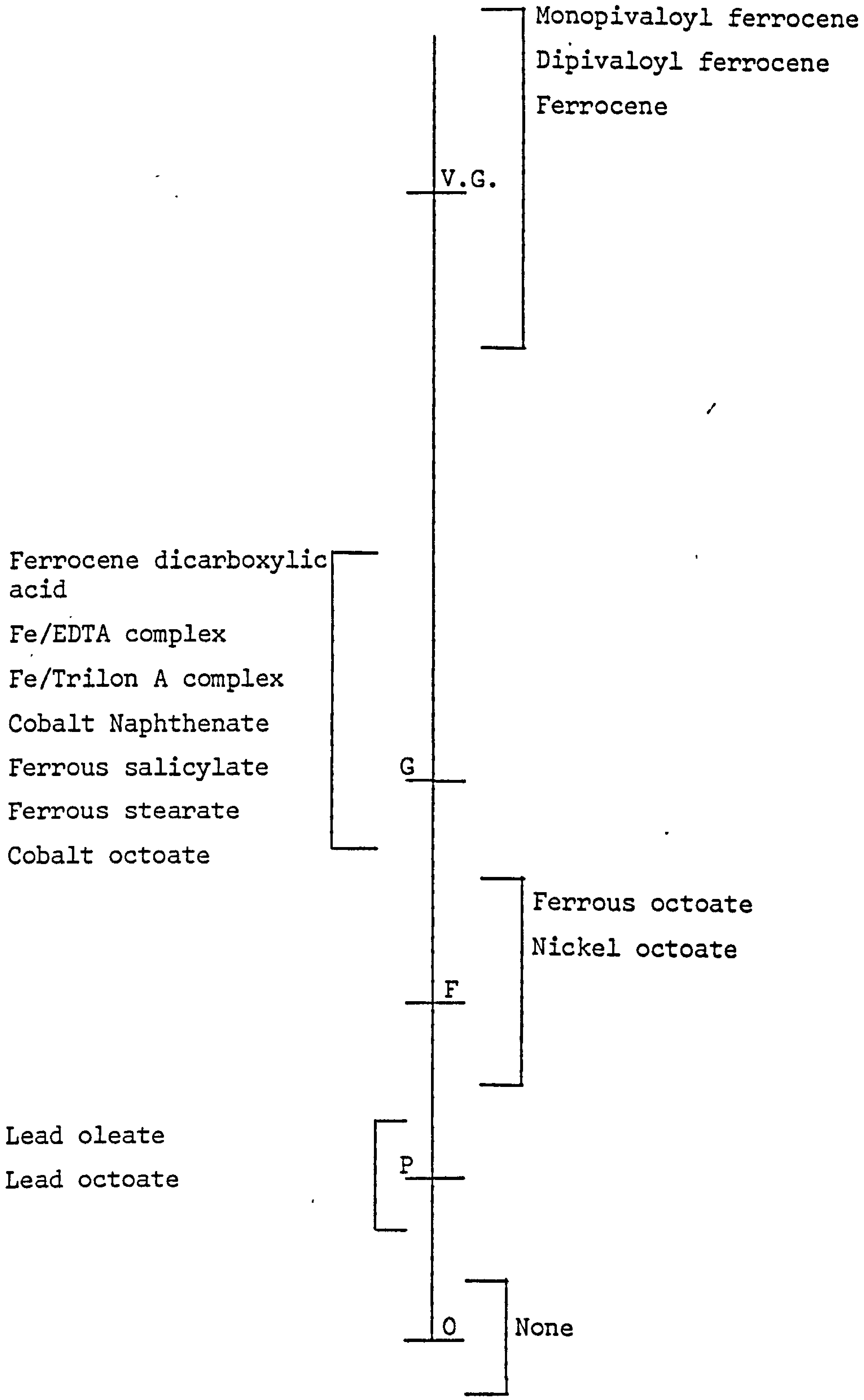
V.G. = Very Good; G = Good; F = Fair; P = Poor and

O = zero oxygen absorption (negligible).

