A mis padres - pasado y presente

A mi esposa e hijo - presente y futuro

STUDIES IN METATHESIS POLYMERISATION

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SUMMARY

The WCl_6 / $AliBu_3$ initiated polymerisation of cyclopentene has been investigated as a chain reaction and attempts have been made to study the reactions of the chain, ie initiation, propagation and termination.

The reactions between alkenes and tungsten hexachloride at low molar ratios of alkene : W have been studied using spectrophotometric techniques and analysis of the products by gas chromatography. These studies showed that a series of reactions takes place between tungsten hexachloride and alkenes and that a number of species are present in the system which, on addition of aluminium alkyl, produce metathesis-active complexes.

Dilatometric and calorimetric techniques have been used to study the kinetics of the reaction. Previous studies concerning the kinetics of the initiation of polymerisation were confirmed using the dilatometric technique. Comparison of the results obtained by these two techniques suggested that more than one active species was formed on the addition of aluminium triisobutyl to a solution originally containing tungsten hexachloride and cyclopentene. It is suggested that these active species produce high and low molecular weight materials independently and that the rate of production of polymer is measured dilatometrically and the overall rate of consumption of monomer calorimetrically.

Polymerisations initiated by WCl_6 / $2AliBu_3$ did not reach an equilibrium conversion of monomer. Addition of a second aliquot of initiator components or oxygen re-initiated polymerisation. The termination was interpreted from kinetic data and shown to be complex. Computer simulation of the reaction indicated second order termination involving both propagating and terminated species.

Studies on the role of oxygen as a catalyst activator indicated the production of a system similar in nature to WCl_6 / EtOH.

KEY WORDS

METATHESIS
TUNGSTEN HEXACHLORIDE
CYCLOPENTENE
RING-OPENING
POLYMERISATION

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CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

(1) INTRODUCTION

The metathesis of olefins and the ring-opening polymerisation of cyclic olefins is a relatively recent development that encompasses the application of inorganic complexes to the synthesis of materials from simple organic chemicals to high molecular weight polymers and many of the techniques used to study the reaction have their origins in modern physical chemistry.

With such a broad spectrum of disciplines involved and interested in metathesis, the area has undoubtedly benefitted from a multi-disciplinary approach, but the interests and emphasis of the research of these subject areas have not necessarily been directed towards a common solution. The industrialist has a different view from the structural inorganic chemist or that of the polymer chemist, but the international symposia organised in recent years have done much to overcome this problem.

The metathesis reaction has many applications that range from the production of high molecular weight synthetic elastomers with similar properties to those of natural rubber, to the preparation of polycondensation monomers and from the analysis of polymer networks to the production of olefins that can be used to produce high molecular weight polymers.

Although the reaction has attracted a lot of interest and several of the initial problems have been solved, there are some points that need further clarification. In particular, the detailed study of the kinetics of the polymerisation, including the initiation and, if any, the termination reactions.

The objective of this project is to try to produce some answers to some of the many questions that studies of this field have produced, with particular interest centred on the kinetics of the polymerisation of cyclopentene.

(2) GENERAL DESCRIPTION OF THE METATHESIS REACTION

The olefin metathesis reaction, also known as the 'olefin disproportionation reaction'(1) and the 'olefin dismutation reaction'(2) can be represented by:

$$2\,R_1CH{=}CH\text{-}R_2 \rightleftharpoons R_1\text{-}CH{=}CH\text{-}R_1 + R_2\text{-}CH{=}CH\text{-}R_2$$

In 1931 Schneider and Frohlich(3) described a non-catalysed reaction for the conversion of propylene to ethylene and 2-butene:

$$2CH_3\text{-}CH{=}CH_2 \rightleftharpoons CH_3\text{-}CH{=}CH\text{-}CH_3 + CH_2{=}CH_2$$

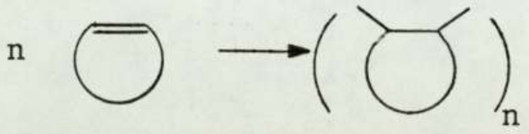
For this reaction to reach equilibrium temperatures of the order of 700°C were found to be necessary. The thermal activation of this entropy-controlled reaction is consistent with the fact that the reaction is symmetry forbidden according to the Woodward-Hoffmann rules(4). The metathesis reaction is athermal and involves the formation and cleavage of carbon-carbon double bonds. Equilibrium can be reached from either side of the reaction giving a random product distribution.

The catalysis of the reaction was first reported by Banks and Bailey(1). Their discovery stemmed from investigations carried out on the catalytic activity of molybdenum hexacarbonyl supported on alumina. It was found, that when this system was used, linear olefins of 3 to 8 carbon atoms were converted to mixtures of lower and higher molecular weight olefins and in particular that propylene was converted into ethylene and 2-butene. Temperatures of 150°C and pressures of 30 atmospheres were employed.

Prior to Banks and Bailey's discovery, Eleuterio(5) disclosed the polymerisation of cyclopentene to polypentenamer with a catalyst obtained from the hydrogen reduction of molybdenum oxide (MoO_3) which was supported on an inert metal oxide such as alumina; the reduced metal oxide was activated by lithium aluminium hydride to produce trans-polypentenamer in low yields after long reaction times. Natta et al(6-8) reported homogeneous catalyst systems based on the reactions of halides of group IV B and VI B transition metals and aluminium alkyls and alkyl halides, that were more efficient for the polymerisation of cyclic alkenes to polyalkenamers.

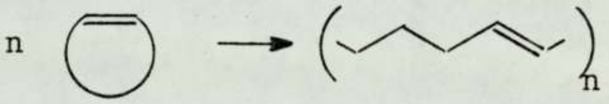
There are two possible modes of polymerisation of cyclic olefins which can be summarised by:

(a) conventional addition across a double bond,



and

(b) ring opening polymerisation,



The first reaction yields a polymer containing cyclic structures and the second results in a polymer containing carbon-carbon double bonds.

Very recently, Tsonis and Farona(9) reported the addition polymerisation of cyclic olefins containing 5, 6, 7 and 8 carbon atoms, using $Re(CO)_5Cl$ / $EtAlCl_2$ as the catalyst system. When polymerisation was carried out at high temperatures, low molecular weight materials, in which the ring structure was retained and no unsaturation was found, were obtained.

Although this evidence suggested a conventional addition across the double bond, the commonly observed mode of polymerisation is that first described by Natta et al(10) in 1964. Sufficient evidence based on infra-red spectroscopy showed that the polymerisation of cyclopentene proceeded by a ring-opening process. It was also suggested that the ring-opening proceeded by scission of the carbon-carbon single bond adjacent to the double bond of the cyclic olefin.

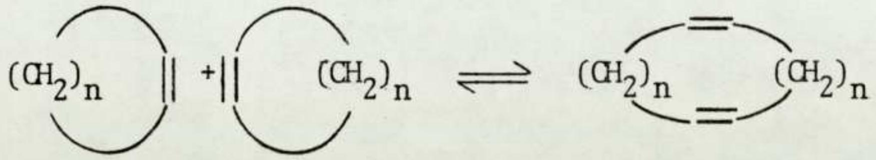
Polymerisation via scission of the double bond was not considered until the discovery by Calderon and co-workers(11) of a new olefin reaction in 1967. This reaction, called for the first time, olefin metathesis, occurred when a linear internal olefin was mixed with the catalyst WCl_6 / EtOH / $EtAlCl_2$, which was essentially similar to those used by Natta for polymerisation of cyclic olefins. Calderon proposed two routes by which the metathesis reaction could occur, either by exchange of alkyl groups or by the exchange of alkylidene groups.

The doubt was resolved when the reaction between 2-butene and perdeuterated 2-butene was carried out in the presence of the same catalyst system. The reaction was described as:

$$\underset{\text{I}}{CH_3\text{-}CH{=}CH\text{-}CH_3} \;+\; \underset{\text{II}}{CD_3\text{-}CD{=}CD\text{-}CD_3} \;\overset{W/Al}{\rightleftharpoons}\; \underset{\text{III}}{2CH_3\text{-}CH{=}CD\text{-}CD_3}$$

The result of the reaction was an equilibrium with molar ratios of I:II:III = 1:1:2 which gave a condition of maximum entropy for the system. Accordingly, the olefin metathesis reaction had to follow the route of alkylidene group exchange.

By analogy with the above reaction system, the ring-opening polymerisation of cycloolefins was described(12) as a special case of the olefin metathesis reaction and the authors suggested a reaction scheme wherein polymerisation took place by scission of the carbon-carbon double bond.



Evidence that this type of polymerisation reaction occurred by scission of the carbon-carbon double bond was supplied by Dall'Asta and Motroni(13). Cyclooctene was copolymerised with cyclopentene, which was (C^{14}) labelled at the double bond, to produce a random copolymer. This copolymer was then broken down by ozonolysis and the ozonolysis products were reduced to the corresponding diols.

Polymerisation by ring cleavage at the double bond would be expected to produce a polymer with units derived from C_8 and C_5 groups as follows:

$$C_8H_{14} + \overset{*}{C}_5H_8 \rightleftharpoons \underbrace{=CH-(CH_2)_6-CH=}_{C_8}\underbrace{\overset{*}{C}H-(CH_2)_3-CH=}_{C_5}\underbrace{CH-(CH_2)_6-CH=}_{C_8}$$

Polymer A

After ozonolysis and reduction of this type of unit, the following products would be obtained:

$HO\text{-}CH_2\text{-}(CH_2)_6\text{-}CH_2OH$ 1,8-octanediol

$HO\text{-}\overset{*}{C}H_2\text{-}(CH_2)_3\text{-}CH_2OH$ (C^{14}) 1,5-pentanediol

Polymerisation by ring cleavage at a single bond would result in the formation of a polymer containing units of the following structures:

$$\underbrace{\text{-}CH{=}CH\text{-}(CH_2)_6}_{C_8}\text{-}\underbrace{\overset{*}{C}H{=}CH\text{-}(CH_2)_3}_{C_5}\text{-}\underbrace{CH{=}CH\text{-}(CH_2)_6}_{C_8}\text{-}$$

Polymer B

and

$$\underbrace{\text{-}CH{=}CH\text{-}(CH_2)_6}_{C_8}\text{-}\underbrace{CH{=}\overset{*}{C}H\text{-}(CH_2)_3}_{C_5}\text{-}\underbrace{CH{=}CH\text{-}(CH_2)_6}_{C_8}$$

Polymer C

After ozonolysis and reduction of the polymers with these structures, the following products would be obtained:

$OH\text{-}CH_2\text{-}(CH_2)_6\text{-}\overset{*}{C}H_2OH$ (C^{14}) 1,8-octanediol
$OH\text{-}CH_2\text{-}(CH_2)_6\text{-}CH_2OH$ 1,8-octanediol
$OH\text{-}\overset{*}{C}H_2\text{-}(CH_2)_3\text{-}CH_2OH$ (C^{14}) 1,5-pentanediol
$OH\text{-}CH_2\text{-}(CH_2)_3\text{-}CH_2OH$ 1,5-pentanediol

Ozonolysis of the polymers of structures B and C followed by reduction to diols would divide the radioactivity equally between 1,8-octanediol and 1,5-pentanediol whereas ozonolysis and reduction of structure A would give only one radioactive product, 1,5-pentanediol.

Dall'Asta and Motroni found that ozonolysis of the copolymer obtained from the reaction, followed by radiochemical anlysis, showed that all the radioactivity was contained in the 1,5-pentanediol, which confirmed that the polymerisation took place by scission of the carbon-carbon double bond in the monomer as predicted by the olefin metathesis reaction theory.

(3) THE CATALYST SYSTEMS

(a) NATURE AND SCOPE OF CATALYST SYSTEMS

The metathesis of olefins and the ring-opening polymerisation reactions are promoted by heterogeneous as well as homogeneous catalysts. The heterogeneous catalysts are normally composed of a promoter, such as MoO_3 or WO_3 deposited on a high surface area refractory support such as alumina or silica. The homogeneous catalysts are composed of a transition metal complex usually of tungsten or molybdenum and an organometallic derivative or a Lewis acid, such as LiBu or $EtAlCl_2$. The range of catalyst systems available has been adequately described in many reviews of the literature(14-17).

It seems that a general theory able to explain all the systems is unlikely to be advanced, particularly if one bears in mind that complexes of W(VI) as well as W(O) are active precursors, and also the cocatalyst used to activate the system may also range from typical Lewis acids such as $AlCl_3$ or $AlBr_3$ to strong reducing agents as LiBu or $LiAlH_4$. Indeed in some instances metathesis has been reported to occur in monometallic systems, either with WCl_6 / cyclopentene(18) or $EtAlCl_2$ / norbornene(19). Every catalyst system must be treated independently with the hope of producing an overall mechanism for metathesis reactions.

(b) REACTIONS INVOLVING CATALYST COMPONENTS

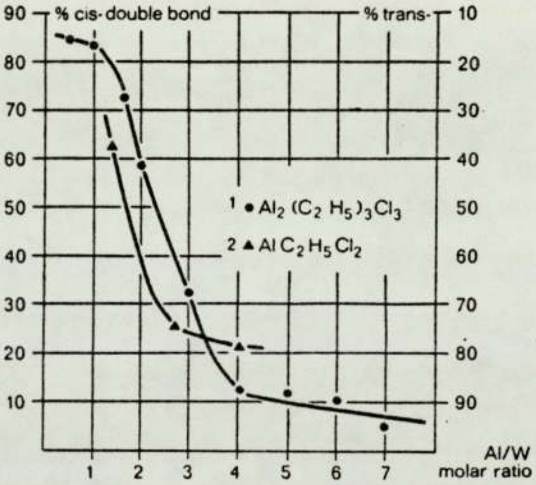
The complexity of the metathesis systems and the problems associated with attempts to assign universal mechanisms can be illustrated by some simple examples wherein apparently slight changes in some facet may render significant changes in the nature of the products and / or the nature of the reactions involved.

(i) Factors Affecting Microstructure of Polypentenamer

WCl_6 / Et_3Al induces the formation of trans-polypentenamer while the WCl_6 / $Na_3W(Ph)_5$ system produces essentially cis-polypentenamer(20).

The stereospecificity of a catalyst system may also vary with the W:Al ratio. Pampus and co-workers(20) observed that when WF_6 was combined with $Et_3Al_2Cl_3$ or $EtAlCl_2$ as cocatalyst, the cis:trans ratio of the polypentenamer obtained, varied continuously from about 85:15 to 10:90 when the Al:W molar ratio was changed from 0.5:1 to 7:1, as shown in Fig I.1.

Fig I.1 POLYPENTENAMER MICROSTRUCTURE AS A FUNCTION OF THE Al:W RATIO(20)



The cis:trans ratio of polypentenamer may also depend on the temperature of polymerisation. Minchak and Tucker(21) reported this effect for the polymerisation of cyclopentene for the temperature range -50 - +40°C.

(ii) Effect of Order of Mixing

Another factor that can influence the course of the metathesis reaction is the way and / or the order in which the different reaction components (ie catalyst, cocatalyst, olefin, activators) are mixed. The normal method consists of the addition of the catalysts to the olefin solution, followed by the incorporation of the cocatalyst(s) and, where appropriate, the activators.

Wang et al$^{(22)}$ showed that the effect of $AlBr_3$ and $AlCl_3$ on a WCl_6 / LiBu system depended on whether the catalysts were premixed. Premixing of the catalyst components (WCl_6 / LiBu) before addition of the aluminium compound greatly improved the selectivity of the system towards metathesis over the premixed system. In contrast to this, Menapace$^{(23)}$ observed that for the system WCl_6 / $Et_3Al_2Cl_3$ / aniline, the poorest selectivity was observed when the WCl_6 and the $Et_3Al_2Cl_3$ were premixed before the addition of the aniline and prior to the addition of the olefin. The maximum selectivity was attained when the tungsten compound was firstly allowed to react with aniline before the addition of the olefin and the aluminium compound (the order of addition of these last two components did not affect selectivity). This effect could be due to the reducing effect shown by some amines$^{(24)}$. It appears necessary therefore to have a prereduced system prior to the addition of the aluminium compound.

Amass and Tuck$^{(25)}$ observed that the dilatometrically determined rate of production of high molecular weight polymer from cyclopentene was practically nil when the catalyst components WCl_6 / $AliBu_3$ were premixed. Similarly, the disproportionation activity of the catalyst, WCl_6 / Et_3Al / O_2 was also dependent on the mixing order of the catalyst components (26). Preparation of the active catalyst was favoured by the presence of the olefin when WCl_6 was treated with Et_3Al and then oxygen.

The order of addition of the catalyst components can also affect the metathesis of ethylenic esters (27). Otton et al showed that the maximum conversion was obtained when the WCl_6 was allowed to react with the ester for 30 minutes to produce a red homogeneous solution before the cocatalyst ($SnMe_4$) was added. A less effective catalyst was obtained by premixing $SnMe_4$ with the olefinic ester prior to the addition of the WCl_6 or when the catalysts were premixed before addition to the ester.

Dolgoplosk (28) observed, however, that when the components of the catalyst $MoCl_3(C_{17}H_{35}COO)_2$ / Et_2AlCl were mixed in the absence of the monomer, at the concentration used for polymerisation of cyclopentene (1 to 7 x 10^{-3} mol dm^{-3}), and kept for several hours at room temperature before the addition of cyclopentene, the yield of polymer was the same as when they were mixed in the presence of the monomer. At higher concentrations (2 x 10^{-2} mol dm^{-3}), however, keeping the catalyst system without the monomer for several hours led to the deactivation of the catalyst. It was suggested that a greater reduction of the molybdenum was attained under these conditions.

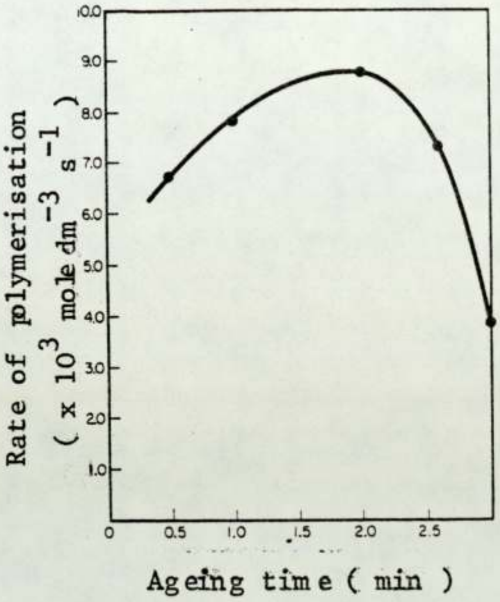
(iii) Reactions Between Transition Metals and Olefins

Results tend to indicate that a series of reactions can take place simultaneously in any system and that reactions can occur not only between the catalyst and cocatalyst, but also between the transition metal compound and the olefin or the activator.

In general, the reactions that can take place between the olefin and the transition metal compound have been neglected, although it has been reported that WCl_6 and $MoCl_5$ can lead to the stereoselective chlorination of olefins(29). In the reaction of cyclopentene with $MoCl_5$, a 66% yield of cis-1,2-dichlorocyclopentane was obtained and less than 1% of the trans-isomer. Similar results(29) were reported for WCl_6, producing with cyclohexane, a 41% yield of cis-1,2-dichlorocyclohexane and no trans-isomer. Such results suggest a common pathway for both these systems that would probably involve a reaction within the co-ordination sphere of the metal in order to provide such a stereoselective reaction and at the same time presumably reduce the metal to a lower oxidation state.

Amass and Tuck(25) reported a strong dependence of the initial rate of polymerisation on the time elapsed between the addition of WCl_6 and $AliBu_3$ to the monomer solutions for the metathetic polymerisation of cyclopentene by WCl_6 / $AliBu_3$. The rate increased to reach a maximum and decayed again as the premixing time of WCl_6 with monomer, as shown in Fig I.2.

Fig I.2 DEPENDENCE OF THE RATE OF POLYMERISATION ON AGEING TIME(25)



These results were associated with an initial reaction of the WCl_6 with a molecule of cyclopentene, followed by reaction of this product with an additional molecule to render a species when reacted with $AliBu_3$, that was less active towards metathesis. It has also been shown(30) that the oxidation state of tungsten changes during the reactions involved in the polymerisation of cyclopentene. These results are shown in Table I.1.

Accordingly, it is likely that the tungsten is present in the polymerisation of cyclopentene as a mixture of oxidation states, and that one of the initial roles of the olefin is to reduce W(VI)to a lower oxidation state, more active towards metathesis.

Table I.1 CHANGES IN THE MEAN OXIDATION STATE OF TUNGSTEN DURING THE REACTIONS INVOLVED IN THE POLYMERISATION OF CYCLOPENTENE(30)

Reaction Conditions	Mean Oxidation State of Tungsten
1 WCl_6 solution	6.0
2 WCl_6 + cyclopentene after 1 min	5.1
3 WCl_6 + cyclopentene after 20 mins	4.3
4 (3) + $AliBu_2OiBu$	4.3
5 (4) after 2 hours	4.4

The reaction of a carbon-carbon double bond with WCl_6 has been reported(31) for the degradation of 1,4-polybutadiene by a WCl_6 / $SnMe_4$ catalyst. The addition of WCl_6 to the polymer solution was followed immediately by an increase in the viscosity of the medium. The viscosity decreased suddenly when only a few drops of ethanol were added, breaking down any complexes and polymer network formed. As soon as the $SnMe_4$ was added, the viscosity started to decrease below the original levels. This reaction between WCl_6 and the double bonds of the polymer produced chlorinated products that were isolated as part of the final degradation products.

(iv) Role and Reactions of Cocatalysts

Although the metathesis reaction has been initiated by systems not containing a metal alkyl cocatalyst (ie Al, Sn, Zn, etc) examples of such, involve the reactions initiated by metal carbenes, WCl_6(18) and $WOCl_4$(32), the exceptionally low activity that is normally shown is greatly increased by the addition of a cocatalyst and sometimes other additives.

The effect of the use of different amounts of cocatalyst on a given system has already been shown in Fig I.1(20) which shows that by changing the W:Al molar ratio, the microstructure of the polymer obtained can change drastically. In the system, WCl_6 / $Et_3Al_2Cl_3$ / aniline(23) the metathesis system is converted into a dimerising system by increasing the amount of aluminium compound in the catalyst.

The role of the cocatalyst has been interpreted as:

(i) a reducing agent,

(ii) alkylating agent,

(iii) complexing agent, either to the olefins or the transition metal compound, or

(iv) creation of a vacant co-ordination site that would allow the incoming olefin to complex with the transition metal.

Again, the problem arises that a simple mechanism will not explain all the experimental facts and what may be true for one system is not necessarily so for another.

The addition of $AlCl_3$ or $AlBr_3$ to the catalyst WCl_6 / 2LiBu increases the metathetic activity sometimes by at least 100 fold(33,34) and WCl_6 is itself activated by these Lewis acids(35,36).

The function of the organometallic cocatalyst in this case would be to reduce W(VI) to W(IV) since maximum activity was observed for a W:Li ratio of 1 to 2(33). The reactions involved are shown below:

$$\begin{tikzcd}
WCl_6 + 2LiR \arrow[r] & R_2WCl_4 + 2LiCl \arrow[d, "2\text{ olefin}"] \\
 & WCl_4(\text{olefin})_2 + 2R\cdot
\end{tikzcd}$$

The increase in the activity of the system after the addition of the aluminium halides was considered to be a way of effecting the rapid isomerisation of trans-$WCl_4(\text{olefin})_2$ to the more active cis-$WCl_4(\text{olefin})_2$ by the mechanism outlined below(22):

$$\begin{tikzcd}
\text{Trans-}[WCl_4(\text{olefin})_2] \arrow[r, shift left, "AlCl_3"] & {[WCl_3(\text{olefin})_2]^+[AlCl_4]^-} \arrow[l, shift left] \arrow[d, shift right] \\
 & \text{cis-}[WCl_4(\text{olefin})_2] \arrow[u, shift right, "-AlCl_3"']
\end{tikzcd}$$

Similarly, because some organoaluminium cocatalysts produce optimum activity at a W:Al ratio of 1:2(26,34,25), the following reactions were proposed(35):

$$WCl_6 + EtAlCl_2 \longrightarrow EtWCl_5 + AlCl_3$$

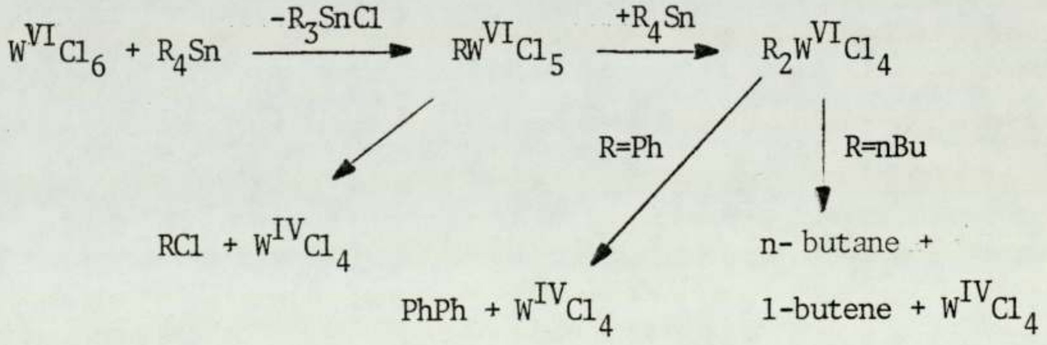
$$EtWCl_5 \longrightarrow WCl_5 + Et\cdot$$

$$2Et\cdot \longrightarrow C_2H_6 + C_2H_4$$

$$2Et\cdot \longrightarrow C_4H_{10}$$

WCl_5 could either undergo further reduction to WCl_4 or W(V) disproportionate to W(IV) and W(VI).

Ichicawa(37) proposed the following mechanism for the formation of the active species ($W^{IV}Cl_4$) from the reactions between WCl_6 and R_4Sn:



The $W^{IV}Cl_4$ species are formed by reductive elimination of RH, 1-alkene, RCl and RR from $RWCl_5$ and for R_2WCl_4.

However, WCl_4 obtained by reduction of WCl_6 with hydrogen or prepared in situ by treatment of WCl_6 with reducing agents, such as zinc, magnesium or sodium amalgam is not a metathesis catalyst(35,38) although the addition of $AlCl_3$ to WCl_4 so prepared gives a highly active catalyst(39).

Bridging between the tungsten compound and the cocatalyst may occur through chloride, hydride or alkyl ligands, or the Lewis acid properties of the organometallic of hydridic species towards the tungsten components may establish the acid-base equilibria of the type shown in the equation:

$$WCl_X + AlCl_3 \rightleftharpoons [WCl_{X-1}]^+ + [AlCl_4]^-$$

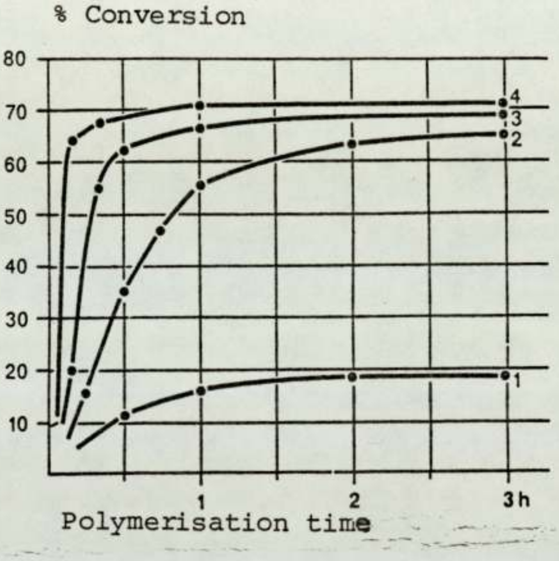
Such reactions would allow the formation of a vacant co-ordination site for the incoming olefin molecule(35).

The effect of the cocatalyst as an alkylating agent is considered in more detail in the section covering the chain initiation of the reaction (I,5).

(v) Role of Oxygen and Oxygen Containing Compounds

Various oxygen containing compounds have been used as activators for the metathesis reaction of olefins. In particular, compounds containing epoxide groups(40,41,20) or hydroperoxides(42) increased the activity of the catalysts for the ring-opening polymerisation of cyclic alkenes. Pampus$^{(20)}$ reported the effect of different catalyst combinations on the polymerisation of cyclopentene. The results are shown in Fig I.3.

Fig I.3 POLYMERISATION OF CYCLOPENTENE IN TOLUENE (TEMPERATURE= 0 °C)$^{(20)}$

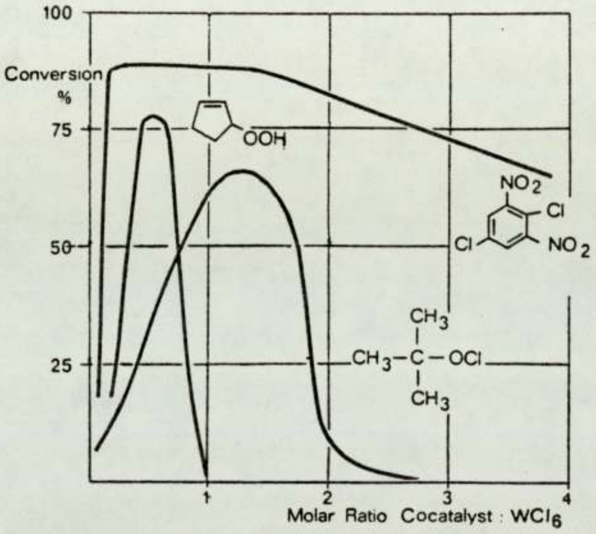


(1) WCl_6 / $AliBu_3$, (2) $WCl_5(OCH_2CH_2Cl)$ / Et_2AlCl, (3) $WCl_{4.75}$ - $(OCH_2CH_2Cl)_{1.25}$ / Et_2AlCl, (4) $WCl_4(OCH(CH_2Cl)_2)_2$ / Et_2AlCl

The systems with oxygen containing compounds were more active and reached a conversion closer to that at equilibrium. Attention should be drawn to the fact that the WCl_6 / $AliBu_3$ system terminated (ie rendered inactive) well before it reached the monomer-polymer equilibrium.

The effect of different activators for the polymerisation of cyclopentene initiated by WCl_6 / $AliBu_3$ is shown in Fig I.4.

Fig I.4 EFFECT OF ACTIVATION OF WCl_6 / $AliBu_3$ / ACTIVATOR SYSTEM ON THE RING OPENING POLYMERISATION OF CYCLOPENTENE (20)



Controlled treatment of WCl_6 with protic compounds such as ethanol, phenol, water or acetic acid, prior to the addition of the organometallic compound increased the catalytic activity of the systems based on WCl_6 / R_XAlCl_{3-X} (11,34,43). The reaction with ethanol (35) produced a stoichiometric quantity of HCl:

$$WCl_6 + EtOH \longrightarrow Cl_5WOEt + HCl$$

The reaction with water also is stoichiometric to produce HCl and $WOCl_4$:

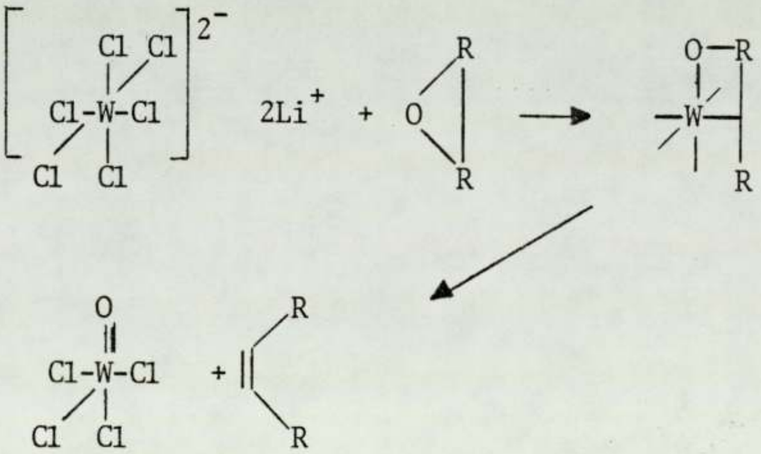
$$WCl_6 + H_2O \longrightarrow WOCl_4 + 2HCl$$

It is not strange, therefore, that compounds such as $WOCl_4$, WO_3, $W(OPh)_6$ and $WO(OPh)_4$ are active metathesis catalysts in the presence of a suitable cocatalysts(44,45).

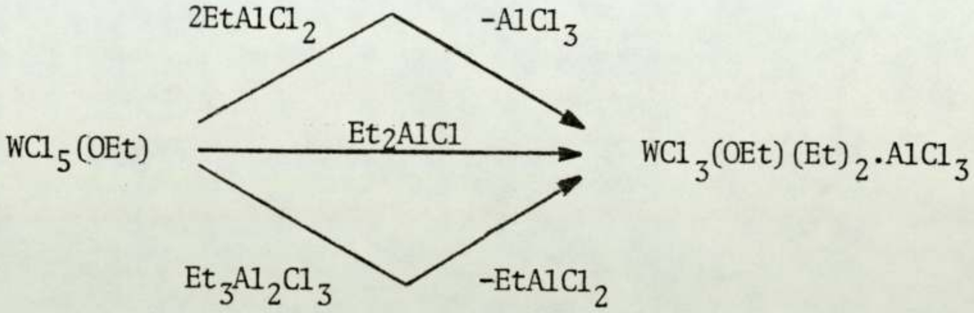
Pampus(20) explained the reaction between the epoxides and WCl_6 according to the following scheme:

$$WCl_6 + 2CH_2\text{-}CH\text{-}CH_2Cl \longrightarrow Cl_4W[OCH(CH_2Cl)_2]_2$$

and in this way provided for the formation of an alkoxide ligand. In a more recent mechanism, it has been proposed(46) that an epoxide would reoxidise the tungsten compound and at the same time provide an oxo-tungsten complex:



The role of the alcoholic or phenolic component, according to Hocker(47), is to disturb the highly symmetrical structure of the octahedral WCl_6 and hence facilitate chlorine-alkyl exchange with the organo-aluminium compound. The formation of the precursor or the active species was proposed as follows:

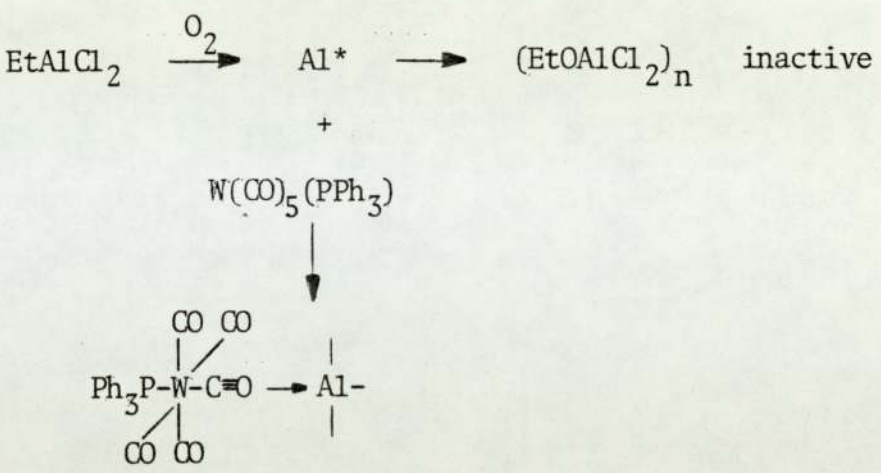


Schrock(48) pointed out that d^0 alkylidine complexes are the most common type of metathesis catalyst. At least one oxo-ligand may be crucial for keeping a group VI metal in a d^0 state. Since reactions with water or oxygen lead to the formation of oxo-complexes, it is not surprising that these should be beneficial to metathesis activity in trace amounts. The use of ethanol may serve primarily as a source of alkoxide ligands which in turn increases the electron density on the central transition metal atom(48).

Muetterties and co-workers found that the standard bimetallic catalyst systems were inactive when prepared under oxygen free conditions(49) and the introduction of oxygen or oxygen-containing species induced high activity. Although this statement could be challenged, especially in systems operated under maximum purity conditions in high vacuum, it is however important since it pointed out the importance of oxygen in the reactions under study. Tungsten carbonyl derivatives, $W(CO_5)L$ or $W(CO)_4L_2$, in the presence of $AlCl_3$ or $EtAlCl_2$ promote the metathesis reaction, provided that trace quantities of oxygen are present(50).

The amount of oxygen added has been shown to be critical in determining the catalytic activity of a metathesis system. Uchida(26) showed that for an Re / Al catalyst the system was still active in the disproportionation of 1-pentene after 72 h when the O_2:Re ratio was 2.6 but at a large O_2:Re ratio, the disproportionation activity was decreased and the catalyst was deactivated by excess oxygen.

Haines(14) suggested that the increased metathesis activity of $W(PMePh)_4(NO)_2$ / $EtAlCl_2$ in the presence of oxygen was the result of the creation of a vacant or potentially vacant site through removal of the organic ligand of the tungsten as its oxide. Basset(51) suggested that it is the aluminium compound and not the tungsten compound which is activated by oxygen. An intermediate species produced during the oxidation of the aluminium compound would then react (or be complexed) with the tungsten complex. The following mechanism was proposed:



The species Al* would act as a Lewis acid, able to decrease the electron density on the tungsten atom by complexing the lone pair of the oxygen of the carbonyl group. This would induce mobility of the carbonyl ligands, favouring co-ordination of one, or more likely two, molecules of olefin. It has been reported(26) that the starting metal chlorides could be reduced to various oxidation states according to the amount of Et_3Al added at Al:W ratio of 0.6. WCl_6 could be reduced to an appropriate oxidation state and exhibit metathesis activity. Subsequently adding oxygen can reoxidise the low valent complex and realise a favourable oxidation state for disproportionation. If oxygen was present in excess, the active species would be further oxidised and destroyed.

The role of oxygen and oxygen-containing compounds has therefore been described to have four main effects:

(i) create or aid the creation of a vacant site for the complexing of an olefin

(ii) act as a ligand to the transition metal creating a more active catalyst centre,

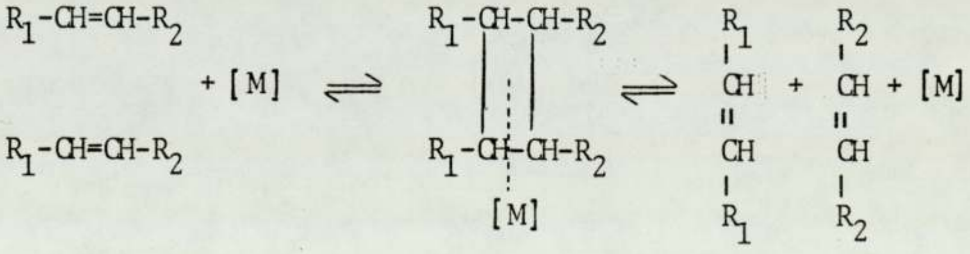
(iii) react with the organometallic compound, which itself would react with the transition metal to help the co-ordination of an olefin, and

(iv) probably the most important, help to reoxidise the active centre that has been previously reduced by the cocatalyst and / or the olefin.

(4) MECHANISTIC ASPECTS OF THE METATHESIS REACTION

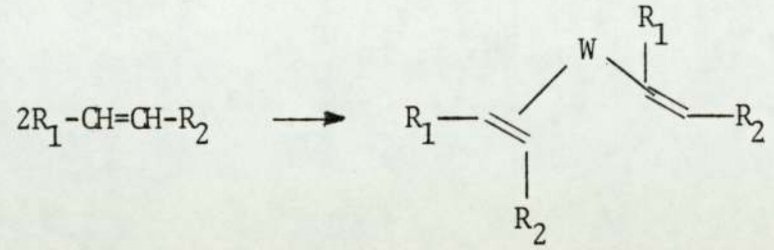
(a) PAIRWISE MECHANISM

Bradshaw and co-workers(2) proposed the first mechanism for olefin metathesis. It was suggested that the formation of an intermediate 'quasi cyclobutane metal complex' would account for the observed products.

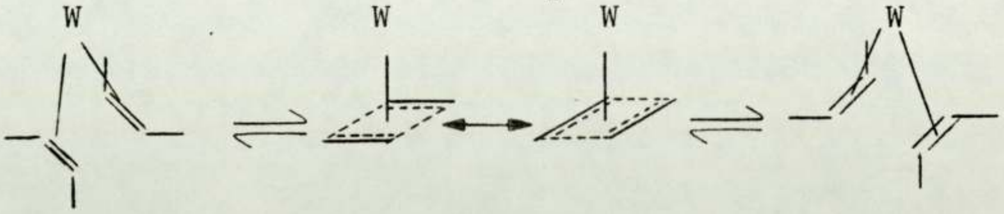


Calderon et al(11,34) contributed important experimental evidence to the metathesis mechanism and proposed a three-stage process namely: (a) bisolefin metal complex formation, (b) trans-alkylidenation and (c) olefin exchange.

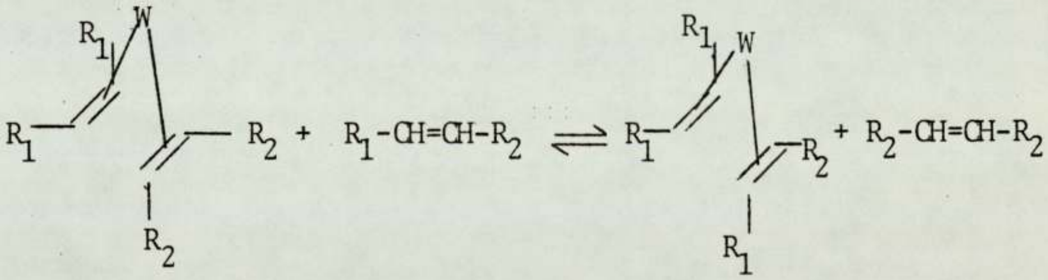
(a)



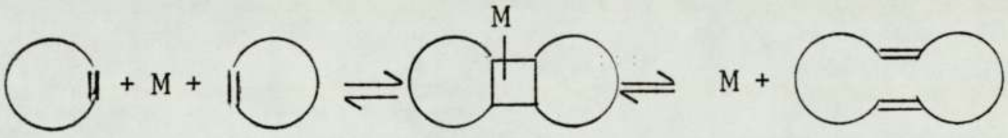
(b)



(c)



Consequently, an extension of the same mechanism was postulated for the ring-opening polymerisation of cyclic olefins:



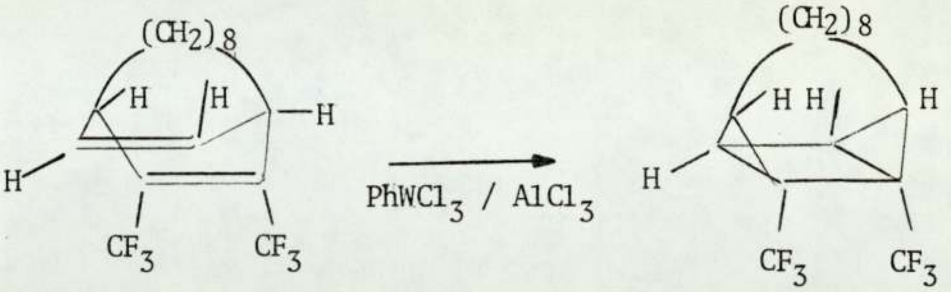
To account for the high catalytic activity of the system, it was proposed that the alternating trans-alkylidenation and olefin exchange steps must occur at very rapid rates.

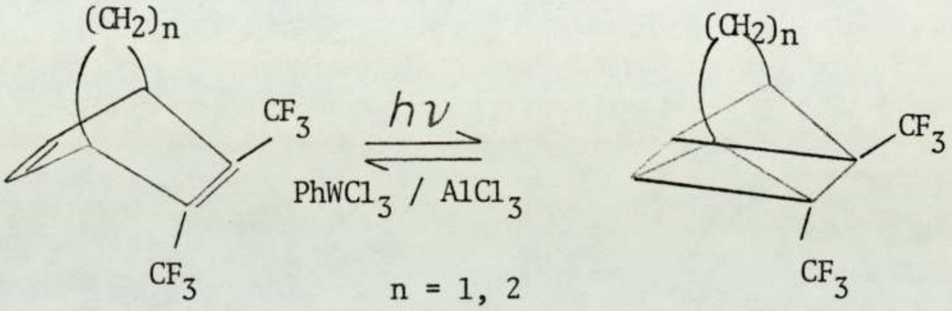
Several authors(52-54) obtained cyclic oligomers with up to

120C atoms when cyclooctene was polymerised in the presence of metathesis-type catalysts. The first studies made to determine whether polyalkenamers were linear or macrocyclic were reported by Scott(55,56), who found that the high molecular weight polyoctenamers were linear. This fact was explained by the reaction of macrocycles with linear olefins produced by reactions involving the metal alkyls, or the presence of very small amounts of olefinic impurities.

Theoretical support for this pairwise mechanism was provided by Mango et al(57). Calculations and orbital symmetry considerations predicted that the reaction could proceed by this mechanism in a concerted fashion with a low activation energy. According to the Woodward-Hoffmann theory, the synchronous making and breaking of double bonds in the manner suggested is thermally forbidden. Mango suggested, however, that the metal d orbitals removed the symmetry restriction to allow for such a reaction to occur in the co-ordination sphere of the metal.

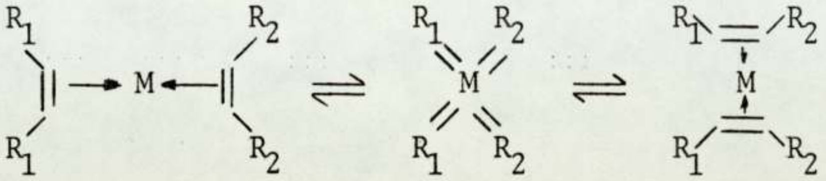
Several authors(44,58,34,59,60,61) have criticised this mechanism on the grounds that cyclobutanes have not been isolated from the reaction and that cyclobutanes do not interconvert with olefins in the presence of metathesis catalysts. However, Gassman and Johnson reported the conversion of cyclobutanes into olefins, previously observed by other workers(62,63), and that two non-conjugated olefinic groups can be converted into a cyclobutane in close to quantitative yield by a commonly accepted metathesis catalyst$^{(64)}$.





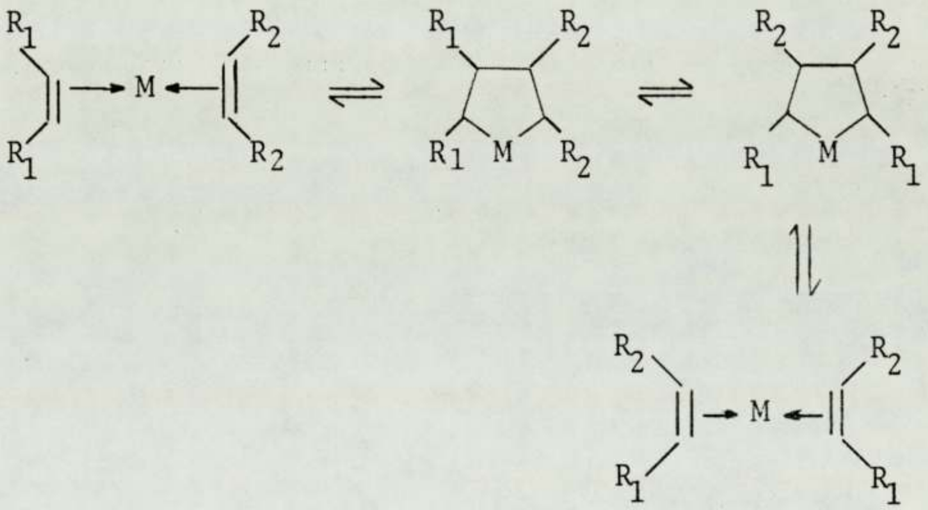
The occurrence of these reactions was suggested by Gassman as evidence for the existence in certain cases of a quasicyclobutane intermediate. This was challenged by Feast and Wilson$^{(65)}$, who reported that the bicyclic dienes (n=1 and 2) polymerised quite readily by a ring-opening mechanism in the presence of a catalyst derived from WCl_6 / $SnPh_4$ and that the substituted norbornadiene could polymerise in the presence of WCl_6 alone. Feast concluded that the cyclobutane-diene interconversions have little relevance to the mechanism of the general metathesis reactions.

Lewandos and Pettit$^{(66,67)}$ based on the fact that cyclobutanes were unreactive under usual metathesis conditions, suggested another scheme involving an intermediate that possessed little cyclobutane character and was represented as a tetracarbene metal complex with each carbon atom bound by three centre bonds.



This mechanism was shown to be symmetry allowed by molecular orbital considerations.

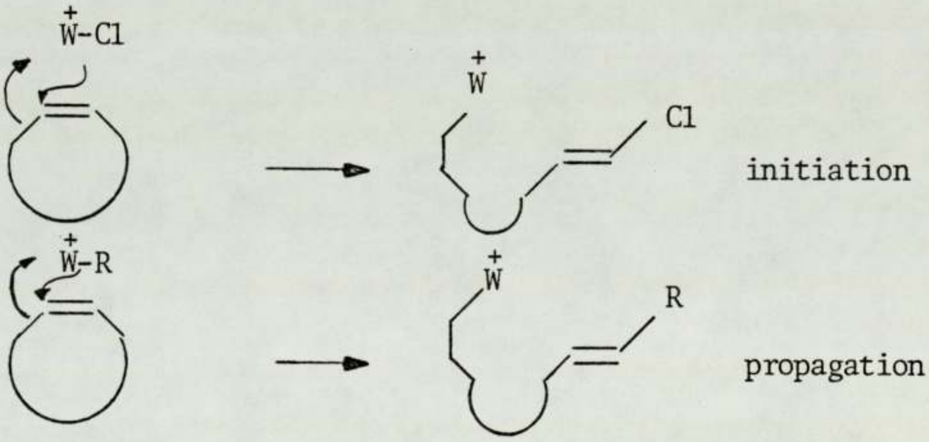
Another pairwise mechanism concerted in this case,was proposed as :



A number of examples of the interconversion of metallocyclopentanes and olefin complexes provided models for the first step of the reaction$^{(38,60,68)}$. The mechanism initially proposed by Grubbs et al$^{(69,70)}$, was largely based on the investigation of the reactions between 1,4-dilithiobutanes with WCl_6. The intermediate produced in the reaction should be similar in structure to the proposed intermediate in metathesis. When the reaction was carried out with 1,4-dilithiobutane in benzene, a quantitative yield of ethylene was obtained. When experiments were carried out with 1,4-dilithio-1,3-dideuterobutanes a mixture that contained 6% D_2, 6% D_o and 88% D_1 ethylene was obtained. This result demonstrated that 12% of the ethylene was arising from a rearranged intermediate.

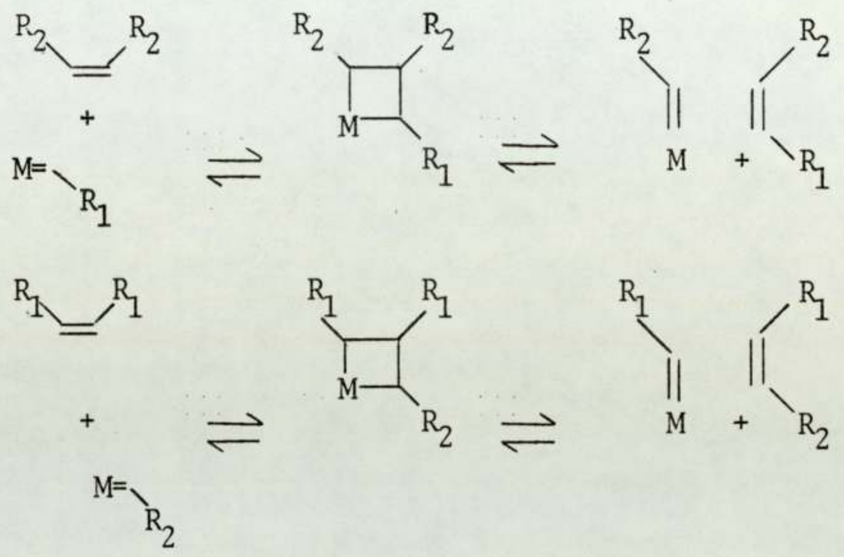
(b) NON-PAIRWISE, CHAIN MECHANISM

The first attempt to explain the polymerisation of cyclic olefins by a chain mechanism was proposed by Marshall and Ridgewell(36) who used WCl_6 / $AlBr_3$ as a catalyst. The mechanism fits closely to that accepted for Ziegler-Natta(71) polymerisations.

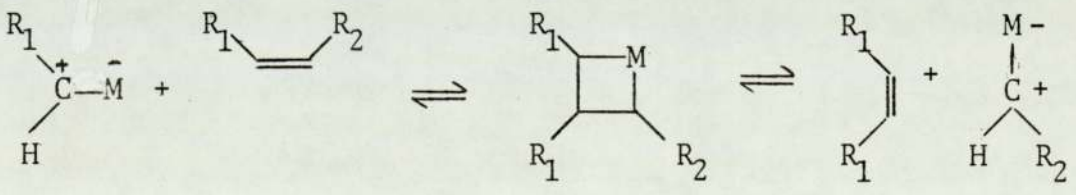


This mechanism explained the absence of vinyl groups and part of the stereochemistry of the reaction. Immediately after this suggestion, Calderon et al(11) proved that the metathesis reaction followed an alkylidene group exchange in which case the mechanism lacks any significance.

In 1970 Chauvin(44) proposed a mechanism involving, for the first time, a metal carbene:



Authors have explained the production of the intermediate metallocycle in two ways. The most commonly accepted is that the olefin first co-ordinates with the metal and in a subsequent step forms the metallocycle(49,72,73). For this explanation, then a vacant co-ordination site is required in a position adjacent to that of the carbene. The other way for metallocycle to be formed is essentially a dipolar attack of a polarised metal-carbene on the olefin as proposed by Katz et al(60).



This scheme does not specify a need for π-complexation of the olefin as a precondition to metathesis, hence it does not need a vacant site.

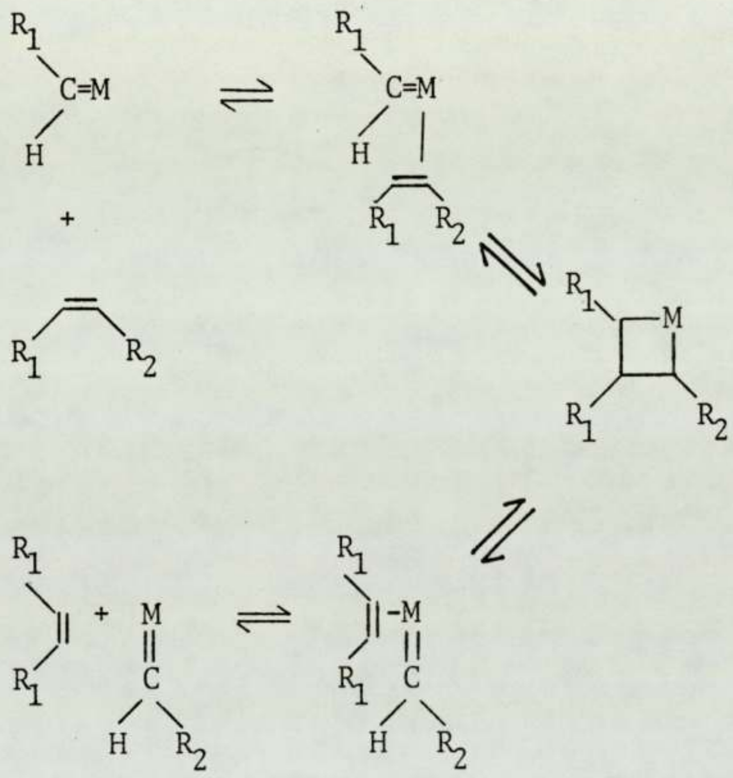
Gassman(74) advocated a nucleophilic character for the active carbon centre attached to the metal, this conclusion was based on 'trapping' the carbenes formed during the metathesis reaction with a Michael acceptor. Although these results do not correspond with the electrophilic carbon atom suggested by Katz, they support the idea of a polarised bond.

The need for a vacant site was concluded from studies with carbonyl complexes of tungsten. Lewandos(67) reported that no metathesis occurred when using toluene-$W(CO)_3$ as a catalyst for the metathesis of 4-nonene in a closed system in which the escape of CO was prevented. Casey(75) demonstrated that carbonyls of $(CO)_5W=CPh_2$ are vulnerable to exchange processes under relatively mild reaction conditions.

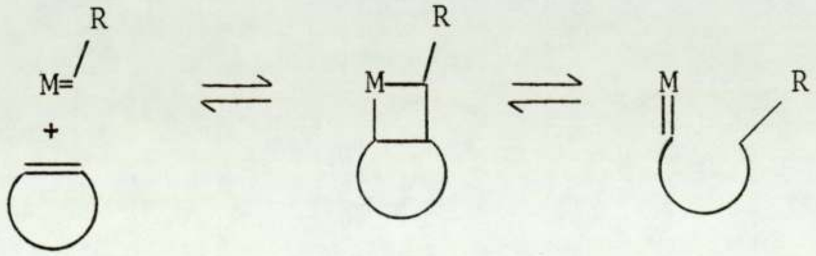
$$(CO)_5W{=}CPH_2 \xrightarrow[33^oC]{^{13}CO} (^{13}CO)(CO)_4W{=}CPh_2$$

At low temperatures, under conditions where carbonyl exchange is suppressed, the highly reactive $(CO)_5W=CHPh$ did not exhibit any carbene exchange with olefins. The necessity for the presence of a vacant co-ordination site was taken to the limit by Calderon(76) when he explained the cis stereospecificity of a WF_6 / $EtAlCl_2$ catalyst. He suggested that not only the incoming olefin complexed with the metal but also the nearest double bond of the polymer chain.

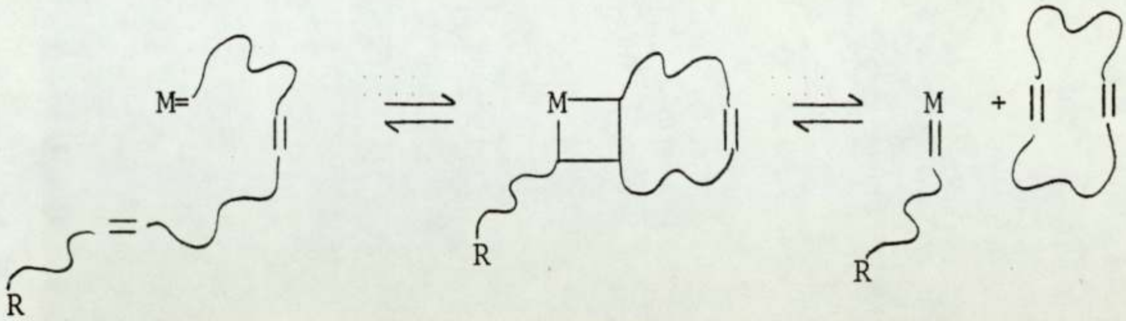
These results render support to the assumption that the metallocyclobutane transition state which provides for metathesis is produced by an internal rearrangement of the complexed carbene and olefin substrates.



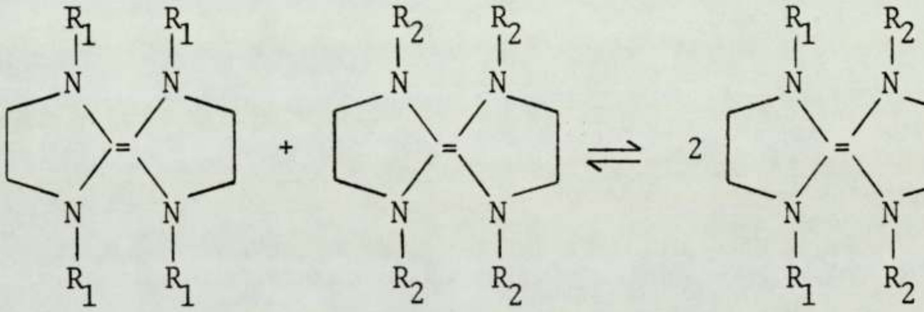
The mechanism could be extended to the polymerisation of a cyclic alkene:



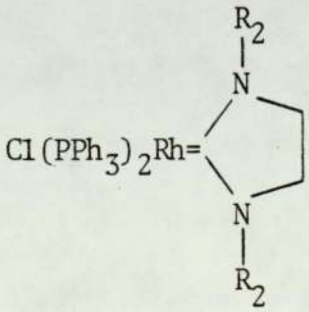
as well as to the formation of cyclic oligomers:



Cardin and co-workers (58) reported results that supported the carbene mechanism. They demonstrated that tetrakisaminoethylenes underwent metathesis with a Rhodium catalyst at high temperature.



They were also able to isolate an intermediate metal carbene complex which would serve as the catalyst for the reaction:



Other evidence for the metal carbene mechanism is found in the oligomer composition in the polymerisation of 1,5-cyclooctadiene(77) in which the ratio of C_{12} : C_{16}, C_{20} : C_{16}, C_{24} : C_{16}, C_{26} : C_{16} and C_{32} : C_{16} are essentially constant throughout the course of the reaction. The fact that the formation of the C_{12} compound would need the cross-metathesis of cyclobutane with 1,5-cyclooctadiene according to the pairwise quasicyclobutane intermediate would indicate the presence of a carbene as the chain carrier for the reaction and the formation of macrocycles as an intramolecular reaction with the double bonds already attached to the metal centre.

O'Neill and Rooney(78) observed that a CoO / MoO_3 supported catalyst which is active in propylene metathesis, readily decomposed diazomethane into ethylene and N_2. Ethylene was also converted directly to propene at higher temperatures on a $Mo(CO)_6$ / Al_2O_3 catalyst(79). The suggested mechanism involved a splitting of one ethylene into methylenes and addition of each of this to another ethylene, followed by rearrangement of the resulting trimethylene into propylene.

Dolgoplosk et al(72) demonstrated that the reactions between WCl_6 and WCl_4 with methyl diazomethane, in the presence of cycloolefins initiates the chain process of ring-opening polymerisation. In the absence of the olefin, the decomposition of the diazomethane resulted in the formation of stilbene. The following reaction was proposed:

$$\text{Ph-CH=WX}_n + \text{PhCHN}_2 \longrightarrow \text{N}_2 + \text{Ph-CH=CH-Ph} + \text{WX}_n$$

Dolgoplosk reported those results as direct proof of the chain initiation in cycloolefins ring-opening polymerisation by metal carbene complexes.

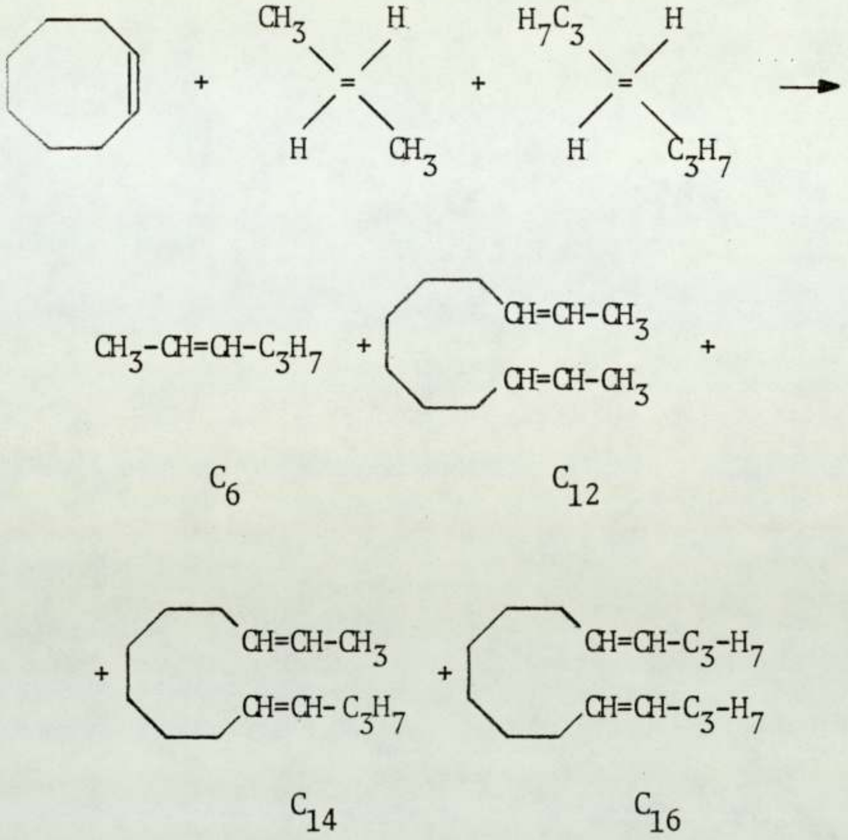
However, the major support for this mechanism comes from kinetic studies and from the reactions of isolable carbenes with cyclic and linear olefins.

(i) Kinetic Studies

The kinetic studies carried out on the metathesis reaction can be divided in two main groups, firstly cross-metathesis of cyclic and acyclic olefins and secondly metatheis of α-ω dienes.

(a) Cross metathesis of cyclic with acyclic olefins

Telomer compositions during the early stages of the reaction between trans-2-butene and trans-4-octene with cyclooctene using $Mo(Ph_3P)_2Cl_2(NO)_2$ as catalyst were reported by Katz(60,80). The work tried to differentiate between the pairwise and the non-pairwise mechanisms. The reaction is summarised as follows:



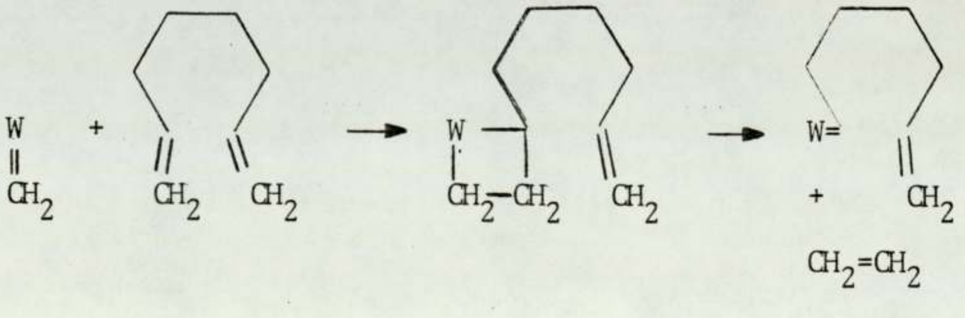
Katz found that in addition to C_6, product from the cross metathesis of the linear olefins, two symmetrical compounds C_{12} and C_{16} and one unsymmetrical C_{14} were formed. If the pairwise scheme were to prevail, the ratios of the unsymmetric to symmetric dienes C_{14}/C_{12} and C_{14}/C_{16} would be initially zero. In fact, the extrapolated values to zero conversion showed that the formation of the unsymmetrical diene was favoured initially. This kinetic study strongly supported a non-pairwise reaction scheme but did not entirely exclude the pairwise scheme. This would only be so if it is assumed that the trans-alkylidenation step in the pairwise mechanism is the rate determining. However if the exchange step is rate determining the data could account for either scheme.

(b) Metathesis of α-ω-dienes

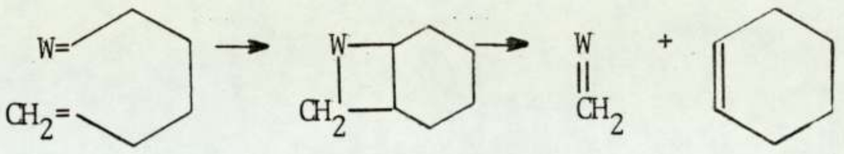
Non-conjugated α-ω dienes can undergo, when treated with a metathesis catalyst, either metathetical polycondensation to form open chain oligomers with terminal double bonds or intramolecular metathesis to form a cycloolefin, both processes yield ethylene as a product.

Kroll and Doyle(81) converted 1,7-octadiene to the stable product cyclohexene with a 99% selectivity. Because cyclohexene cannot undergo any further metathesis, 1,7-octadiene is a very good substrate for the mechanistic studies on metathesis. Based on these facts, Grubbs(61,82) studied the metathesis of a mixture of 1,7-octadiene with (1,1,8,8-D_4)-1,7-octadiene. From a consideration of the two different mechanisms, the expected ratios of ethylene D_4 D_2 and D_0 were predicted and compared with experimental values.

According to the carbene mechanism, the reaction could be summarised as follows:



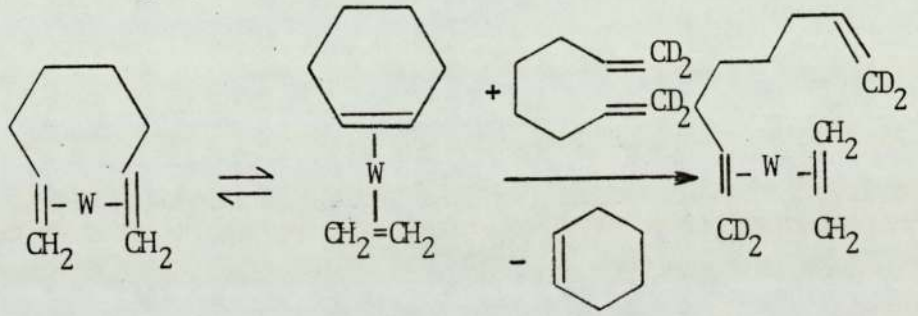
(A)



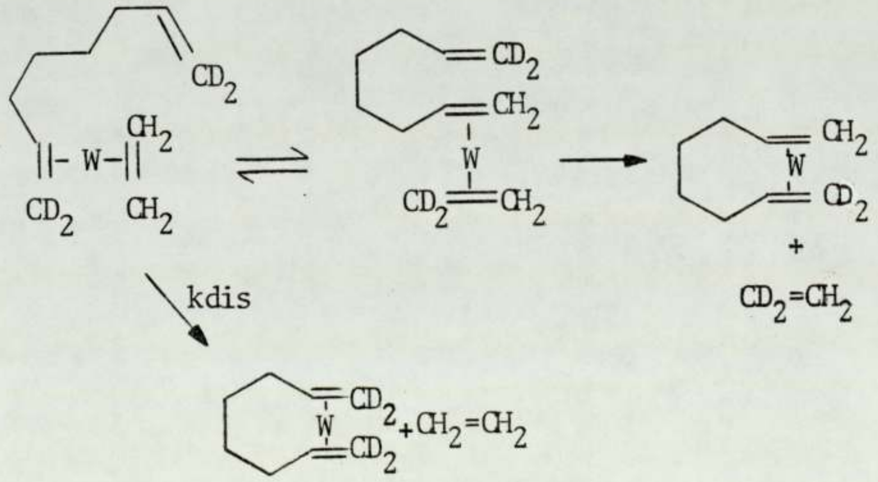
(B)

For an equimolar mixture of 1,7-octadiene and (1,1,8,8-D_4)-1,7-octadiene a statistical distribution of 1:2:1 for $D_4 : D_2 : D_0$ is expected at low conversions even without taking into account any ethylene redistribution reactions.

For the pairwise mechanism, different distributions of ethylene are predicted, depending on the relative rates of metathesis (km) to exchange (kdis). The mechanism is described as:



(C)



(D)

The di-deuterated and tetra-deuterated bidentate bisolefin complexes produced according to equation (D), will then metathesise yielding cyclohexene and the respective ethylenes in accordance with equation (C).

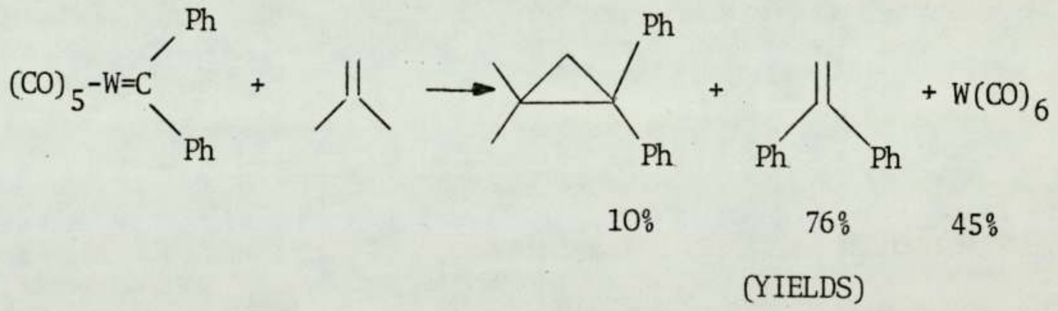
If the intramolecular exchange were rapid and the trans-alkylidenation step were rate determining ($k_{dis} >> k_m$), then a distribution of 1:0:1 for the $(-D_4):(-D_2):(-D_0)$ ratio would be expected for the ethylenes in the initial stages of the reaction. Thus as cyclohexene is displaced by 1,7-octadiene (eq (C)), the new complex rapidly eliminates ethylene and forms a bidentate species. In the case that $k_m >> k_{dis}$ the bisolefin complex would undergo trans-alkylidenation forming some $CH_2=CD_2$. Grubbs calculated for this case a limiting value for the $(-D_4):(-D_2):(-D_0)$ ratios of 1:1.6:1.

The experimental results showed on ethylenes distribution, close to the statistical value (1:2:1), these results being consistent with a non-pairwise mechanism. He also found that the $(-D_4):(-D_2):(-D_0)$ distribution of the residual 1,7-octadiene did not vary from start to finish in this particular metathesis experiment. This series of experiments carried out by Grubbs is probably the best evidence to support the non-pairwise mechanism because the results cannot be accounted for by any pairwise scheme.

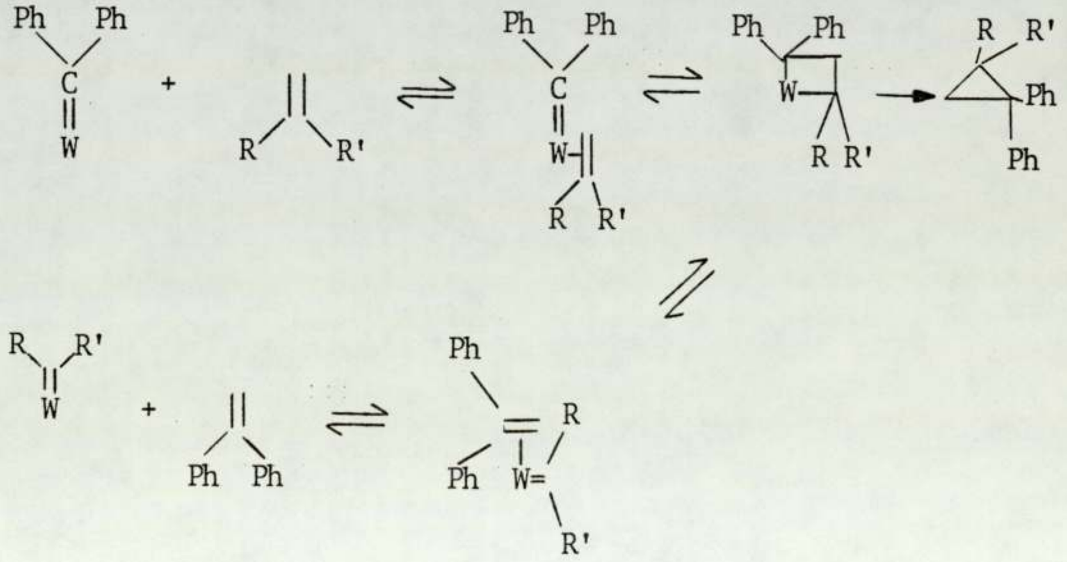
(ii) Metathesis Induced by Metal Carbenes

One of the major breakthroughs in support of the carbene and the metallocyclobutane theory was made by Casey who synthesised diphenylcarbenepentacarbonyltungsten (0) and assessed its reactivity towards alkenes$^{(73)}$.

Upon heating $(Ph)_2C{=}W(CO)_5$ with isobutene, a mixture of products was obtained, indicating a net transfer of (CH_2) group.



Casey explained these results according to the following scheme:



After Casey's experiments, Katz(83) used the same catalysts, not stoichiometrically but catalytically for the metathesis of linear olefins. He also used this catalyst to polymerise 1-methylcyclobutene and 1-methyl-trans-cyclooctene(84) as well as cyclobutene, cyclopentene, cycloheptene, cyclooctene and norbornene(85), that were converted to linear high molecular weight polymers which stereochemistries are largely cis. In some cases (cyclooctene) a polymer containing more than 97% cis double bond was obtained.

Katz also used (phenylmethoxycarbene)pentacarbonyltungsten(86) for the polymerisation of cyclobutene and norbornene. He found that while the stereochemistry of the polybutenamers obtained by both catalysts were about the same for the norbornene were different. The polynorbornenamer formed by the diphenylcarbene had 95% of its double bonds cis but the polymer formed when the phenylmetoxycarbene was used had only 75% of its double bonds cis. According with the metal carbene chain reaction, the only difference between these polymers should have been the initiating end, because the chain carrying carbene had to be identical. The reasons for this difference have yet to be determined.

More recently(87) it has been reported that a titanacene methylene complex can catalyse terminal group exchange in α-olefins and that nickel carbenes prepared from nickelacyclohexane(88) will catalyse the metathesis of 1,7-octadienes.

(c) SELECTIVITY AND STEREOCHEMISTRY

(i) Competition Between Terminal and Internal Olefins

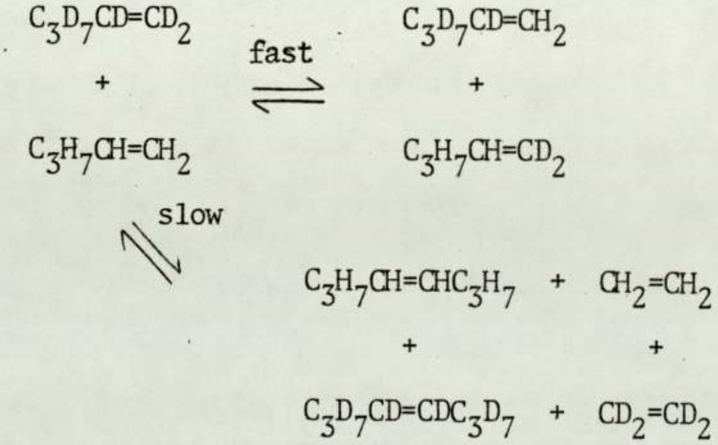
It has been observed that internal olefins produce their corresponding metathesis products faster than terminal olefins(49,83,89,90). This finding contrasts with most metal catalysed reactions, which show higher rates for terminal olefins than for more highly substituted olefins.

Calderon(89) observed that when a mixture of 1-pentene and 2-pentene was subjected to metathesis conditions, the major products were the cross products:

$$CH_3\text{-}CH{=}CH\text{-}C_2H_5 \;+\; C_3H_7\text{-}CH{=}CH_2 \;\rightleftharpoons$$

$$\underset{\text{HOMO PRODUCTS}}{\left[\begin{array}{l} CH_3\text{-}CH{=}CH\text{-}CH_3 + C_2H_5\text{-}CH{=}CH\text{-}C_2H_5 \\ C_3H_7\text{-}CH{=}CH\text{-}C_3H_7 + CH_2{=}CH_2 \end{array}\right]} \quad \underset{\text{CROSS PRODUCTS}}{\left[\begin{array}{l} C_2H_5CH{=}CH_2 + CH_3CH{=}CH_2 \\ C_2H_5CH{=}CHC_3H_7 + CH_3CH{=}CHC_3H_7 \end{array}\right]}$$

The results indicated that a terminal olefin competes with the internal olefins in the cross reaction but does not undergo observable metathesis with itself. The results could be explained by the so-called 'non productive metathesis' for the terminal olefin in which $=CH_2$ groups could be exchanged without affecting the composition of the original mixture. Calderon(89) demonstrated that this terminal exchange takes place in the examination of the cross metathesis between 1-pentene and 1-pentene-D_{10}. A random mixture of 1-pentene-D_0, D_2, D_8 and D_{10} was produced before any significant amount of C_8 olefins were formed. The results can be represented in the following scheme:

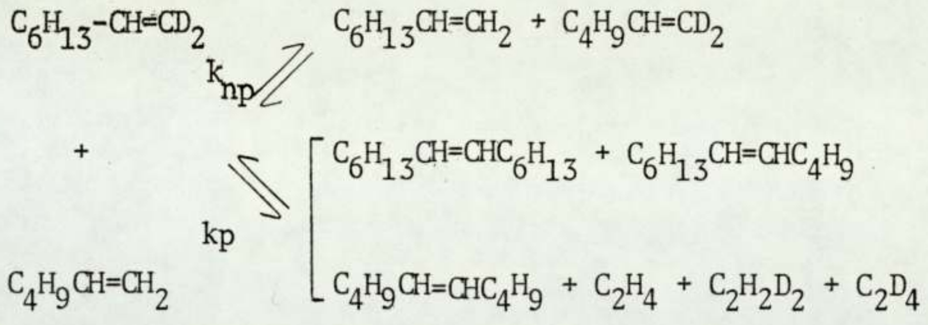


$$C_3D_7CD{=}CD_2 + C_3H_7CH{=}CH_2 \overset{\text{fast}}{\rightleftharpoons} C_3D_7CD{=}CH_2 + C_3H_7CH{=}CD_2$$

$$C_3D_7CD{=}CD_2 + C_3H_7CH{=}CH_2 \overset{\text{slow}}{\rightleftharpoons} C_3H_7CH{=}CHC_3H_7 + CH_2{=}CH_2 + C_3D_7CD{=}CDC_3D_7 + CD_2{=}CD_2$$

Consequently, during the reaction between a terminal and internal olefin, although the primary olefin may react more rapidly than the internal olefin, the apparent rate of such metathesis is zero. The internal olefin will however compete with the terminal olefin and trap the intermediate as observable cross products. The rate of such a reaction is measurable and apparently greater than the rate of non productive metathesis, as observed experimentally.

Katz$^{(83)}$ determined the relative rates of productive (kp) and non productive (knp) metathesis for five catalyst preparations.



$$\begin{tikzcd} C_6H_{13}\text{-}CH{=}CD_2 + C_4H_9CH{=}CH_2 \arrow[r, shift left, "k_{np}"] \arrow[r, shift right, "k_p"'] & {\begin{array}{l} C_6H_{13}CH{=}CH_2 + C_4H_9CH{=}CD_2 \\ \left[\begin{array}{l} C_6H_{13}CH{=}CHC_6H_{13} + C_6H_{13}CH{=}CHC_4H_9 \\ C_4H_9CH{=}CHC_4H_9 + C_2H_4 + C_2H_2D_2 + C_2D_4 \end{array}\right. \end{array}} \end{tikzcd}$$

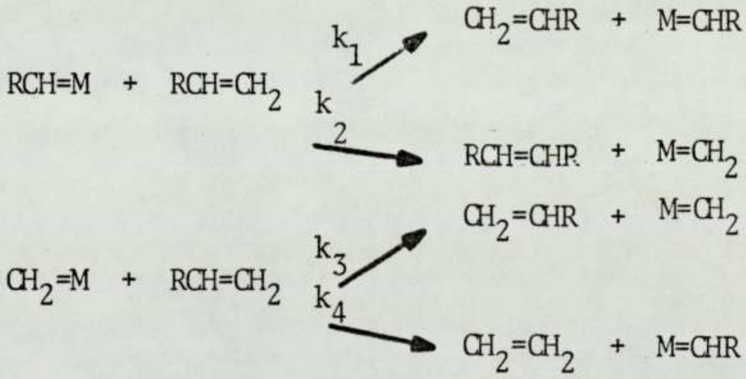
The rate at which a concentration of 1-hexene and (1,1-D_2),1-octene formed products when treated with different metathesis catalysts was measured and the ratio of the rate constants calculated. The results are shown in Table I.2.

Table I.2 RATIOS OF RATE CONSTANTS k_{np}/k_p (83)

Catalyst (Temperature)	knp/kp
$Mo(Ph_3P)_2Cl_2(NO)_2 + Me_3Al_2Cl_3(0^oC)$	26.5 ± 6
$Ph_2C{=}W(CO)_5(50^oC)$	75.2 ± 4
WCl_6 + nBuLi(RT)	80.0 ± 8
$WCl_6 + Ph_3SnEt$(RT)	103 ± 20
WCl_6 + EtOH + $EtAlCl_2$(RT)	155 ± 33

The Table shows that for all catalysts, the degenerate metathesis is faster than the productive metathesis. The molybdenum catalyst that is known to be the most effective for the metathesis of terminal olefins is the least selective. The Calderon catalyst WCl_6 / EtOH / $EtAlCl_2$ which is very effective in bringing about the metathesis of primary olefins, is the most selective of the catalysts studied.

The results can be interpreted in two ways, considering a metal carbene as the chain carrier. Either the main carrier is a methylene complex, CH_2=M, and the reaction to form another methylene complex is preferred or that the main carrier is an alkylidene complex, RCH=M, and the reaction to form the alkylidene complex is preferred.



In order to explain the results obtained, k_1 must be much bigger than k_2 or k_3 much bigger than k_4 or both.

Bencze et al$^{(91)}$ based on studies of the minor products from cross metathesis of norbornadiene with 1-hexene and cyclopentene with 1,7-octadiene respectively, showed that complexed alkylidenes RCH=M, are much preferred to complexed methylene, CH_2=M, as chain carriers formed by the reaction of the terminal olefins. The methylene complex, when formed, is highly reactive towards primary alkenes with the strongly electrophilic methylene ligand selectively adding to the terminal olefins at the C-1 position in a non productive fashion.