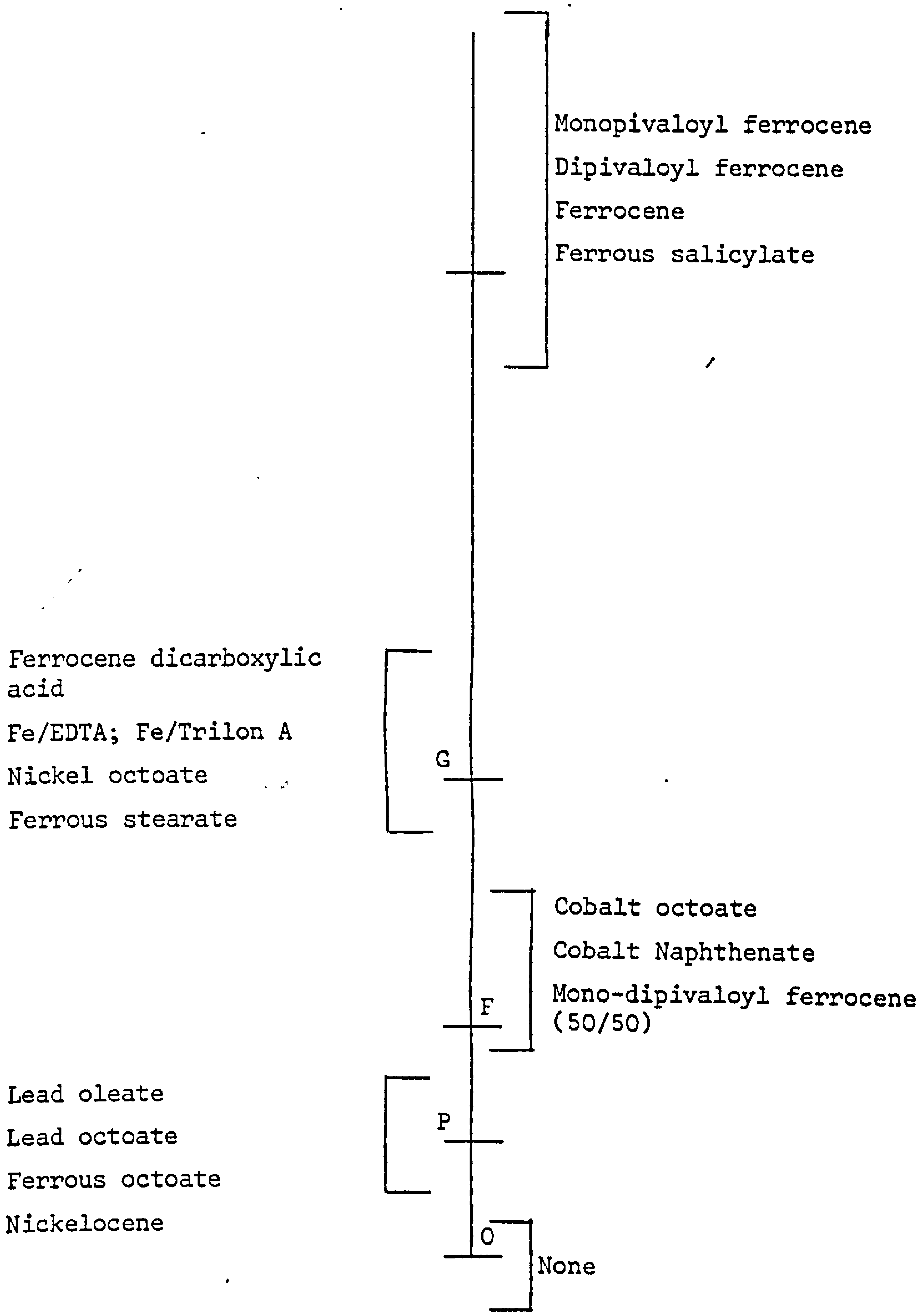
Oxygen absorption at $60^{\circ}C$



Oxygen absorption at 80°C

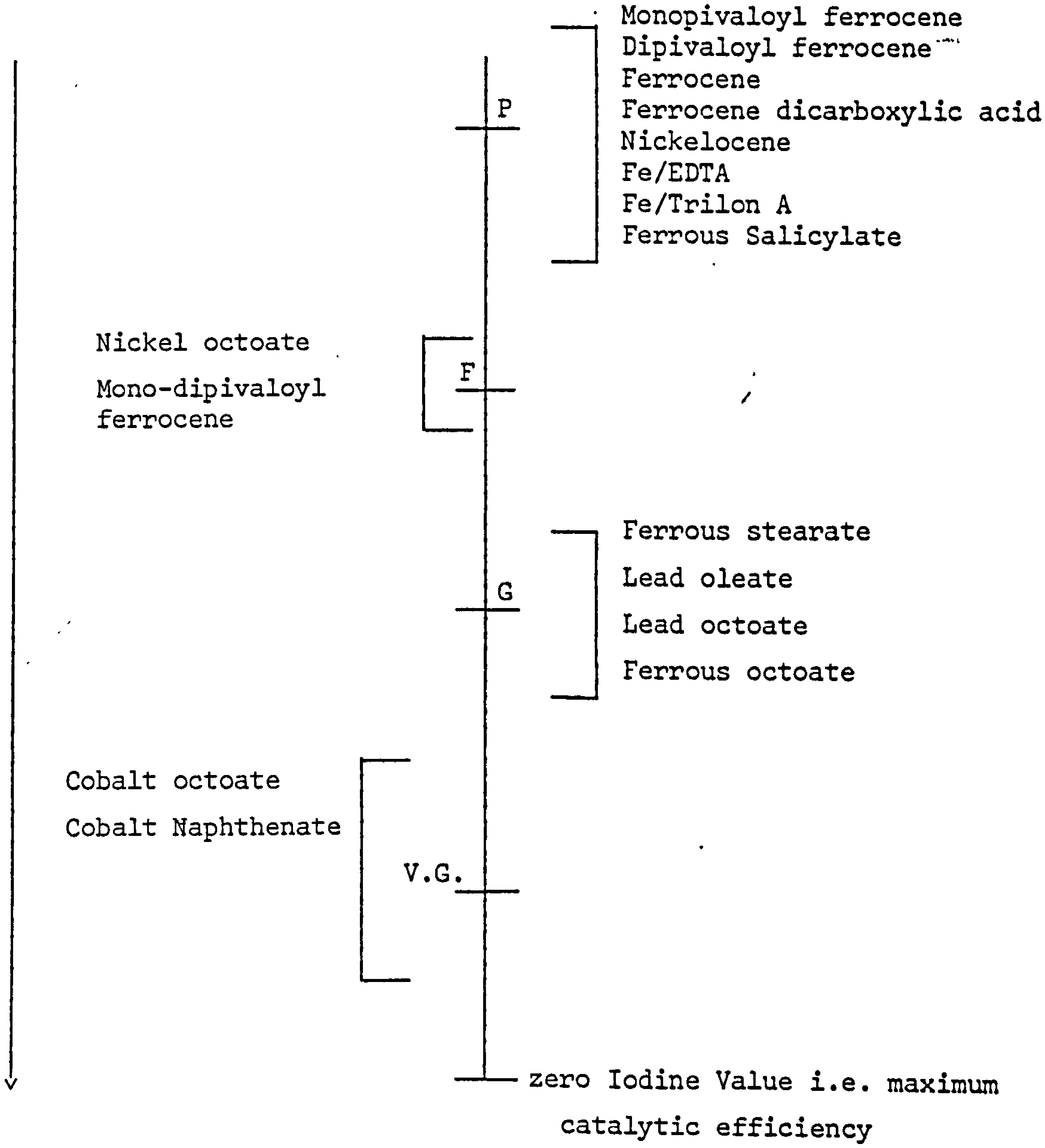


Oxygen absorption at 120°C



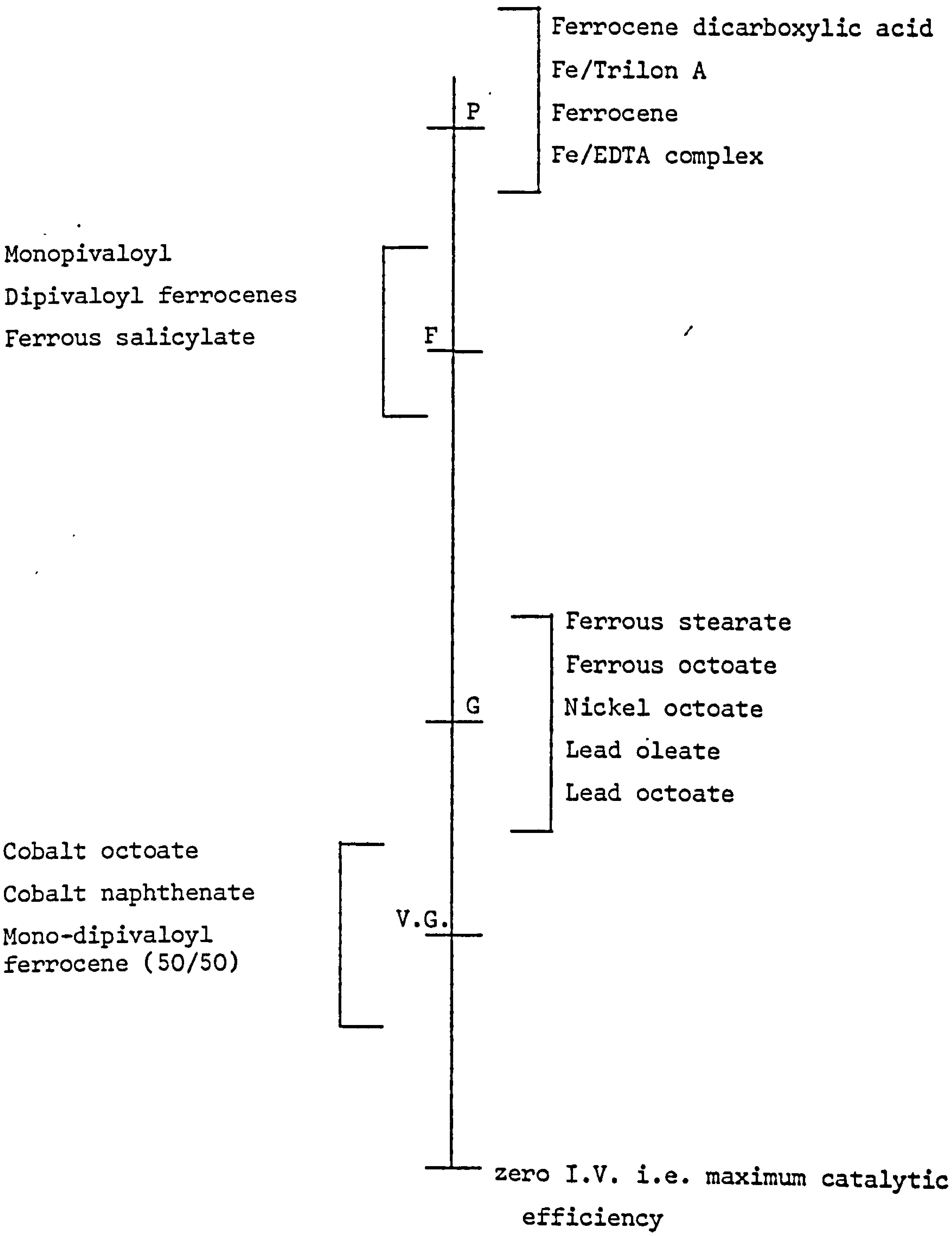
Changes in Iodine Values at room temperature

(Catalytic Rating Performance)



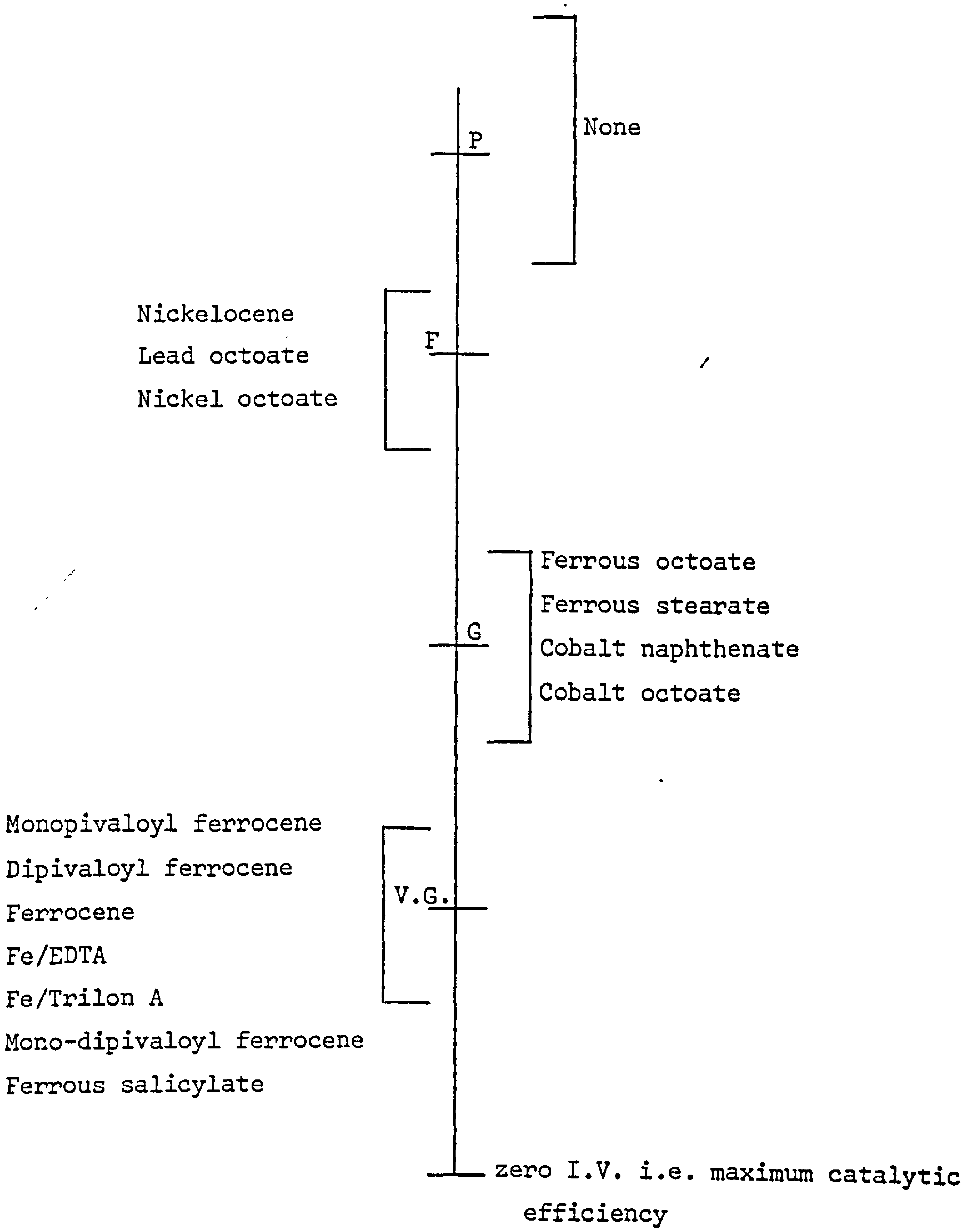
Changes in Iodine Values at 60°C

(Catalytic Rating Performance)



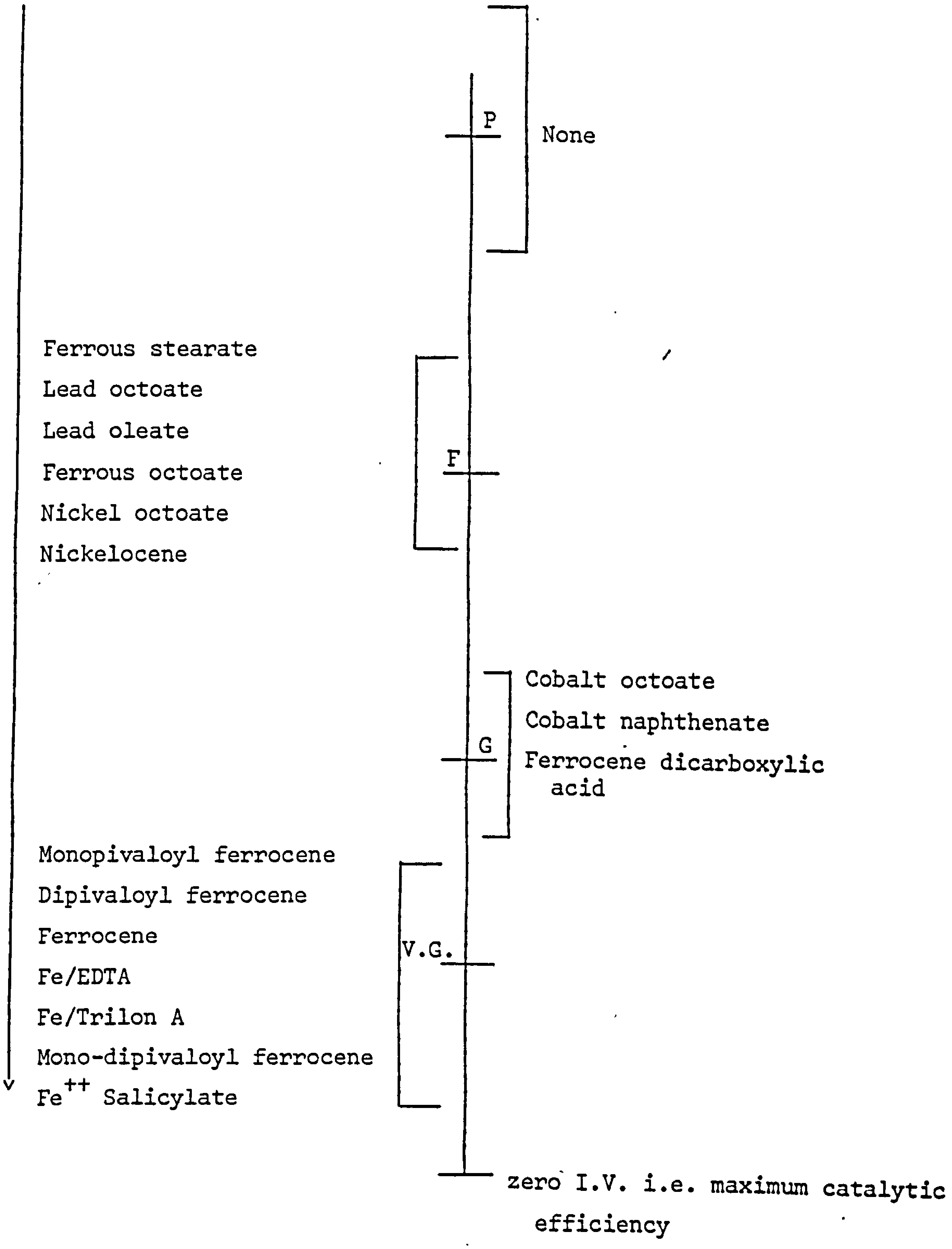
Changes in Iodine Values at 80^{0}C

(Catalytic Rating Performance)