Casey et al$^{(92)}$ provided a model to show the relative rates of reactions of carbenoid complexes. They discovered that (diphenylcarbene)pentacarbonyltungsten, reacted with olefins forming 1,1-diphenylethylenes$^{(73)}$, they measured the ratio of the olefin products, $CH_2{=}C(Tol)_2$ and $CH_3(CH_2)_2CH{=}C(Tol)_2$, to determine the rate constant ratios between non productive and productive metathesis. The ratio found for this experiment was of the order of 600. When compared with the Katz's results, this indicates that the more highly substituted carbene is in fact the more selective as could be predicted.

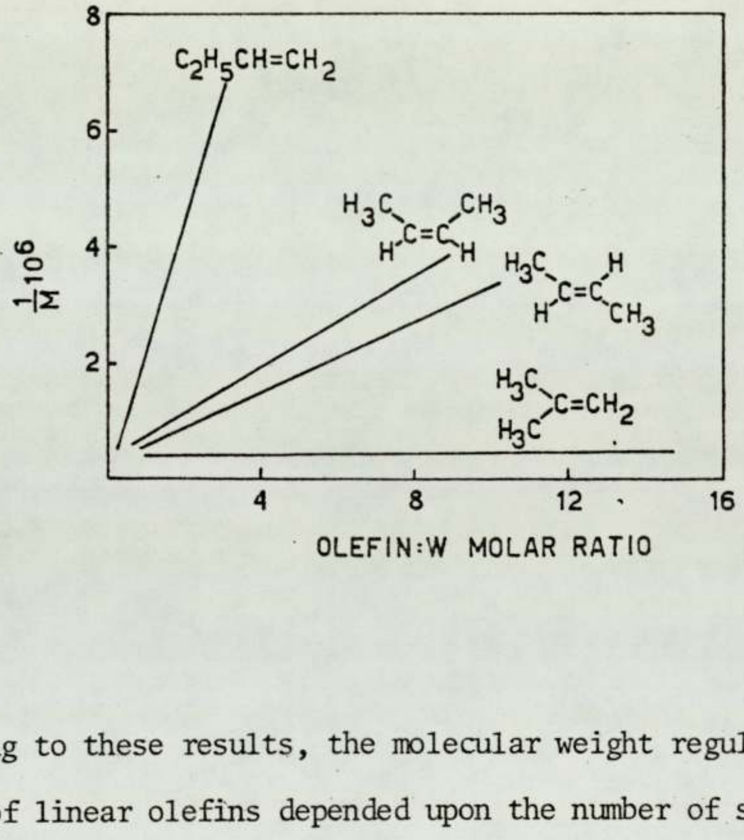
Casey et al$^{(92)}$ also measured the reactivities of different olefins by combining their mixtures with $(Tol)_2C{=}W(CO)_5$ and measuring the ratios of the olefin products. The following results were obtained:

$$\underset{49 \pm 5}{CH_2{=}CH{-}C_3H_7} \;>\; \underset{10.4 \pm 5}{CH_2{=}C(CH_3)_2} \;>\; \underset{1}{\text{cis-}CH_3CH{=}CHCH_3} \;\gg\; \underset{\sim 0}{(CH_3)_2C{=}CHC_5H_7}$$

These results demonstrate the faster reaction of primary olefins with metal carbon double bonds as required for the selectivity observed in metathesis.

Similar results were obtained by Pampus and co-workers$^{(93)}$ for the studies on the molecular weight regulating action of different substituted olefins in the ring-opening polymerisation of cyclopentene induced by $WCl_5(OCH_2CH_2Cl)$ / $AliBu_3$. The results are shown in Fig I.5.

Fig I.5 MOLECULAR WEIGHT REGULATING ACTION OF DIFFERENT OLEFINS ON THE POLYMERISATION OF CYCLOPENTENE(93)



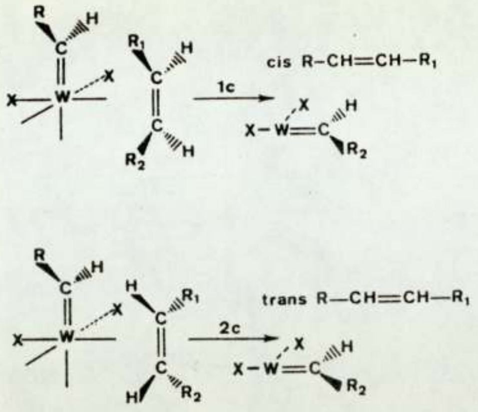
According to these results, the molecular weight regulating action of linear olefins depended upon the number of substituents on the double bond. The difference with Casey's results was the inversion in the order of isobutene and cis-2-butene in the given orders.

(ii) Stereoselectivity

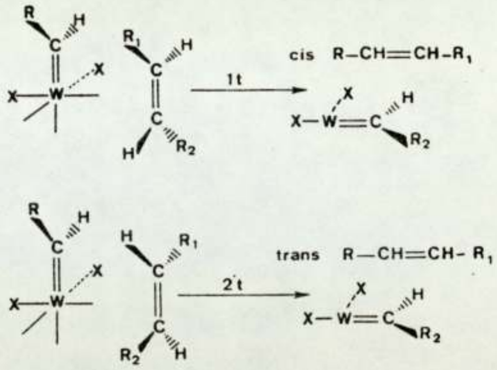
Several studies have been carried out on the stereoselectivity of linear olefins. In general, these observations have been based on the metathesis of 2-pentene and studies of the products obtained at low conversions and extrapolated to zero conversion.

Basset and co-workers(94,95) have formulated a reaction model for the stereoselectivity of trans- and cis-2-pentene. It was assumed that the carbon atom of the co-ordinated carbene had an sp^2 character, having therefore a rigid conformation with a high barrier to rotation.

Basset and co-workers found when starting from cis-2-pentene the production of cis-isomers is slightly favoured (trans : cis C_4 = 0.74, trans : cis C_6 = 0.88); starting from trans-2-pentene trans-isomer is favoured (trans : cis C_4 = 2.0). These facts could be interpreted in terms of the steric effect for the co-ordination of the olefin or in terms of the stability of the metallocyclobutane formed as intermediate in the reaction. For the first alternative, two possible approaches were suggested, for a cis or a trans olefin to the tungsten.



Approach of a cis-olefin

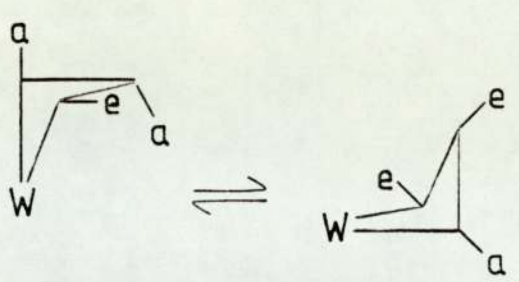


Approach of a trans-olefin

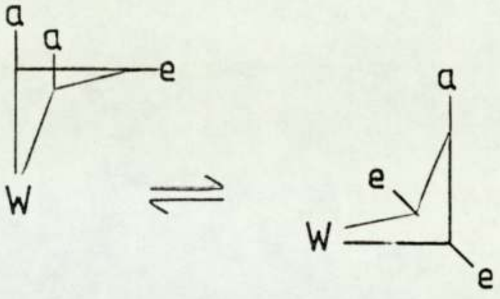
The model suggested two kinds of steric interaction: (a) between the alkyl group of the co-ordination carbene and that of the olefin or (b) between the metal and / or its ligands and the alkyl groups of the olefin.

Since reaction '1c' is slightly favoured, compared with reaction '2c', it was assumed that the major steric effects were due to the ligands co-ordinated to the metal (X) and not to the R group of the co-ordinated carbene. This conclusion was supported by the fact that cis-2-pentene showed higher stereoselectivity in favour of cis-isomers on supported complexes or when chloride ligands were substituted by bromide ligands for homogeneous tungsten catalysts.

The second alternative proposed was to consider the stability of a tungstacyclobutane intermediate. In this case, the cis or trans approach of a cis olefin will result in two different metallocyclobutanes:

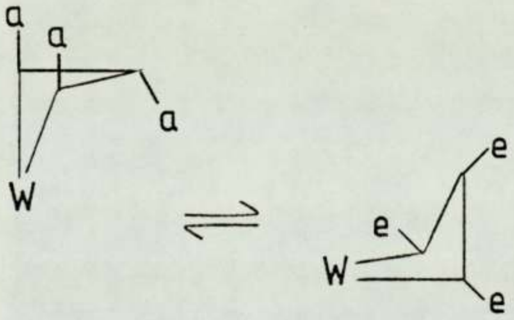


I, TRANS APPROACH

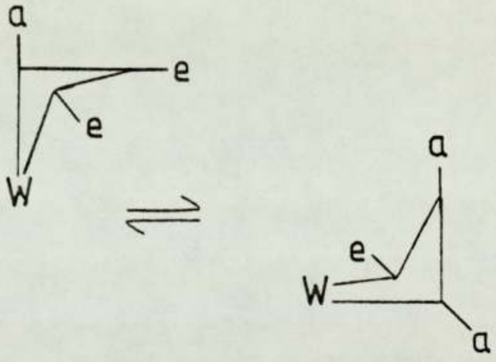


II, CIS APPROACH

In the same way the cis or trans approach of a trans-olefin will result in two different metallocycles:



IV, TRANS APPROACH

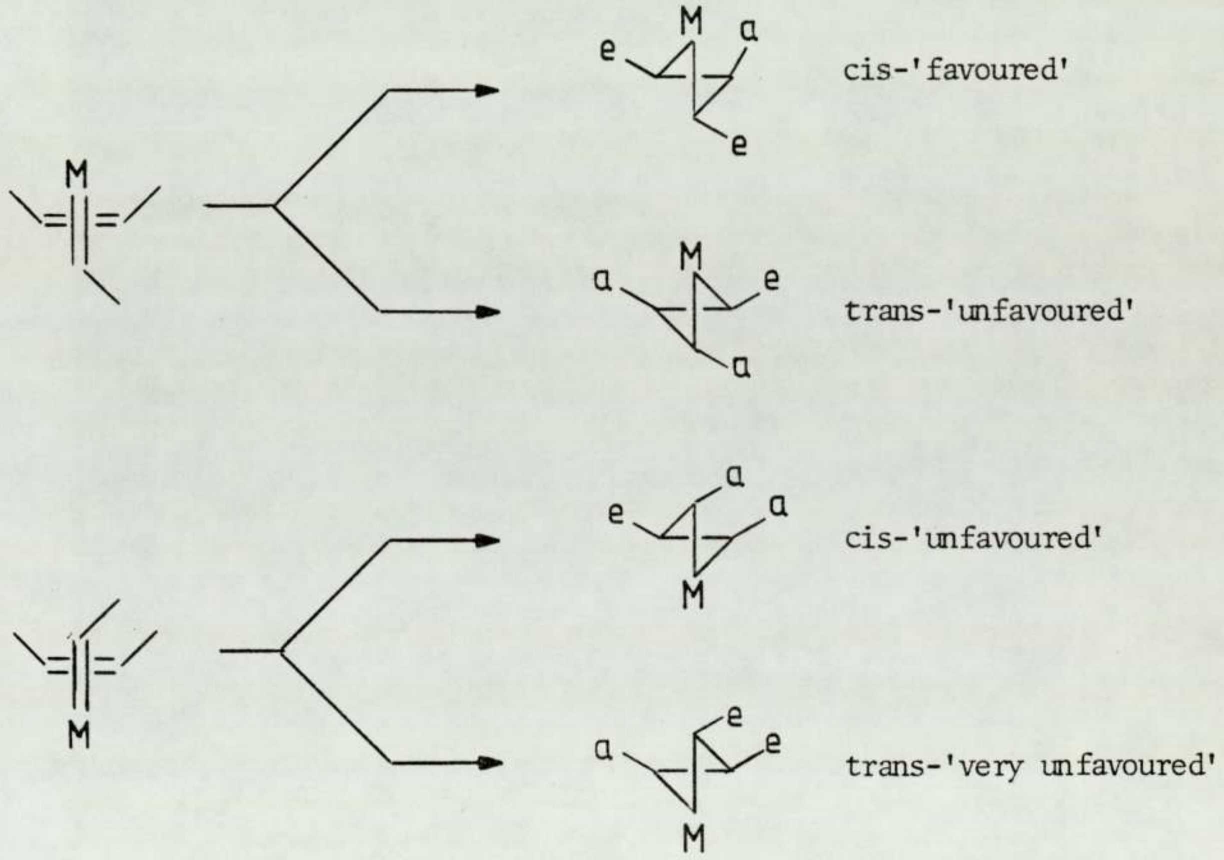


III, CIS APPROACH

Such considerations accounted for the trans stereoselectivity with trans-olefins since IV is more stable than III but no definitive conclusions were drawn for cis-olefins. The authors suggested that the analysis of the metallocyclobutanes could not explain the steric effect of a bulky ligand such as surface or a halogen and it could not either explain the respective rates of cis-trans-isomerisation and metathesis.

A very similar explanation for the stereoselectivity of cis-1,2-disubstituted ethylenes was proposed by Katz and co-workers (96).

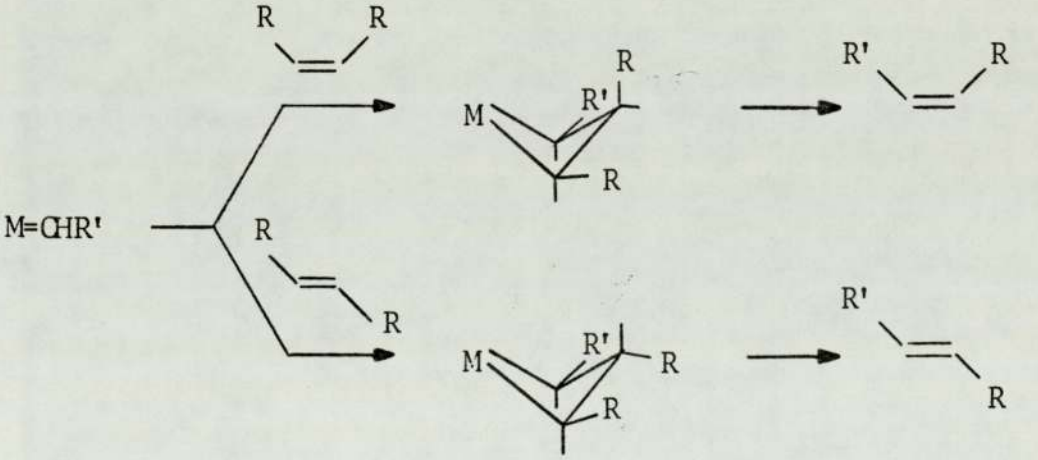
They considered the latent cis-specificity in reactions of cis-olefins with (diphenylcarbene)pentacarbonyltungsten to be very high (92%). They also proposed that the lack of stereospecificity normally observed was mainly a consequence of cationic processes inherent in the metathesis step, masking stereospecificity. The reaction was described as a rearrangement which is preceded by the approach of an olefin oriented perpendicular to the metal carbene. Previous formation of an olefinic complex with the incoming olefin prior to the formation of the metallocyclobutane was not considered necessary. The pathway for reaction of cis-olefins was proposed as follows:



In the scheme, a metallocycle possessing pseudoaxial and equatorial substituents was used and the reaction pathway was favoured which minimised the following effects: (a) 1,3-diaxial interactions of substituents on the two α-carbons; (b) axial substituent interactions with juxtaposed ring carbons and (c) 1,2-diequatorial interactions.

Casey et al^(97) explained the stereochemistry of 2-pentene in terms of the relative stabilities of the various substituted metallocycle derivatives. Only those reaction pathways which provided conformations possessing the fewest axial substituents on the α-carbons in the ring were considered.

Retention of configuration was provided by this scheme:



Calderon^(98) reported results obtained for the metathesis of 4-methyl-2-pentene that were not reconcilable with any of the steric model that predicted stereospecificity with retention of configuration.

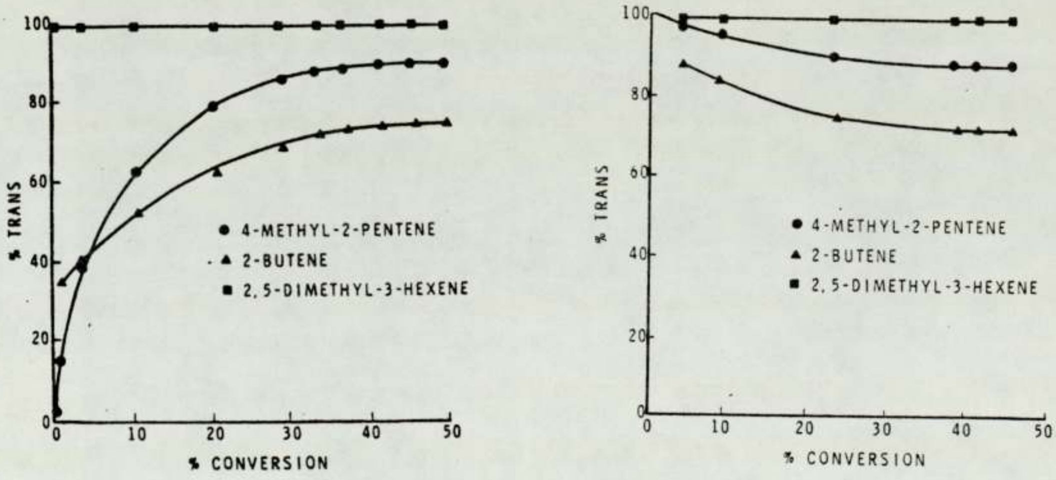
4-Methyl-2-pentene yielded the expected products, 2-butene and 2,5-dimethyl-3-hexene which is a highly hindered olefin (the equilibrium cis content of 4-methyl-2-pentene and 2,5-dimethyl-3-hexene are 11.8 and 6.3% respectively). The reaction can be underlined as follows:

$$(CH_3)_2CHCH{=}CHCH_3 \rightleftharpoons (CH_3)_2CHCH{=}CHCH(CH_3)_2 + CH_3CH{=}CHCH_3$$

The composition of metathesis reaction mixtures over a range of conversions starting with cis- and trans-4-methyl-2-pentene are shown in Fig I.6.

Fig I.6 (A) METATHESIS OF CIS-4-METHYL-2-PENTENE

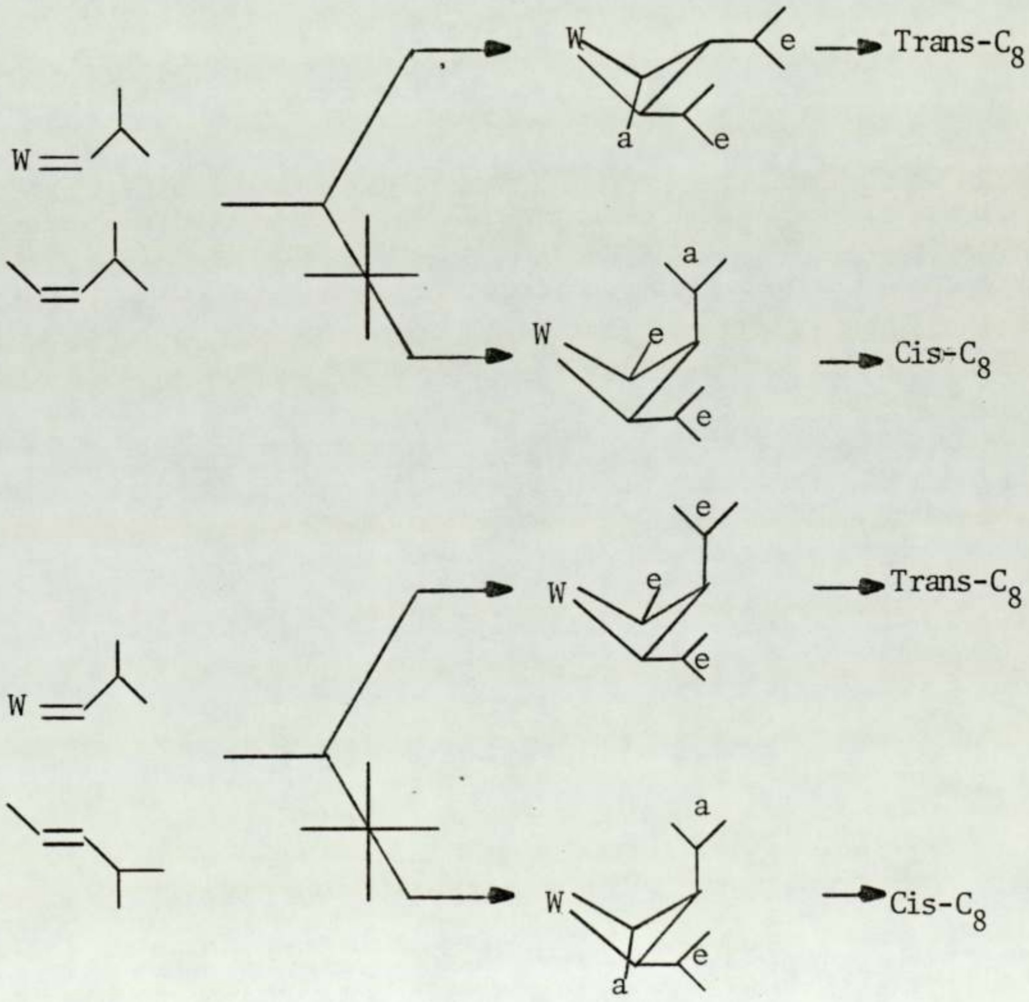
(B) METATHESIS OF TRANS-4-METHYL-2-PENTENE



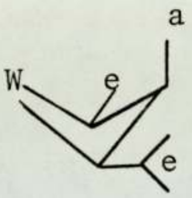
(A) (B)

Calderon(78) based on these results criticised the Katz proposal, mainly because the results previously described for the metathesis of cis-4-methyl-2-pentene, which selectively gave pure trans-C_8 as one of the products would be entirely unexpected. The Casey mechanism does not, either, anticipate the non specific formation of 50% trans-3-hexene from cis-2-pentene, nor the course of reaction for cis-4-methyl-2-pentene mentioned earlier.

Calderon(98) pointed out that the lack of formation of 2,5-dimethyl-cis-3-hexene indicated that cis-1,3-diisopropyl substitution on the metallocycle ring formed is highly unfavourable and trans-1,2-susbstitution leading to adjacent diequational substituents was permissible.

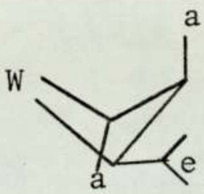


The moderate cis-specificity for cis-2-butene observed initially in the metathesis of 4-methyl-cis-2-pentene, in contrast with the high trans-specificity for trans-2-butene as observed with 4-methyl-trans-2-pentene metathesis (Fig I.6) was explained by Calderon by examining the respective transition states. For the cis case, the structure on the left appeared to be slightly preferred over the one on the right.



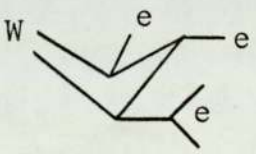
CIS

≃



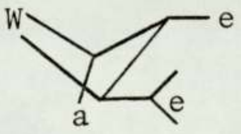
TRANS

The tendency to minimise eclipsing in the 1,3-positions, thus favouring equatorial methyl and isopropyl orientations, was offset by weak repulsions caused by cis-1,2-dimethyl substitution. For the trans case, the intermediate with all substituents on the equatorial position was preferable over the one containing one substituent in an axial position.



TRANS

$\gg$



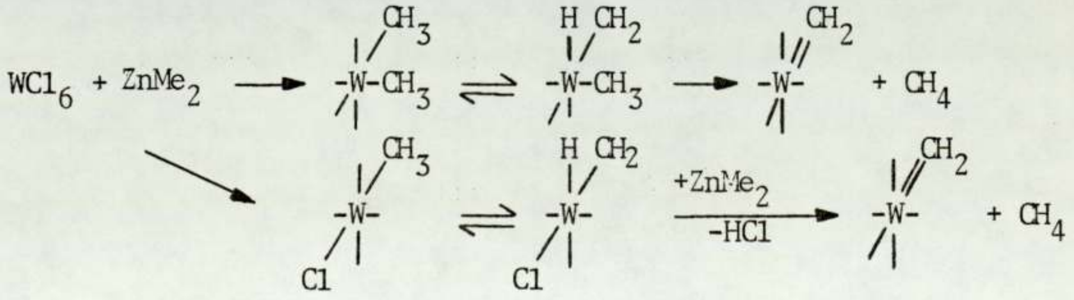
CIS

Leconte and Basset(99) studied the stereoselectivity of metathesis of cis and trans R-CH=$CHCH_3$ with the catalyst $M(NO)_2X_2(PPh_3)_2$/ $EtAlCl_2$ (M=Mo or W and X = Cl, Br or I) by determining cis : trans ratio of the 2-butenes (C_4) formed at 0% conversion. When R=H, the trans : cis ratio was equal to 1. For R=Et, trans : cis ratios of C_4 depended on the stereochemistry of the olefin and were 0.20 and 12.5 for the cis and trans-olefins respectively. Increasing the bulkiness of R resulted in a significant decrease in stereoselectivity and activity with a cis-olefin. The trans : cis ratio of C_4 increased with the bulkiness of R, with a trans-olefin but the trans : cis ratio of the other product olefin decreased when the size of R increased. Although with cis or trans-2-pentene, the trans : cis ratio of 3-hexene was always higher than the trans : cis ratio of 2-butene. This result was related to a 1-2 repulsive axial-equatorial, equatorial-axial interaction in the metallocyclobutane intermediate. The conclusion was corroborated by the stereoselectivities of the metathesis of the terminal olefins: propylene, 1-butene and 1-pentene. The trans : cis ratio of the products increased in the order: 2-butene (1.1) < 3-hexene (1.42) < 4-octene (2.0). The authors concluded that the stereoselectivity reflected steric interactions in the metallocyclobutane intermediate and that simultaneous steric repulsions between the 1-2 and 1-3 positions on the metallocycle and olefin-metal seemed to account for the observed selectivities.

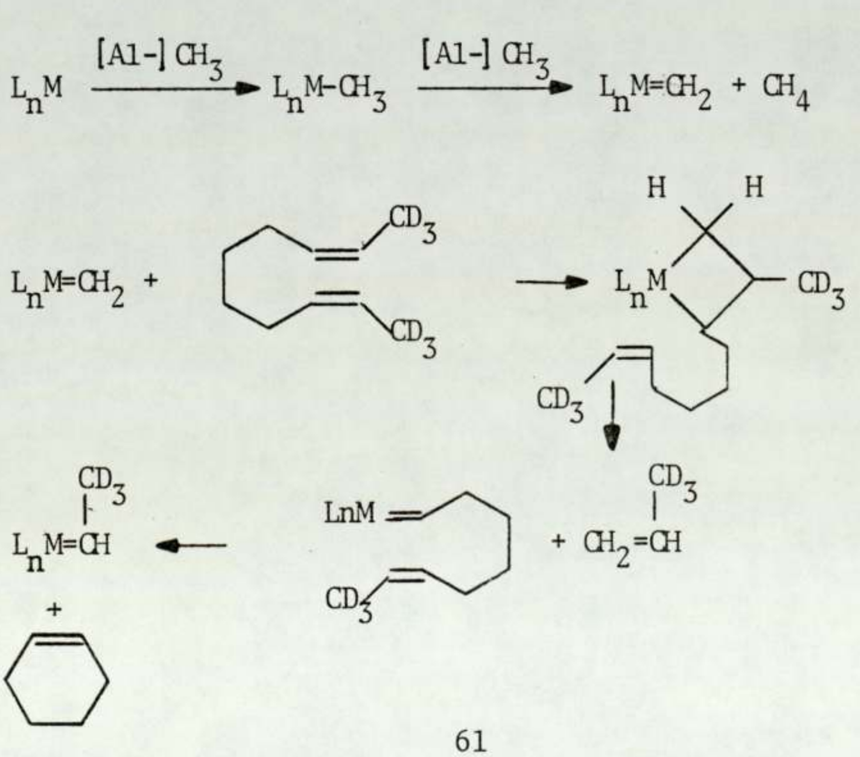
(5) CHAIN INITIATION

All the new mechanistic evidence tends to confirm the metathesis reaction of linear olefins and the polymerisation of cyclic olefins as chain processes. In any chain reaction, an initiation step is required for the formation of the chain carrying species. Whereas in some chain reactions, for example, the free radical cationic or anionic polymerisation of vinyl monomers, this initiation step can be considered to be well understood, this is not the case for the reaction under study. It is nowadays commonly accepted that a metallocarbene is involved in the propagation step of the metathesis reaction of olefins; the way in which this first metal carbene is formed is, however, the subject of a great deal of discussion.

Muetterties(100) found that when WCl_6 was allowed to react in benzene with $Zn(Me)_2$, in the presence or absence of an olefin methane was produced. When the reaction was allowed to proceed in deuterated benzene, the methane produced contained no deuterium. The author proposed that the hydrocarbon resulted from the formation of a carbene by one of the pathways given below:



This mechanism of initiation although feasible, proposes some intermediates and reactions that have not been characterised and are of somewhat dubious structure. Additional evidence for this kind of initiation was found in the metathesis of 2,8-decadienes when the catalyst was prepared by the reduction of $L_2(NO)_2Cl_2M$ (M=Mo or W and L = a neutral organic ligand) with $Me_3Al_2Cl_3$. The catalyst was prepared by allowing the two components to react before the addition of the olefins. Schrock et al(101) discovered that methane was produced during the initial reaction and when 2,8-decadiene was added there was an initial production of propylene; after which the expected compounds, cyclohexene and 2-butene were the only products of the reaction. When a similar experiment was carried out using (1,1,1,10,10,10-D_6) 2,8-decadiene, (3,3,3-D_3) propylene was produced in addition to the normal products (102). The ratio of propylene to 2-butene was near the value of the initial Mo to olefin ratio. The following schemes explained these facts and the formation of the original metallocarbenes:

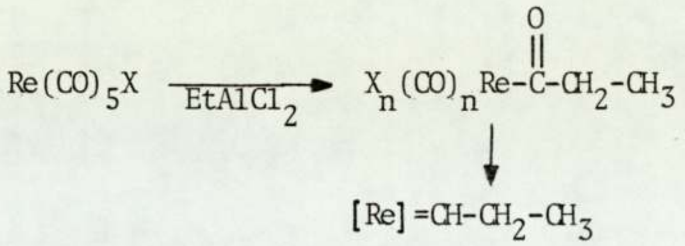


The mechanism proposed by Grubbs and supported by Schrock suggests that the production of metal carbene proceeds to 100% yield if 1 mole of propylene is produced per mole of transition metal. If the metal carbene formation is the initiation reaction, then the catalyst efficiency in this reaction would be expected to be close to 100%. Considerable evidence from metathesis polymerisation reactions suggests that this is not so, otherwise the metathesis polymers would have much lower degrees of polymerisation than usually recorded. Pakuro and Dolgoplosk(28) have used a molybdenum catalyst ($MoCl_3(C_{17}H_{35}COO)_2$) / $2EtAlCl_2$ and quoted efficiencies of less than 1% for the polymerisation of cyclopentene.

A similar scheme was also suggested by Menapace et al(23) for the WCl_6 / $Et_3Al_2Cl_3$ catalyst system and by Dolgoplosk and co-workers(103) for the reaction between WCl_6 and Me_3SiCH_2Li:

$$\begin{aligned}
&Me_3SiCH_2Li + WCl_6 \longrightarrow Me_3SiCH_2WCl_5 + LiCl \\
&Me_3SiCH_2WCl_5 \longrightarrow Me_3SiCH{=}WCl_4 + HCl \\
&HCl + Me_3SiCH_2Li \longrightarrow Me_4Si + LiCl
\end{aligned}$$

Farona and Greenlee(104) observed the formation of trace products containing an extra three carbon fragments when using the system $Re(CO)_5X$ / $EtAlCl_2$. The most reasonable source of these initial, unusual products was the production of a propylene carbene in the initiation step. Because the alkylating agent contained only 2 carbon atoms, the source of the extra carbon atom was one of the carbonyl groups. The initial alkylation of a carbonyl ligand by the aluminium compound was suggested.

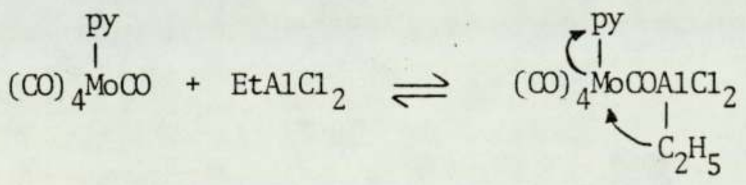


$$Re(CO)_5X \xrightarrow{EtAlCl_2} X_n(CO)_nRe-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \;\downarrow\; [Re]=CH-CH_2-CH_3$$

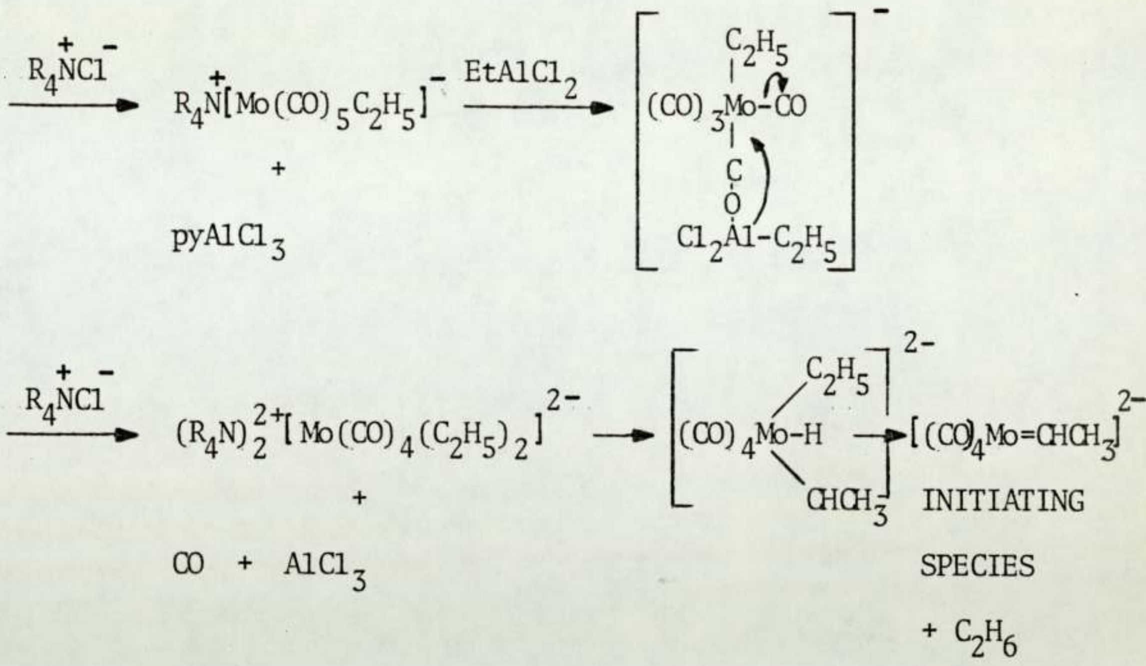
This scheme would not apply universally but only to systems containing carbonyl groups.

More recently, Motz and Farona(105) proposed processes for the formation of the initial carbene in chlorobenzene and heptane for the system $Mo(CO)_5py$ / $RAlCl_2$ / $(Bu)_4NCl$ for the metathesis of 1,7-octadiene based on studies of the first formed olefins. They found that in chlorobenzene, the initial carbenes were ethylidene and methylidene depending on the cocatalyst used (R=Et or Me) but in heptanes co-ordinated propylidene and ethylidine arose from the respective cocatalysts. They found that the amount of the initially formed products varied directly with the amount of catalyst added to the solution. The following processes were proposed for the formation of the initial carbenes in chlorobenzene and heptane:

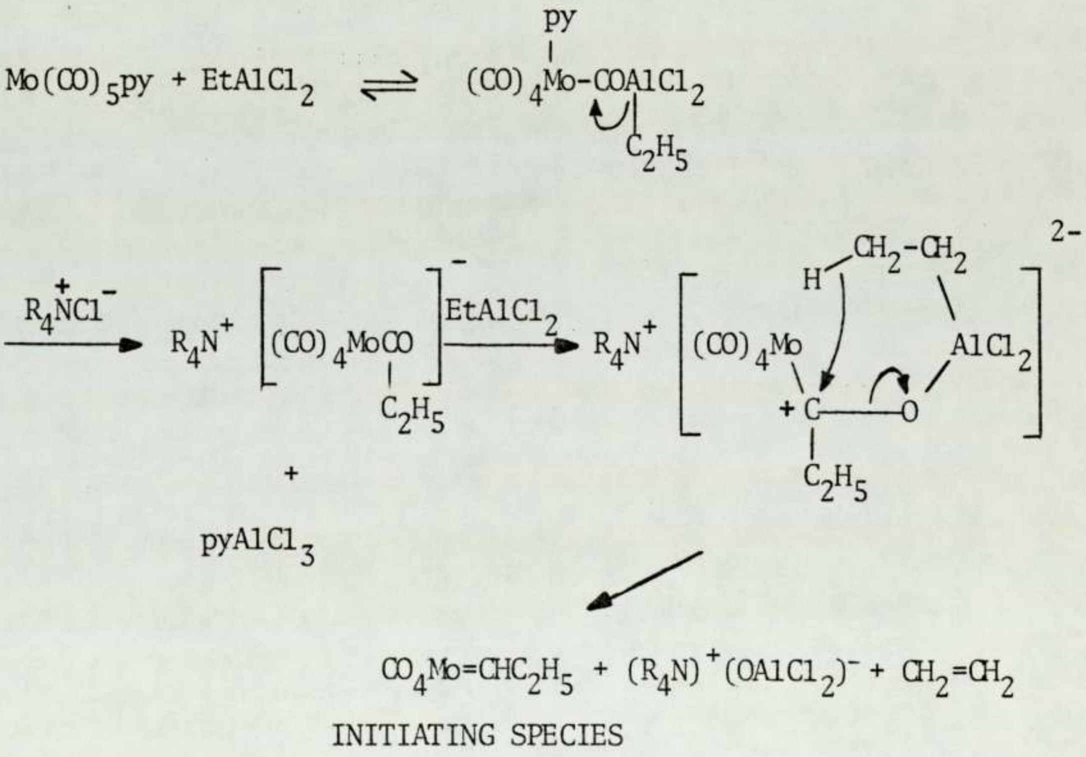
IN CHLOROBENZENE



$$(CO)_4\overset{py}{\overset{|}{Mo}}CO + EtAlCl_2 \rightleftharpoons (CO)_4\overset{py}{\overset{|}{Mo}}CO\underset{\underset{C_2H_5}{|}}{AlCl_2}$$


$R_4\overset{+}{N}\overset{-}{Cl}$
$R_4\overset{+}{N}[Mo(CO)_5C_2H_5]^-$
+
$pyAlCl_3$
$EtAlCl_2$
C_2H_5
$(CO)_3Mo-CO$
C
O
$Cl_2Al-C_2H_5$
-
$R_4\overset{+}{N}\overset{-}{Cl}$
$(R_4N)_2^{2+}[Mo(CO)_4(C_2H_5)_2]^{2-}$
+
$CO + AlCl_3$
C_2H_5
$(CO)_4Mo-H$
$CHCH_3$
2-
$[(CO)_4Mo=CHCH_3]^{2-}$
INITIATING
SPECIES
$+ C_2H_6$

IN HEPTANE

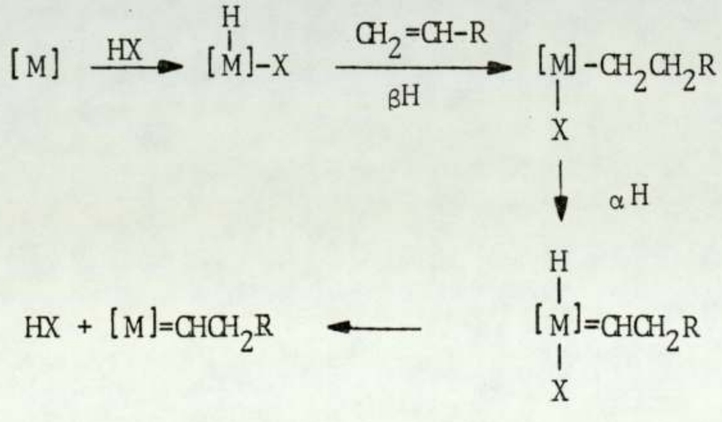

$Mo(CO)_5py + EtAlCl_2$
py
$(CO)_4Mo-COAlCl_2$
C_2H_5
$R_4\overset{+}{N}\overset{-}{Cl}$
R_4N^+
$(CO)_4MoCO$
C_2H_5
-
+
$pyAlCl_3$
$EtAlCl_2$
R_4N^+
CH_2-CH_2
H
$(CO)_4Mo$
$AlCl_2$
+C
O
C_2H_5
2-
$CO_4Mo=CHC_2H_5 + (R_4N)^+(OAlCl_2)^- + CH_2=CH_2$
INITIATING SPECIES

In general, systems that consider only the reaction between catalyst and cocatalyst as the source of the carbene have severe drawbacks. Systems containing no alkylating agent are known to initiate the metathesis reaction. For example, WCl_6 / $AlBr_3$(36) initiates the ring opening polymerisations of cycloolefins, in some cases with a 100% yield. As previously explained, the role of the olefin is more than just to be a substrate for the reaction but one that can also take part in the initiation process in some cases acting as a reducing agent. Another point in favour of involving the olefin in the initial stages of the reaction can be taken from the observations of Basset et al(95,106). They found that the catalytic systems $W(CO)_5(P(Ph)_3)$ / $EtAlCl_2$ / O_2 and $W(CO)_3$(mesitylene) / $EtAlCl_2$ / O_2 displayed no catalytic activity towards metathesis when the starting olefin was pure trans-2-pentene. However, when small amounts of a cis or a terminal olefin were present, the reaction took place after an induction period of varying lengths; then the reaction was autocatalytic during the initial period. A similar observation was mentioned by Pampus(107) for the inactivity towards the metathesis of pure trans-2-butene with the system WCl_6 / $MeAlCl_2$. Additionally Katz(96) did not report any complications for the metathesis reaction of trans-olefins when (diphenylcarbene)pentacarbonyltungsten was used as the catalyst system.

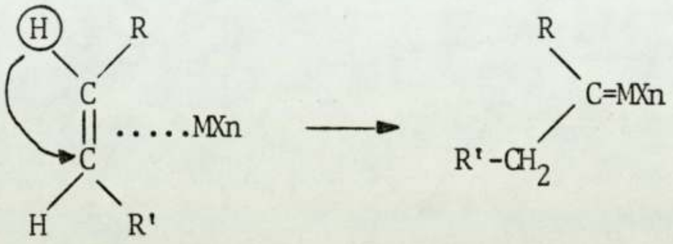
Basset(95) explained this behaviour to be associated with the initiation step and the formation of the first metallocarbene. Steric factors did not allow trans-2-pentene alone to produce the first metallocarbene, whereas a very small amount of the cis isomer could do so and thus promote metathesis. The cis isomer could reproduce the carbene responsible for the propagation step explaining the autocatalytic aspect of the metathesis reaction of trans-olefins.