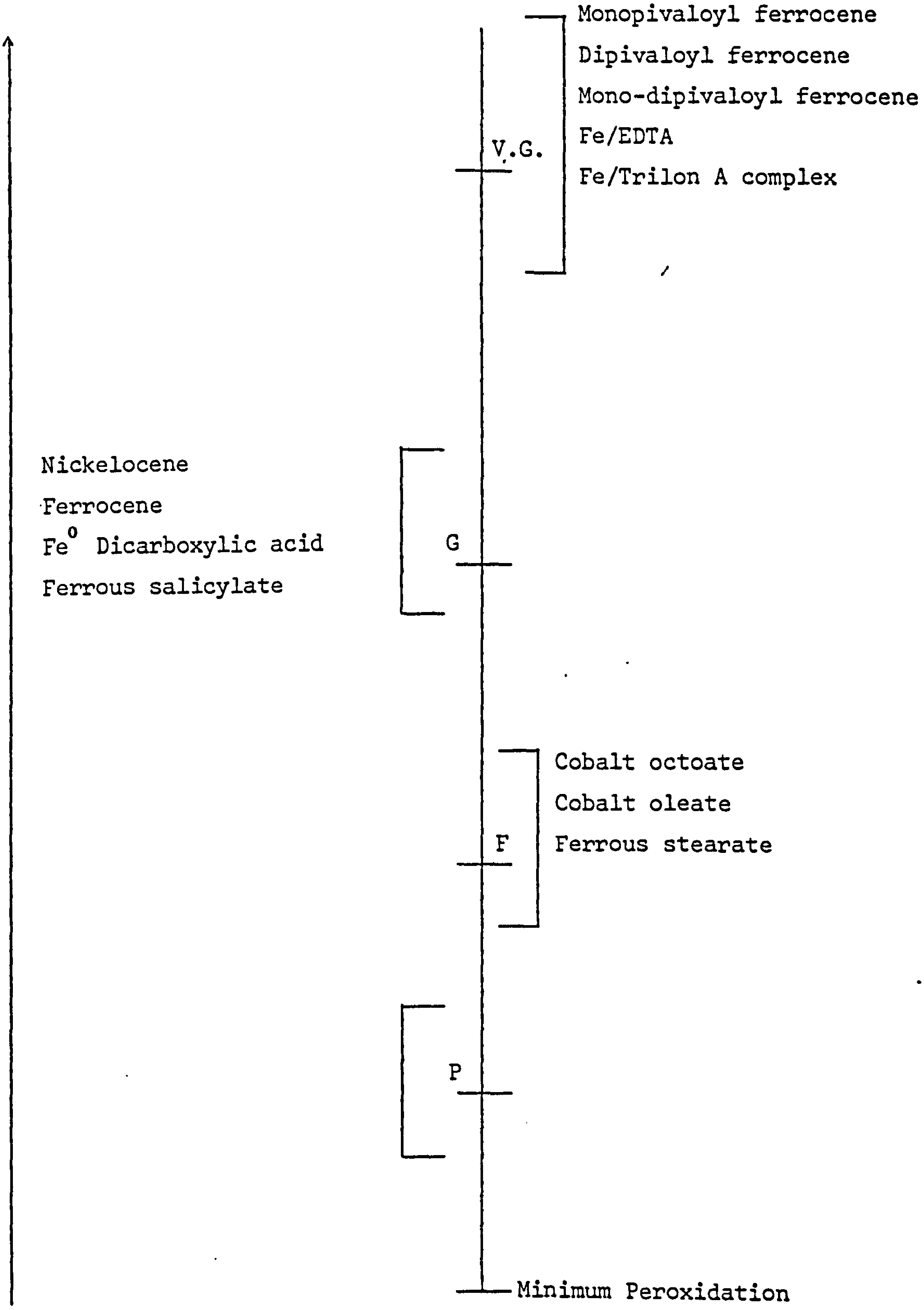
Changes in Iodine Values at 120°C

(Catalytic Rating Performance)



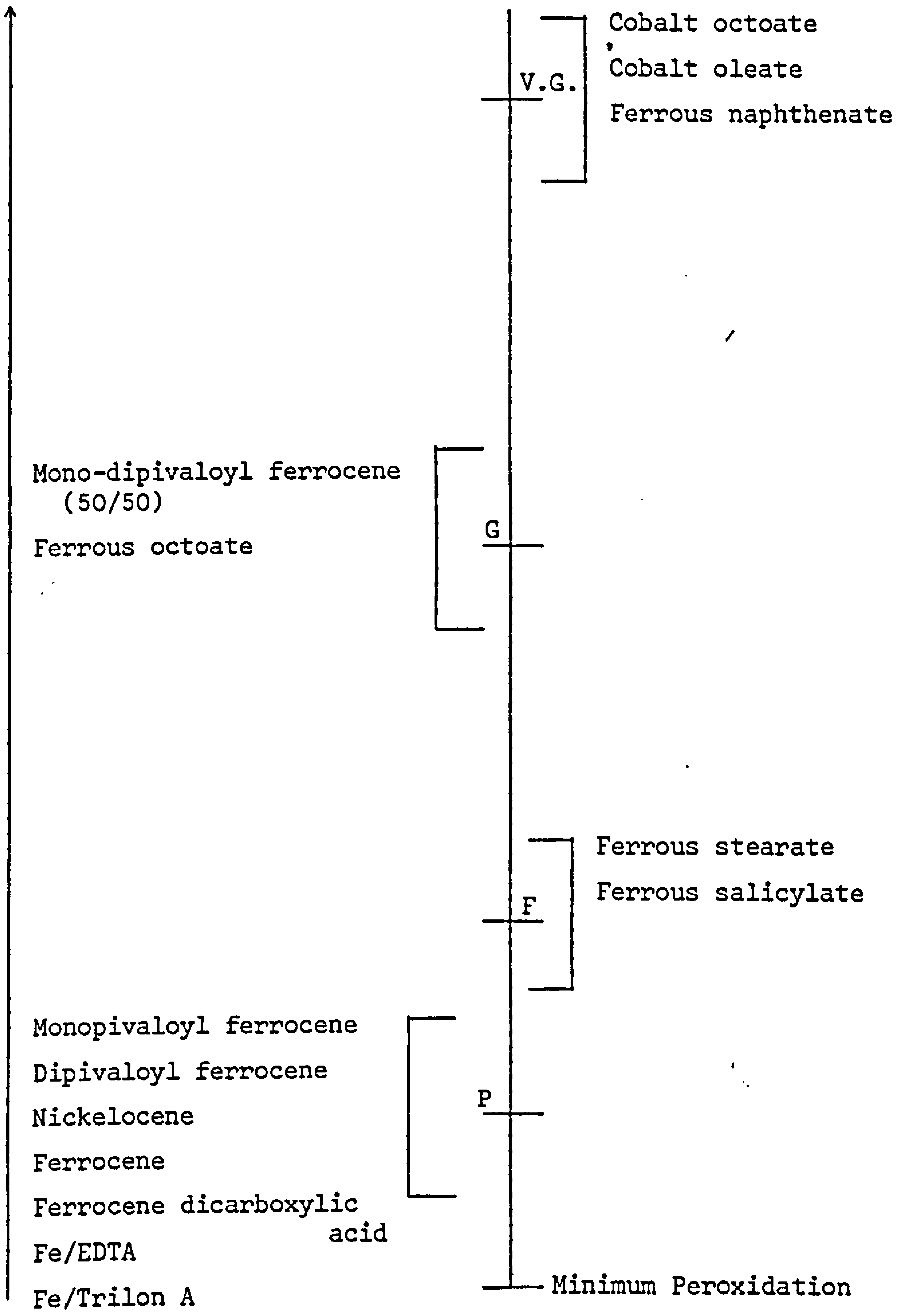
Changes in Peroxide Value at 80^0C

(Catalytic Rating Performance)