If one considers that the first metallocarbene was produced by reaction between the transition metal compound and the organometallic cocatalyst, this observation cannot be accounted for, and the metathesis of trans-olefins should start in a similar way to the cis-olefin and an induction period followed by an autocatalytic process should not be expected.

Another proposed route for the initial carbene production has been suggested for those reactions that do not require an alkylating agent. These reactions involved a β-hydrogen addition of a metal hydride to the olefin followed by an α-hydrogen elimination(108). This sequence requires a source of the hydride. Oxidation involving addition of HX (X = alkoxy, phenoxy, carboalkoxy, H, halide etc) to the transition metal ion which is in a low or immediate oxidation state would take place.

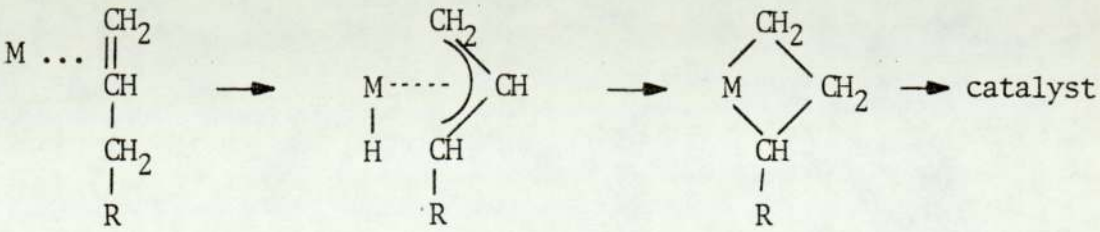


A simpler explanation, suggested by Dolgoplosk et al (72) proposed a step, involving the isomerisation of a π-olefin complex, that does not require much energy.



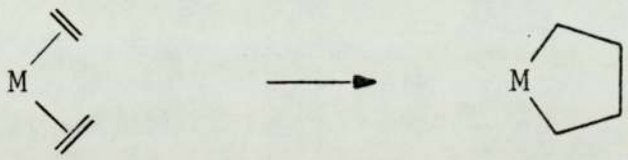
Dolgoplosk compared this reaction with the sequence adopted by Chisholm and Clark (109) to explain the formation of some stable complexes of platinum. Further evidence was that the carbene ligand in the transient compound, RCH_2-(Ph)C=W(CO)$_5$, changed to the corresponding olefinic ligand, RCH=CH(Ph) (110). However this route involved a considerable distortion from the planarity of the olefinic group in sterically constrained highly reactive cycloalkenes, making the scheme inapplicable universally.

Green and co-workers (111,112) demonstrated that metallocyclobutanes can be produced by the reduction of $Cp_2W(allyl)^+$ complexes. This coupled with the isomerisation of metal olefin complexes to allyl hydride complexes by allylic hydride abstraction provided an initiation mechanism:

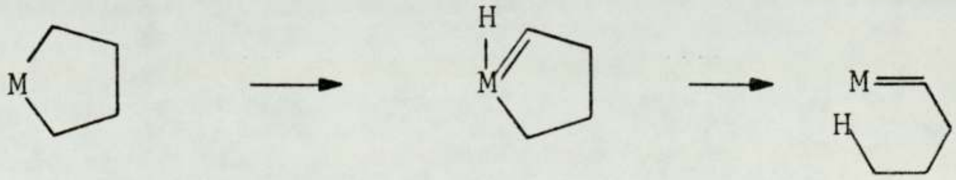


This mechanism has received support by Sherman and Schreiner(113) and more recently by Farona and Tucker(114) using a $Mo(CO)_6$ on γ-alumina catalyst and based on the results of the first formed olefins and first formed metathesis products for the metathesis of 2,4,4-trimethyl-2-pentene. They found that only the predicted products were observed and concluded that these results were in strong support of the Green mechanism.

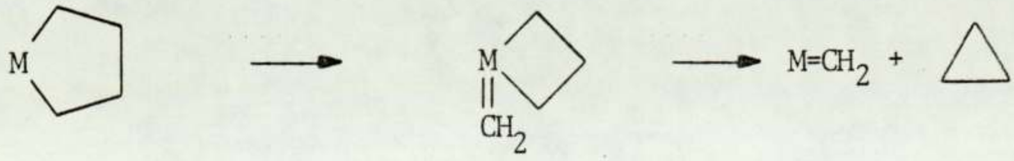
A method that could provide the formation of the initial metallocarbene involves the formation of a metallocyclopentane from metal olefin complexes. This reaction has been described in several publications(68,69,82,115,116):



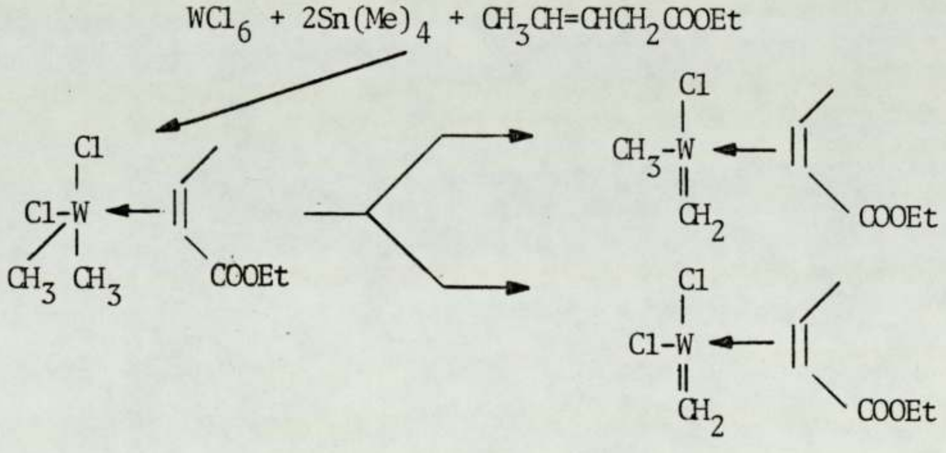
The metallocyclopentene could then rearrange to form the active species. One way involves a α-hydrogen transfer(68):



Another would involve an α-carbon-carbon bond cleavage and the formation of a cyclopropane:

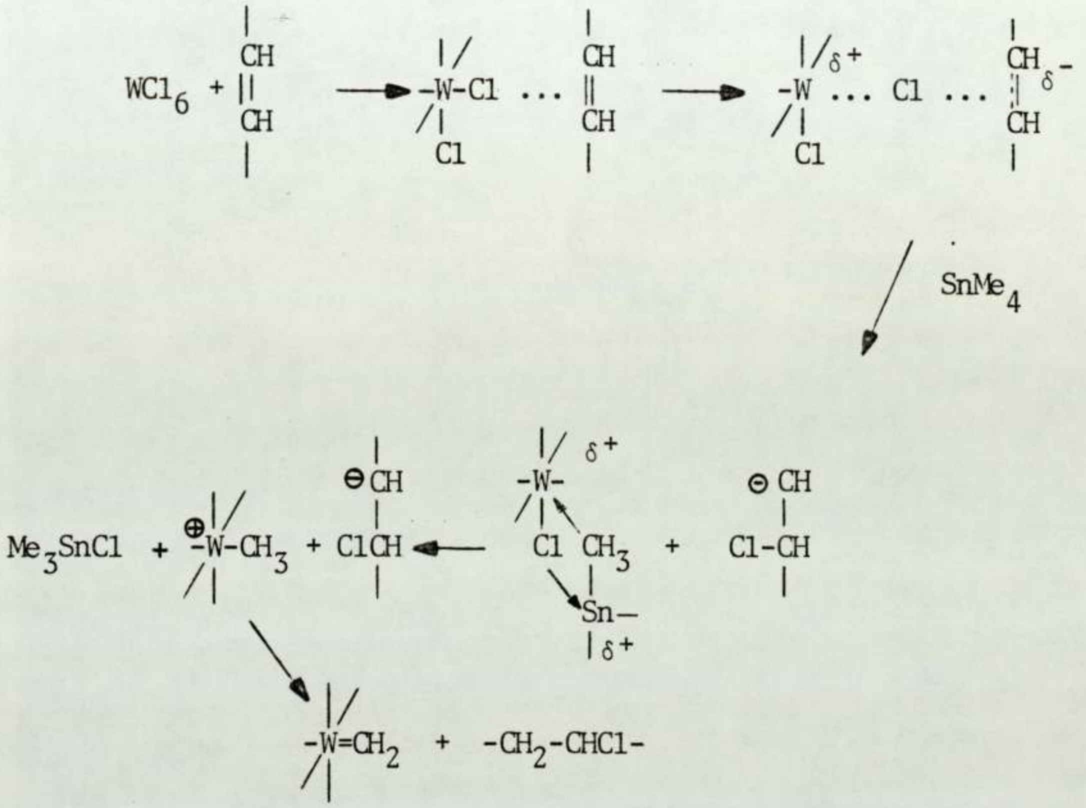


The mechanisms explained above had one common criticism, that they do not take into account the role of the cocatalyst in the reaction. These schemes do not explain the requirement of a cocatalyst but it could be assumed that the cocatalyst would produce the vacant co-ordination site(s) for the olefin(s) to complex with the transition metal which is not normally in its maximum oxidative state. Very recently two initiation mechanisms have been published that would involve both the reaction with the cocatalyst and with the olefin. Otton(27) proposed an active precursor for the metathesis of ethylenic esters with the WCl_6 / $SnMe_4$ system in which two chlorine atoms of the original WCl_6 must be removed in order to accommodate the olefin. This process would be carried out either by $SnMe_4$ or by the olefin itself acting as a reducing agent. The active precursor initially formed would then form the metal carbene through α-hydrogen abstraction leading to chloroform or methane (both detected).



Hummel(31) based on observations for the degradation reactions of 1,4-polybutadiene with WCl_6 / $SnMe_4$, proposed a mechanism involving complexation of the olefinic double bonds of the polymer to WCl_6

before the reaction with $SnMe_4$ took place. The initial process involved hydrochlorination of the double bonds.



These mechanisms, although they have not been thoroughly tested, could explain several facts, for example the necessity of a cis-olefin to form the first carbene, the presence of the alkyl groups of the cocatalyst in the final products and the formation of chlorinated compounds in the reaction mixtures. They are also the first attempts to explain the initiation in terms of both the initial olefin and the cocatalyst, but could not explain reactions not involving an alkylating agent.

(6) CHAIN TERMINATION

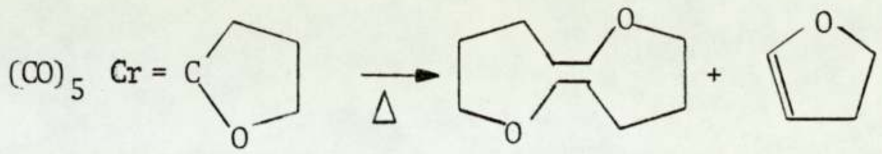
Any chain reaction is normally considered to have three main steps namely, initiation, propagation and termination. For the metathesis reaction, and in particular the ring opening polymerisation of cyclic alkenes, the propagation reaction is considered to be well understood and the presence of metal carbenes and metallocycles as intermediates for the reaction has been amply documented by several authors and their implications and importance explained previously. Similarly, there have been several plausible explanations for the initiation reaction already covered in this introduction. One point that has not been taken into consideration until recently has been the termination step. Some authors have not considered this step at all or have described the systems under study as 'living systems'.

The rate of catalyst production from the various WCl_6 based systems varies substantially. Catalyst quickly forms and dies in the WCl_6 / EtOH / $4EtAlCl_2$ system(49,100) (catalyst lifetimes in the WCl_6 / EtOH / $4EtALCl_2$ are approximately 30 mins at 25°C), whereas in the WCl_6 / $Zn(Me)_2$ system(100) an insoluble catalyst is slowly generated over at least 24 h. Muetterties suggested for these systems more than one catalytically active species, each having a distinguishable metathesis chemistry, each one with a different life time, hence having different rates not only in formation but also in termination of the active species.

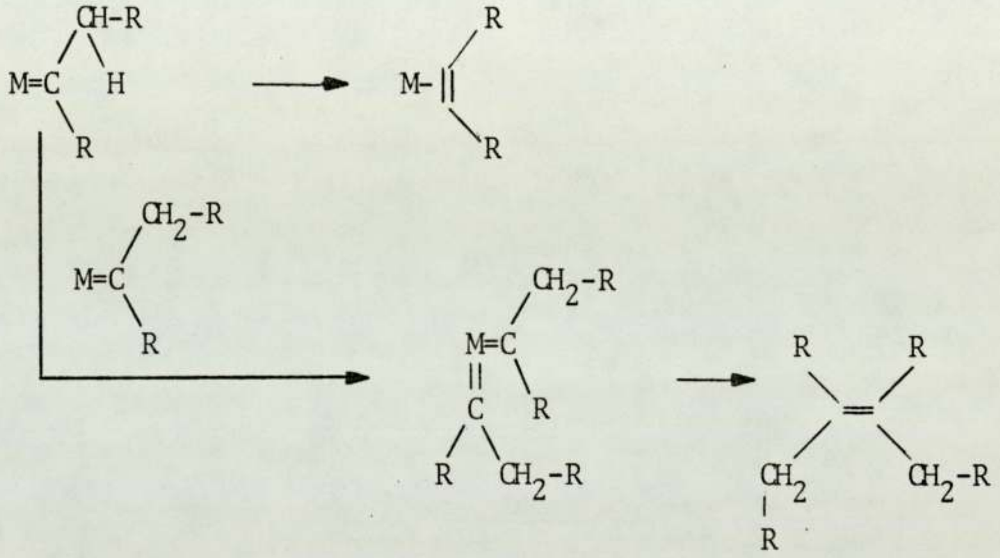
Termination processes can be considered to be of two kinds: (i) those in which the chain process is interrupted but the catalyst species remains active and (ii) those in which the activity of the catalyst is actually destroyed. The first kind of termination should not be considered a proper termination step but a transfer reaction. This process is normally used to explain the control of the molecular weight in polymerisation of cyclic olefins and generally involves the reaction of a growing polymer (attached to the metal centre) with a linear olefin (impurity) or with a double bond in the growing polymer itself to produce a low molecular weight carbene that could carry on the polymerisation process.

Termination reactions that destroy the catalytic intermediates are more critical. These can again be subdivided into two main groups: (i) those reactions that involve the presence of impurities such as oxygen, water, organic molecules containing polar groups etc, and (ii) those that can take place in a completely 'impurities free' environment. The first type of reaction, especially those involving oxygen and water, have been described previously. The reactions that are going to be considered here are those for which there is no need to involve any impurities or alien species to the system.

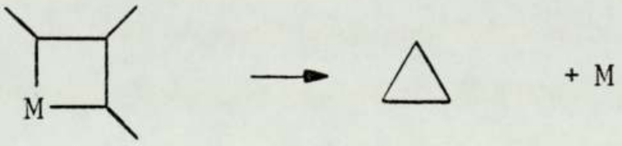
There are a number of side reactions open to metal carbenes and metallocycle intermediates that can account for the deactivation of the active intermediates. Carbene complexes can show hydrogen transfer and dimerisation(117):



where the general schems suggested for these reactions are:



In general the termination of the metathesis reaction is considered to be either first or second order with respect to the carbene or active species concentration. First order reactions may involve the formation of cyclopropanes from metallocycles.



This process has been suggested by Dolgoplosk(118) based on the transformation of cyclopropanes derivatives under the influence of tungsten halides. Cyclopropane formation was also found to be the result of reactions between model metal carbene compounds and olefins(92).

Another route for a first order termination reaction is connected with the reduction of the transition metal and the formation of a free radical(119).

$$R\text{-}CH = WCl_n \longrightarrow R\text{-}\dot{C}HCl + WCl_{n-1}$$

A process opposite to the initiation step proposed involving the migration of a hydrogen atom into the carbene complex can also be proposed:

$$R\text{-}CH_2\text{-}CH{=}MX_n \longrightarrow R\text{-}CH{=}CH_2 + HMX_n$$

The same kind of reaction has been found for the decomposition reaction of tantalum compounds. Schrock(120) found that $TaCp_2(C_2H_4)Me$ rearranges to $TaCp_2$(propylene)H, by migration of the alkyl to the alkylidene ligand followed by β-hydride elimination.

The second order termination reactions would be those involving a bimolecular carbene decomposition.

Grubbs reported the formation of ethylene in the reaction of $(Me)_3Al_2Cl_3$ and $Mo(Ph_3P)_2Cl_2(NO)_2$ as well as $(Me)_4Sn$ and WCl_6(121). It was suggested that dimerisation of methylene-metal complexes was responsible for this formation.

$$2M{=}CH_2 \longrightarrow CH_2{=}CH_2$$

Grubbs(16) also explained the formation of ethylene in the reaction of norcaranene with a catalytic amount of $PhWCl_3$ / $AlCl_3$ by means of the combination of the methylene carbenes. Schrock(120) explained the presence of certain olefinic products from the reactions of model metal-carbenes of Nb and Ta with terminal olefins, by a bimolecular decomposition of the alkylidene complexes involved in the metathesis reaction. The author showed that this decomposition reaction can be slowed down by the addition of a tertiary phosphine ligand that could complex with the metal centre. If this donor efficiently blocked some of the bimolecular decomposition is likely that an oxo ligand, known to be a powerful π-electron donor would then do likewise.

Additional support for a bimolecular termination can be drawn from results obtained by Amass(122) and Lotfipour for the polymerisation of cyclopentene with WCl_6 and oxygen without the use of any aluminium compound. When the reaction between cyclopentene and WCl_6 was carried out in toluene in a sealed, all glass apparatus, some polymerisation took place. A precipitate formed on the walls of the vessel and after 24 h, when oxygen was allowed into the system a very rapid polymerisation to very high conversions took place. The polymer obtained had a molecular weight determined by viscosity using toluene as solvent of about 5×10^6. No polymerisation took place if oxygen was admitted to the supernatant clear solution if this solution was not in contact with the solid. The active sites for the polymerisation were then considered to be formed from the precipitate.

When a similar reaction was carried out in chlorobenzene, no precipitate was formed and after the addition of O_2, a polymerisation took place, but this time neither the conversion nor the molecular weight of the polymer was as high as in the previous case. These results have been explained by the presence of a bimolecular termination process that could take place in the chlorobenzene homogeneous system but, because of the heterogeneous nature of catalysts, could not take place in the toluene system. In the heteregeneous system, the reaction would go not only to high conversions but to very high molecular weights, because active sites could not diffuse to allow termination.

(7) THERMODYNAMICS AND MOLECULAR WEIGHT DISTRIBUTION OF POLYALKENAMERS

The polymerisation of cycloolefins is a ring-opening polymerisation and like many other ring-opening polymerisations, the metathesis of cyclicalkenes differs from conventional addition polymerisations with respect to the changes in chemical bonds involved. In addition polymerisations, a double bond in the monomer is converted into two polymeric in-chain single bonds, thus providing a reaction that is normally exothermic but might show an overall decrease in entropy. The polymerisation of cyclic olefins by a ring-opening process may be favourable from both an enthalpic and in many cases also an entropic term. The only unsubstituted cycloalkene that will not undergo polymerisation is cyclohexene, and even when it is incorporated into a copolymer, such as the one obtained by the polymerisation of cis, trans-1,5-cyclodecadiene it reverts to cyclohexene and polybutenamer(123). This is due to the strain free condition of this particular ring.

The enthalpy of polymerisation is high for 4 and 5 membered rings but relatively small for the higher membered cycles. The entropy change involved in polymerisation is negative for small rings up to cyclohexene, close to zero for cycloheptene and positive for rings with greater than seven carbon atoms. The entropy change derives from two types of structural changes in the polymerisation: (i) the change due to translational entropy since the mobility of small rings is greatly reduced when incorporated into a polymer chain but for the larger rings the translational freedom is not affected to any great extent, and hence this negative value has greater importance for smaller rings and (ii) torsional and vibrational entropies which are always positive, decrease to a much smaller extent going from small to large rings. As a consequence of this, the polymerisation of cyclopentene is an antientropic and proenthalpic determined reaction whereas cyclooctene polymerises with a positive value for both entropy and enthalpy.

Ofstead and Calderon(124) determined the equilibrium monomer concentration for the polymerisation of cyclopentene catalysed by the WCl_6 / EtOH / $EtAlCl_2$ system at different temperatures. The results are shown in Table I.3.

Table I.3 DEPENDENCE OF EQUILIBRIUM CYCLOPENTENE CONCENTRATION ON TEMPERATURE(124)

Temperature °C	$[M]_e$ (mol dm^{-3})
0	0.51 ± 0.01
10	0.70 ± 0.01
20	0.88 ± 0.01
30	1.19 ± 0.04

Theory predicts the relationship:

$$\ln [M]_e = \frac{\Delta Hp}{RT} - \frac{\Delta Sp^o}{R}$$

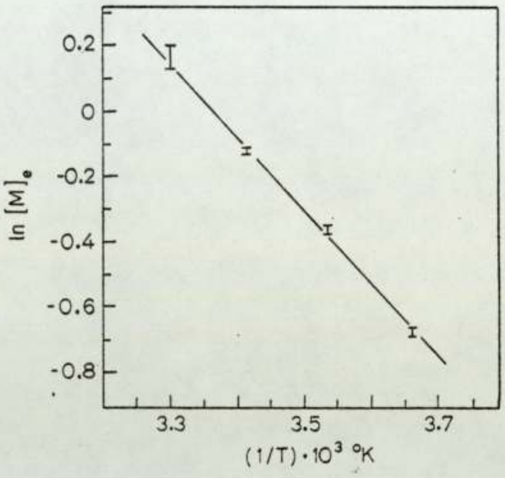
where $[M]_e$ - equilibrium monomer concentration

ΔHp - enthalpy change during polymerisation

ΔSp - the standard entropy change for a $[M] = 1$ mol dm^{-3}

When $\ln[M]_e$ was plotted against T^{-1} for the data in Table I.3 (Fig I.7), the values of -4.4 Kcal mol^{-1} and -14.9 cal mol^{-1} deg^{-1} were derived for ΔHp and ΔSp^o respectively. A ceiling temperature of approximately 150°C was obtained by extrapolation. The enthalpy of polymerisation calculated by Calderon corresponded to the ring strain value for cyclopentene (4.9 Kcal mol^{-1}) reported by Cox(125).

Fig I.7 VARIATION OF MONOMER CONCENTRATION WITH TEMPERATURE FOR THE POLYMERISATION OF CYCLOPENTENE(124)



Studies concerned with the molecular weights of polyalkenamer were carried out as far back as 1968(64,53). Calderon(12) treated several cycloolefins, including cyclooctene, with a metathesis catalyst and reported the formation of low molecular weight 'extractables'. In a subsequent paper(54) the formation of monocyclic compounds possessing molecular weights of up to 1200 from various cycloolefins was reported. The formation of these macrocycles was initially believed to result from the intermolecular ring enlargement of two smaller rings, according to the pairwise mechanism considered at the time to be the intermediate.

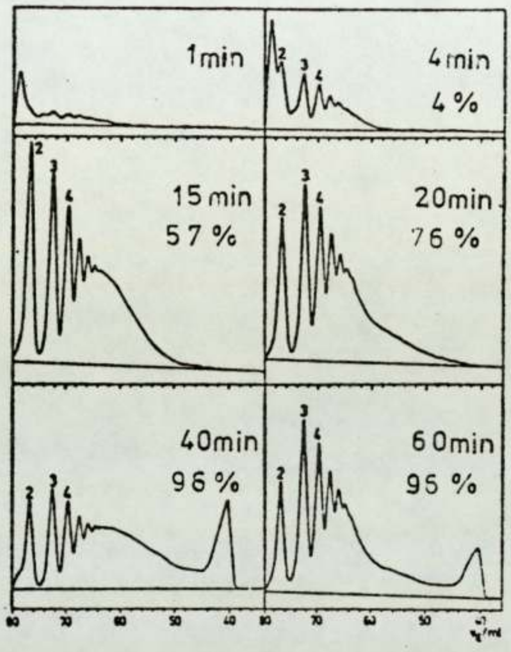
Studies on the molecular weight distribution of polyalkenamers have helped to corroborate the carbene mechanism and it is now commonly proposed that the macrocycles obtained in the polymerisation of cycloolefins are produced by a 'back biting' mechanism.

Chauvin(126) and co-workers showed that polyoctenamer prepared either from cyclooctene or from a polymer of high molecular weight, shows a bimodal molecular weight distribution, which was considered to be the sum of two single distributions. The authors however found a single distribution for polypentenamer with the molecular weight and molecular weight distribution decreasing with increasing conversion. Similar results were found by Hocker and co-workers for the polymerisation of cyclooctene and cyclododecene(77).

Witte and Hoffmann(127) found contrasting results from those obtained by Chauvin for the polymerisation of cyclopentene induced by a series of homogeneous catalysts. The resulting polymers formed showed bimodal distributions consisting of linear macromolecules and small amounts of cyclic oligomers. The oligomers were formed more slowly than the linear high polymers for the range of concentrations used (10-15%). The molecular weight distribution of the oligomer fraction showed a maximum at a degree of polymerisation of 6, broadening to higher molecular weights with increasing reaction time.

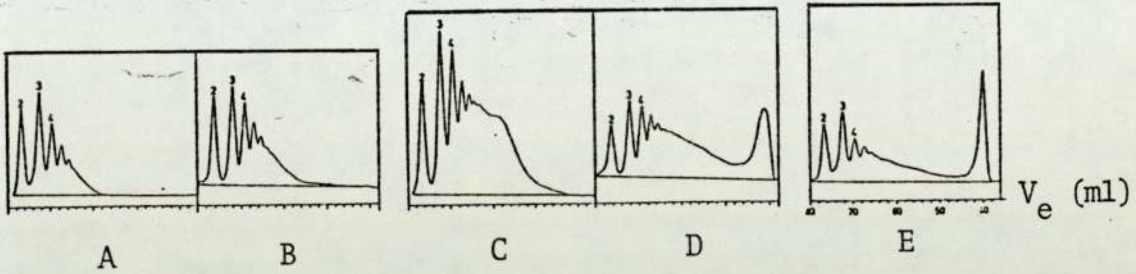
Hocker(128) showed that the formation of oligomers and high molecular weight products is initially kinetically controlled with the distribution being generated gradually. At low conversions, the oligomers were formed with no polymer present but as the polymerisation proceeded the polymeric peak developed, Fig I.8.

Fig I.8 DISTRIBUTION OF OLIGOMERS AND POLYOCTENAMERS FUNCTION OF TIME AND CONVERSION (CYCLOOCTENE CONCENTRATION, 0.25 mol dm^{-3})(128)



This result also applied when the initial monomer concentrations of cyclooctene were low. The authors found that the final molecular weight distribution obtained for the metathesis polymerisation of cyclooctene depended on the initial monomer concentration (Fig I.9) and that the results were identical whether the starting material was pure monomer, the equivalent monomer concentration as high molecular weight polymer or a particular oligomer.

Fig I.9 FINAL MOLECULAR WEIGHT DISTRIBUTION OBTAINED FOR THE METATHESIS OF CYCLOOCTENE AT DIFFERENT INITIAL MONOMER CONCENTRATIONS ($[COE]_o$: A = 0.05; B = 0.075; C = 0.1; D = 0.25; E = 0.5 mol dm^{-3})(128)



Similar results were obtained by Chauvin and co-workers(129) for the metathesis of 1,5-cyclooctadiene. It was found that the amount of high molecular weight material produced depended on the initial concentration of monomer and that below a certain value no polymer could be detected. The results are shown in Fig I.10.

They also showed that the ratio of oligomers to high molecular weight products was initially kinetically controlled and that the final equilibrium concentration could be obtained either from monomer, high molecular weight products or pure macrocyclic oligomers. The results are summarised in Fig I.11.

These authors concluded that the results could only be explained by a chain reaction and invoked the presence of a metal carbene as the chain carrier for the reaction and that an equilibrium between monomer, polymer and an oligomer was established after

Fig I.10 EQUILIBRIUM CONCENTRATION OF OLIGOMERS AS FUNCTION OF THE INITIAL CONCENTRATION OF 1,5-CYCLOOCTADIENE(129)

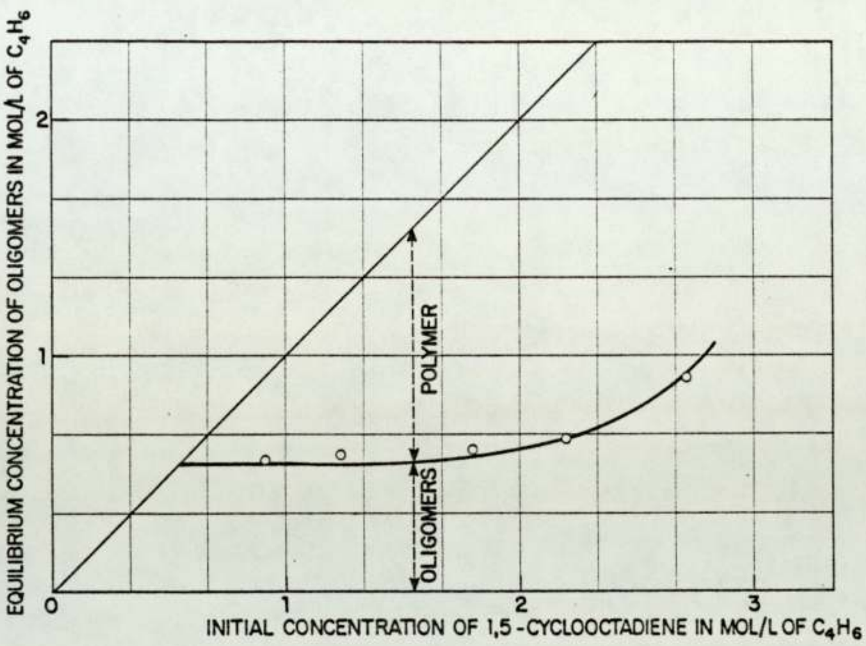
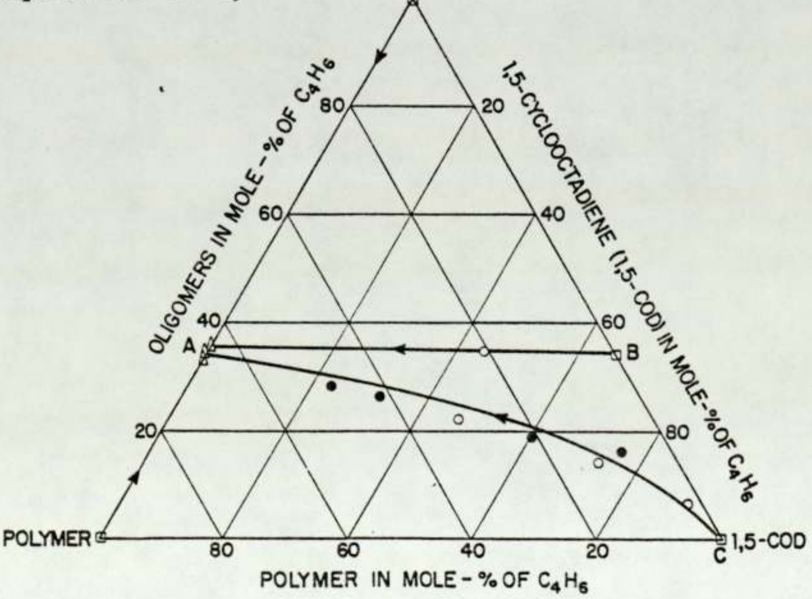


Fig I.11 METATHETIC INTERCONVERSION OF MIXTURES OF POLYMERS AND OLIGOMERS OF 1,5-CYCLOOCTADIENE(129) (□ = starting points; Δ = final equilibrium points; ○ = reactions in chlorobenzene ● = reaction in benzene. Initial monomer conc, 2.7 mol dm^{-3} temperature 30°C)



long reaction times. In all cases, except for that of cyclopentene, the equilibrium concentration of monomer was close to zero and it was not considered in the equilibrium calculations.

(8) KINETICS OF THE RING-OPENING POLYMERISATION OF CYCLIC ALKENES

A lot of work has been carried out on the kinetics of the metathesis reaction of linear olefins, the results obtained have provided very important additional information on the mechanism. In this respect, the kinetics of the formation of products from metathesis of cyclic olefins as well as the cross-metathesis of different acyclic olefins, and acyclic and cyclic olefins were of great interest.

Although the polymerisation of cyclic olefins have received plenty of attention, the majority of the studies have been directed towards optimisation of conversion in the minimum time rather than detailed kinetic studies of the polymerisation itself. This is probably due to the fact that cyclic alkenes normally polymerise to very high conversions in the early stages of the reaction, which makes it difficult to obtain samples for accurate kinetic studies. Therefore the major obstacle has been to obtain data from the polymerisation reaction in a system that can be continuously monitored as the decrease in the concentration of monomer or the formation of high polymer takes place. Dilatometry is a technique which allows the continuous determination of the conversion to high molecular weight materials in the polymerisation mixture, without disturbing the system by the introduction of needles in order to withdraw samples from the system.

The first published results using this technique were reported by Pakuro et al$^{(28)}$ for the polymerisation of cyclopentene in toluene under the action of the homogeneous system $MoCl_3(C_{17}H_{35}COO)_2$ / $2Et_2AlCl$. It was shown that there is a linear relationship between the initial rate of polymerisation and the initial concentration of the monomer, the extrapolation of the straight line obtained to zero initial rate corresponding to the concentration of monomer at equilibrium (0.6 mol dm^{-3} at $2.7^{o}C$). The system also showed a linear dependence of the rate of polymerisation on the instantaneous concentration of monomer. They concluded that there is a first order reaction with respect to the monomer concentration.

Pakuro observed an order of reaction close to 0.6 with respect to the catalyst. The activity of the catalytic system depended strongly on the conditions of the formation of the catalytic complex which affected the degree of reduction of the molybdenum. With an increase in the catalyst concentration, the degree of reduction of the molybdenum component apparently raised and the relative activity of the system fell. The fractional observed order with respect to the catalyst concentration was thus explained by this reaction sequence.

Amass and Tuck$^{(25)}$ studied the polymerisation of cyclopentene in toluene catalysed by WCl_6 / $AliBu_3$ and reported a first order dependence of the initial rate of polymerisation on the concentration of WCl_6 when the molar ratio W:Al was maintained at 1:2.

The initial studies of the determination of the order of reaction with respect to monomer led to irreproducible results, this was found to be due to the variations in time between the addition of WCl_6 and $AliBu_3$ to the monomer solution. It was suggested that a series of reactions could take place between the WCl_6 and the olefin prior to the addition of the $AliBu_3$, the schematical representation is given below (cyclopentene is represented as CP).

$$WCl_6 + CP \xrightarrow{k_1} W_1 \xrightarrow{2AliBu_3} W^* / Al_2 \quad \text{— Polymerises}$$

$$W_1 + CP \xrightarrow{k_2} W_2 \xrightarrow{AliBu_3} W^{**} / Al_x \quad \text{— Unknown activity}$$

The overall change in concentration of W_1 before the addition of $AliBu_3$ is given by:

$$\frac{d[W_1]}{dt} = k_1[WCl_6][CP]_o - k_2[W_1][CP]_o$$

Because CP was present in a large excess, the concentration of cyclopentene before the addition of $AliBu_3$ remained approximately constant (ie $[CP]_o$) but $[WCl_6]$ varied and could be expressed by:

$$[WCl_6] = [WCl_6]_o \exp(-k_1[CP]_o t)$$

Where $[WCl_6]_o$ is the initial concentration of WCl_6. When these equations are substituted and the differential equation solved, it leads to:

$$[W_1] = \frac{k_1}{k_2-k_1} [WCl_6]_o \exp(-k_1[CP]_o t)-\exp(-k_2[CP]_o t)$$

The concentration of W_1 is therefore expected to be a function of $[CP]_o$, $[WCl_6]_o$ and t the time elapsing from the addition of WCl_6 to the monomer. If upon the addition of the $AliBu_3$ to the solution W_1 is immediately converted to W^* / Al_2, the rate of polymerisation would be expected to show a maximum when:

$$\frac{d[W_1]}{dt} = 0$$

Differentiation of the equation for $[W_1]$ with respect to time leads to:

$$t_{max} = \frac{1}{[CP]_o} \quad \frac{1}{k_1-k_2} \quad \ln \frac{k_1}{k_2}$$

Under a given set of conditions, ie of constant monomer and catalyst component concentrations, the rate of polymerisation will be expected to show a maximum after a delay time (t_{max}) that is dependent upon the initial concentration of monomer. Experiments were carried out in which the concentrations of the catalyst components were maintained constant and the elapsed time between the additions of the catalyst component was varied. It was found that a linear relationship existed between t_{max} and the reciprocal of the monomer concentration. It was concluded that a kinetic scheme similar to that described could apply for the reaction under study.

Amass and Tuck also concluded from their studies that the catalytically active species were consumed during the polymerisation but that the rate did not decrease to zero but to a constant value, lower than the initial rate.

Hocker et al(130) studied the kinetics of the metathetical polymerisation of cyclooctene in chlorobenzene with three different catalysts, WCl_6 / EtOH / $EtAlCl_2$ (1:1:4), $(Ph_3P)_2(NO)_2MoCl_2$ / $EtAlCl_2$ (1:5) and WCl_6 / $Sn(Me)_4$ (1:5). The reactions showed induction periods of 5 seconds, 5 minutes and 10 minutes respectively. The reaction is first order with respect to the catalyst concentration for the WCl_6 / EtOH / $EtAlCl_2$ system. The order with respect to the monomer concentration was 1 for the molybdenum and WCl_6 / $Sn(Me)_4$ system while for the WCl_6 / EtOH / $EtAlCl_2$, the observed order was 2. The Arrhenius parameters were also determined for this last system in the temperature range -15 to +60^{o}C. The activation energy was found to be 5.2 Kcal mol^{-1}, the frequency exponent 7.2 and an activation entropy of -55 eu.

(9) SCOPE OF THE PRESENT STUDY

In recent years some very important aspects of the metathesis reaction have been solved but there remains many unanswered questions, especially concerning the polymerisation of cycloolefins.

The initiation of the reaction has still many unexplained points, amongst which are the source of the first carbene capable of initiating polymerisation and the role, if any, of the cocatalyst in its formation, how different cocatalysts ranging from AlX_3 to AlR_3 to LiR can act to produce similar results with the same transition metal compound and the nature of reactions involving the olefins. The vast amount of information on the subject tends to suggest that a common mechanism for the initiation is very unlikely.

The propagation step nowadays considers the presence of a carbene as the chain carrier of the reaction but serious studies on the particular activity of any catalyst-cocatalyst combination have not been carried out, especially concerning kinetic studies on the polymerisation of cycloolefins. It has been suggested that more than one active centre can be present at any time during the reaction but this suggestion has still to be proved.

The termination stage of the reaction represents an area in which little work has been carried out and this could be one of the most interesting fields of study in the area of metathesis.

The object of this project was mainly to develop an overall understanding of the system WCl_6 / $2AliBu_3$ for the polymerisation of cyclopentene.

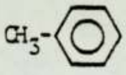
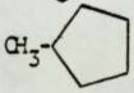
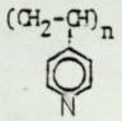
CHAPTER II

EXPERIMENTAL

(1) MATERIALS

Table II.1 shows the list of chemicals used in this project, their sources and properties and the abbreviations used for them in this thesis.

Table II.1 LIST OF CHEMICALS

NAME	FORMULA	ABBREVIATION	SOURCE	MW	MP	BP	DENSITY
Cyclopentene		CP	Koch Light Labs	68.13	-135	44.2	0.772
Toluene		TOL	BDH Chemicals	92.15	-95	110.6	0.867
Cyclohexene		CHE	Hopkin & Williams	82.15	-103.5	83.0	0.810
Cyclohexane		CHA	Hopkin & Williams	84.16	6.6	80.7	0.779
Methyl cyclopentane		MCP	Hopkin & Williams	84.16	-142.4	71.8	0.749
Ethanol	CH_3-CH_2OH	ETOH	James Burrough	46.07	-117.3	78.5	0.789
Aluminium triisobutyl	$Al(CH_2-CH(CH_3)_2)_3$	ATB	Schuchart	198.33	6	42^{1}	0.79
Ethyl aluminium chloride	$CH_3CH_2AlCl_2$	AEDC	Schuchart	126.95	22	80^{12}	1.23
Tungsten hexachloride	WCl_6	THC	Cambrian Chemicals	396.6	275	346.7	3.52
Tungsten oxytetrachloride	$WOCl_4$	TOC	-	341.66	211	227.5	-
Polyvinyl pyridine		PVP	-	-	-	-	-

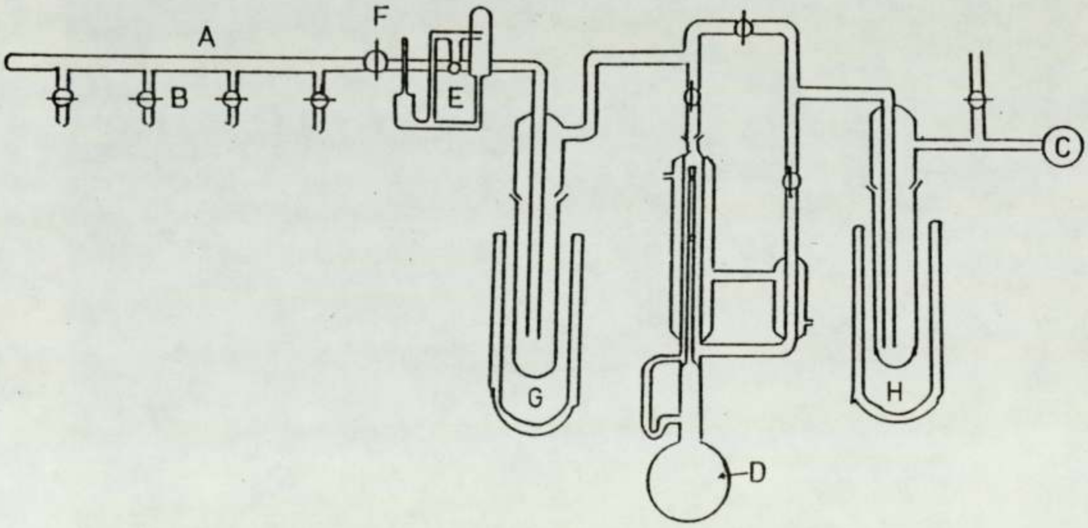
(2) GENERAL TECHNIQUES

(a) THE VACUUM LINE

The purification and preparation of monomers, solvents and catalyst solutions as well as all reactions were carried out, wherever possible, using high vacuuum techniques.

The high vacuum line shown in Fig II.1 consisted of a manifold (A) with four taps (B) which was evacuated by a rotary vacuum pump (C) assisted by a mercury diffusion pump (D). Two liquid nitrogen traps were used to condense any vapours from the manifold (G) and the mercury diffusion pump (H).

Fig II.1 THE VACUUM LINE



The pressure achieved using this system, of the order of 10^{-5} mm Hg, was measured by a 'Vacustat' (E).

(b) FREEZE-THAW DEGASSING PROCESS

The flask containing the liquid to be degassed was attached to the manifold at one of the taps. With the main tap of the manifold (F) closed, the flask was immersed in liquid nitrogen and the contents were allowed to freeze. When frozen, the appropriate taps were opened to allow the gases to be evacuated. With the main tap of the manifold closed, the flask was immersed in methanol and any dissolved gases then passed into the evacuated manifold. These freezing, warming and evacuating procedures were repeated until no gases escaped from the liquid when it was warmed to room temperature.

(c) TRAP TO TRAP DISTILLATION

Two flasks, one of which contained the degassed liquid to be distilled, were attached to the evacuated manifold. The receiver flask was immersed in liquid nitrogen and when the main tap of the manifold was closed, solvent distilled into the receiver.

(d) TREATMENT OF GLASSWARE

All glass apparatus used in the experiments was clean before use with concentrated NaOH solution and / or chromic acid. Thoroughly rinsed with water and dried when possible in an air oven at 240°C. (Quartz cells for spectroscopy and double jacketed silvered apparatus did not receive this treatment.)

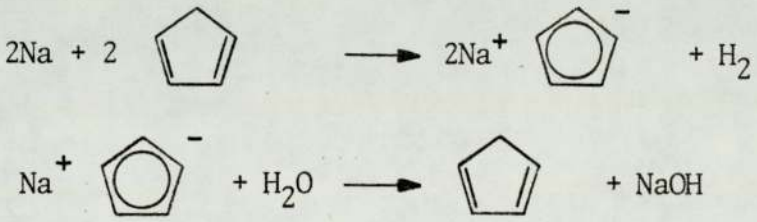
When dry, the apparatus was attached to the vacuum line and flamed (when possible) in order to remove any water still remaining on the walls. The apparatus was subsequently left under high vacuum for a minimum period of 2 h and for not less than 6 h when quartz cells or double jacketed apparatus was used.

(3) PURIFICATION, PREPARATION AND STORAGE TECHNIQUES OF MATERIALS

(a) CYCLOPENTENE (CP)

Cyclopentadiene and water are impurities normally found in CP which can deactivate the different catalysts used.

Cyclopentadiene reacts with sodium to form cyclopentadienyl sodium, which is a very good drying agent because it forms a self-regenerating drying system with sodium.



CP was allowed to stand over sodium for no less than 2 days, the solution was then degassed and distilled into another vessel containing fresh sodium. The monomer purified in this manner was stored under vacuum and ready for use when required.

(b) TOLUENE (TOL)

(i) Procedure A

TOL was distilled from a flask containing sodium, through a 2 m fractionation column and the middle fraction was collected and dried using fine slices of sodium. Because sodium reacts rapidly with water and is covered with a fine layer of sodium hydroxide, it is quickly rendered an ineffective drying agent, leaving traces of water in solution. THC can react with water to produce different oxy chlorides and ultimately WO_3 plus HCl, hence the residual amount of water could destroy the solution of catalyst normally used (10^{-4} mol dm^{-3}). For this reason, this method was not sufficiently effective.

(ii) Procedure B

A similar procedure to procedure A was used, but in this case, some cyclopentadienyl sodium or benzophenone was added to the TOL containing sodium slices. Although the solvent was dried well, this procedure did not produce TOL of sufficiently high purity because traces of olefins that could react with THC were thought still to be present. This had a special significance when the TOL was used as the solvent for the preparation of very dilute WCl_6 solutions.

(iii) Procedure C

In order to obtain an even purer TOL, the TOL obtained using procedure B was distilled into another flask and solutions of ATB and THC were injected through a rubber septum (the molar ratio of THC:ATB being higher than 1) and the TOL distilled when required.

Using this system proved to be more disadvantageous than advantageous. Analysis of the TOL produced by this method showed more unknown impurities than in the original solvent after either following procedures A or B.

(iv) Procedure D

The TOL obtained after procedure B was distilled into a flask containing pure THC, the traces of water reacted with the THC to form HCl and TOC and more importantly, any olefin present could react with the THC.

The TOL was then distilled again over sodium slices containing some benzophenone. This last step was necessary to remove any HCl that could have been formed and because some of the oxy chlorides produced distilled together with the TOL. Those oxy chlorides were destroyed by the drying system to produce species that did not distill in subsequent steps.

The solvent in this form was sufficiently dry and pure to be used when required. GLC analysis did not detect any impurities above 1 part in 10,000.

(c) CYCLOHEXENE (CHE)

The CHE was distilled and collected in a flask to which slices of sodium and a small amount of benzophenone were added. The solution was degassed and allowed to stand for at least 2 days after which it was degassed again and stored under high vacuum until required.

(d) CYCLOHEXANE (CHA)

A procedure similar to that used for CHE was used to purify and dry this compound.

(e) METHYL CYCLOPENTANE (MCP)

A procedure similar to that for CHE was used to purify and dry this compound.

(f) ETHANOL (ETOH)

ETOH was purchased as pure absolute ethyl alcohol and was subsequently dried by the following method.

The method depends upon the reactions:

$$\mathrm{Mg} + 2\mathrm{CH_3CH_2OH} \quad\text{——}\quad \mathrm{H_2} + \mathrm{Mg(OCH_2\text{-}CH_3)_2}$$

$$\mathrm{Mg(OCH_2\text{-}CH_3)_2} + \mathrm{H_2O} \quad\text{——}\quad \mathrm{Mg(OH)_2} + 2\mathrm{CH_3\text{-}CH_2OH}$$

The first reaction usually proceeds readily when activated by iodine and the original water content is less than one per cent.

One gram of pure magnesium and a small amount of iodine were placed in a dry flask, provided with a reflux condenser, 10 ml of ETOH were added and the mixture was allowed to reflux under a stream of dry nitrogen. When all the magnesium was converted into the ethoxide, an extra 140 ml of ETOH were added and the mixture refluxed for 30 minutes. The alcohol was distilled directly under nitrogen to a flask containing 4Å activated molecular sieves, degassed and stored under vacuum.

(g) TUNGSTEN HEXACHLORIDE (THC)

(i) Purification

Commercially obtained THC (nominal purity 99%) was used initially as provided, but because it was apparent that the amounts of impurities (TOC and WO_2CL_2) were well above 10%, further purification was required.

WO_2Cl_2, TOC and THC sublime under high vacuum, the sublimation temperature increasing in this order. The normal procedure for purification of THC is to sublime the impurities onto a cold-finger

Fig II.2 APPARATUS USED FOR THE SUBLIMATION OF THC

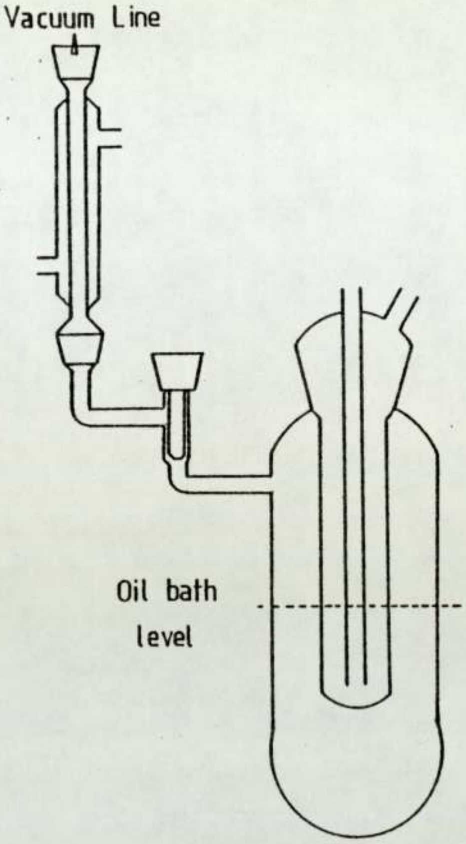
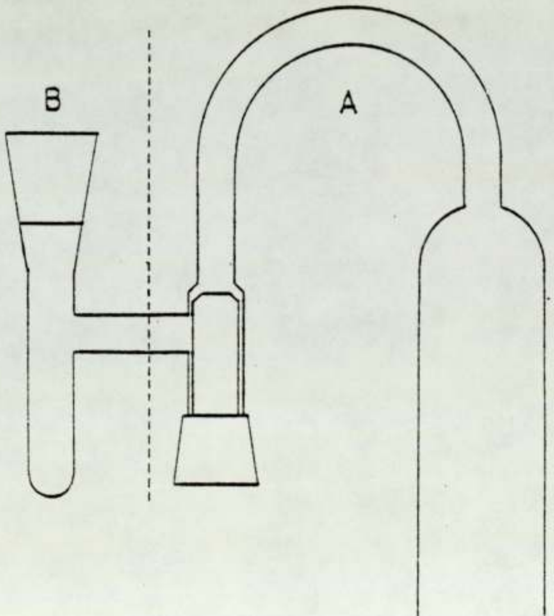


Fig II.3 APPARATUS USED FOR STORAGE OF CATALYST SOLUTIONS



which is then replaced by a clean dry cold finger on to which is sublimed pure THC. However, by this procedure sufficiently pure THC could not be obtained. A simple modification of the above procedure is to use a 'hot finger' which is maintained at a temperature between 75 and 80°C, instead of the series of cold fingers. The TOC and the WO_2Cl_2 sublime to the walls of the apparatus (shown in Fig II.2) above the oil level and away from the 'hot finger' on to which pure THC sublimes. The purified THC was transferred to different ampoules which were sealed under vacuum.

(ii) Preparation of solutions

PROCEDURE A: The preparation and storage of THC solutions presented many problems. In the initial experiments, a 100 ml flask stoppered by a rubber septum was used as a storage vessel but this method proved inadequate because once perforated, the rubber septum was a source of leaks leading to a rapid destruction of the catalyst solutions.

PROCEDURE B: The apparatus shown in Fig II.3 was designed and used for the preparation and storage of the solutions.

A weighed amount of THC was introduced under nitrogen into the apparatus which was then evacuated. TOL was then distilled under vacuum and the greaseless tap securely closed.

When the solution was required the part 'B' of the apparatus was fitted with a rubber septum and flushed with dry nitrogen. The greaseless tap was opened and an excess of solution poured in the side tube. The tap was then closed and the required volume of solution was withdrawn by syringe through the rubber septum. The excess solution in part B was rejected and not returned to the bulk.

(h) TUNGSTEN HEXACHLORIDE-ETHANOL (THC/ETOH)

After a solution of THC was prepared using the method previously described, the necessary amount of dry ETOH was added to the solution and stored in the usual manner.

(i) TUNGSTEN OXYTETRACHLORIDE (TOC)

TOC is the main impurity found in commercial THC. In order to obtain this product of good purity, a sample of non-purified THC was introduced into the apparatus described for the sublimation of THC. Using a cold finger and controlling the temperature of the oil bath between 75 and 80°C it is possible to obtain TOC of a high purity. This is due to the fact that WO_2Cl_2 reacts readily with THC to produce TOC. A method similar to the one described for THC was used for the preparation and storage of TOC solutions.

(j) ALUMINIUM TRIISOBUTYL (ATB)

The ATB solutions were prepared by a similar method to the THC solutions with the difference that the TOL was first distilled and then the required amount of ATB was injected under nitrogen through a rubber septum.

(k) ETHYL ALUMINIUM DICHLORIDE (EADC)

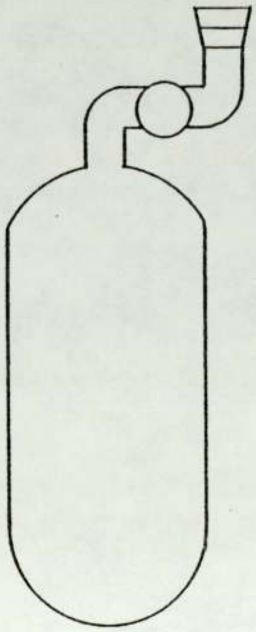
A procedure similar to that described for ATB was used for the preparation and storage of EADC solutions.

(1) STOCK SOLUTIONS

For some of the experimental techniques, stock solutions of monomer were required for the polymerisation reactions.

The preparation of these solutions assumed the use of a constant concentration in which any possible remaining impurities that escape the purification procedures were kept constant. In this way it was much easier to compare observations from the results obtained.

Fig II.4 APPARATUS USED FOR STORAGE OF STOCK SOLUTIONS



For the preparation of these solutions, a flask of the type shown in Fig II.4 was attached to the vacuum line and the necessary amounts of monomer and solvent were distilled into the apparatus. The concentration of the solutions were calculated by weighing the flask before and after each distillation.

The solutions were stored under vacuum and the required amount of solution was poured using greaseless joints and taps into the different pieces of apparatus in which the reactions were carried out.

(4) ANALYTICAL TECHNIQUES

(a) GAS LIQUID CHROMATOGRAPHY (GLC)

In gas chromatography, the components of a vaporised sample are fractionated as a consequence of partition between a mobile gaseous phase and a stationary phase held in a column. The stationary phase is a liquid, supported on an inert solid matrix, in this case gas liquid equilibria are important.

The method was used to determine the purity of the different liquid materials to be used and as a way of determining the concentrations of monomers and reactants in samples taken from the reactions under study.

When the concentrations of olefins in reactions involving tungsten compounds were required, an internal standard was generally used.

The internal standard had to be inert towards the reactions taking place as well as having retention times that made them easily identifiable from the rest of the components of the reaction mixture. The compounds chosen were cyclohexane when the olefin used was cyclopentene and methylcyclopentane when the olefin was cyclohexene. Both internal standards are alkanes that cannot take part in the reactions under study.

Two different gas liquid chromatographs were used. Conditions were chosen depending on the apparatus and columns used, two different examples are described here. The instruments used were:

(i) Perkin Elmer 456 with a flame ionisation detector fitted with a 12 ft, $\frac{1}{8}$ inch internal diameter column packed with silicone gum rubber E301 on AW-DMCS chromosorb G, 80-100 mesh colums. Before use, the columnwas initially conditioned for 12 h at 210°C with a flow of nitrogen used as carrier gas, a mixture of hydrogen and air was used to operate the detector.

The conditions for the analysis of a cyclopentene solution in toluene were: Injection temperature 150°C, detection temperature 200°C, flow rate 10 cm^3 min^{-1} and a temperature programme with initial temperature of 45°C held for 5 mins, a rate of heating of 8°C min^{-1} to a final temperature of 125°C for 15 mins.

(ii) Pye Unicam GDC Chromatograph with a flame ionisation detector fitted with a 7 ft, $\frac{1}{4}$ inch internal diameter, 2.5% silicone grease on phase prep A, 60-80 mesh column. The column was conditioned using the procedure described above.

The condition for the analysis of cyclohexene solution in toluene were: Injection temperature 130°C, detection temperature 150°C, flow rate 30 ml min^{-1} and a temperature programme with an initial temperature of 40°C held for 5 mins, a heating rate of 8°C min^{-1} to a final temperature of 120°C.

The data from the chromatograph was evaluated by cutting out the peaks and comparing the masses of the appropiate peak with the mass of the internal standard.

(b) INFRA-RED SPECTROSCOPY

Infra-red spectra of polymer samples were obtained to determine the relative proportion of cis and trans double bonds in the polymers obtained under different reaction conditions, as well as to detect the presence of cyclic structures.

The instrument used was a Perkin Elmer 237 or 457 grating infra-red spectrophotometer, provided with its own recorder.

Samples were prepared either by dissolving the polymer in chloroform and casting films on a sodium chloride cell or in the case of high concentration of oligomers that made the sample practically a high viscous liquid, by placing the required amount of material directly onto a sodium chloride cell.

(c) GEL PERMEATION CHROMATOGRAPHY (GPC)

(i) Principles

This is currently one of the most important techniques for the determination of molecular weights and molecular weights distributions of polymer samples. It is based on the diffusion of the polymer molecules into the capillary interstices of a cross-linked swollen polymer gel, which is used as a packing material in a column and which permits a particularly sharp separation into fractions of different molecular weights and therefore allows an approximate determination of the molecular size distribution curve.

When a sample consisting of a mixture of small and large molecules has been injected onto the end of the column, initially there is a concentration gradient between the mobile phase and the solvent in the pores of the beads causing diffusion of polymer into the porous beads of the polymer gel. But, the large molecules cannot penetrate the beads. A continuous flow of solvent sweeps the large molecules along more rapidly and reverses the concentration gradient for the small ones so that they diffuse out of the beads. This process is continuously carried out until eventually the sample is eluted from the column and the largest molecules are eluted before the low molecular weight material.

Under conditions of constant temperature, flow rate and concentration for the same physical system, the retention volume Vr, the volume of the solvent that must be eluted from the system between the time the sample was introduced and the time it appears in the eluent is a function only of the molecular size of the polymer molecules in solution. The eluent can be analysed continuously using either an ultra-violet detector or a differential refractometer. Calibration of the columns using well characterised polymer samples allows the elution volume (Vr) to be related directly to molecular weight.

By definition:

$$\bar{M}_n = \frac{\Sigma\ NiMi}{\Sigma\ Ni} \quad \text{and} \quad \bar{M}_w = \frac{\Sigma\ NiMi^2}{\Sigma\ NiMi}$$

where: $\bar{M}_n$ is the number average molecular weight

$\bar{M}_w$ is the weight average molecular weight

Mi is the molecular weight of a given fraction

and Ni is the number of moles in a given fraction of molecular weight Mi

If Wi is the weight of polymer of molecular weight, Mi in a given fraction, then:

$$Ni = \frac{Wi}{Mi}$$

and $\bar{M}_w$ and $\bar{M}_n$ can be written as follows:

$$\bar{M}_n = \frac{\Sigma\ Wi}{\Sigma Wi/Mi} \qquad \bar{M}_w = \frac{\Sigma WiMi}{\Sigma\ Mi}$$

The differential refractive index gives a relative measure of concentration of polymer in units of mass per unit of volume. It is then possible to substitute Wi by hi, where hi is the deflection corresponding to the refractive index of the eluent relative to that of pure solvent.

Hence:

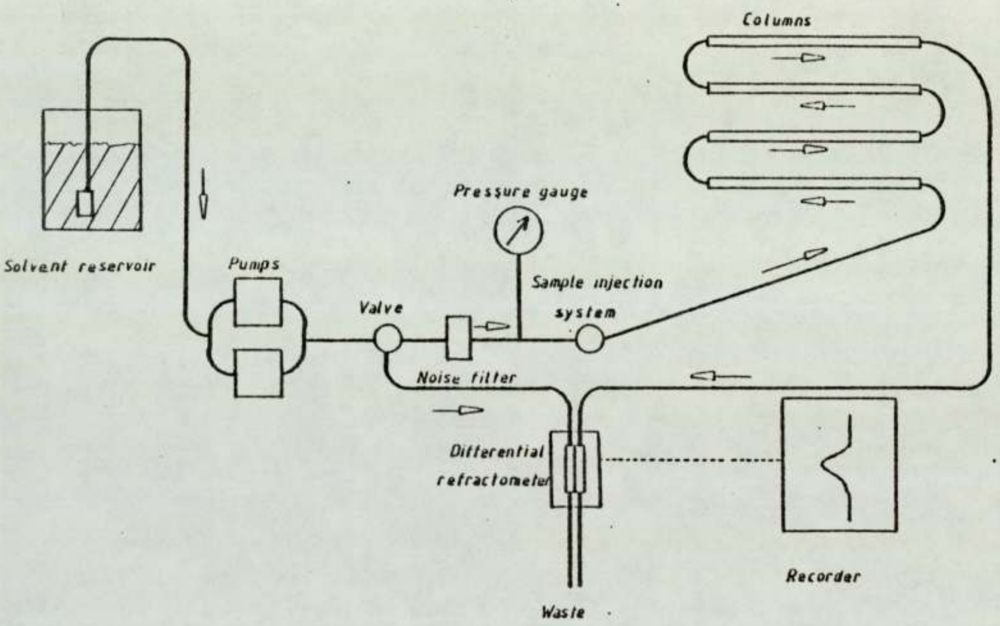
$$\bar{M}_n = \frac{\Sigma\ hi}{\Sigma\ hi/Mi} \quad \text{and} \quad \bar{M}_w = \frac{\Sigma hiMi}{\Sigma\ Mi}$$

Therefore from a typical GPC trace, it is possible to obtain all the necessary information for the calculation of molecular weights and molecular weight distributions of polymer samples, providing that a calibration curve exists for the molecular weight against elution volumes for the particular polymer under study.

(ii) Experimental

The instrument used was a Waters 6000 fitted with 4μ Styragel columns of exclusion limites of 10^2, 10^3, 10^4 and 10^5 Å. 250 μl of a solution of 0.2 g polymer in 100 cm^3 chloroform were injected with an attenuator factor of the differential refractometer of 8. A diagram of the apparatus is shown in Fig II.5. The results were recorded and analysed by means of a computer program.

Fig II.5 GEL PERMEATION CHROMATOGRAPH



(iii) CALIBRATION

The columns in the GPC instrument were calibrated in order to obtain average molecular weights of the samples. For the high molecular weight materials, samples of polystyrene of known molecular weight (M) obtained from Water Associates, USA, were injected into the system and their respective retention volumes recorded. Calibration curves of log M against elution volumes were drawn.

In order to calibrate the columns for the low molecular weight regions, samples of linear alkanes from C_6 to C_{28} were used.

This form of calibration has the problem that is not directly applicable to the polypentenamer samples. Therefore all results obtained are not actual molecular weights of polypentenamer but their related values in polystyrene terms. (The calibration curves are shown in Appendix I.)

(5) EXPERIMENTAL TECHNIQUES

(a) ULTRA—VIOLET VISIBLE SPECTROSCOPY

(i) Principles

When radiation passes through a medium, certain frequencies may be selectively absorbed. Energy is transferred to the molecules of the sample and as a result these are promoted to a higher energy or excited state.

Molecules have a limited number of discrete quantized energy levels; for absorption of radiation to occur, the energy difference between the ground state and one of the excited states of the absorbing species must match the energy of the exciting photon. Since these energy differences are unique for each species, a study of the frequencies of absorbed radiation provides a means of characterising the constituents of a sample.

The fundamental law governing the absorption of all types of electromagnetic radiations is known as the Beer-Lambert law.

$$\log \frac{Io}{I} = \varepsilon lc = A$$

where: Io is the incident intensity

I is the transmitted intensity

ε is the extinction coefficient

c is the concentration of absorbant

l is the path length

and A is the absorbance $= \log \frac{Io}{I}$

The Beer-Lambert law applies to a solution containing more than one kind of absorbing substance provided there is no interaction among the various species. Thus, for a multicomponent system:

$$\begin{aligned} A\ \mathrm{TOTAL} &= A_1 + A_2 + \quad \ldots\ldots + A_n \\ &= \varepsilon_1 lc_1 + \varepsilon_2 lc_2 + \ldots\ldots + \varepsilon_n lc_n \end{aligned}$$

where the subscripts refer to absorbing components 1, 2, ... n.

One of the applications of uv-visible spectroscopy is the elucidation of the composition of complex metal species in solution. The power of the technique lies in the fact that quantitative absorption measurements can be performed without disturbing the equilibria under consideration.

One of the most common techniques employed for studies of complexes is the 'mole ratio method'. A series of solutions are prepared in which the concentration of one of the reactants (often the metal component) is held constant while that of the other is varied. A plot of the absorbance against mole ratio of the reactants is then prepared. If the formation constant is reasonably favourable, two straight lines of different slopes are obtained; the intersection occurs at a mole ratio corresponding to the combining ratio in the complex.

(ii) Instrumentation

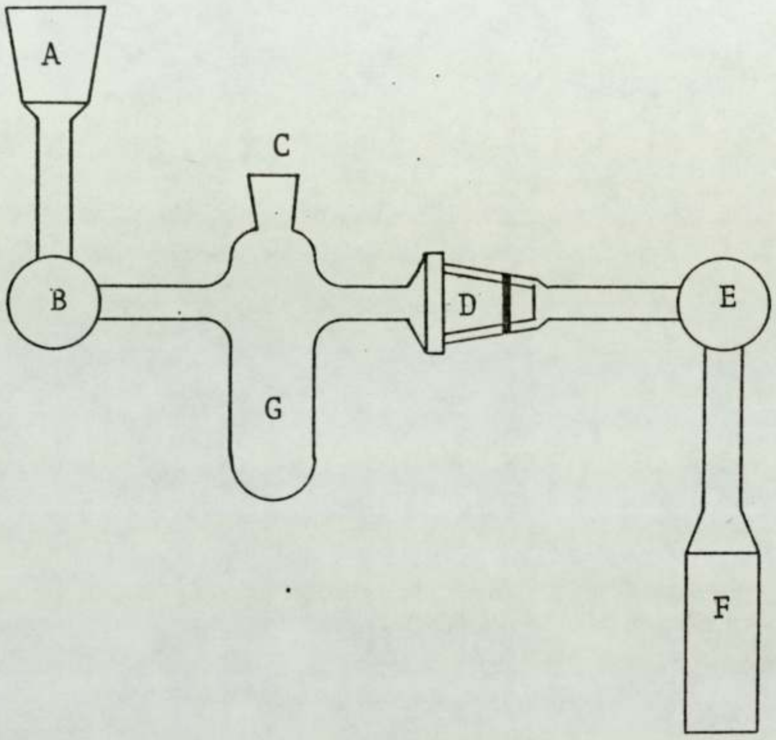
The uv visible spectra were recorded using a Unicam SP800 spectrophotometer provided with its own recorder.

(iii) Experimental

The apparatus used for the determination of the uv-visible spectral changes taking place in the reaction of THC with CP and ATB is shown in Fig II.6.

After evacuation of the system, tap (B) was closed and the required amount of THC solution was injected through the rubber septum (C), into the mixing bulb (G) and the cell (F) was filled and isolated using tap (E). The uv-visible spectrum was recorded using toluene as reference. If the experiment involved the reaction of THC with other reagents, these would have been added by injection through the rubber septum before the cell was filled.

Fig II.6 APPARATUS USED FOR UV-VISIBLE STUDIES



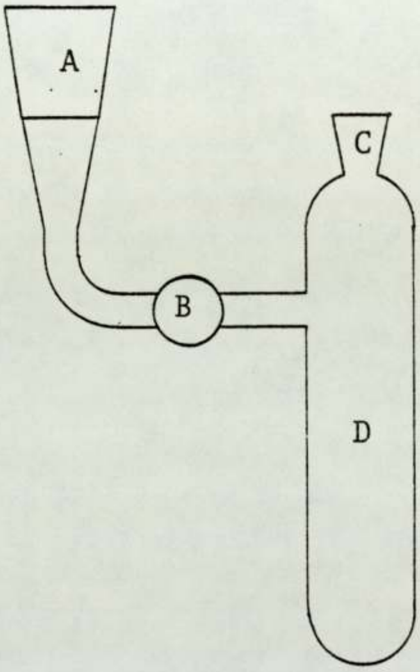
A - glass joint, B and E - greaseless taps, C - rubber septum, D - greaseless joint, F - 1 mm quartz cell, G - mixing bulb.

(b) REACTIONS BETWEEN OLEFINS AND THC

(i) Procedure A

A simple apparatus was designed for carrying out reactions between THC and CP when the concentration of THC was of the order of 10^{-2} mol dm^{-3} and molar ratios of CP:THC less than 6:1 were used. The apparatus used is shown in Fig II.7.

Fig II.7 APPARATUS USED FOR REACTIONS BETWEEN CP AND THC (PROCEDURE A)



A - glass joint, B - greaseless tap, C - rubber septum, D - reaction bulb.

A weighed amount of THC was placed into the previously weighed apparatus and the required quantity of toluene was distilled into the reaction bulb (D). The apparatus was then placed in a constant temperature bath at 25°C and after thermal equilibrium was reached, the volume of CP solution containing a known concentration of internal standard (CHA) required to produce the desired molar ratio THC:CP was injected through the rubber septum (C).

Samples were withdrawn from the reaction mixture at various times by syringe whilst the reaction vessel was continuously purged with dry nitrogen. The samples were then added to 1 ml of a dilute solution of NaOH (0.5%) and the organic phase was immediately analysed by GLC.

(ii) Procedure B

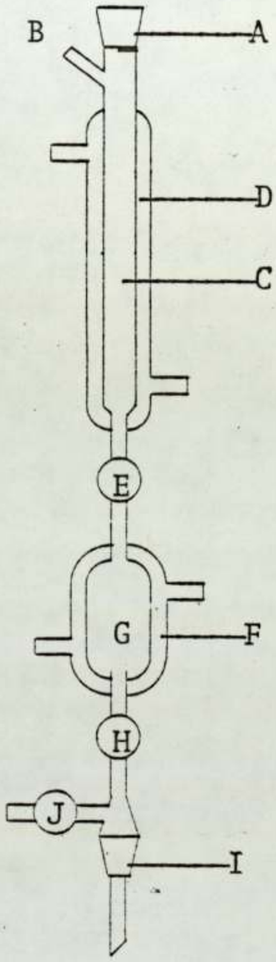
The apparatus shown in Fig II.8 was designed in order to avoid contact between the reacting solution and the rubber septum (B) which could be a source of impurities and leaks.

A flask containing THC solution was connected to the apparatus by means of greaseless joint (A). The system was evacuated through valve (J) and with taps (J), (H) and (E) then closed the required amount of THC solution was poured into the mixing bulb (C). After thermal equilibrium was achieved, the solution containing the olefin and the internal standard was added through the rubber septum (B). After mixing, the reaction mixture was immediately transferred to the reaction bulb (G) and the greaseless tap (E) securely closed. At various times, a small amount of solution was poured through tap (H) into an evacuated flask connected to glass joint (I). The solution was analysed by GLC.

When the olefin was CP, CHA was used as an internal standard, when the olefin used was CHE, MCP was chosen as the internal standard.

Fig II.8 APPARATUS USED FOR REACTIONS BETWEEN THC AND OLEFINS (PROCEDURE B)

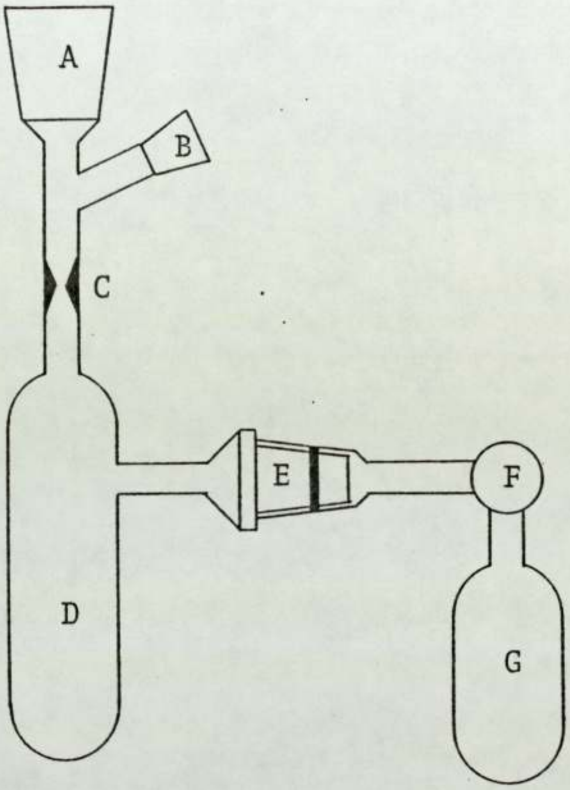
A	Greaseless joint
B	Rubber septum
C	Graduated mixing bulb
D,F	Constant temperature double jacket
E,H,J	Greaseless taps
G	Reaction bulb
I	Glass joint



(iii) Procedure C

Because evolution of HCl from the reaction between THC and CP was suspected, a reaction was carried out in the apparatus shown in Fig II.9.

Fig II.9 APPARATUS USED FOR REACTIONS BETWEEN THC AND OLEFINS (PROCEDURE C)



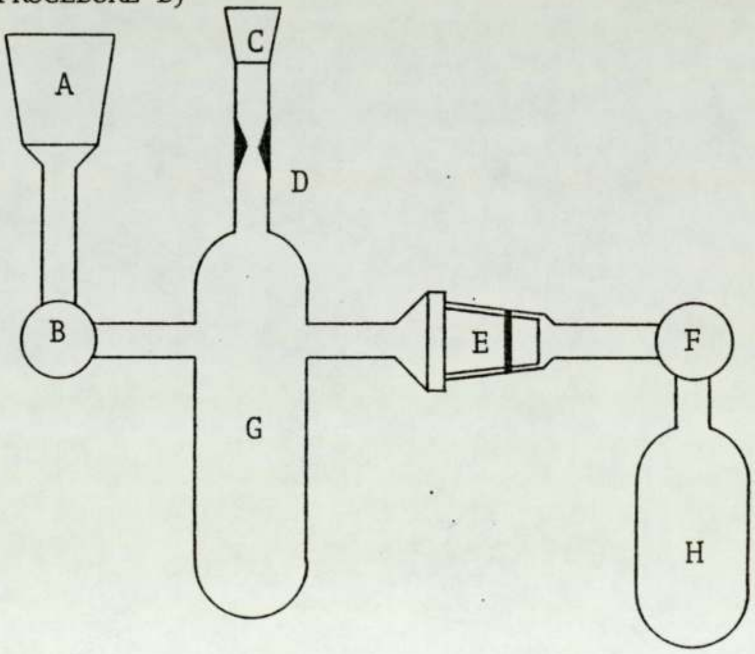
A - glass joint, B - rubber septum, C - sealing off point,
D - reaction bulb, E - greaseless joint, G - PVP bulb

For this experiment, polyvinylpyridine (PVP) cross-linked with 2% divinylbenzene was used in order to absorb the HCl produced. The required amount of PVP was placed in bulb (G) which was evacuated until a constant weight was obtained (± 0.2 mg). The bulb was connected to the rest of the apparatus through the greaseless joint (E) and a known amount of THC was introduced into the reaction flask (D). After the required amounts of toluene and CP had been distilled into the apparatus, the reaction mixture was frozen with liquid nitrogen and isolated by sealing through the sealing off point (C). Tap (F) was opened and the system was allowed to stand for a period of two days in the dark. After this period, tap (F) was closed and the two parts of the apparatus were separated. The PVP bulb was then evacuated and weighed until a constant weight was obtained. The amount of HCl absorbed by the PVP was calculated.

(iv) Procedure D

A slight variation of the system previously described was used which allowed easier analysis of the reaction mixture. The apparatus is shown in Fig II.10.

Fig II.10 APPARATUS USED FOR REACTIONS BETWEEN THC AND OLEFINS (PROCEDURE D)



A-glass joint, B,F-greaseless taps, C-rubber septum, D-sealing off point, E-greasless joint, G-reaction bulb, H-PVP bulb

THC and CP were introduced into the reaction bulb (G) as solutions in toluene, through the rubber septum (C) and sealed off through (D). After the reaction was carried out, the liquid components were distilled out and analysed by GLC. The procedure was otherwise similar to that in 'Procedure C'.

(c) DILATOMETRY

(i) Principles

Dilatometry is a technique used to measure the contraction or expansion of liquids or solids. During polymerisation, a contraction in volume normally occurs when the monomer is converted to polymer. It has been established as a very sensitive technique to measure the extent of conversion. The accuracy of the technique depends upon a number of factors:

(i) the temperature must be kept constant, usually by carrying out the experiment in a constant temperature bath, in which the dilatometer is immersed, to avoid thermal fluctuations in the meniscus,

(ii) when the polymerisation reaction is highly exothermic, the heat evolved should be controlled by means of a slower reaction, ie lower monomer and / or initiator concentration, as well as having a high heat transfer medium surrounding the system that can ensure isothermal conditions,

(iii) the capillary must be sufficiently small in diameter to enable a high sensitivity and also have a uniform diameter, and

(iv) the extent of conversion must be kept low because a highly viscous medium could prevent the movement of the meniscus.

The decrease in volume that occurs during polymerisation is associated with the difference in density of the monomer and the polymer produced. The density of the polymer should refer to its density in solution which is not necessarily that of the solid polymer. The error that arises from these density differences is small compared with other sources of error in the measurement of rates of polymerisation. The dilatometric method can be very useful for the study of polymerisation kinetics, because the volume change originates solely from the conversion of monomer molecules to monomer units in the polymer chains.

(ii) Treatment of data

In a dilatometer if the menicus moves from point A to a point B, the decrease in volume (ΔV) would be:

$$\Delta V = \pi r^2 \Delta h$$

where Δh is the distance from A to B, and r the radius of the capillary.

If m grams of monomer are completely polymerised to m grams of polymer, the volume contraction would be:

$$\Delta V = V_p - V_m$$

$$= \frac{m}{\rho_p} - \frac{m}{\rho_m} = m\left(\frac{\rho_m - \rho_p}{\rho_p\,\rho_m}\right)$$

Then $m = \Delta V\left(\frac{\rho_p\,\rho_m}{\rho_m - \rho_p}\right)$

where: V_p - volume of polymer

V_m - volume of monomer

ρ_p - density of polymer

ρ_m - density of monomer

If ΔM is the number of moles of monomer polymerised then,

$$\Delta M = \frac{m}{M_m} = \frac{\Delta V}{M_m}\left(\frac{\rho_p\,\rho_m}{\rho_m - \rho_p}\right)$$

M_m being the molecular weight of the monomer.

If the volume of the dilatometer (V) is much bigger than the total change of volume ($\Delta V << V$) then the change in concentration of monomer ($\Delta[M]$) can be written as:

$$\Delta[M] = \frac{\Delta M}{V} = \frac{\Delta V}{V}\;\frac{1}{M_m}\left(\frac{\rho_p\,\rho_m}{\rho_m - \rho_p}\right)$$

$$\Delta[M] = \frac{\pi r^2}{V M_m}\left(\frac{\rho_p\,\rho_m}{\rho_m - \rho_p}\right)\Delta h$$

where $\frac{\pi r^2}{VM_m} \left(\frac{\rho_p \ \rho_m}{\rho_m - \rho_p}\right)$ is a constant for the system under study.

So that $\Delta[M] = k\Delta h$.

The rate of polymerisation (Rp) can then be obtained from a plot of Δh as a function of time since:

$$Rp = -\frac{d[M]}{dt}$$

so that Rp is proportional to $\frac{\Delta h}{\Delta t}$.

(iii) Experimental

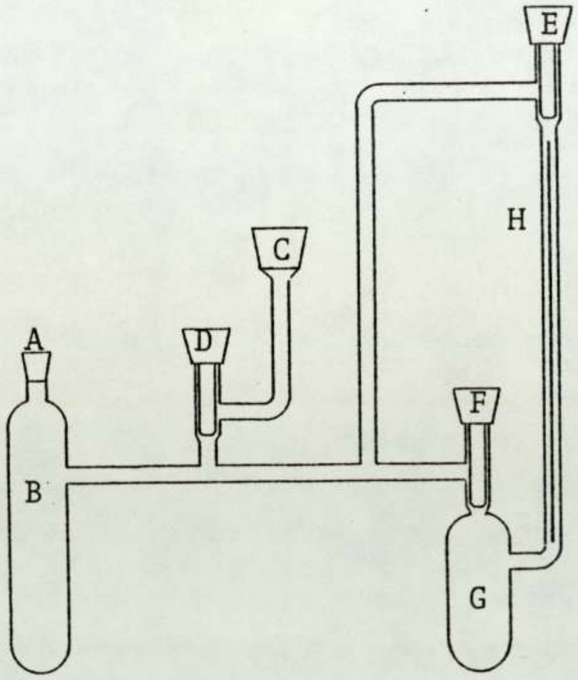
Two different dilatometers were used to observe the decrease in volume during the polymerisation of monomers in solution. The main difference between them being the way in which the solution to be polymerised was introduced into the dilatometer.

DILATOMETER A

The apparatus used is shown in Fig II.11.

The required amounts of CP and toluene were distilled into the graduated mixing bulb (B) and after reaching thermal equilibrium in the constant temperature bath at 25°C, calculated volumes of THC and ATB solutions were injected through the rubber septum (A). After mixing, the solution was transferred to the polymerisation

Fig II.11 DILATOMETER A



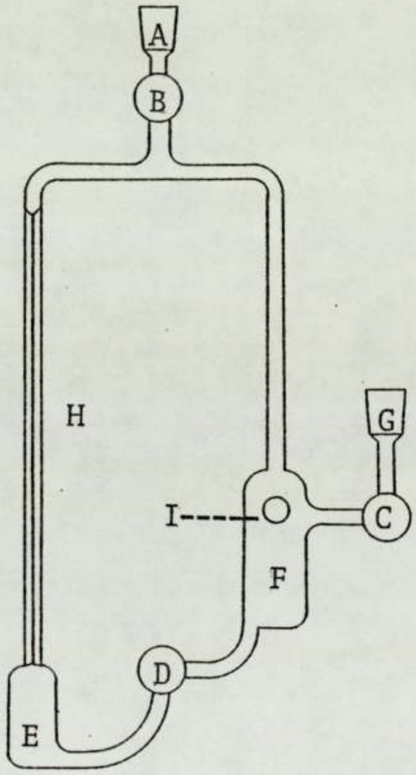
A - rubber septum, B - graduated mixing bulb, C - glass joint,
D,E,F - greaseless taps, G - polymerisation bulb, H - capillary tube

bulb (G), isolated from the rest of the system by means of greaseless taps (E) and (F), replaced in the bath and the decrease in the height of the meniscus of the capillary tube (H) was followed using a cathetometer.

DILATOMETER B

The difference between this system and the one previously described resides in the possibility of pouring the monomer solution instead of the series of distillations required in the first method. Another advantage was that the bulb in which the polymerisation took place was filled from the bottom, making it easier and quicker to complete that part of the procedure, a factor that enabled readings to be taken within two or three minutes of the injection of the catalysts. Otherwise the procedure was identical to the one described for Dilatometer 'A'. The apparatus used is shown in Fig II.12.

Fig II.12 DILATOMETER B



A - glass joint, B,C,D - greaseless taps, E - polymerisation bulb, F - graduated mixing bulb, G - greaseless joint, H - capillary tube, I - rubber septum

In some cases, after the polymerisation had apparently ended, (ie

$\Delta h / \Delta t = 0$), additional amounts of catalysts were added. The polymerisation solution was taken back to the mixing bulb, the catalysts injected and the procedure repeated.