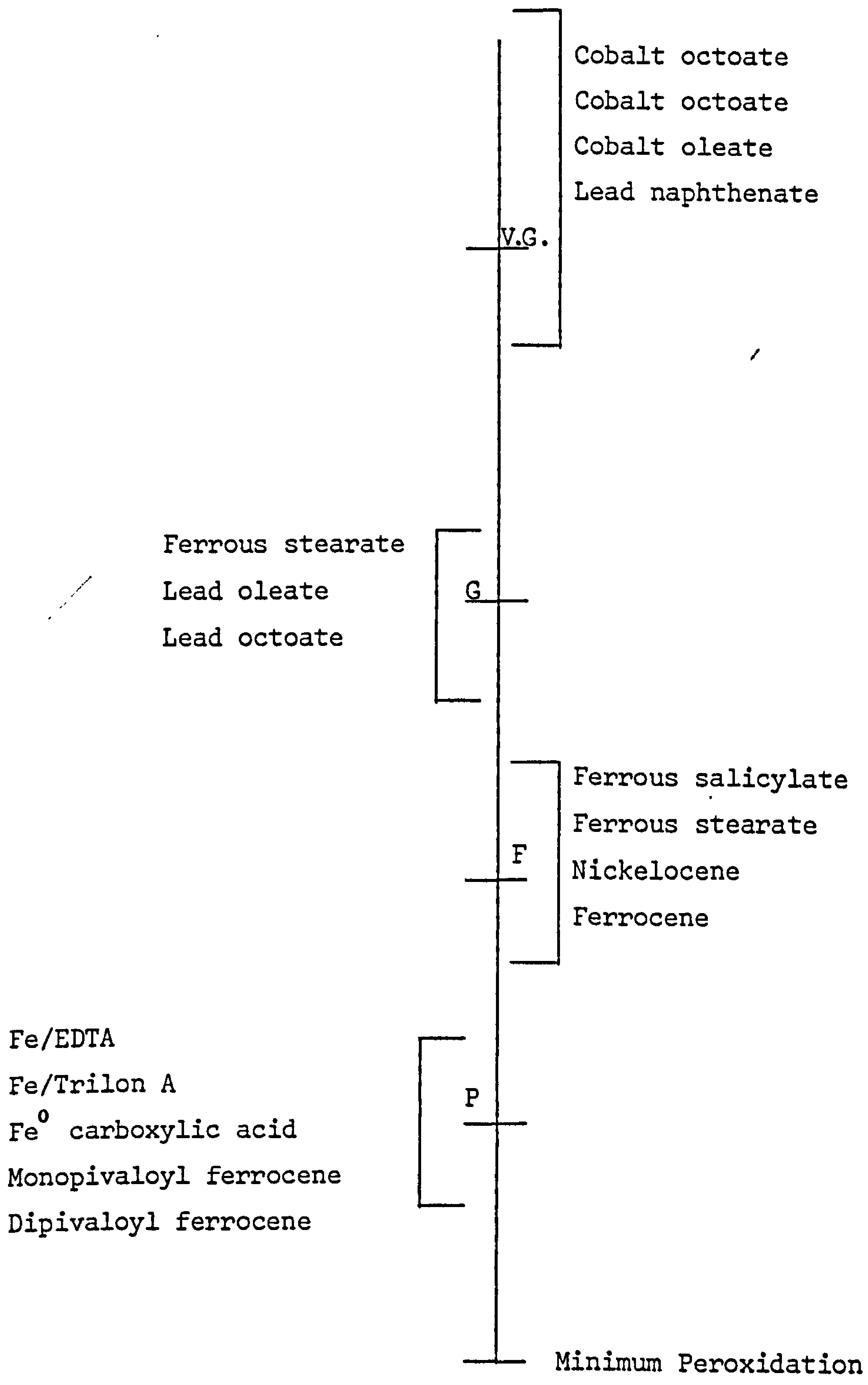
Changes in Peroxide Value at room temperature

(Catalytic Rating Performance)



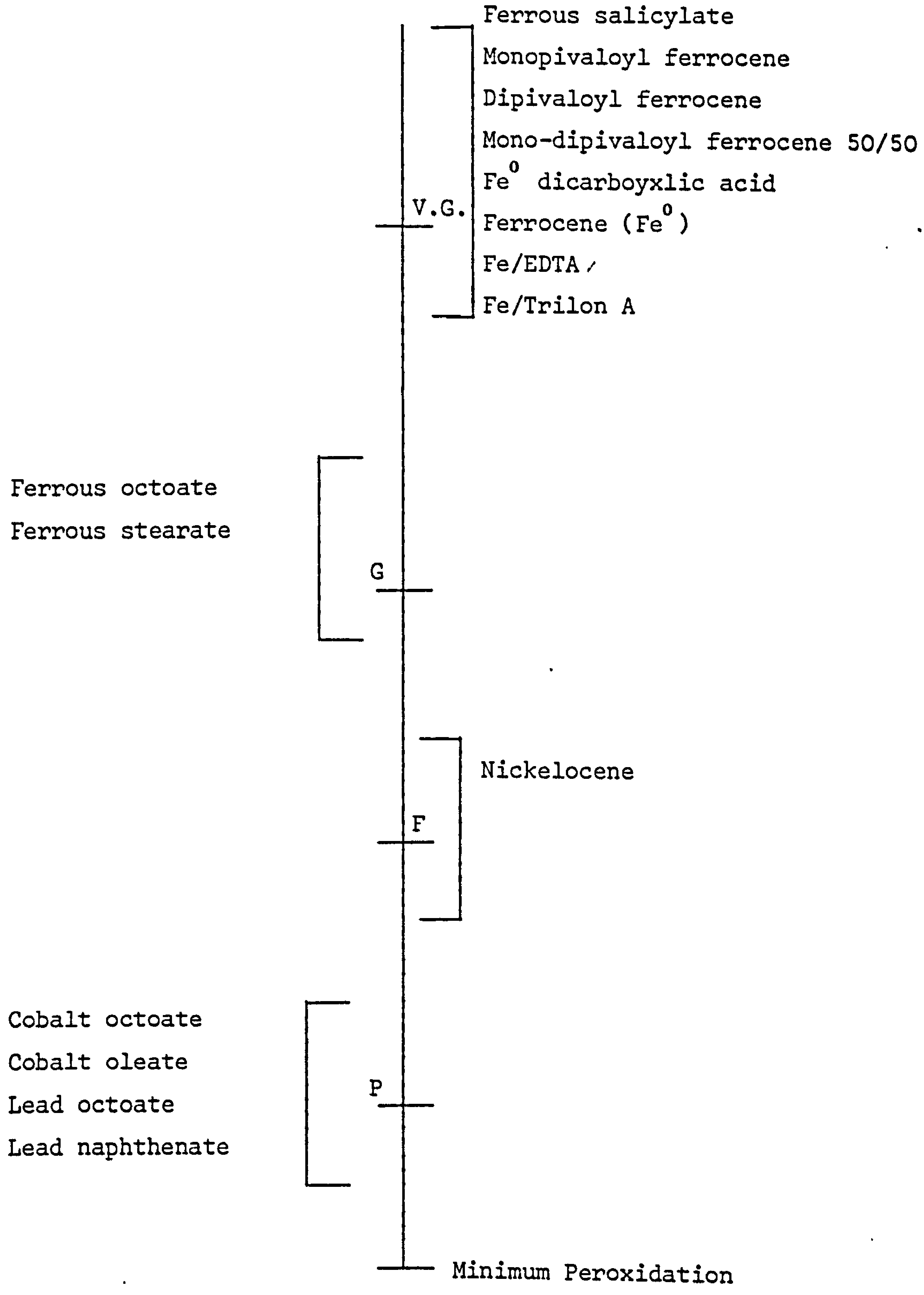
Changes in Peroxide Value at 60^0 C

(Catalytic Rating Performance)



Changes in Peroxide Value at 120°C

(Catalytic Rating Performance)



BIBLIOGRAPHY

1. W.M.F. Petri; Diospolis Parua, p.15.
2. Aetius; Introduction to history of science; Carnegie Int. Wash. Pub. 376, pp.1927-1931. Edited by G. Sarton.
3. A.E. Rheineck and R.O. Austine; Treatise on Coatings, Vol. 1 (ii) p.183. Edited by Myers and Long.
4. Ibid. Vol. 1 (ii) p.183.
5. Emulsions and water soluble paints and coatings. Edited by C.R. Martens, pp.1-6 (1964).
6. Ibid. pp.1-6.
7. Ibid. pp.1-6.
8. J. Liebig; Prep. and Application of Drying Agents in Paints; Prag. in Organic Coatings 4 (1976) pp.137-160.
9. S.B. Elliot; The Alkaline Earth and Heavy Metal Soaps; Reinhold, New York (1946).
10. Eibner and Pallauf; Chem. Umschaufette, Olele, Waschse, Harze, 32, pp.81, 97 (1925).
11. Sanda; M.Phil. Thesis; Bradford University (1981).
12. R.P.A. Sins and W.H. Hoffman; Oxidative polymerisation in autoxidation and antioxidants. Vol. 1 (ii) Edited by W.O. Lundberg; Wiley (Interscience), New York (1962).
13. H.R. Rawls and P.J. Van Santen, JAOCS, 47: 121 (1970).
14. H.R. Rawls and P.J. Van Santen; Ann. New York Acad. Sci. 171: 135 (1970).
15. A.H. Clements; R.H. Van den Engh; D.J. Forst, K. Hoogenhout and J.R. Nooi; JAOCS 50: 325 (1973).
16. D.J. Carson; T. Suprunchuk and D.M. Wiles; JAOCS 53: 656 (1976).
17. M.L. Kaplan; "Single Oxygen", Chem. Tech. 621 (1971).

18. C.S. Foote; W.A. Pryor; ed. Vol. (ii) Academic Press, New York (1976).

19. I. Fridovich; W.A. Pryor, ed. Vol. (i) Academic Press, New York (1976).

20. J. Bland; J. Chem. 53: 274 (1976).

21. N.I. Krinsky; Trends in Biochem. Sci. 2: 35 (1977).

22. L. Packer and J. Walton; Antioxidants vs Ageing; Chem. Tech. 276 (1977).

23. P.A. Leighton; Academic Press, New York (1961).

24. R.H. Kummerler; M.H. Bortner and T. Baurer, Environ. Sci. Technol. 3: 248 (1969).

25. J.N. Pitts Jr.; A.V. Khan, E.B. Smith and R.P. Wayne, Environ. Sci. Technol. 3: 241.

26. W.A. Pryor, ed.; Vol. 1, Academic Press, New York (1976).

27. E. Lee-Ruff; Chem. Sci. Rev. 6: 195 (1977).

28. M.B. Korycka-Dahl and T. Richardson; CRC Crit. Rev. Food Sci. Nutr. 11: 209 (1978).

29. A. Singh and A. Petkan; Photochem. Photobiol. 28: 429-934 (1978).

30. B. Ranby and J.F. Rabeck. Edited by John Wiley and Sons, New York (1978).

31. H.H. Wasserman and R.W. Murray. Edited by Academic Press, New York (1979).

32. H.N. Stephens; J. Am. Chem. Soc. 50: 568 (1928).

33. R. Criegee; Ann. 75: 522 (1936).

34. R. Criegee and Pilz H. Ber; 72: 1799 (1939).

35. A. Reiche; Angew. Chem. 50: 520 (1937).

36. E.H. Farmer and Sundraligam; J. Chem. Soc. 121 (1942).

37. E.H. Farmer; Trans. Faraday Soc.; 38; 356 (1942).

38. E.H. Farmer; Trans. Faraday Soc.; 38: 340 (1942);
Ibid.; 42: 228 (1946); Rubber Chem. and Technol.; 19: 267 (1946).
39. E.H. Farmer et al.; J. Chem. Soc.; 541 (1943).
40. D.A. Sutton and E.H. Farmer; J. Chem. Soc.; 119 (1943).
41. C.O. Willits et al.; Anal. Chem. 24: 785 (1952).
42. W.R. Lewise et al.; Ibid. 21: 762 (1949).
43. H. Nogami et al.; J. Pharm. Soc. Japan 71: 818 (1951).
44. C. Paquot and J. Mercier; Compt. rend; 236: 1802 (1953);
J. recherches centre natl. recherceh - sci., labs. Bellvue
(Paris) No. 24: 113 (1953).
45. C.O. Willits et al.; JAOCS 30: 420 (1953).
46. D.H. Saunders et al.; JAOCS 32; 79 (1955).
47. J.L. Bolland and G. Gee; Trans. Faraday Soc.; 42: 244 (1946).
48. J.L. Bolland and G. Gee; Ibid. 42: 236 (1946).
49. E.H. Farmer; Trans. Inst. Rubber Ind.; 21: 122 (1945).
50. E.H. Farmer; Trans. Faraday Soc. 42: 288 (1946).
51. F.D. Gunstone and T.P. Hilditch; J. Chem. Soc. 10 (1946).
52. C.S. Foote; Pure Appl. Chem. 27: 635 (1971).
53. N.A. Khan; W.O. Lundberg, R.T. Holmann; J. Am. Chem. Soc.
76: 1779 (1954).
54. D. Cobern, J.S. Hobbs, R.A. Lucas and D.J. Mackenzie;
J. Amer. Chem. Soc. (C): 1897 (1966).
55. G.E. Hall and D.G. Roberts; J. Am. Chem. Soc. (B): 1109 (1966).
56. E. Federi; G. Gamurati and G. Jacini; J. Am. Chem. Soc. 48:
787 (1973).
57. J. Terao and S. Matsuchita; Agric. Biol. Chem. 41: 2467 (1977).
58. H.W.S. Chan; J. Am. Chem. Soc. 54: 100 (1977).
59. J. Terao and S. Matsuchita; Agric. Biol. Chem. 42: 667 (1974).

60. R.T. Holman et al.; JAOCS 67: 1285 (1945).

61. C. Merritt et al.; JAOCS 44: 141-4 (1967).

62. R.J. Horvat; W.H. McFadden et al.; JAOCS 42: 1112-5 (1965).

63. R.J. Horvat et al.; Ibid. 46: 273-6 (1969).

64. D.A. Forss et al.; Ibid. 44: 572-5 (1967).

65. R.T. Holman; Progress in the Chem. of fats and other lipids. Eds. Pergamon Press Limited, London, Vol. II p.51 (1954).

66. J.L. Bolland and M.P. Koch; J. Chem. Soc. 445-7 (1945).

67. N.P. Butasku; Sbornik Khim. Fakul'teta 3: 33 (1953).

68. S.B. Crecelius et al.; Ind. Eng. Chem. 47: 1643 (1955).

69. H. Wexler, Chem. Rev.; 64: 591 (1964).

70. E.N. Frankel, W.E. Neff, M.K. Rohwedder; B.P.S. Khamboy, R.F. Garwood and B.C.L. Weedon; Lipids 12: 1055 (1977).

71. T. Umehara, J. Terao and S. Matsushita; J. Agric. Chem. Soc. Japan 53: 51 (1979).

72. J. Terao and S. Matsushita; Agric. Biol. Chem. 42: 667 (1978).

73. R.S. Morrell and H. Samuels, J. Chem. Soc., (1932) 2251.

74. O.S. Privett, JAOCS; 36: 507 (1959).

75. H. Hock and M. Siebert, Chem. Ber., 87: 554 (1954).

76. J.E. Myers, J.P. Kass and G.O. Burr. Oil and Soap 18: 107 (1941).

77. R.R. Allen and F.A. Kummerow, JAOCS 28: 101 (1951).

78. R.W. Brauer and L.T. Steadman, JAOCS 66: 563 (1944).

79. H.P. Kaufmann and J. Baltes, Fette Seifen, 43: 93 (1936).

80. J.D. Von Mikusch, Z. Anal. Chem., 130: 412 (1950).

81. E.T. Clocker, U.S.P. 2, 188, 882-90 (1940).

82. H. Plimmer, J. Oil Colour Chem. Assoc. 32: 99 (1949).

83. J.W. Shaw and M.W. Formo; JAOCS 31, 448 (1954).

84. A.E. Rheineck, Progress in Chem. of Fats, Vol. V (R.T. Holman ed.), Pergamon Press, London, 1959, Chapter 9.

85. R.S. Taylor and J.G. Smull, Ind. Eng. Chem; 28, 193 (1936).

86. A.E. Rheineck; Unpublished data.

87. J.L. Bolland, Quart. Rev., 3, 1 (1949).

88. L. Bateman, Ibid. 8: 147 (1954).

89. N. Uri; Autoxidation and Antioxidants, Lundberg Ed. (1961).

90. S.S. Stavala and L. Reich; Autoxidation of hydrocarbons and polyolefins, Marcel Dekker, New York, 247 (1969).

91. J.L. Bolland, India Rubber J., 213-8 (1946).

92. G.W. Grams and K. Eskins. Biochem. 11: 606 (1972).

93. C.S. Foote and R.W. Denny. JAOCS 90: 6233 (1968).

94. R.H. Young and D.H.R. Brewer. The mechanism of quenching of singlet oxygen. B. Ranby and J.F. Rabek, eds.; J. Willis and Sons, Chichester (1978).