(d) CALORIMETRY

(i) Principles

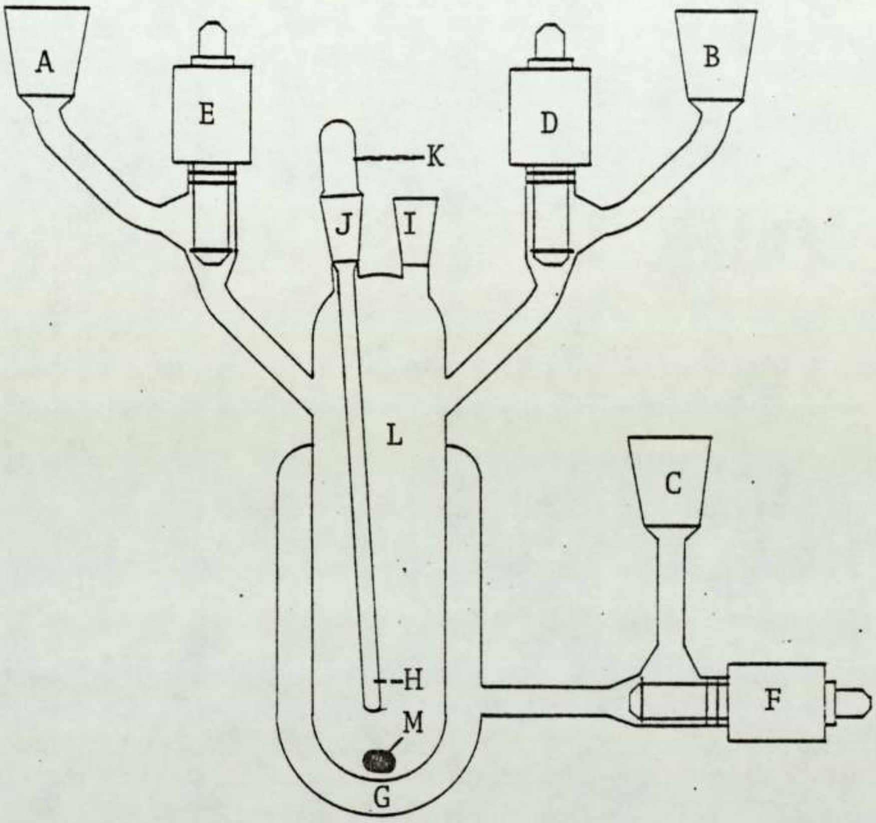
The polymerisation of cyclopentene to produce polypentenamer is exothermic with a $\Delta H \simeq -4.4$ Kcal mol^{-1}(124). Therefore a system capable of measuring the change in temperature while the reaction is taking place in adiabatic conditions could be used to measure rates of reaction for the system under study.

(ii) Apparatus and instrument

A modification of the techniques described originally by Biddulph and Plesch(131) was used. The calorimeter is shown in Fig II.13.

The thermistor used was of 2 K Ω(GL23, RS Components Limited), and was connected to a Knauer auto-potentiometer bridge adapted with a Servoscribe IS recorder.

Fig II.13 CALORIMETER



A, C - glass joints, B, J - greaseless joints, E,D,F - greaseless taps, G - double jacket, H -thermistor, I - rubber septum, K - glass prove and leads, L - reaction flask, M - magnetic follower

(iii) Experimental

NORMAL POLYMERISATION

A flask containing a stock solution was connected to the calorimeter through joint (B). The system was evacuated through (A), tap (E) closed and the required amount of monomer solution

(18 ml) poured into the reaction flask (L). Tap (D) was then closed and the double jacket (G) evacuated through (C) and (F). The apparatus was then placed on a magnetic stirrer and the thermistor connected to the balancing bridge. When a stable base line was obtained, the required amount of catalyst and cocatalyst were injected through the rubber septum (I) and the change in temperature was automatically recorded as a function of time.

If subsequent additions of monomer solution were needed, the flask containing stock solution was left attached to the apparatus and when required monomer solution was added by opening the greaseless taps separating the stock solution from the polymerisation mixture. If more catalyst was needed, it was injected directly through the rubber septum (I).

POLYMERISATIONS USING OXYGEN

In some experiments different amounts of oxygen were added at different stages of the reaction. For these experiments the apparatus shown in Fig II.14 was used in addition of the system already described.

The internal volume of the oxygen bulb was calculated by weighing the apparatus with and without water. The calorimeter was filled in the usual way and was connected to the vacuum line through the oxygen apparatus. After evacuation, tap (D) was closed and a mercury manometer and a dry oxygen supply were connected to the

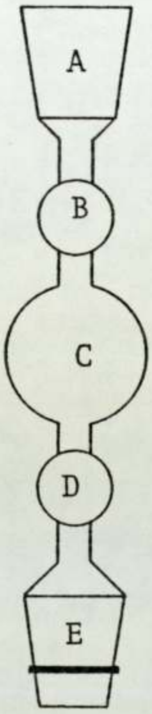
Fig II.14 APPARATUS USED FOR OXYGEN ADDITION

A - glass joint

B,D - greaseless taps

C - calibrated oxygen bulb

E - greaseless joint



manifold. The required pressure of oxygen was allowed into the system and tap (B) was closed. In this way, the oxygen needed was stored in the calibrated part (C) of the oxygen flask.

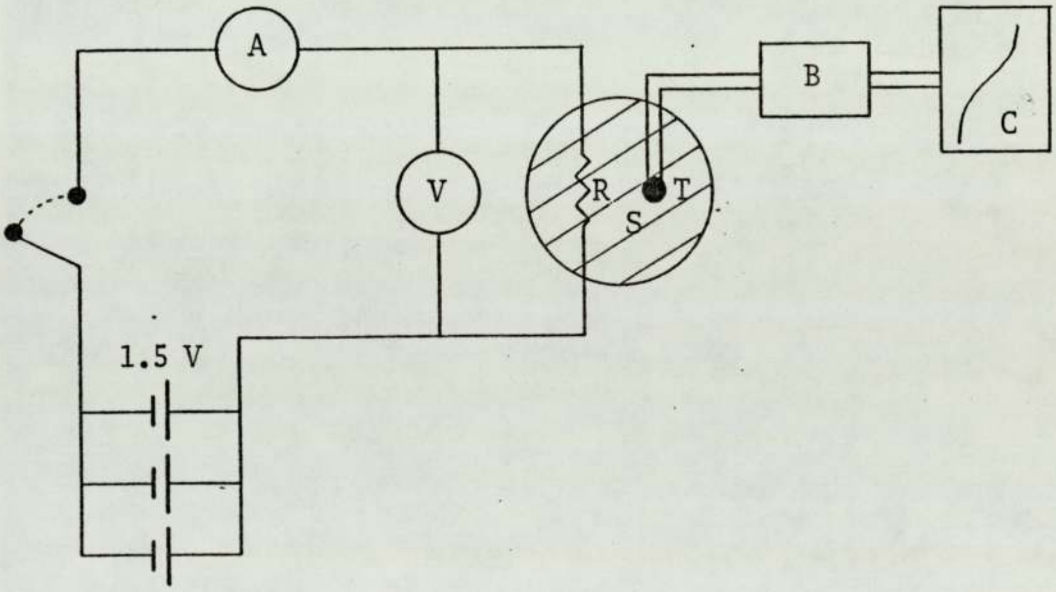
Oxygen could be allowed into contact with the solution by opening the two greaseless taps separating the oxygen bulb from the polymerisation mixture.

In all cases, the number of moles of oxygen used was calculated using the law for ideal gases. The errors introduced this way were considered to be within normal experimental error.

(iv) Calibration

In order to calibrate the calorimeter, a known amount of energy had to be introduced into the system and the deflection caused in the measuring system calculated. A very simple circuit illustrated in Fig II.15 was employed.

Fig II.15 CALIBRATION SYSTEM FOR THE CALORIMETER



A - ammeter, V - volt meter, R - 1Ω resistance, T - thermistor
S - monomer solution, B - balancing bridge, C - recorder

The voltage and current across the system were measured by two digital multimeters (Solatron 704S) with internal resistance for the ammeter of 0.1 Ω and for the volt meter of 1 M Ω. The multimeters were calibrated with a Weston standard cell.

The heating resistance was immersed in the monomer solution, the power supply switched on and the voltage and current were registered against time. The change in temperature was recorded simultaneously by means of the thermistor balancing bridge recorder system. After switching the power off, the amount of energy introduced could be calculated by the equation:

$$Q = \int_0^t VIdt \simeq \Delta t \, \Sigma \, Vi \, Ii$$

where: Q is the energy dissipated as heat by the resistance

Δt is the time between readings in seconds

Vi is the voltage reading in volts

and Ii is the current intensity reading in amps

The amount of heat necessary to produce a full scale deflection on the recorder chart could be calculated for a given system.

No corrections were made for the change of heat capacity of the system during the polymerisation. In the calcuations it was considered that the heat capacity was that of the monomer solution-calorimeter system.

(e) MOLECULAR WEIGHT STUDIES

(i) Procedure A

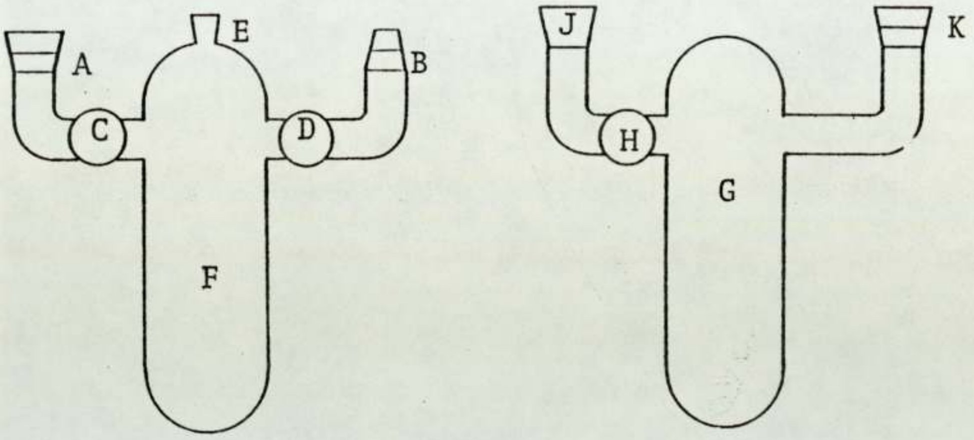
A 150 ml flask fitted with a rubber septum and a greaseless tap was used as a reaction vessel. The required amounts of CP and toluene were distilled into the flask and the THC and ATB solutions were then added through the rubber septum with predetermined intervals between additions. The flask was filled with dry nitrogen and samples taken out at various reaction times. The problems involved with this method were that once the rubber septum had been perforated, it became a source of leaks for moisture and secondly that the solutions became too viscous making it impossible to syringe them out.

(ii) Procedure B

The pieces of apparatus described in Fig II.16 were used in this procedure.

The reaction vessel (F) was connected to the stock solution container via the greaseless joint (B) and the system evacuated. Tap (C) was then closed and the required amount of monomer solution poured into the reaction vessel. Tap (D) closed and the THC and ATB solutions injected through the rubber septum (E).

Fig II.16 APPARATUS USED FOR OBTAINING SAMPLES FOR M_W DETERMINATION STUDIES



A,B,K - greaseless joints, C,D,H - greaseless taps, E - rubber septum, F - reaction flask, G - collecting flask, J - glass joint

Samples could be taken at different stages of the reaction. The collecting flask (G) was connected to the reaction flask (F) via the greaseless joints (B) and (K) and evaculated through (H) and (J). When a good vacuum was obtained, tap (H) was closed and the whole apparatus removed from the vacuum line. A sample of solution was taken through tap (D). In order to quench the reaction, wet chloroform was introduced. The solvent and remaining monomer were steam distilled. The polymer sample was then dried under vacuum and stored in sealed ampoules in the refrigerator until solutions were prepared.

Analysis of the polymer samples were carried out by gel permeation chromatography (GPC).

CHAPTER III

KINETIC STUDIES

(1) DILATOMETRY

(a) INTRODUCTION

The kinetic treatment proposed by Amass and Tuck$^{(25)}$ suggested that the initial rate of the polymerisation of CP initiated by the system THC / 2 ATB depended on the time allowed for the THC to react with the CP (ageing time) before the addition of the ATB solution. It was shown that at a given set of conditions, CP and THC constant, the rate of polymerisation showed a maximum as the ageing time was increased, this time was defined as t_{max}. The authors derived an expression for t_{max} that shows a reciprocal relation for t_{max} on the concentration of CP and independence on the THC concentration. However, studies on the effect of the concentration of THC on t_{max} have not been carried out.

The first objective of this project was to check this assumption using the techniques developed by Tuck$^{(132)}$.

(b) EFFECT OF TUNGSTEN HEXACHLORIDE CONCENTRATION ON t_{max}

Amass and Tuck reported that for a CP concentration of 1.97 mol dm^{-3} and a THC concentration of 3×10^{-4} mol dm^{-3}, the rate of polymerisation reached a maximum when the ageing time of THC to CP was 2 mins. The initial experiments were carried out using the same CP concentration but changing the THC concentration to 1.0×10^{-3} mol dm^{-3}.

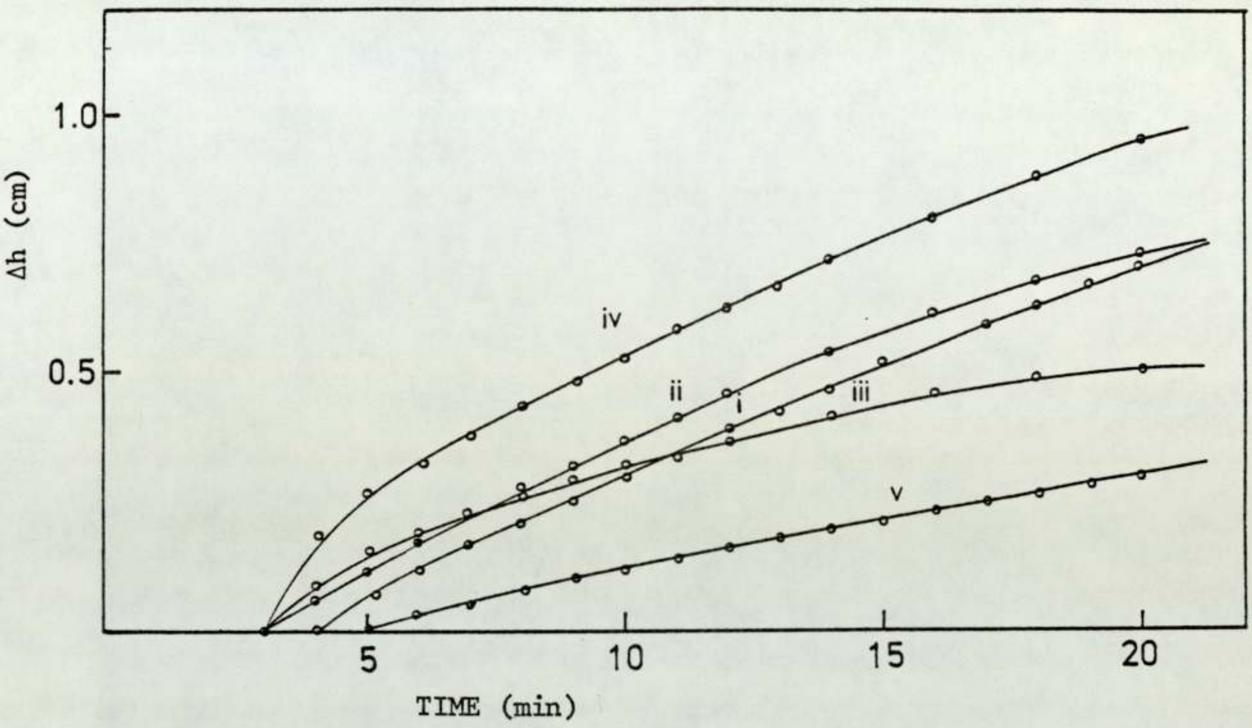
The technique used by Tuck involved the use of a dilatometer similar to that described in Section II,5,c,iii. dilatometer A, and the catalyst solutions were stored in a flask stoppered by a rubber septum. Using these techniques, 5 different polymerisations were carried out with a series of ageing times; the dilatometer curves are shown in Fig III.1. It can be seen that they did not show any particular trend and did not have any relation with any previous observations.

Because of the number of manipulations that had to be performed it took a minimum of 3 mins to fill the dilatometer and readings could only be taken 5 mins after the initiation when thermal equilibrium had been achieved. It was apparent that a rapid polymerisation was taking place immediately after addition of ATB while the dilatometer was being filled because the viscosity of the system increased. It was therefore concluded that the measurements made at an advanced stage of the reaction did not necessarily correspond to the behaviour of the system in the initial period, and any rates of polymerisation quoted are meaningless.

It was considered that to obtain meaningful results, it was necessary to reduce the rate of polymerisation by decreasing the concentrations of monomer and / or catalyst.

For this series of experiments, two different concentrations of THC were used ([THC] = 8×10^{-4} and 5×10^{-4} mol dm^{-3}) at a constant CP concentration ([CP] = 1.75 mol dm^{-3}). Every experiment was

Fig III.1 DILATOMETRIC CURVES FOR THE POLYMERISATION OF CP

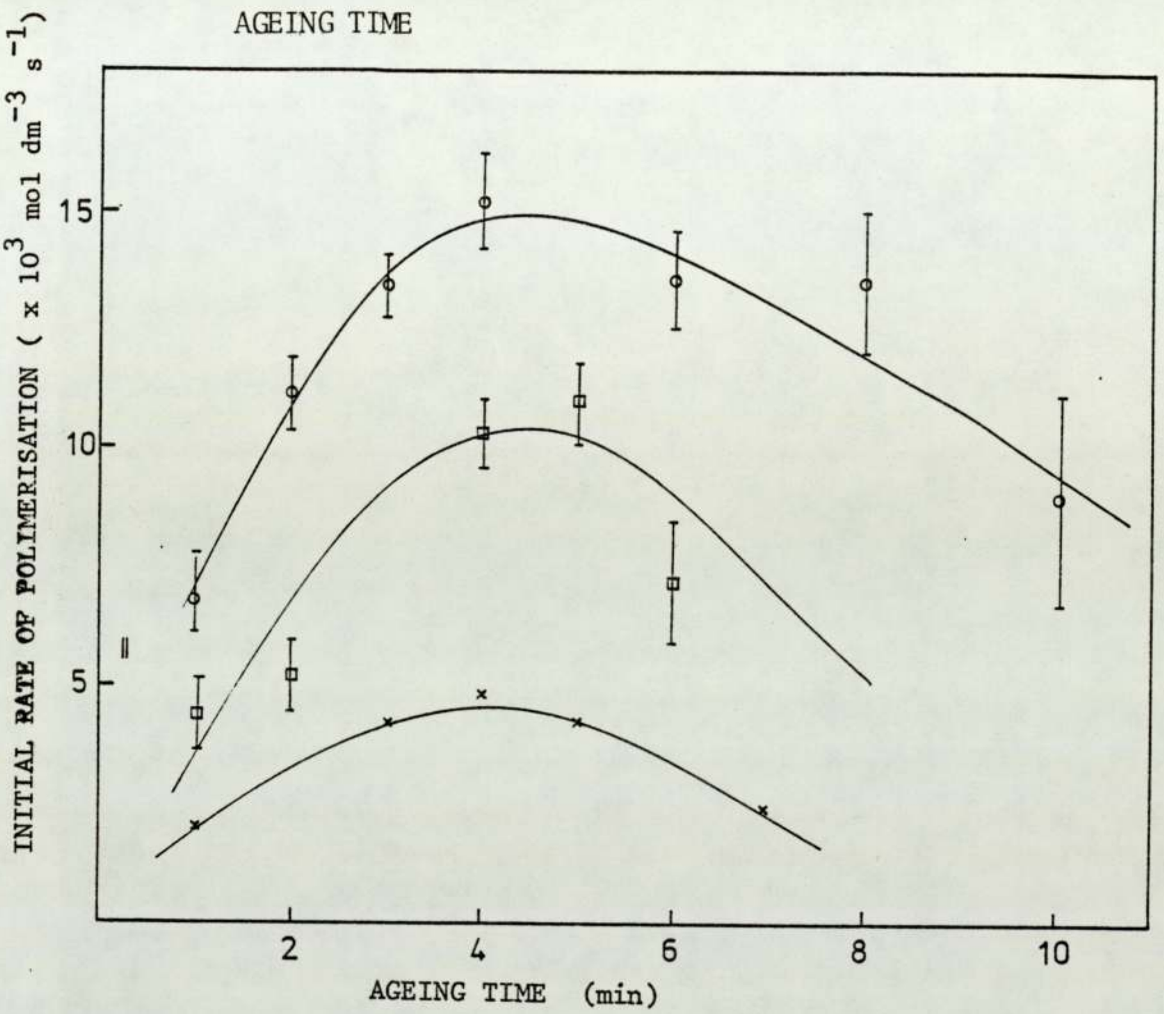


([CP] = 1.93, [THC] = 9.65 x 10^{-4}, [ATB] = 1.93 x 10^{-3} mol dm^{-3}; ageing times (mins): i = 1, ii = 2, iii = 3, iv = 4, v = 5)

repeated a minimum of 3 times, the results showing the deviations from the average and including Amass and Tuck(25) results for this CP concentrations are shown in Fig III.2.

The results obtained in this way showed good agreement with those obtained by Amass and Tuck(25) and tend to confirm the kinetic treatment suggested. However, there was a relatively large irreproducibility within a series of polymerisations carried out under apparently identical conditions and some of the results were well outside the range quoted. There may be many causes for the irreproducibility of the system:

Fig III.2 DEPENDENCE OF INITIAL RATES OF POLYMERISATION ON AGEING TIME



([CP] = 1.75 mol dm^{-3}, [THC] = ○ 8 x 10^{-4}, □ 5 x 10^{-4}, × 2.5 x 10^{-4} mol dm^{-3}; × is taken from Amass and Tuck(25).

(i) The practical impossibility of maintaining a constant concentration of impurities.

(ii) Successive distillations were needed in order to obtain the exact monomer concentration required for the experiment and thus increased the likelihood of introducing impurities into the system.

(iii) The purity of the THC used varied from batch to batch.

(iv) The method of storage of the catalyst solutions (a flask stoppered by a rubber septum) was a continuous source of leaks for water and oxygen and catalyst solutions rapidly decomposed.

(v) The system of filling the bulb in which the reaction was to take place did not allow a constant time for the manipulations required and subsequently the first readings were not made at exactly the same time.

In an attempt to improve the reproducibility of this series of experiments, the following procedures were adopted:

(i) THC was purified by the technique described in Section II,3,g,i.

(ii) The solutions of catalyst were stored as described in the procedure B in Section II,3,g,ii.

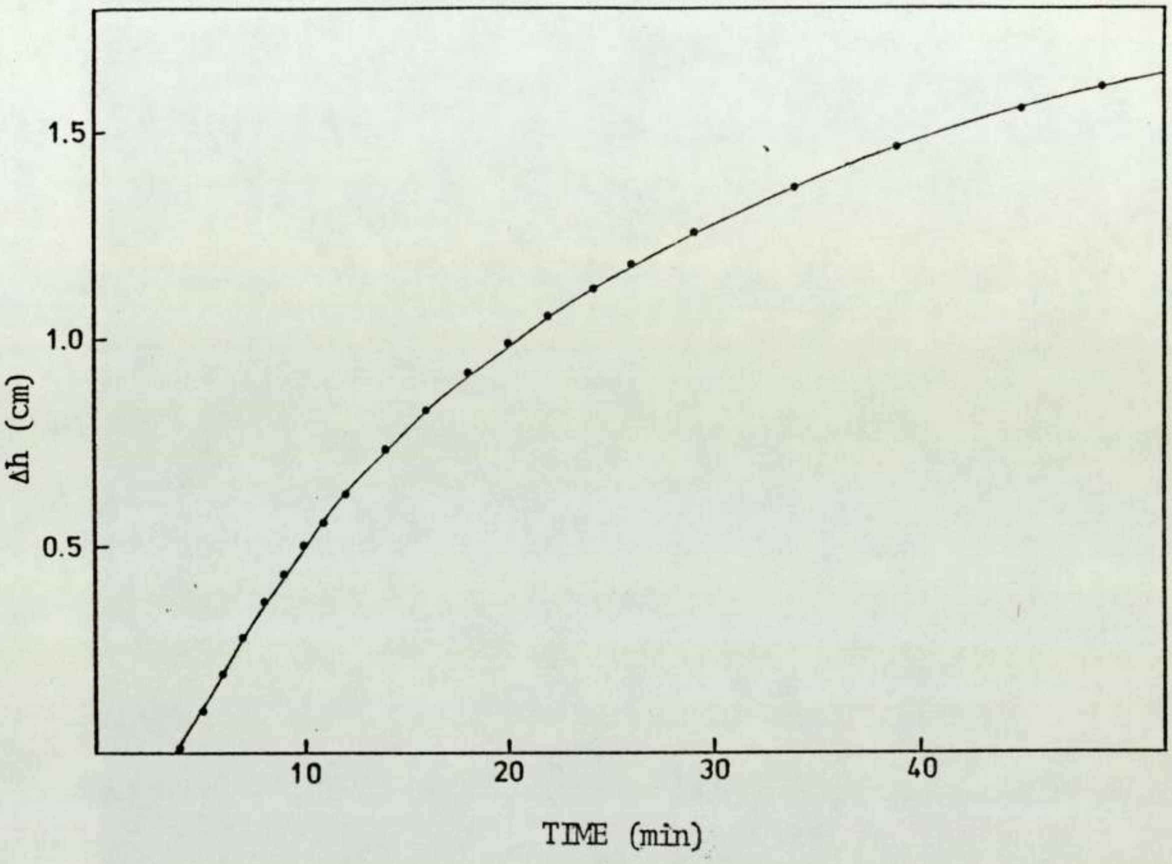
(iii) The rate of polymerisation was measured using dilatometer B described in Section II,5,c,iii.

(iv) The monomer was stored and used as a stock solution.

A typical dilatometric curve using the improved technique is shown in Fig III.3. The curve is readily extrapolated to zero conversion and the initial rate of polymerisation can be estimated.

Fig III.4 shows the dependence of the initial rate of polymerisation on ageing time of THC and CP at constant CP concentrations and at different concentrations of THC. The reproducibility of the system was greatly increased and the results tend to confirm the

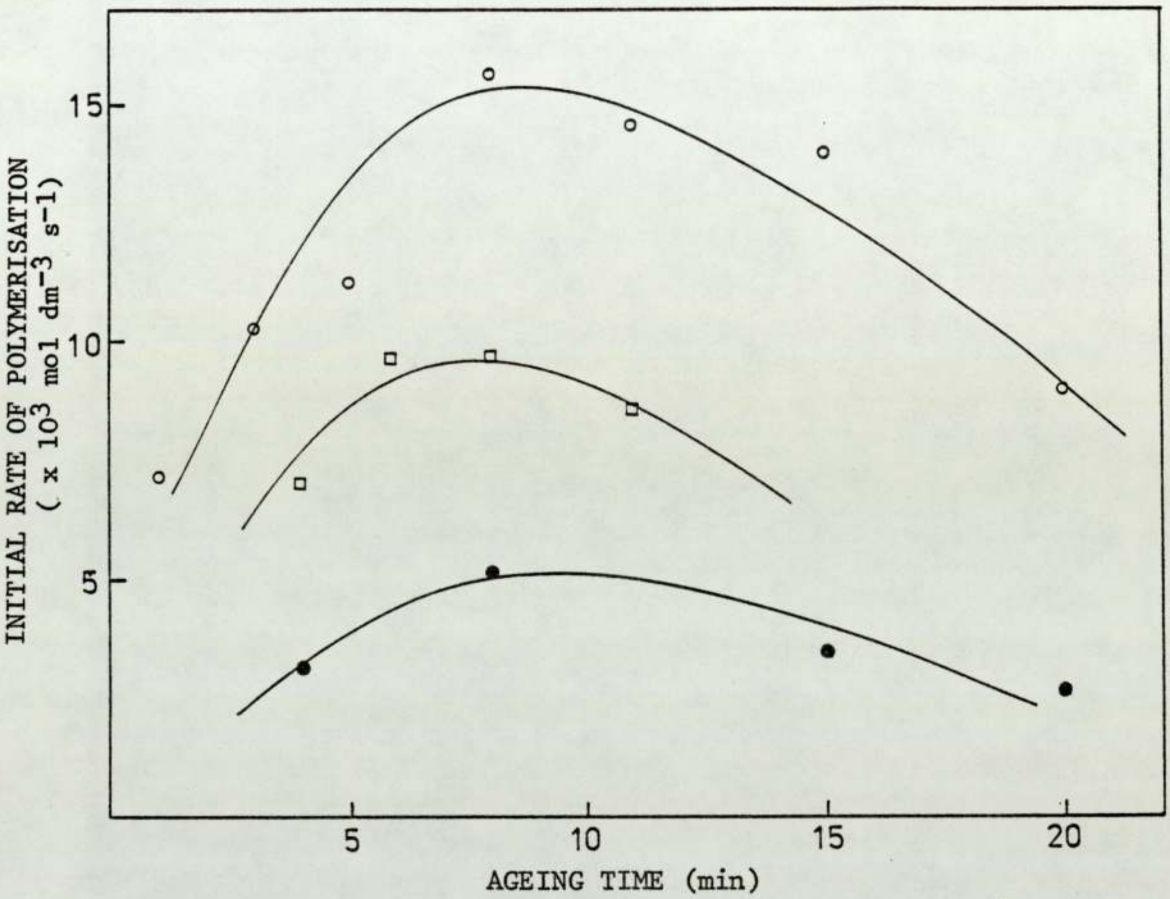
Fig III.3 TYPICAL DILATOMETRIC CURVE



([CP] = 1.82,[THC] = 2×10^{-5} mol dm^{-3}; ageing time = 2 mins)

kinetic mechanism proposed by Amass and Tuck, ie at a given CP concentration, t_{max} is independent of the initial concentration of THC.

Fig III.4 DEPENDENCE OF INITIAL RATES OF POLYMERISATION ON AGEING TIME



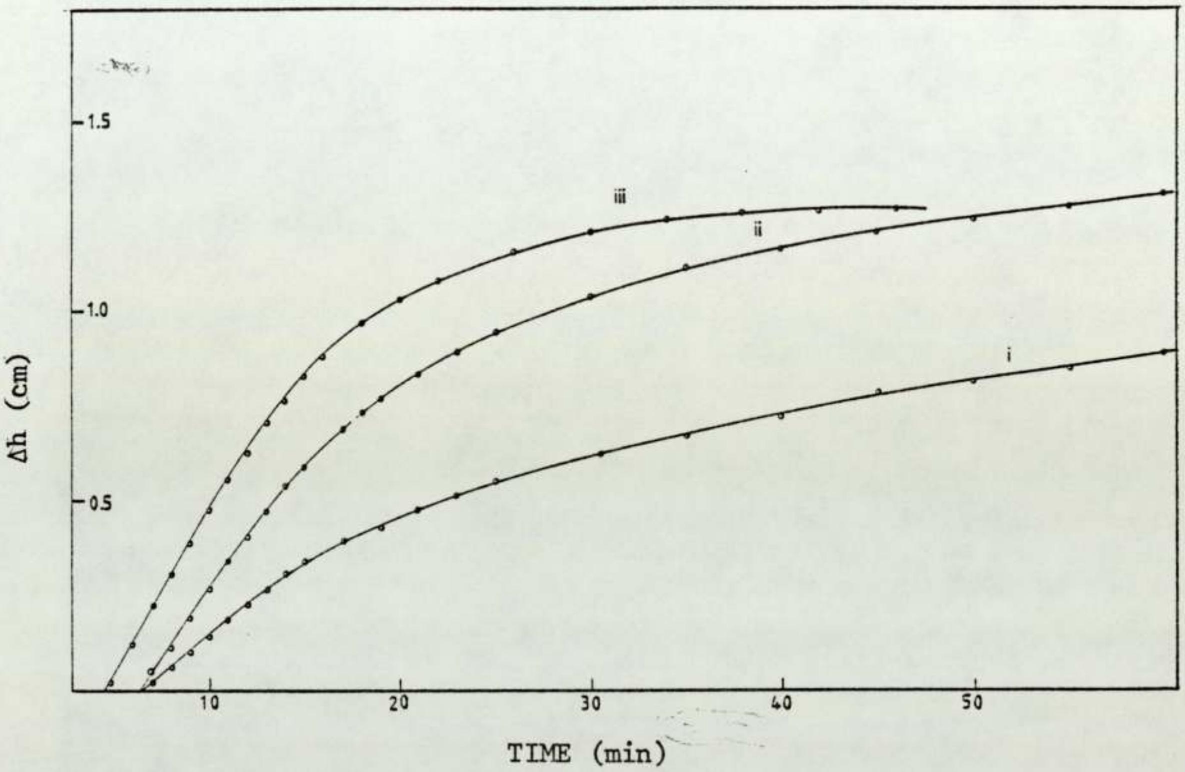
([CP] = 1.12 mol dm^{-3}, [THC] = ○ 11.2 x 10^{-4}, □ 7.5 x 10^{-4}, ● 4.5 x 10^{-4} mol dm^{-3})

(c) STUDIES OF THE DILATOMETRIC CURVES

Fig III.5 shows a series of polymerisation curves which are typical of many obtained in the previous section.

An inspection of these curves shows that in general there is a decrease in the rate of polymerisation with conversion which is greater than can be accounted for by the consumption of monomer

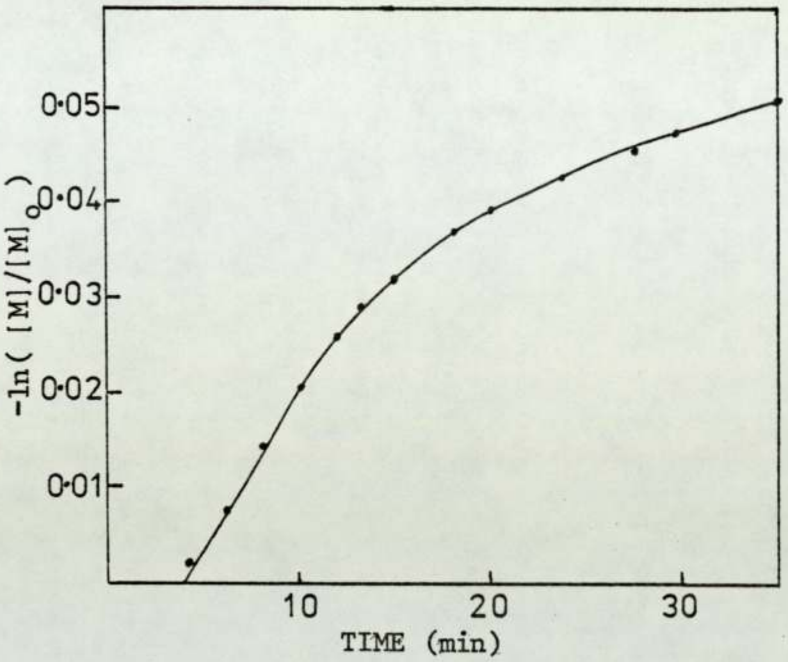
Fig III.5 DEPENDENCE OF CONVERSION TIME CURVES ON INITIAL CONCENTRATION OF ACTIVE SPECIES



([CP] = 1.3 mol dm^{-3}, [THC] = 4 x 10^{-4}, T = 25^{o}C, ageing times:
i = 2 mins, ii = 6 mins, iii = 4 mins)

alone that in general was less than 15%. Fig III.6 shows the decrease in the logarithm of the monomer concentration with time for a particular polymerisation. This plot should have been linear if the concentration of the active species remained constant during the polymerisation. It was considered that this deviation from linearity can only be accounted for by the destruction of the catalyst during the polymerisation process or by the removal of catalyst by non-productive reactions.

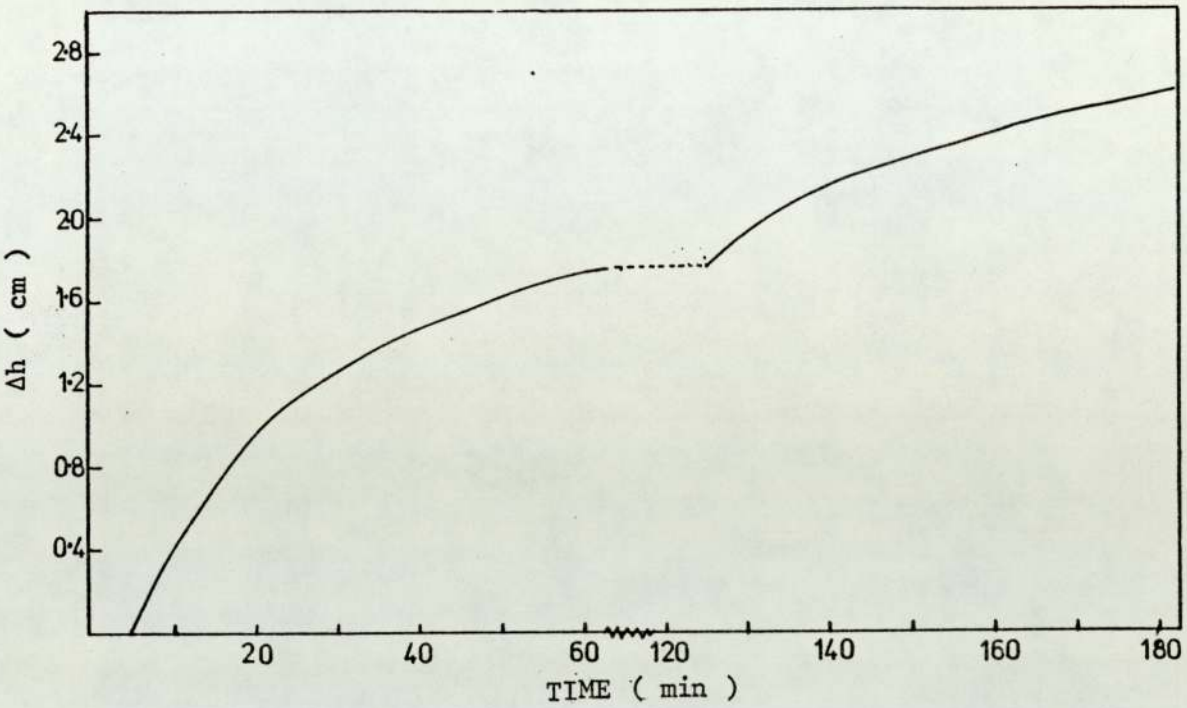
Fig III.6 DEPENDENCE OF LOG [CP] UPON REACTION TIME



All the polymerisations reached a stage in which there was no change in the volume of the system. At this stage, two possibilities existed: (i) the reaction had reached the monomer-polymer equilibrium while still possessing a 'living catalyst' or (ii) the catalyst was rendered inactive before the reaction reached the monomer-polymer equilibrium.

To distinguish between these two possibilities, two experiments were carried out on solutions which had reached this state of zero rate. To one system fresh CP solution was added and to the other, further aliquots of catalyst solution were added. After each experiment the resulting change in volume was monitored. Addition of fresh CP solution did not produce any subsequent change in the volume of the system with time. The addition of a new aliquot of catalyst however produced further polymerisation as shown in Fig III.7.

Fig III.7 EFFECT OF SEPARATE ADDITIONS OF CATALYST ON THE POLYMERISATION OF CP



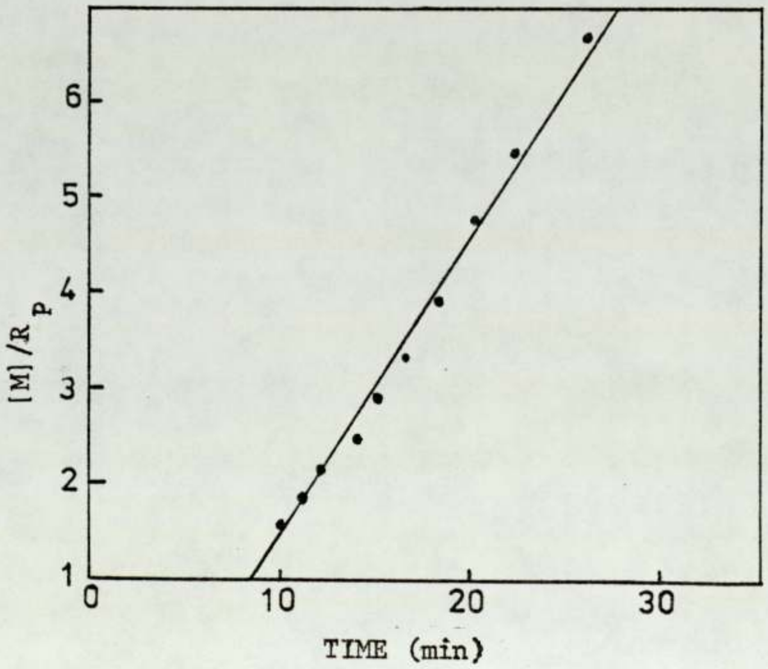
([CP] = 1.82, [THC] = 2 x 10^{-5}, [ATB] = 4 x 10^{-5} mol dm^{-3}, ageing time = 2.5 mins, after second addition [THC] = 4 x 10^{-5}, [ATB] = 8 x 10^{-5} mol dm^{-3})

It would appear reasonable to assume that the polymerisation of CP initiated by THC / 2ATB has associated with it a termination reaction.

The nature of this termination may be gauged from the manner in which the rate of polymerisation decays with time. The kinetics of the termination in all polymerisations studied do not follow a simple first order decay, whereas some polymerisations exhibit a second order decay of the rate of polymerisation. If the rate of polymerisation is proportional to the concentration of propagating species, then a plot of [CP] / Rp against time should be linear if the decay is second order in the concentration of propagating species. Such a plot is shown in Fig III.8.

It is reasonable to assume that the linear tendencies would indicate that a termination reaction that is second order in active species could take place in this metathesis system. However, an inspection of other polymerisation curves would not fit perfectly a simple second order decay of the rate of polymerisation. From an inspection of the curves shown in Fig III.5 it would appear that the greater the initial rate of polymerisation, the faster is the decay of the rate of polymerisation.

Fig III.8 DEPENDENCE OF [CP] / Rp UPON REACTION TIME



(2) CALORIMETRY

(a) INTRODUCTION

Calorimetry was used as a way of measuring rates of reaction for the polymerisation of CP. This system was used because it had the following advantages over dilatometry:

(i) measurements could be taken continuously in a fully automatic manner,

(ii) the rates could be measured immediately after the addition of the catalyst components, and

(iii) when any changes were introduced into the system, their effects could be monitored immediately.

Unfortunately the system also has the following disadvantages that have to be taken into account when any results are analysed:

(i) the experimental impossibility of achieving a completely adiabatic system,

(ii) the heat capacity of the reaction mixture changes with reaction time,

(iii) the temperature is not constant during the reaction. This has the opposite effect of increasing the rate of reaction and increasing the base line shift because of increased difference in temperature between the reaction and the surrounding medium,

(iv) the rate measured would be the consumption of monomer and not the rate of polymerisation that might include the conversion of oligomers to polymer and

(v) because the viscosity of the system increases with reaction time, the efficiency of the stirrer decreases and enhances the possibility of the formation of 'hot' and 'cold' spots in the system.