95. M.G. Simic; Autoxidation in Food and Biological Systems. p.17 (1980).

96. W.W. Nawar and A. Witchwoot. Ibid. p.207 (1980).

97. Crossley et al.; JAOCS 39: 9 (1962).

98. K. Kitamura; Bull. Chem. Soc. Japan 44: 1606 (1971).

99. Breitbart and Nawar; 1977 (Unpublished data).

100. Crnjar et al.; Thermal oxidation of a series of saturated triacylglycerols (1980). Submitted for publication.

101. Y.C. Lien and Nawar; JAOCS 50: 76 (1973).

102. Kleinau and Neitzel; Fette, Seifen, Anstrichimittel, 72: 1025 (1970).

103. M.C. Paquot and F. de Goursac; Bull. Soc. Chem. France, 41: 172 (1950).

104. E. Selke et al.; JAOCS 54: 62 (1977).

105. E. Selke et al.; Ibid. 52: 232 (1975).

106. M.H. Brodnitz et al.; Lipids 3: 59 (1968); 3: 65 (1968).

107. N.E. Jewell and W.W. Nawar; Paper presented at the Combined Meeting of the Inter. Soc. for Fat Res.; Amer. Oil Chem. Soc., New York, May (1980).

108. Watanabe and Y. Sato; Agric. Biol. Chem. 34: 464 (1970).

109. Sen Gupta; Fette, Seifen, Anstrichmittel, 69: 907 (1967).

110. Sen Gupta; Ibid. 68: 475 (1966).

111. Nawar and M.F. Dubravcic; JAOCS 45: 100 (1968).

112. Sen Gupta and H. Scharman; Fette, Seifen, Anstrichmittel, 70: 265 (1968).

113. Frankel et al.; Lipids 12: 1055 (1977); 12: 901 (1977); 12: 908 (1977).

114. Chang et al.; JAOCS 55: 718 (1978).

115. Swoboda et al.; J. Sci. Fd. Agric. 16: 680 (1965).

116. Nawar et al.; Volatiles from frying fats. A Comparative Study in "Lipids as a source of flavour". M.K. Supran, ed.; ACS Symposium Series No. 75 (1978).

117. Henderson et al.; The Autoxidation of linoleates at elevated temperatures. Paper submitted for publication (1980).

118. Lomanno and Nawar; Effect of heating temperature and time on the oxidative decomposition of linoleate. Paper presented at the Inst. of Food Technol. Meeting, New Orleans, June (1980).

119. Chang et al.; JAOCS 53: 572 (1976).

120. K. Figge; Lipids 6: 164 (1971).

121. Witchwoot et al.; The influence of polyunsaturation on thermal decomposition of saturated triacylglycerols. Submitted for publication (1980).

122. D. Swern, J.T. Scanlon and H.B. Knight; J. Am. Oil Chemists' Soc. 25, 193 (1948).

123. S.S. Chang and F.A. Kummerow; J. Am. Oil Chemists' Soc. 30, 403 (1953).

124. G.J. King; J. Chem. Soc. 1954 (2114).

125. B. Lathlean; Paint J. Australia New Zealand 3(1), 12 (1958); CA, 52, 21156e (1958).

126. O.S. Pivett, W.O. Lundberg, N.A. Khan, W.E. Tolberg and D.H. Wheeler; J. Am. Oil Chemists' Soc. 30, 61 (1953).

127. C.D. Miller; J. Am. Oil Chemists' Soc. 36, 596 (1959).

128. H.T. Bandings; J. Am. Oil Chemists' Soc. 36, 648 (1959).

129. E.N. Frankel et al.; J. Am. Oil Chemists' Soc. 38, 161 (1961).

130. R.W. Keith and E.A. Day; J. Am. Oil Chemists' Soc. 40, 121 (1963).

131. G. Hoffman; J. Am. Oil Chemists' Soc. 36, 439 (1962).

132. J.H. Skellon; J. Oil Colour Chemists' Ass. 46, 1001 (1963).

133. F. Franks and B. Roberts; J. Applied Chem. (London) 13, 302 (1963).

134. R.J. Horvat et al.; J. Am. Oil Chemists' Soc. 43, 350 (1966).

135. M. Gomberg; Ber., 33, 3150 (1900).

136. M. Gomberg; J. Am. Chem. Soc., 22, 757 (1900).

137. H. Weiland; Ber., 48, 1098 (1915).

138. J. Weiss and F. Haber; Proc. Roy. Soc. (London) A147, 332 (1934).

139. M. Bodenstein; Z. Physik. Chem. 85, 329 (1913).

140. P. George, E.R. Rideal and A. Robertson; Proc. Roy. Soc. (London), 42, 201 (1946).

141. L. Bateman and H. Hughes; J. Chem. Soc. 4594 (1952).

142. V. Stannett and R.B. Mesrobian; Discus. Faraday Soc., 2, 242 (1947).

143. K.R. Hargrave and A.L. Morris; Trans. Faraday Soc., 52, 89 (1956).

144. A.V. Tobolsky et al.; J. Am. Chem. Soc. 72, 1942 (1950).

145. R.G. Bauman and S.H. Maron; J. Poly. Sci. 22, 1 (1956).

146. H. Winn and J.R. Shelton; Ind. Eng. Chem., 38, 71 (1946).

147. T.P. Hilditch and F.D. Gunstone; J. Chem. Soc. 836 (1945).

148. C.A. Russel; J. Am. Chem. Soc., 77, 4583 (1955).

149. J. Alagy et al.; Bull. Soc. Chim. France 1495 (1965).

150. C.H. Bramford and M.J.S. Dewar; Proc. Roy. Soc. (London), A198, 252 (1949).

151. H.W. Melville and S. Richard; J. Chem. Soc., 944 (1954).

152. V.F. Tsepalov, V.Y. Shiyapintokn and C. Pei-Huang; Russ. J. Phys. Chem.; 38, 26 (1964) & 38, 184 (1964).

153. J.G. Alagy and J.C. Balaceanu; Bull. Soc. Chem. France, 1495 (1965).

154. P.D. Bartlett and P. Gunther; J. Am. Chem. Soc. 88, 3288 (1966); L. Bateman and J.L. Bolland, Proc. XIth Intern. Congr. Pure and Appl. Chem. (1947).

155. Van Wuellen-Scholten; Am. Ink Maker; 18(1), 43 (1940).

156. J.H., Mon. peinture, 18, 189-92 (1930).

157. H.P. Kaufman; Ger. Pat. 870, 312.

158. H.P. Kaufman and E. Gulinsky; Fette, Seifen, Anstrichmittel 55, 593 (1953).

159. F. Haurowitz, P. Schwerin and M.M. Yenson; J. Biol. Chem. 140, 353 (1941).

160. M.E. Robinson; Biochem. J., 18, 255 (1924).

161. A.C. Zettlemoyer and D.M. Nace; Ind. Eng. Chem.; 42, 491 (1950).

162. C.A. Coffey et al.; USP 2, 694, 015 Nov. (1954).

163. C.A. Coffey et al.; USP 2, 631 944, March (1953).

164. (i) R.R. Myers and A.C. Zettlemoyer; Ind. Eng. Chem.; 46, 2223 (1954).
    (ii) D.G. Nicholson, Ibid. 31, 1300 (1939).
    (iii) G.K. Wheeler, Ibid. 39, 1115 (1947).
    (iv) D.G. Nicholson; J. Am. Chem. Soc. 64, 2820 (1942).

165. Loc. cit.

166. Tanaka, Kobayashi and Furihata; J. Soc. Chem. Ind. Japan, 38, Suppl. binding, 417 (1935); C.A., 29, 8301,(1935); Brit. Chem. Abs. B, 1032 (1935).

167. W. Krumbhaar; USP 2, 024, 103.

168. H.C. Bryson; Official Digest Federation Paint and Varnish Production Clubs, 183, 95 (1939).

169. P. Gunther, P.D. Bartlett; J. Am. Chem. Soc., 88, 3288 (1966).

170. M.S. Kharasch, F.S. Arimoto and W. Nudeburg; J. Organic Chem., 16, 1566 (1951).

171. J.W.L. Fordham and H.L. Williams; J. Am. Chem. Soc., 72, 4465 (1950).

172. R.J. Orr and H.L. Williams; Can. J. Chem., 30, 985 (1952).

173. M.S. Kharasch and A. Fono; J. Org. Chem.; 16, 1556 (1951).

174. A.F. Bickel and E.C. Kooyman; J. Chem. Soc., 3211 (1953).

175. E.C. Horswill and K.U. Ingold; Can. J. Chem., 44, 263 (1966).

176. G. Skirrow and M.H. Dean; Trans. Faraday Soc., 54, 849 (1958).

177. A.G. Korsun et al., Izv. Akad. Nauk. SSSR Otd. Khim. Nank. 788 (1961).

178. W.H. Richardson; J. Am. Chem. Soc., 88, 975 (1966).

179. A.E. Woodward and R.B. Mesrobian; Ibid., 75, 6189 (1953).

180. Z.K. Maizus, Russ. J. Phys. Chem. (Leipzig) 85, 329 (1913).

181. Y. Kamiya et al.; Can. J. Chem.; 41, 2034 (1963).

182. L.N. Denisova et al.; IVS. Akad. Nank SSSR Ser. Khim., 1095 (1966).

183. N. Michaels; Ph.D. Thesis, University of Florida, Gainesville (1961).

184. M.S.A. Kharasch, A. Fono and W. Nudenberg; J. Org. Chem., 15, 763 (1950).

185. M.S.A. Kharasch et al., Ibid., 17, 207 (1952).

186. H. Zuidema; Chem. Rev., 38, 197 (1946).

187. C.E.H. Bawn and J.E. Jolley; Proc. Roy. Soc. (London) A237, 297 (1956).

188. J.A. Sharp; J. Chem. Soc., 2026 (1957).

189. G.H. Twig and W.S. Wise; Ibid., 2172 (1953).

190. C.E.H. Bawn et al.; Discus. Faraday Soc., 10, 282 (1951).

191. L. Reich and S.S. Stavila; Autoxidation of Hydrocarbons and Polyolefins, Marcel Dekker, New York, 247 (1969).

192. Y. Kamiya et al.; Can. J. Chem., b034 (1963).

193. B.F. Erofeer and T.I. Soroko; Zh, Prikl, Khim; 33, 903 (1960).

194. Arthur Martell; Dept. of Chem.; Texas A & M, University College Station, Texas 77843.

195. F.R.J. Duke; J. Am. Chem. Soc., 69: 2885 (1947).

196. H. Taube; Ibid., 69: 1418 (1947).

197. H. Taube; Ibid., 70: 1216 (1948).

198. M.M. Taqui Khan and A.E. Martell; Ibid., 89: 4176 (1967).

199. F.R. Duke and A.A. Forist; Ibid., 71: 2790 (1949).

200. F.R. Duke and R.F. Bremer; Ibid., 73: 5179 (1951).

201. M. Anbar, R. Munoz and R.J. Roma; J. Phys. Chem. 67: 2708 (1963).

202. M.M. Taqui Khan and A.E. Martell; J. Am. Chem. Soc., 89: 7104 (1967).

203. R.R. Grinstead; Biochem. 3: 1308 (1964).

204. C.A. Tyson and A.E. Martell; J. Am. Chem. Soc.; 94: 939 (1972).

205. J.P. Wibut and A. Strong; Koninki Ned. Akad. Wetenschap. Proc., 55B, 207 (1952).

206. A.J. Chalk and J.F. Smith; Trans. Faraday Soc., 53, 1214 (1957).

207. B.G. Freidin; Zh. Priklad. Khim., 30, 768 (1957).

208. T.J. Wallance et al.; Chem. Ind. (London) 1764 (1965).

209. Y. Kamiya et al.; Can. J. Chem., 41, 2034 (1963).

210. W.H. Richardson; J. Am. Chem. Soc., 87, 247 (1965).

211. E. Dyer et al.; J. Org. Chem., 23, 1464 (1958).

212. Y. Kamiya; Tetrahedron, 22, 2029 (1966).

213. Sol Panush; J. Coating Tech.; 52: 666 (1980).

214. M.M. Taqui Khan and A.E. Martell; J. Am. Chem. Soc.; 90: 6011 (1968).

215. M.M. Taqui Khan and A.E. Martell; Ibid., 91: 4468 (1969).

216. H.J. Almquist and G.E.K. Branch; J. Chem. Soc.; 54, 2293 (1932).

217. D.G. Knorre et al.; Zh. Fiz. Khim.; 33, 213 (1959).

218. C.E.H. Bawn and A. White; J. Chem. Soc., 343 (1951).

219. G. Hargraves and L.H. Sutcliffe; Trans. Faraday Soc.; 51, 786 (1955).

220. E.T. Denisov and N.M. Emmanuel; Russ. Chem. Rev.; 29, 645 (1960).

221. Z. Hausmann; Angew Chem., 27, 63 (1914).

222. P. Nylen and E. Sunderland; Modern Surface Coatings, p.701.

223. Keal y and Pauson; Nature 168, 1039 (1951).

224. G. Wilkinson et al J. Am. Chem. Soc., 74, 2125 (1952).

225. Woodward et al.; Ibid., 74; 3458 (1952).

226. H.G. Kirschenbauer; Fats and Oils: An Outline of their Chemistry and Technology, 2nd Edition. Reinhold Publishing Corporation.

227. B. Hubl; Dinglers Polytech. J., 253, 281 (1884).

228. J.J.A. Wijs; Ber., 31, 750 (1898); Z. Angew. Chem., Heft 13, p.290 (1898).

229. C.E. Kendall; Proc. XIth Intern. Congr. Pure and Appl. Chem. (London), 5, 343 (1947).

230. D. Benson and L.H. Sutcliffe; Trans. Faraday Soc., 55, 2107 (1959).

231. H.W. Melville and S. Richard; J. Chem. Soc., 944 (1954).

232. V.F. Tsepalov; Russ. J. Phys. Chem.; 35, 710 (1961).

233. G.L. Hills and C.C. Thiel; J. Dairy Research, 14, 340 (1960).

234. A. Lips et al.; Oil and Soap (JAOCS), 20, 240 (1943).

235. Tanaka, Kobayashi and Furihata; J. Soc. Chem. Ind., Japan 38, Suppl. binding, 417 (1935); C.A. 29, 8301 (1935); Brit. Chem. Abs. B, 1032 (1935).

236. M.M. Taqui Khan and A.E. Martell; J. Am. Chem. Soc., 90: 6011 (1968).

237. M.M. Taqui Khan and A.E. Martell; Ibid., 91: 4468 (1969).

238. Bawn and Williamson; Trans. Faraday Soc. (1951) 47, 721, 735.

239. Kagan and Lubarsky; J. Physic. Chem., 1953, 39, 387.

240. Strang and Wibaut; Proc. Kon. Neder. Akad. Wet B, 1951, 54(2), 101; 1952, 55(3), 207.

241. Walsh; Trans. Faraday Soc.; 1946, 42, 269.

242. K.J. Moulton, R.E. Beal and E.L. Griffin; J. Amer. Oil and Chem. Soc., Vol. 50, November 1973.

243. D. Swern; "Bailey's Industrial Oil and Fat Products". Third Edition, Interscience Publishers, New York, (1964), pp.845,846.

244. W.J. Paterson; U.S.P. 2, 357, 352 (1944).

245. K.J. Moulton, D.J. Moore and R.E. Beal; JAOCS 46: 662 (1969).

246. P. Nylen and E. Sunderland; Modern Surface Coatings, Interscience Publishers, New York, 1965.

247. BP. 861833.

248. S.M. Arghande, Ph.D. Thesis, 1977. Bradford University.

249. J. Skalsky; Progress in Organic Coatings, 4, (1974) 137-160.

250. G.G. Hawley; The Condensed Chemical Dictionary, 9th Edition.

251. P.M. Fisk; Advanced Paint Chemistry, p.94, Leonard Hill (Books) Ltd., Eden Street, London NW1.

252. G. Garner, Textile Laboratory Manual, Vol. 2, Resins and Finishes p.59.

253. C.F. Bell, Principles and applications of metal chelation. Oxf. Chem. Series p.78.

254. F.A. Bavey and I.M. Kalthoff, Chem. Rev.; 42, 491 (1948).

255. W.A. Waters, "The Chem. of Free Radicals" Clarendon Press, Oxford, England.

256.

257. I.M. Kolthoff and A.I. Medallia; J. Am. Chem. Soc., Vol. 71, 3784 (1949).

258. E.H. Farmer; J. Chem. Soc., p.228 (1945).

259. C. Lea; J. Chem. Ind., 64, 106 (1945).

NKÉ RE̲DU LU UFFIA.