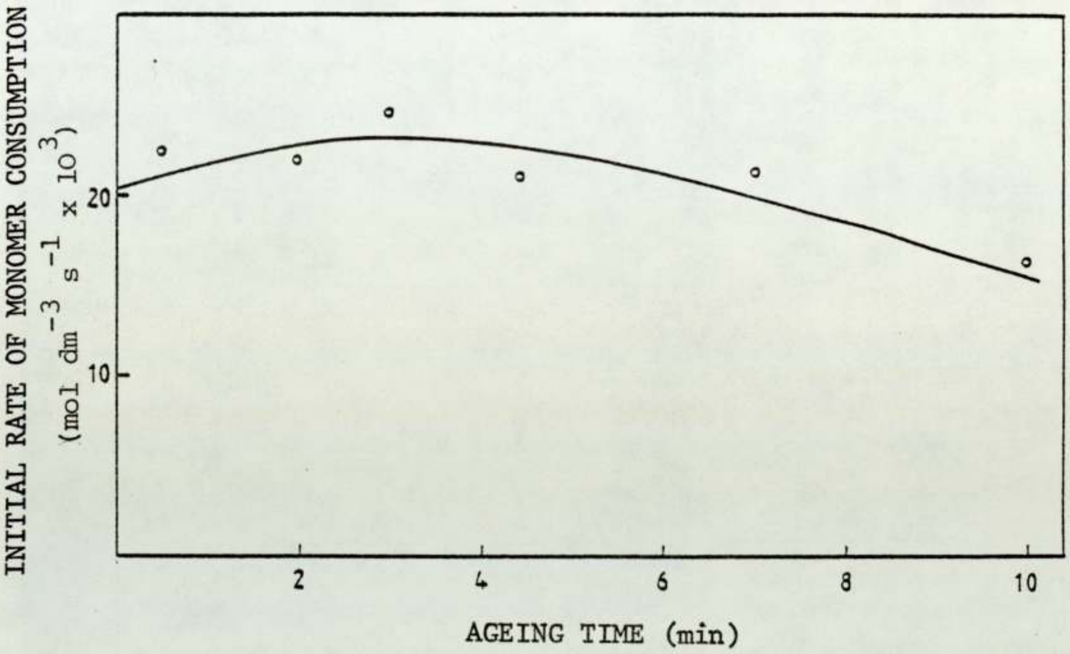
Although the system has some limitations, very valuable information can be obtained by the use of this technique. In general, the problems are minimised if only the data during the initial stages of the reaction is used. When results at high conversions are considered, special attention should be given to the different factors that can affect the results.

(b) EFFECT OF AGEING TIME ON THE INITIAL RATE OF MONOMER CONSUMPTION

The first series of experiments carried out using this technique were designed to test the reproducibility of the system and compare the effect of ageing of THC with CP and the initial rate of monomer consumption. Under a given set of conditions, a particular experiment was repeated three times and the measured rates of consumption of monomer, were within an error of 5%, which was considered accurate enough for the purpose of this study.

Fig III.9 shows the effect of ageing time on the initial rate of monomer consumption. Although there is some change, the variation is not of the same magnitude as for the polymerisations

Fig III.9 DEPENDENCE OF THE INITIAL RATE OF MONOMER CONSUMPTION ON AGEING TIME



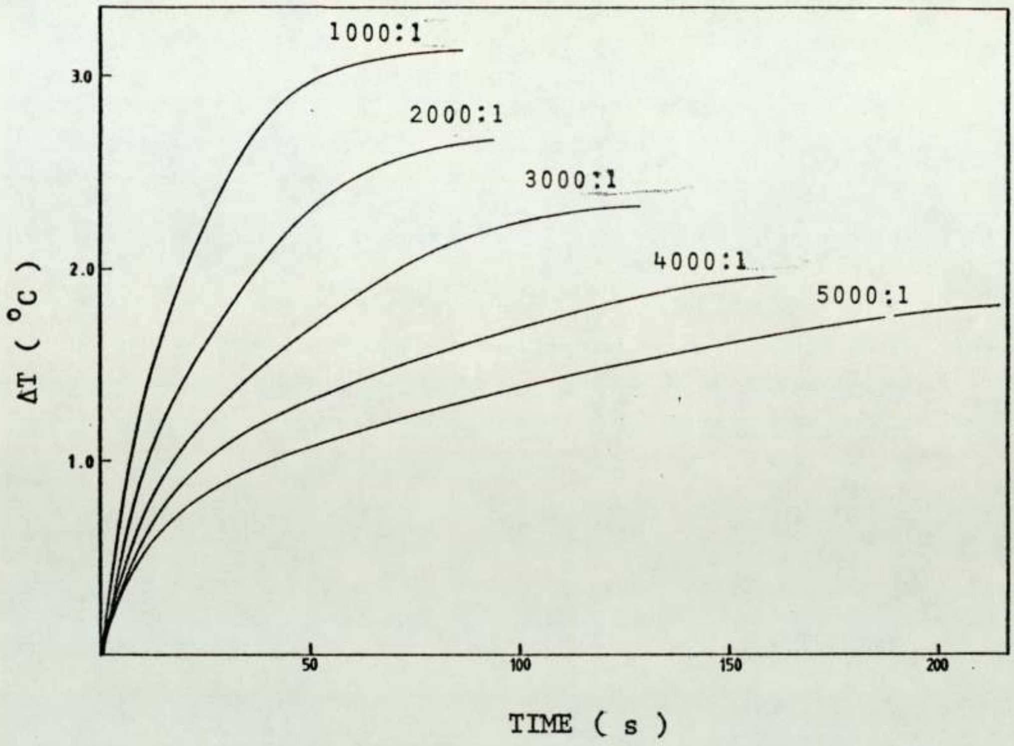
([CP] = 1.9, [THC] = 7×10^{-4}, [ATB] = 1.4×10^{-3} mol dm^{-3})

followed by dilatometry. This difference in behaviour can be correlated with the production of low molecular weight oligomers that will be expanded further in a later section.

(c) EFFECT OF TUNGSTEN HEXACHLORIDE CONCENTRATION

Polymerisations were carried out at constant CP concentration with an ageing time of 2 mins betwen CP and THC. Fig III.10 shows the calorimetric curves for a CP concentration of 2.05 mol dm^{-3} with an ageing time of 2 mins for 5 different concentrations of THC.

Fig III.10 CALORIMETRIC POLYMERISATION CURVES



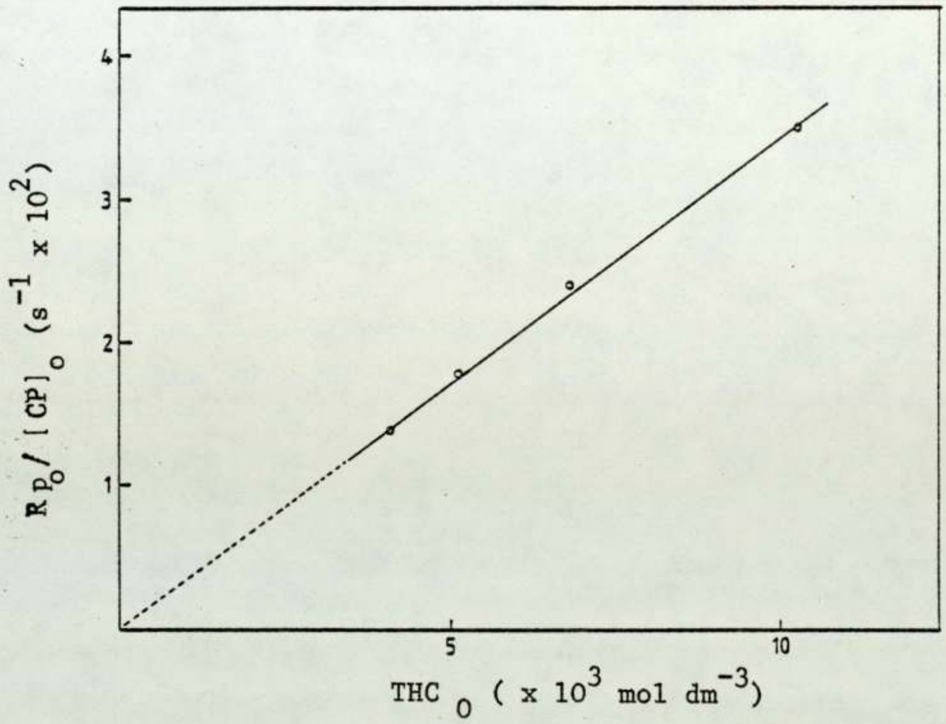
([CP] = 2.05 mol dm^{-3}; figures on the curves represent CP:THC initial molar ratios)

When the initial rate of reaction is plotted against the initial THC concentration (Fig III.11) a linear relationship is obtained. Furthermore, the straight line obtained can be extrapolated to zero concentration of THC and corresponded with a zero rate of reaction. It can therefore be concluded that the reaction is overall first order with respect to catalyst concentration.

(d) THE EFFECT OF PREMIXING OF CATALYSTS

It has been reported$^{(25)}$ that the rate of production of high molecular weight polymer for the system THC / ATB / CP when the catalysts were premixed was practically zero. For this reason, it was

Fig III.11 DEPENDENCE OF THE INITIAL RATE OF MONOMER CONSUMPTION ON THE INITIAL CONCENTRATION OF THC

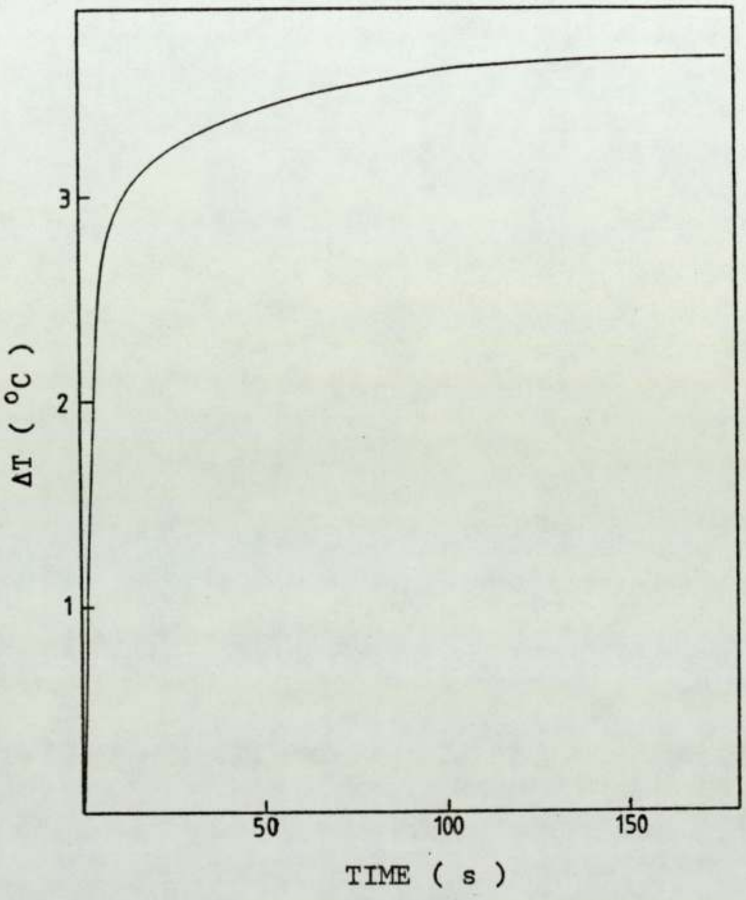


assumed that the premixed catalyst was inactive towards metathesis at least for the system under study.

When the catalysts were premixed and allowed to react for 1 min, and subsequently added to the CP solution, a very rapid exothermic reaction took place. The calorimetric curve for this reaction is shown in Fig III.12.

This reaction was the fastest of all the reactions under study and required only 3 minutes to reach zero rate. When the reaction had stopped, the CP consumption was determined after quenching, by GLC. The analysis showed that the concentration of CP had decreased by 8.7%. Two new broad, but high boiling peaks appeared in the

Fig III.12 CALORIMETRIC DETERMINATION OF THE RATE OF REACTION FOR A CATALYST PREMIXED SYSTEM

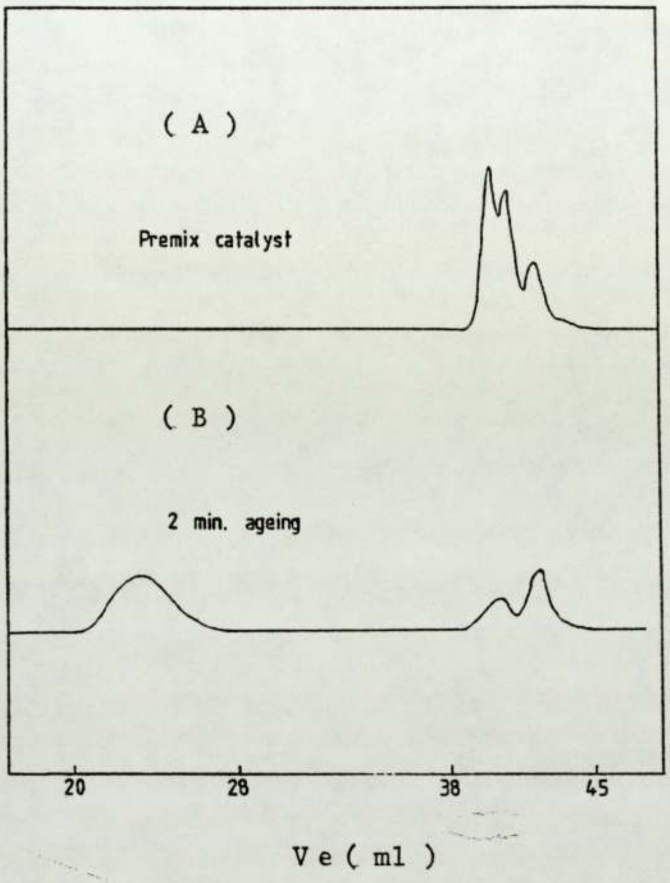


([CP] = 2.05, [THC] = 2.05×10^{-3}, [ATB] = 4.1×10^{-3} mol dm^{-3})

chromatograph. The product was isolated by distilling the more volatile materials leaving an oily substance.

The oil was analysed by GPC and no high molecular weight material could be detected. However, peaks in the low molecular weight region corresponding to the exclusion volumes of the dimer, trimer and tetramer of CP were observed. Fig III.13 shows the

Fig III.13 GEL PERMEATION CHROMATOGRAPHS OF THE POLYMERISATION PRODUCTS



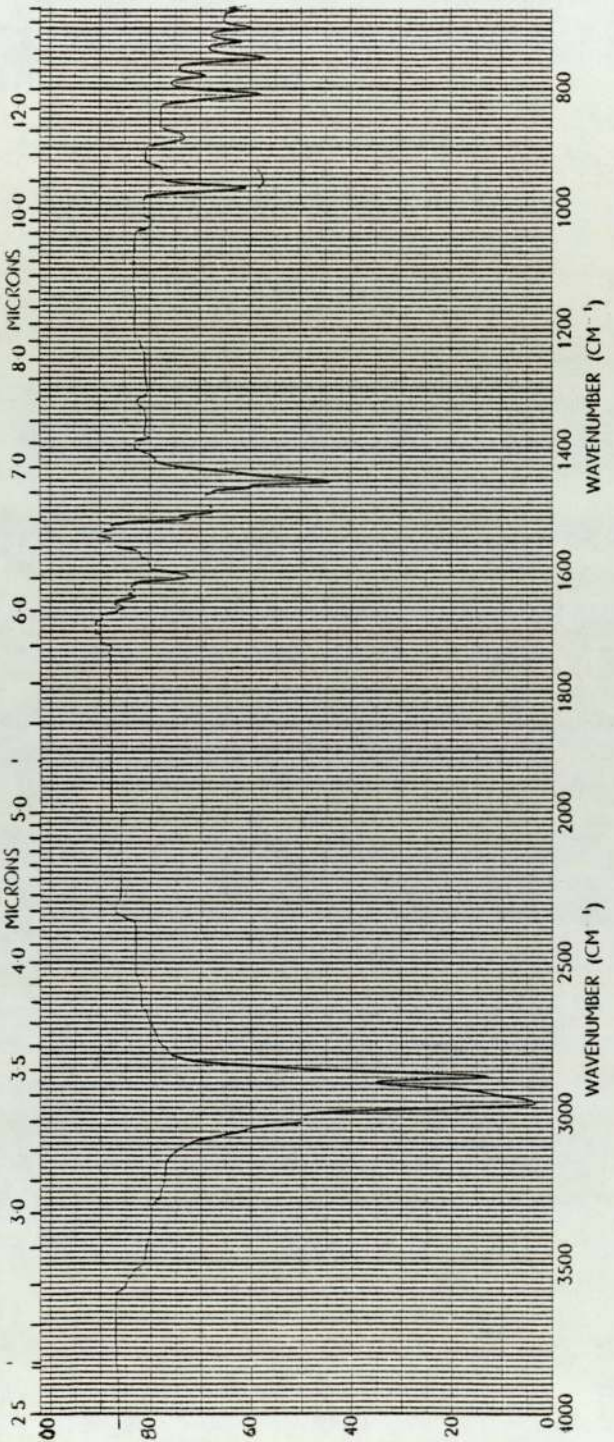
(A - premixed system, B - 2 mins ageing time)

chromatographs for the premixed material and for a polymer obtained under similar conditions but with an ageing time of 2 mins.

The infra-red spectrum of the oil, shown in Fig III.14 is similar in many aspects to that of polypentenamer and the product is assumed to be oligomers of cyclopentene.

The results tend to indicate that when the catalysts are premixed

Fig III.14 INFRA-RED SPECTRUM OF PRODUCTS OBTAINED WITH A PREMIX CATALYST SYSTEM



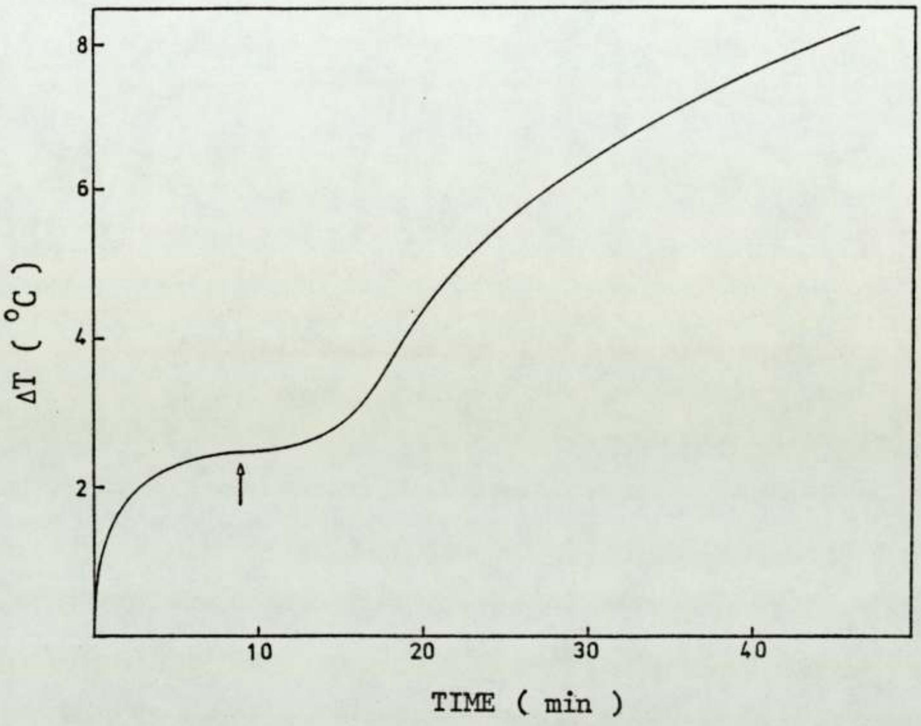
a very fast reaction takes place which dies rapidly. The analysis of the products suggests the presence of a very active catalyst that would produce metathesis with the double bond of adjacent monomer units in the growing chain rather than with a new molecule of monomer. This may be due to the fact that the rate of polymerisation (ie addition of a new monomer unit to the growing chain) is determined in this case by the rate of diffusion of the monomer to the active metal centre and since the double bonds of the growing chain were more readily available, oligomers formed by an intramolecular reaction rather than high molecular weight polymer, which was not detectable by GPC. The results also suggest that this very active species has a very high termination rate, rendering it inactive after a very short reaction time.

(e) THE EFFECT OF OXYGEN

As previously described, the polymerisation of CP initiated by the system THC / 2ATB does not reach the monomer-polymer equilibrium, before the catalyst is rendered inactive. This termination process could possibly be attributed to a reduction of the tungsten to a lower oxidation state in which it is no longer active.

In this experiment, dry oxygen was added to the system after it reached zero rate for the consumption of monomer. Fig III.15 shows the effect that the addition of oxygen has on the polymerisation of CP.

Fig III.15 TYPICAL CALORIMETRIC CURVE SHOWING THE EFFECT OF OXYGEN ADDITION (the arrow indicates the point of addition)

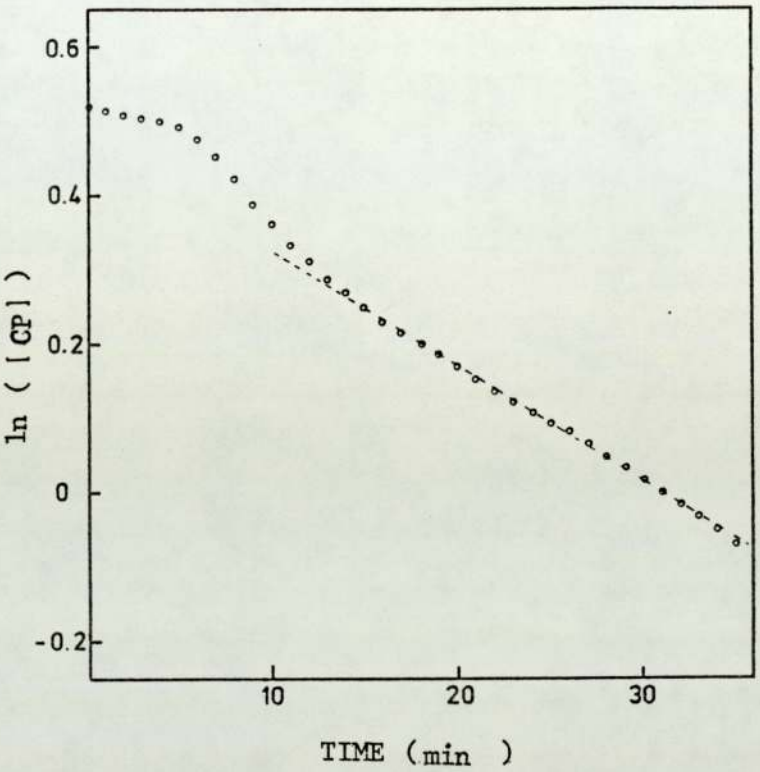


The new catalyst formed after the addition of oxygen did not show the same fast initial rate of reaction, but it allowed the reaction to reach the monomer-polymer equilibrium.

Fig III.16 shows a plot of ln (CP) against time, after the addition of oxygen to the system. The plot shows that after an initial 'activation period' followed by a short period of 'fast reaction', the reaction becomes first order with respect to the monomer and that the catalyst remains stable throughout the reaction.

Fig III.17 shows a plot of $\frac{-Rm}{[THC]_o\ [CP]}$ against $[THC]_o$ where

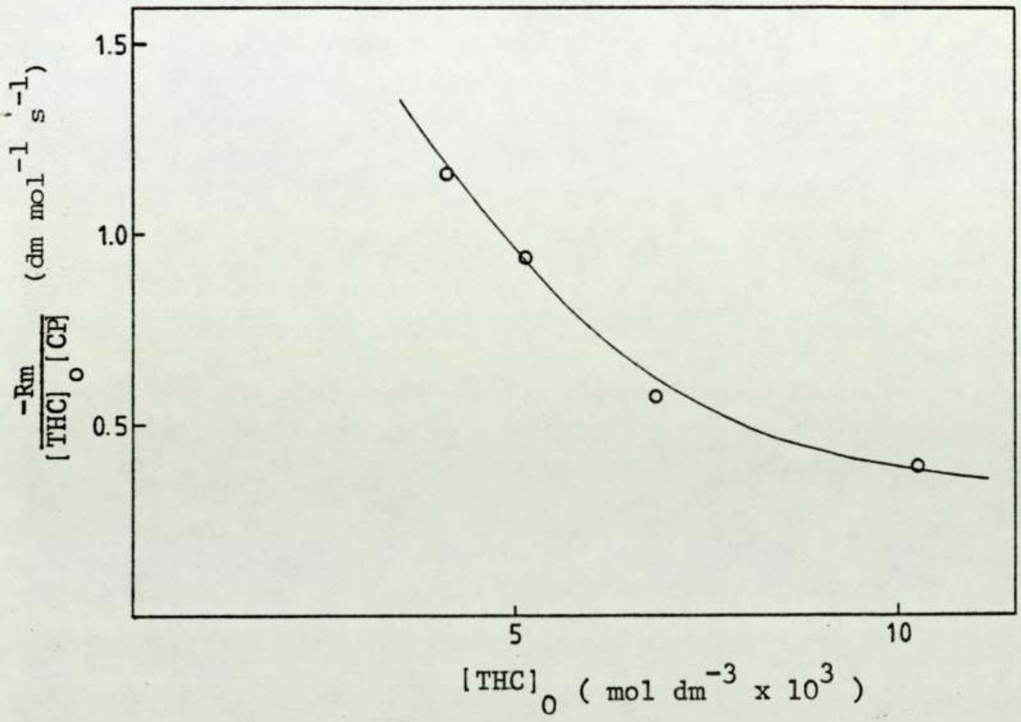
Fig III.16 DEPENDENCE OF ln [CP] ON REACTION TIME AFTER ADDITION OF OXYGEN



$-R_m$	is the rate of monomer consumption after addition of oxygen,
$[THC]_0$	is the initial THC concentration and
$[CP]$	is the concentration of monomer at the moment of addition of oxygen.

This plot shows that there is a decrease in the ratio of catalyst that is 'recovered' as the initial concentration of THC increases, which suggests that only a fraction of the catalyst recovers activity and that this fraction depends on the initial catalyst concentration.

Fig III.17 DEPENDENCE OF $\frac{-Rm}{[THC]_o[CP]}$ on $[THC]_o$ AFTER ADDITION OF OXYGEN



The amount of oxygen necessary to provide maximum activation was measured by introducing different aliquots of oxygen to the system and measuring the resultant rate of monomer consumption.

The effect of the amount of oxygen added did not show any stoichiometric relation with the catalyst used and only a large excess of oxygen provided the maximum rate for a given system. When only low amounts of oxygen were added, some activity was recovered but the rate of monomer consumption was so small that it could not be measured accurately.

(f) EFFECT OF SEPARATE ADDITIONS OF CATALYST AND MONOMER SOLUTIONS

Fresh solutions of monomer and catalyst were added to reaction mixtures that had reached zero rate of reaction to compare the results with those of similar rexperiments carried out by dilatometry.

When fresh monomer solution was added no change was observed. When fresh THC solution was added, a very fast reaction took place as shown in Fig III.18.

The results tend to confirm that there is a termination reaction involved in the polymerisation of CP initiated by the THC / 2ATB.

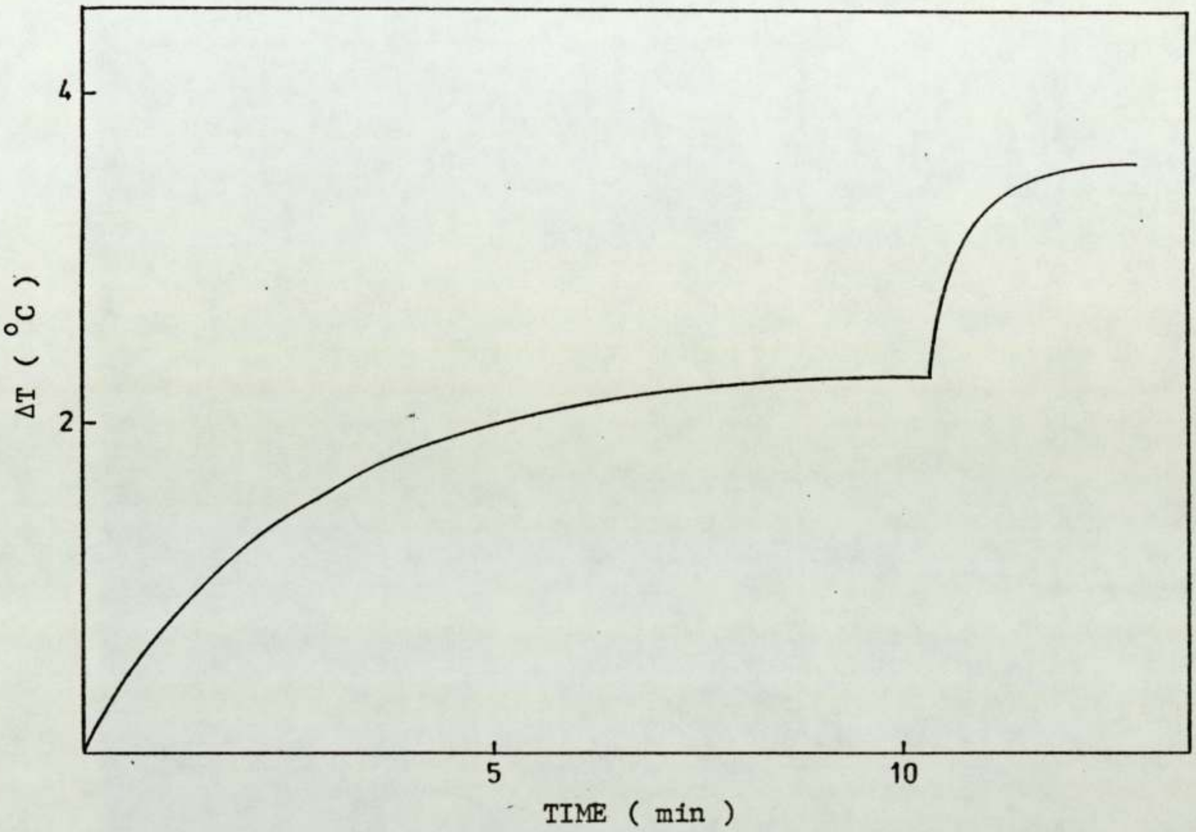
(g) STUDY OF CALORIMETRIC CURVES

Fig III.10 shows a typical series of calorimetric curves for the polymerisation of CP at a constant monomer concentration and ageing time ([CP] = 2.05 mol dm^{-3}, ageing time = 2 mins) and different catalyst concentrations.

As it has been previously shown the reaction reaches zero rate before the monomer-polymer equilibrium is achieved. Therefore, a termination process has to take place to account for the rapid change in the activity of the system.

For a typical polymerisation,

Fig III.18 EFFECT OF ADDITION OF THC TO A REACTION AFTER REACHING ZERO RATE



$$-Rm = \frac{-d[CP]}{dt} = kp\ [W^*]\ [CP]$$

where $-Rm = \frac{-d[CP]}{dt}$ is the rate of monomer consumption

kp is the rate constant for the polymerisation

and $[W^*]$ is the monomer concentration.

Then $\frac{-Rm}{[CP]}$ has to be proportional to the concentration of active species (W^*).

If a second order termination process is taking place,

$$W^* + W^* \longrightarrow W_{inactive}$$

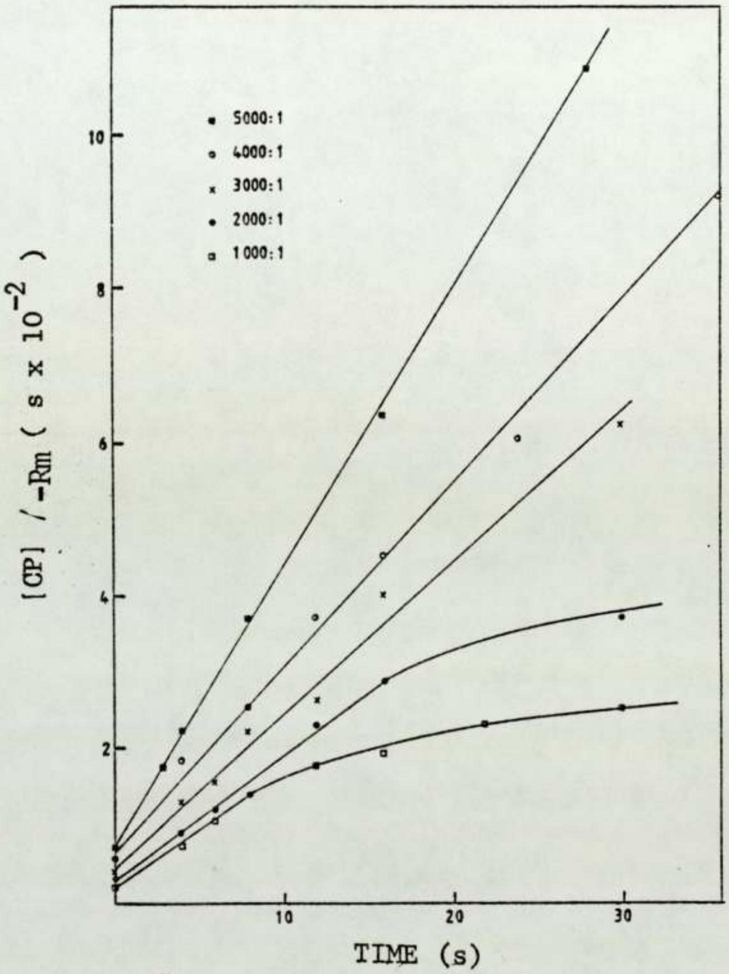
and $$\frac{-d[W^*]}{dt} = k_t [W^*]^2$$

Then for a second order reaction, a plot of $\frac{1}{[W^*]}$ against time should be linear and the slope should correspond to k_t. Then a plot of $\frac{[CP]}{-Rm}$ against time should be linear and the slope would represent k_t / k_p. Such a plot for the family of curves in Fig III.10 is shown in Fig III.19.

Fig III.19 shows that for low catalyst concentrations, the relation is linear over the entire range. However, at higher catalyst concentrations there is deviation from linearity. The family of lines should be parallel with a slope equal to $\frac{k_t}{k_p}$ however this is not so.

This result shows that the system is more complex than a simple second order termination and that a kinetic mechanism more complicated than the one described would probably apply to the reaction under study. Probably the reaction would involve more than one active species, each one with a particular rate of propagation and termination.

Fig III.19 DEPENDENCE OF [CP] / -Rm ON REACTION TIME



(CP = 2.05 mol dm^{-3} ; ageing time = 2 min)

(h) EFFECT OF DIFFERENT CATALYST SYSTEMS ON THE POLYMERISATION OF CYCLOPENTENE

The addition of oxygen greatly affects the kinetics of cyclopentene consumption when the THC / 2ATB catalyst system is used. Apparently the effect of oxygen is to produce a stable catalyst that stays active throughout the reaction allowing the reaction to reach the monomer-polymer equilibrium.

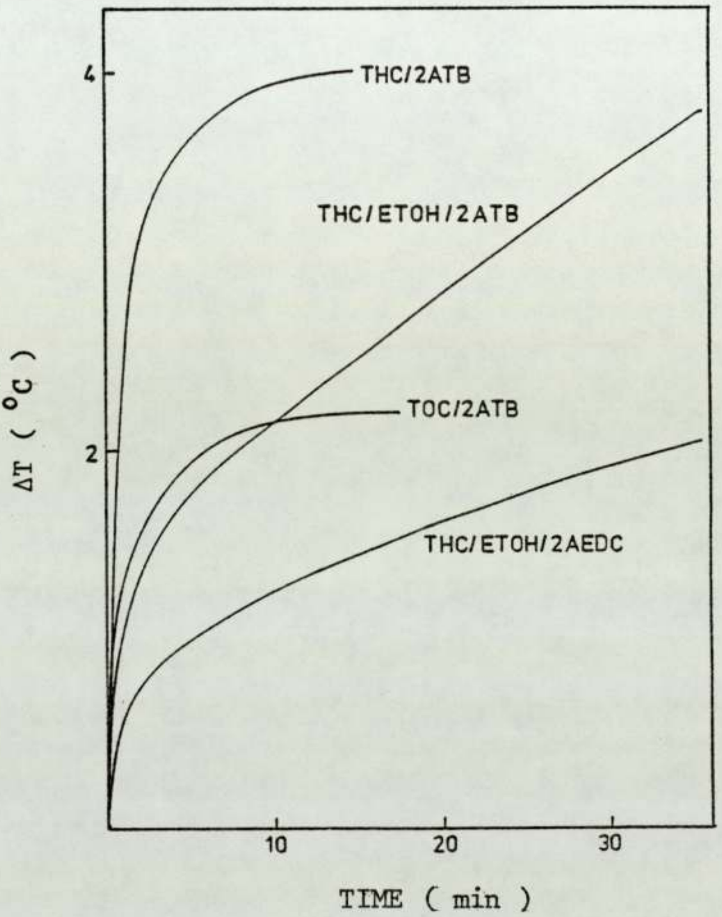
To compare the effect of oxygen present in other forms in the reaction system, tungsten oxychloride (TOC) and tungsten hexachloride-ethanol (THC / EtOH) were used as catalyst. The effect of a different cocatalyst was also studied. Fig III.20 shows the calorimetric curves for systems initiated with different catalyst combinations at constant CP concentration ([CP] = 2.8 mol dm^{-3}) and constant catalyst concentration (catalyst concentration = 1.12×10^{-3} mol dm^{-3}) The results clearly indicate that the TOC / 2ATB system behaves quite similarly to the THC / 2ATB system, ie it provides a rapid initial rate of consumption of monomer followed by a rapid decay in the activity of the catalyst.

However, the polymerisations initiated by the system THC / EtOH with either 2ATB or 2AEDC as cocatalyst showed a slower initial rate but reached a point at which polymerisation took place at a rate depending only on the concentration of CP. When this polymerisation was allowed to react for a long reaction time, the equilibrium monomer polymer was achieved.

From these results it could be concluded that the presence of oxygen containing compounds does not necessarily guarantee that a system will maintain its activity during the polymerisation reaction, but that the way in which it is introduced will determine the behaviour of the system.

Another point that could be drawn is that the cocatalyst apparently does not have a significant effect on the stability of the system

Fig III.20 CALORIMETRIC CURVES SHOWING THE EFFECT OF DIFFERENT CATALYST SYSTEMS



but it affects the activity of it.

(3) STUDIES ON MOLECULAR WEIGHT CHANGES

A complete understanding of the kinetics of a polymerisation reaction should include a study of the kinetic dependence of the molecular weights and molecular weight distribution of the polymers formed.

Several authors have shown that the ring-opening polymerisation of a cycloolefin produces a material which, when analysed by GPC, shows a bimodal molecular weight distribution. It was also found that the ratio of high to low molecular weight material changes with conversion.

The object of these experiments was to observe the effect of ageing time on the molecular weight and molecular weight distribution of the products of the reaction to study the ratios of high to low molecular weight materials and compare these results with those obtained from the kinetic studies carried out by dilatometry and / or calorimetry.

The polymerisation of CP was carried out, at a constant concentration of monomer and catalysts, ($[CP] = 2.6$, $[THC] = 1.04 \times 10^{-3}$, $[ATB] = 2.08 \times 10^{-3}$ mol dm^{-3}) for a series of ageing times. Samples were taken at different polymerisation times using the technique described in Section II,5,a,ii, and analysed by gel permeation chromatography.

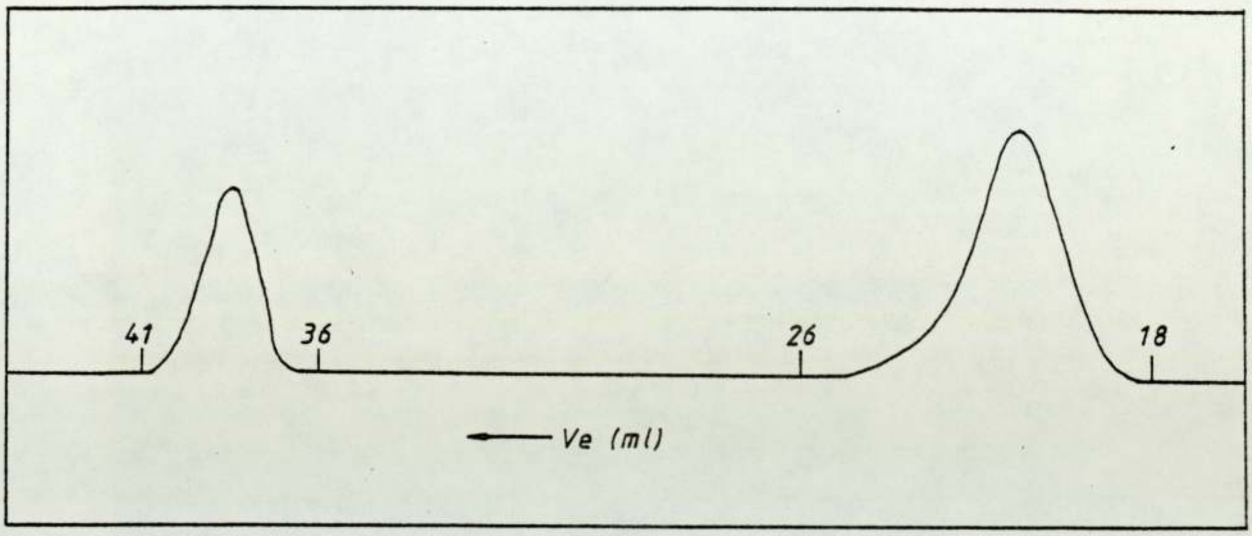
Fig III.21 shows a typical GPC trace obtained for samples of the polymers obtained. The chromatograph shows two different peaks, one corresponding to high molecular weight (exclusion volume from 18 to 26 ml) and the other corresponding to low molecular weight oligomers (exclusion volume from 36 to 41 ml).

Table III.1 RESULTS FOR THE MOLECULAR WEIGHT STUDIES

Ageing time min	Reaction time,min	High m wt fraction			Fract area of high to low mol wt peaks
		$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	
1	2	7.8	16.7	2.1	6.9
	6	5.6	13.9	2.5	2.4
	20	5.5	12.8	2.4	1.4
	50	4.3	10.7	2.5	2.1
	24 x 60	4.0	10.4	2.7	3.7
2	1.5	4.5	11.0	2.5	10.1
	20	5.3	12.9	2.5	2.3
	50	5.9	14.0	3.4	2.0
	200	4.6	12.4	2.8	3.2
	72 x 60	3.3	9.0	2.8	3.7
3	3	6.1	14.6	2.4	4.5
	10	4.7	11.0	2.4	2.1
	20	5.0	12.0	2.4	2.0
	50	4.1	10.2	2.5	2.0
	24 x 60	3.7	9.4	2.6	3.4
5	4	7.5	16.4	2.2	4.5
	20	4.4	11.3	2.5	1.6
	50	5.0	12.1	2.4	1.5
	24 x 60	3.7	8.9	2.4	3.7
15	10	6.1	13.9	2.3	2.4
	20	4.9	11.9	2.4	1.9
	50	4.0	9.7	2.4	1.6
	24 x 60	2.9	7.3	2.5	3.8

The results obtained for the molecular weight studies are shown in Table III.1. The table contains the results for the number average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$) and polydispersity (Mw/Mn) for the high

Fig III.21 TYPICAL GPC TRACE

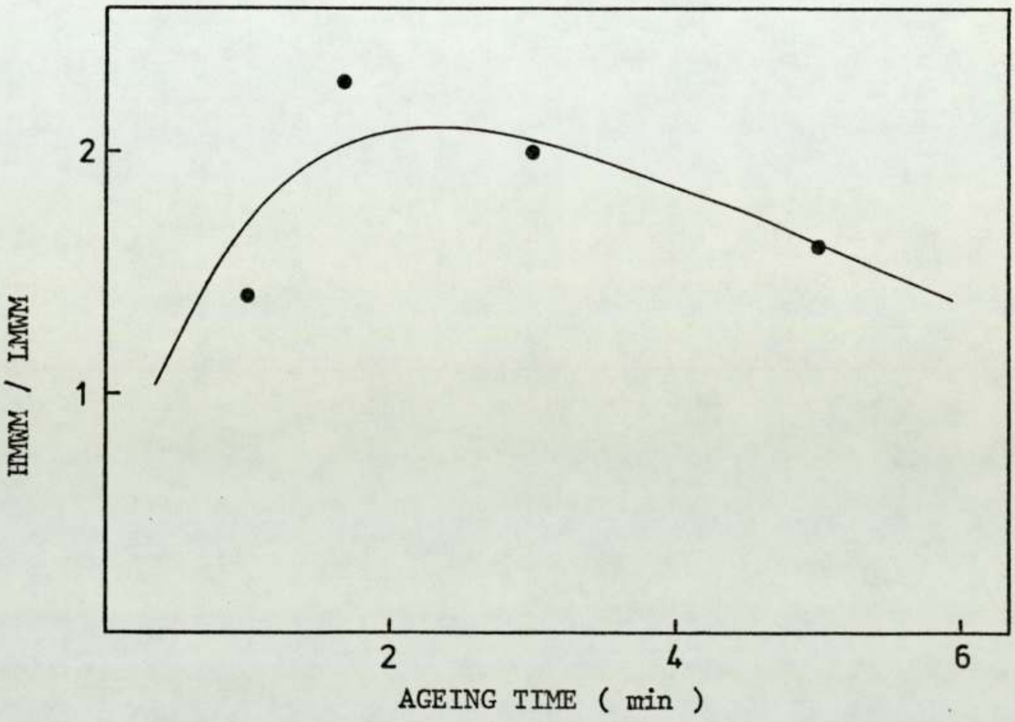


molecular weight peak and the ratio of the area under the curve of the high molecular weight peak to that of the low molecular weight peak. Because the differential refractive index $(\frac{\Delta n}{\Delta c})$ produced by the high and low molecular weight species is not necessarily the same, the values of the ratios cannot be considered as the ratio of the masses of high to low molecular weight material. Nevertheless it is very useful for comparison between different samples.

From the results obtained, it is possible to indicate some trends that if not conclusive, can point to the general behaviour of the system:

(i) Within experimental error, the number average molecular weight of the high molecular weight fraction decreases with conversion and the molecular weight distribution broadens.

Fig III.22 DEPENDENCE OF THE RATIO OF HIGH TO LOW MOLECULAR WEIGHT MATERIAL AFTER 20 MINS OF REACTION ON AGEING TIME



(ii) The ratio of the areas under the high to the low molecular weight peaks decreases initially and subsequently increases at high conversions and / or reaction times for all ageing times.

(iii) Comparison of the ratios of the areas under the peaks of a common reaction time (20 mins) indicates that this ratio depends on the ageing time of the initiator as shown in Fig III.22. Although the figures are not available, a similar marked dependence can be seen to occur in the earlier stages of the reaction.

(iv) The ratio of the areas are practically identical after long reaction times for all ageing times.

The observation that the ratio of the peaks firstly decreases and then increases to a constant value for all the polymerisations, suggests the existence of two different stages of the reaction: the initial stage of the reaction is kinetically controlled and the second leading the system eventually to equilibrium thermodynamically controlled.

It has been shown that during polymerisation the active sites are consumed at a rate faster than monomer and hence the decrease with time of the number average molecular weight of the higher molecular weight fraction cannot be accounted for by a change in [CP] / [W*] that would be predicted by a simple second order termination reaction. An explanation that could account for the small decrease in the number average molecular weight would be that there is a progressive change in the kinetic nature of the system. This could occur if more than one active species is present in the reaction mixture and the ratio of their concentrations changes with reaction time, consequently changing all overall rate constants.

Fig III.22 shows the dependence of the ratio of the areas under the chromatograph for high to low molecular weight material on ageing time. The shape of the curve is similar to those obtained by dilatometry (Fig III.2) and calorimetry (Fig III.9), for the dependence of the initial rate of polymerisation and rate of monomer consumption on ageing time respectively. All curves show a maximum suggesting a common explanation for the phenomenon.

The shapes of the curves could be explained by the presence of more than one active species in the system. One capable of producing high molecular weight material (HMWM) and other(s) capable of producing low molecular weight material (LMWM). The initial concentration of the species capable of producing HMWM could depend on ageing time in a similar manner to that suggested by Amass and Tuck(25).

In this way, the ageing time at which the maximum initial rate of polymerisation is obtained (t_{max}) would be that at which the ratio of the catalyst capable of producing HMWM to the catalyst capable of producing LMWM is a maximum. The calorimetric curves would not be expected to show the same magnitude of dependence because the network does not differentiate practically between the production of polymer or oligomers (the enthalpy change from monomer to polymer and from monomer to oligomers is very similar) and the rate of production of oligomers may be substantial.

The attainment of a true monomer-oligomer-polymer equilibrium is suggested because the ratios of the peak areas at long reaction times are practically identical. It has been shown previously that the catalyst used (THC / 2ATB) terminates before the reaction reached equilibrium, however, in this case, equilibrium could have been achieved if small amounts of air leaked into the system to produce a long-lived catalyst.

CHAPTER IV

REACTIONS BETWEEN COMPONENTS OF THE POLYMERISATION SYSTEM

(1) INTRODUCTION

The metathesis reaction is described by many authors as involving a metal carbene complex, derived from a reaction between the components of the catalyst system. Very rarely is any mention made of the possible source of such carbenes or moreover the role the olefin may play in their formation. An indication that there is a reaction between THC and the olefin is the colour change that takes place on the addition of THC solution to CP. Furthermore, kinetic evidence suggests that a series of reactions takes place between CP and THC and attempts have been made in this project to try to characterise further the nature of these reactions, for to do so would be of great value in the elucidation of the mechanism of metathesis. The reactions were studied by:

(i) an analysis of the visible spectral changes that take place during the initial stages of the reaction between THC and CP and

(ii) investigating the consumption of the olefin by gas liquid chromatography, most often at low ratios of olefin : THC and high concentrations of THC.

(2) SPECTROPHOTOMETRIC STUDIES

(a) THE SPECTRUM OF TUNGSTEN HEXACHLORIDE IN TOLUENE

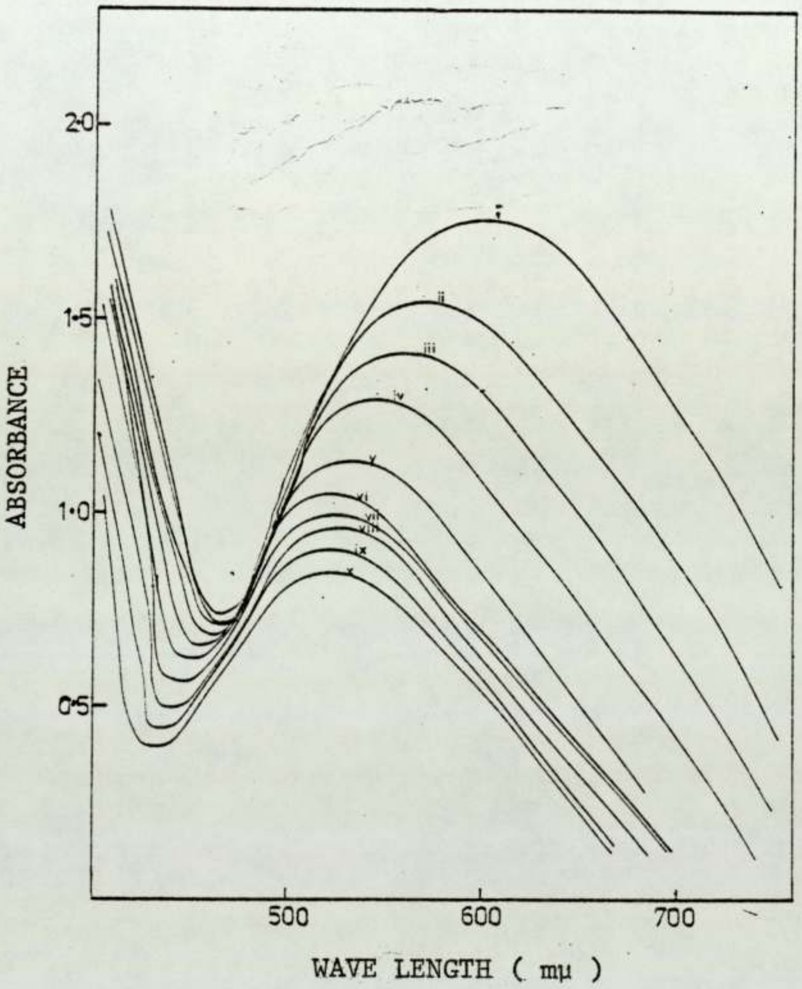
The spectrum of THC in toluene was produced by the technique described in Section II,5,a,iii. These studies were initially found to be extremely difficult to perform with any degree of reproducibility because λ_{max} for THC in toluene could be found at random between 600 and 540 mμ. It was felt that the solvent used contained traces of olefinic impurities. Because THC is such a powerful chromophore very dilute solutions had to be used, which could lead to high impurities to THC molar ratios. Spectrum (i) in Fig IV.1 shows the visible absorption of spectrum of WCl_6 in toluene (λ_{max} = 600 mμ) when the solvent used was purified by successive distillations from THC. In this way the maximum possible λ_{max} and ε were obtained.

(b) REACTION BETWEEN TUNGSTEN HEXACHLORIDE AND CYCLOPENTENE

Samples of CP solution ([CP] = 9.6×10^{-2} mol dm^{-3}) were added with a microsyringe to 5 ml of a THC solution ([THC] = 5.0×10^{-3} mol dm^{-3}) following the procedure described in Section II,5,a,iii. The visible spectrum was recorded after each addition until the molar ratio CP : THC was 4 : 1, these spectra are shown as (ii) to (x) in Fig IV.1. It appeared that there was a gradual shift in λ_{max} as the addition of CP took place, however, on further investigation it would appear that curves (ii) to (iv) are in fact the resultants of the appropriate proportional additions for a multicomponent system of curves (i) and (v) which have λ_{max} at 600 and 520 m μ respectively.

The change from (i) to (ii) or any of the other spectra in the series was instantaneous at room temperature. When the absorbance

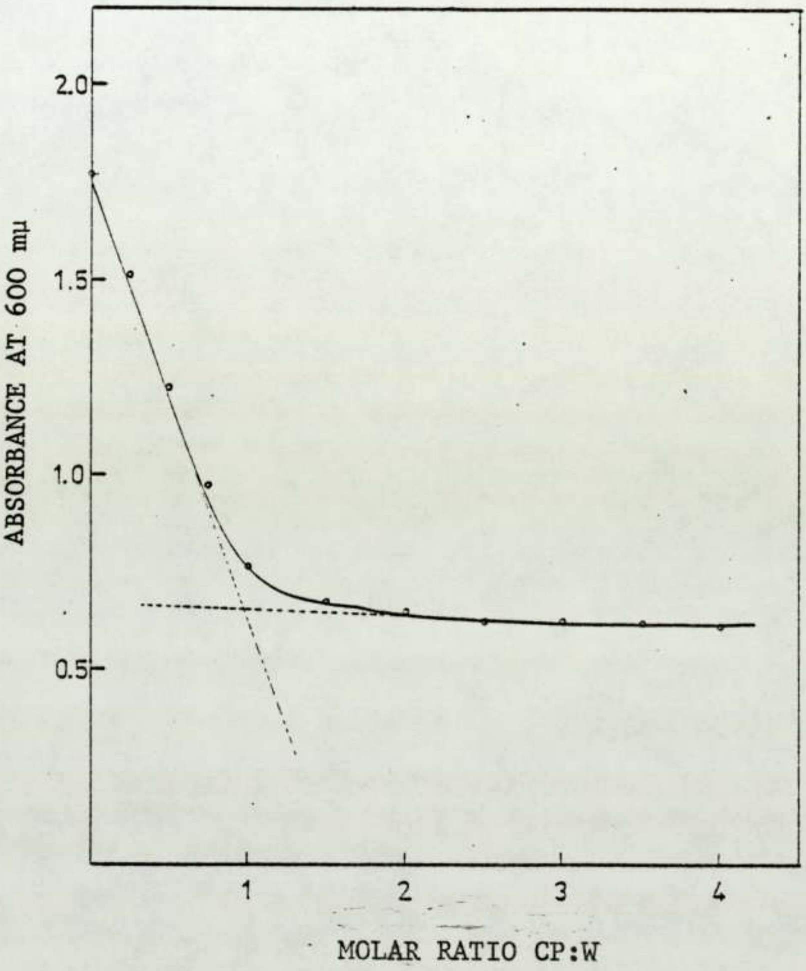
Fig IV.1 SPECTROPHOTOMETRIC STUDIES OF THE REACTION BETWEEN THC AND CP



(CP : THC molar ratio ⇒ i = 0, ii = 0.25, iii = 0.5, iv = 0.75, v = 1, vi = 1.5, vii = 2.0, viii = 2.5, ix = 3.0, x = 4.0)

at 600 m μ for the different molar ratios is plotted against the CP : THC (Fig IV.2) molar ratio and the 'mole ratio' method is used, the formation of a simple complex between THC and the olefin with a molar ratio THC : CP equal to 1 : 1 is revealed. Whatever the structure, the species formed is not stable, for there is a

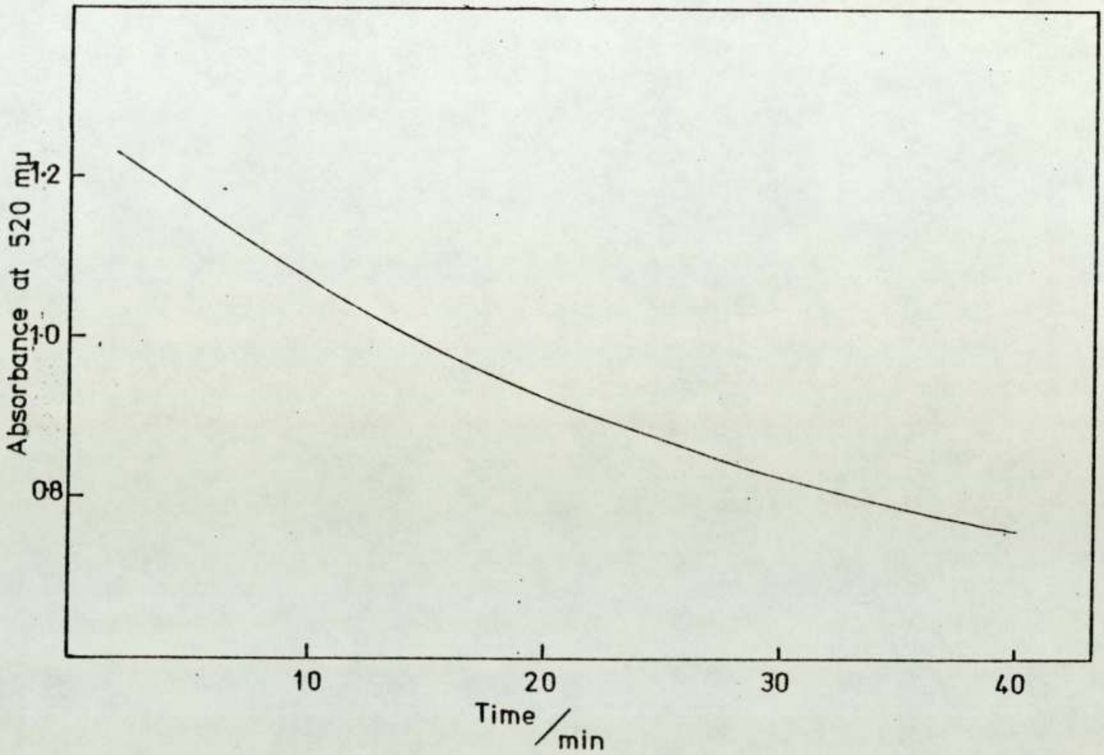
Fig IV.2 EFFECT OF THE CP : THC MOLAR RATIO ON ABSORBANCE AT 600 m μ



further change in the absorbance if the system is allowed to stand. Fig IV.3 shows the change that takes place in the absorbance at 520 mμ , when enough CP was added to a THC solution ([THC] = 5×10^{-3} mol dm^{-3}) to provide a CP : THC molar ratio of 4 : 1, and the reaction mixture was allowed to stand.

The disappearance of the peak at 520 mμ occurs in a first order manner with respect to the species giving rise to this peak, since a plot of log (absorbance) against time, shown in Fig IV.4 is

Fig IV.3 CHANGE IN ABSORBANCE AT 520 mμ WITH REACTION TIME

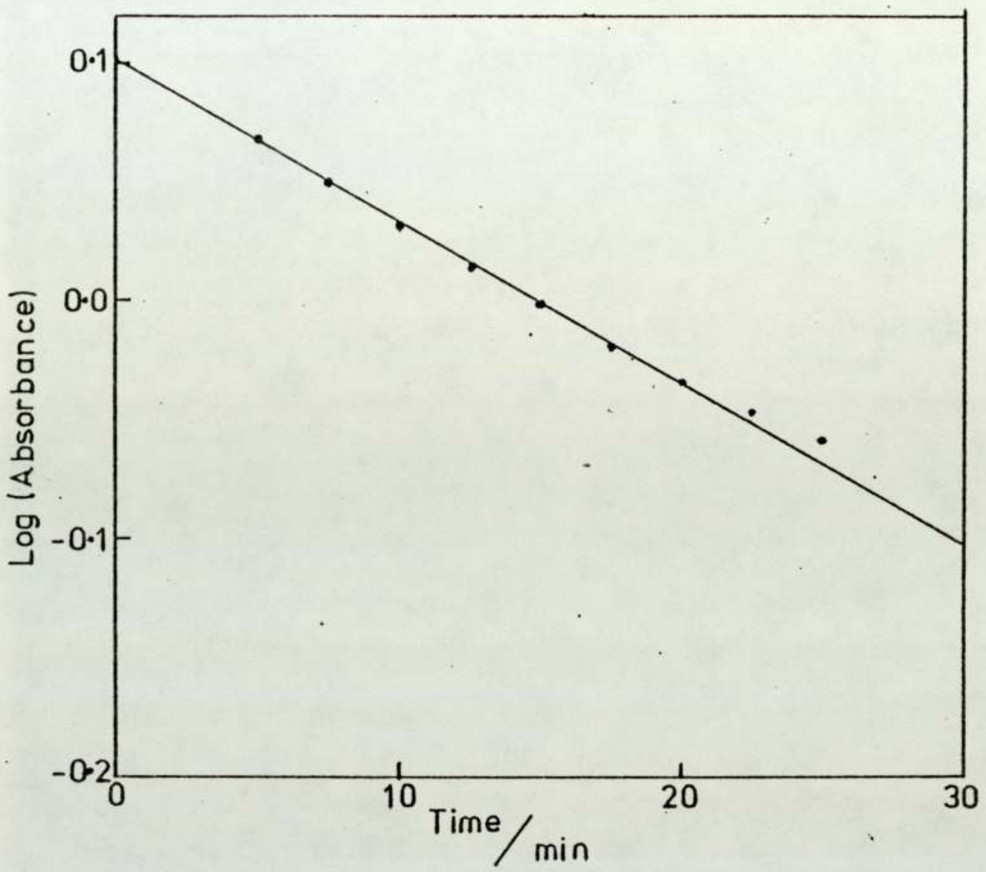


linear. It is not clear whether this reaction involves another molecule of cyclopentene but it is likely that such a reaction could account for the deviation from linearity after long reaction times.

(c) REACTIONS INVOLVING ALUMINIUM TRIISOBUTYL

Samples of ATB solution ([ATB] = 9.6×10^{-2} mol dm^{-3}) were added to 5 ml of THC solution ([THC] = 5.0×10^{-3} mol dm^{-3}) following the procedure described in Section II,5,a,iii. The visible spectrum was recorded after each addition. The results are shown in Fig IV.5.

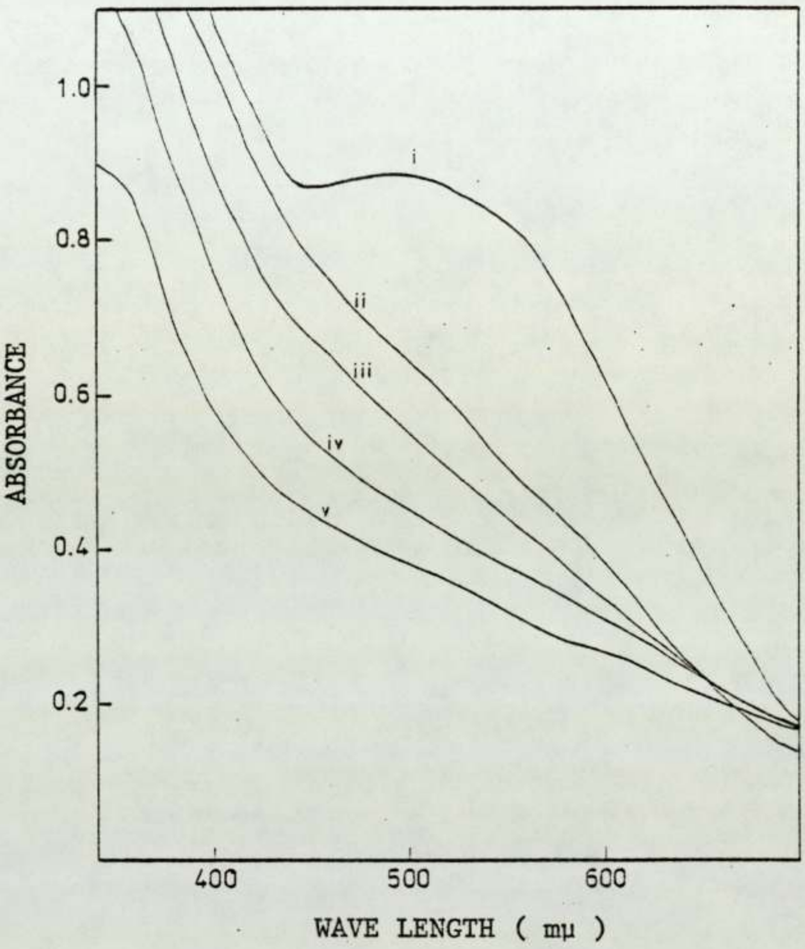
Fig IV.4 DEPENDENCE OF LOG (abs_{520}) ON REACTION TIME



When the ratio ATB and THC was 0.25 (spectrum (i), Fig IV.5), a shift of the original spectrum of THC (spectrum (i), Fig IV.1) towards shorter wave lengths and lower absorbance is apparent, while a broad shoulder still remains. Upon further addition of ATB, the visible absorption corresponds to a broad band with a maximum in the uv region (λ_{max} = 360 mμ). A precipitate was observed at ATB : THC molar ratios greater than 0.5 : 1.

When THC was premixed with CP (THC : CP = 1 : 4) immediately before the addition of the ATB, the spectra recorded (Fig IV.6) showed

Fig IV.5 VISIBLE SPECTRA OF THE ADDITION OF ATB TO THC SOLUTION

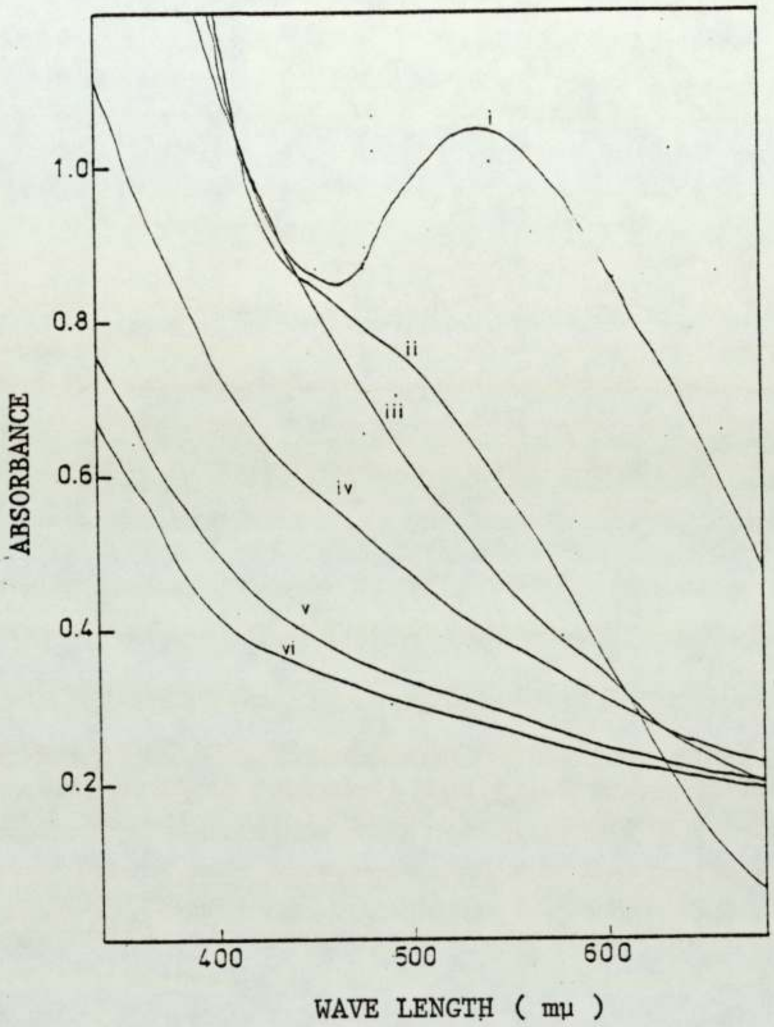


(ATB : THC molar ratio = i = 0.25, ii = 0.5, iii = 0.75, iv = 1.0, v = 1.25)

similar results to those obtained in the absence of CP. When the ratio ATB : THC was 0.5 : 1 or greater, some precipitation was observed.

When THC was allowed to react with CP (CP : THC = 4 : 1) for one hour, before the addition of ATB, a distinctive shoulder appeared

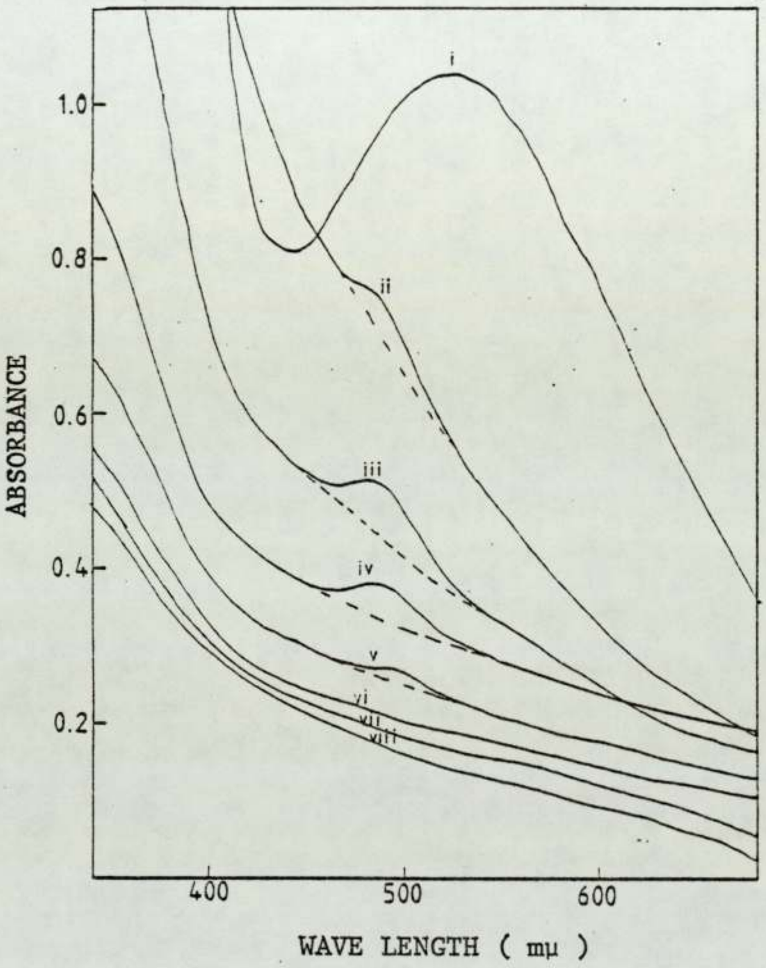
Fig IV.6 SPECTROPHOTOMETRIC STUDIES OF THE REACTION BETWEEN (THC/4CP) AND ATB



(ATB : THC molar ratio - i = 0, ii = 0.25, iii = 0.5, iv = 1.0, v = 1.5, vi = 2.0)

on the visible spectra recorded (Fig IV.7). The maximum for this absorption was observed at a wavelength of 490 mμ , and it only disappeared when the molar ratio ATB : THC was greater than 2 : 1. In this case precipitation was observed when the ATB : THC molar

Fig IV.7 SPECTROPHOTOMETRIC STUDIES OF THE REACTION BETWEEN (THC / 3CP) AGED FOR 60 MINS, AND ATB



(ATB : THC molar ratio - i = 0, ii = 0.5, iii = 1.0, iv = 1.5, v = 2.0, vi = 2.5, vii = 3.0, viii = 3.5)

ratio was of the order of 1.5 : 1.

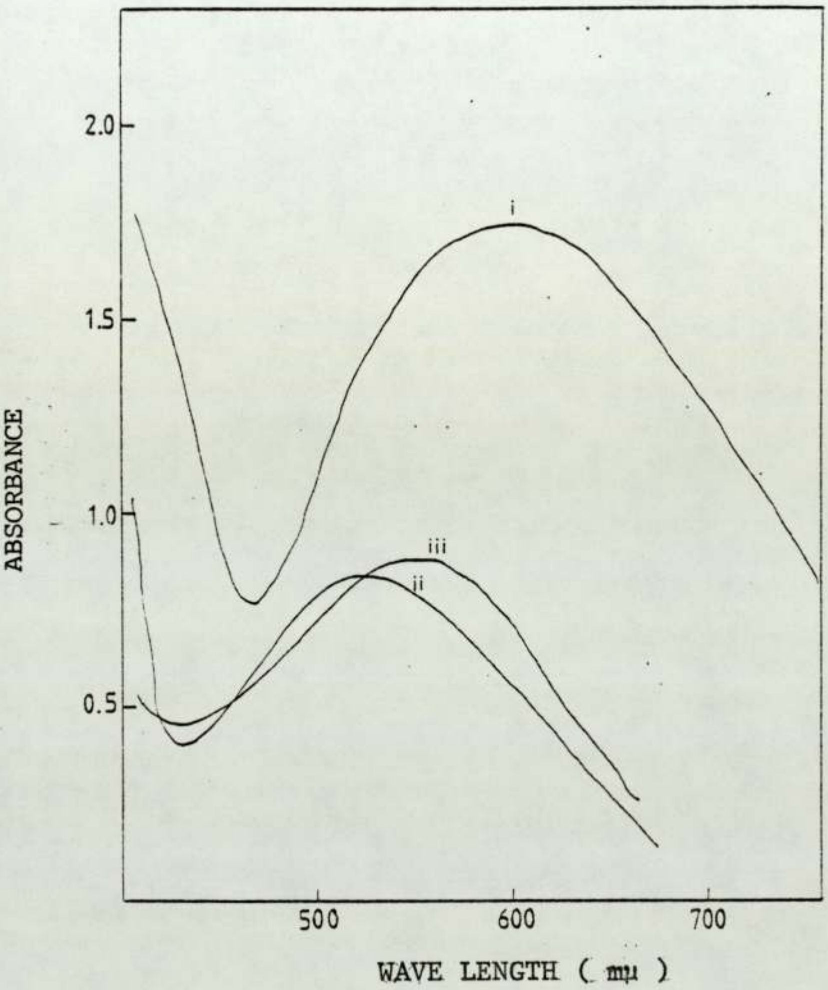
These results tend to suggest that a species that absorbs in the visible region appears from the reaction of THC, CP and ATB only when the THC is allowed to react with the CP prior to the addition of the cocatalyst. This would indicate that at least two reactions take place between THC and CP. One of them will give rise to an immediate shift of λ_{max} from 600 mμ to 520 mμ, probably involving the reaction of THC with only one molecule of CP but that a slower reaction would later take place to produce a species that when reacted with ATB will absorb in the visible region (λ_{max} = 490 mμ).

Unfortunately, detailed studies of the uv region were not carried out because the very high extinction coefficients of the species under study in this region would involve working with very dilute solutions (10^{-4} to 10^{-5} mol dm^{-3}) bringing irreproducibility into the system due to the impossibility of eliminating completely all sources of impurities.

(d) THE PRESENCE OF OXYGEN

CP was added ([CP] = 9.6×10^{-2} mol dm^{-3}) to 5 ml of THC solution ([THC] = 5.0×10^{-3} mol dm^{-3}) to provide a THC : CP ratio of 1 : 4, allowed to stand for 20 mins and the spectrum recorded (Fig IV.8, spectrum (ii)). Dry oxygen was then added and the spectrum taken (Fig IV.8, spectrum (iii)). The maximum shift from 520 mμ to 550 mμ and the absorbance at the maximum increased slightly from 0.84 to 0.88.

Fig IV.8 SPECTROPHOTOMETRIC STUDIES ON THE EFFECT OF OXYGEN



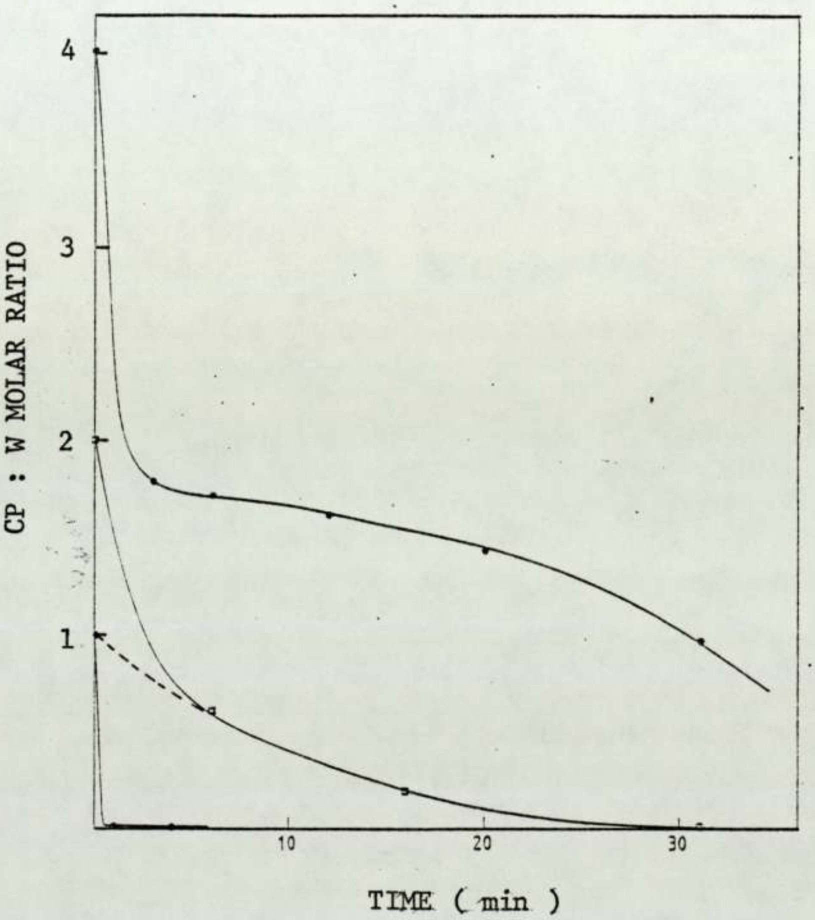
(i = THC; ii = THC : CP, 1 : 4; iii = ii after 20 mins + oxygen)

(3) GAS CHROMATOGRAPHIC STUDIES

(a) REACTIONS BETWEEN TUNGSTEN HEXACHLORIDE AND CYCLOPENTENE

Gas chromatography was used to study the disappearance of olefins during their reactions with THC. The procedure described in Section I,5,b,i was used to allow CP and THC to react at different

Fig IV.9 REACTIONS BETWEEN CP AND THC; CHANGE IN CP : W RATIO WITH TIME



molar ratios. The concentration of CP remaining in the solution was analysed as a function of reaction time and the results are shown in Fig IV.9 (above).

The results show that at least one mole of CP is consumed immediately after the addition of CP solution to THC. When the initial CP : THC ratio was 4 : 1, it appears that 2 moles of CP are consumed immediately. However, when the initial ratio was 2 : 1, the second mole of CP appears to be consumed more slowly.

If it is assumed that one mole of CP is instantaneously consumed after mixing, then the consumption of the remaining mole of CP can be considered to follow the broken line shown in Fig IV.9. The subsequent decay in the concentration of cyclopentene can be shown to follow a first order manner, (Fig IV.10).

This result shows a first order decay for the CP concentration, if the order with respect to tungsten is zero, it indicates that it is acting as a catalyst, ie its concentration does not change with time. However, if the product formed from any reaction between CP and the first formed THC/CP product is similar in chemical characteristics to the initial one the same or similar sort of kinetic behaviour could be expected.

A plateau is observed after 5 mins of reaction, when the CP : THC initial molar ratio was 4 : 1, although the CP concentration eventually decreased to zero. This result can be interpreted in two ways: (i) a catalyst is produced that can metathesise CP or (ii) the CP is chlorinated by the THC(29).

Fig IV.11 shows a typical product analysis for a reaction of CP in toluene with THC after 48 h. The dotted lines represent the initial CP and toluene peaks. The CP was practically totally consumed, probably by one of the reactions already discussed. The toluene peak also appears to be consumed.

It is quite possible that some of the products may be chlorinated

Fig IV.10 DEPENDENCE OF LOG [CP] ON REACTION TIME (CP : THC INITIAL MOLAR RATIO = 2 : 1)

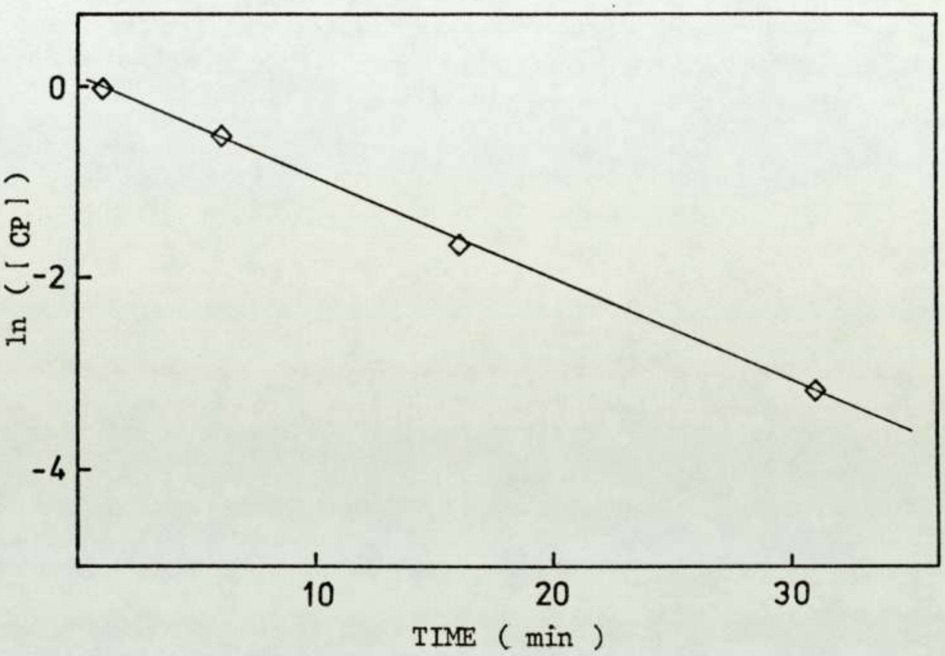
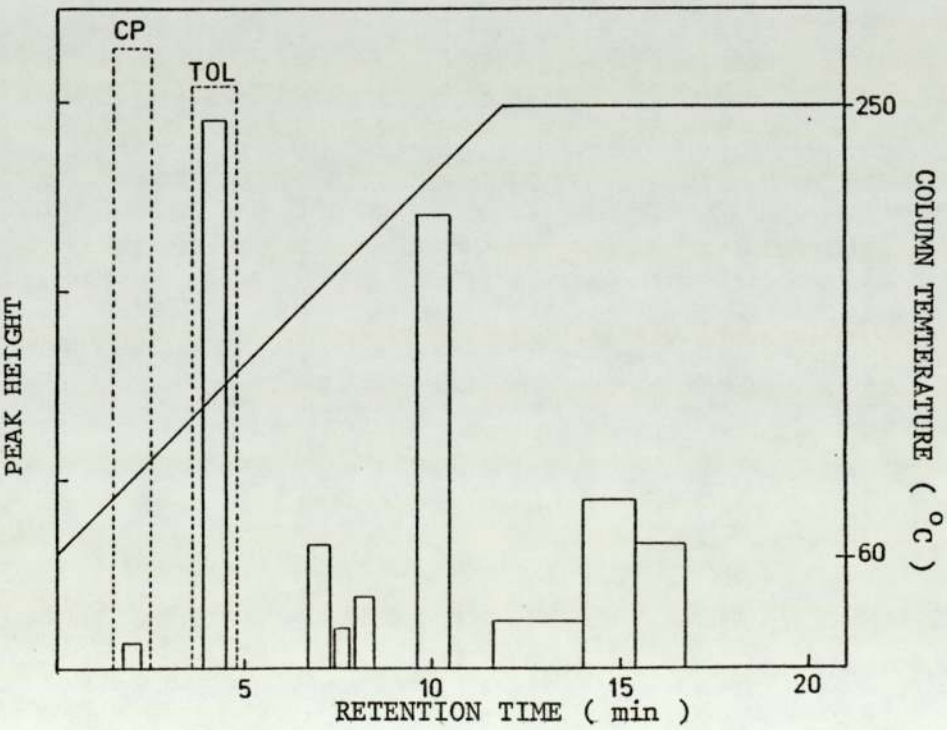


FIG IV.11 PRODUCT ANALYSIS FOR THE REACTION BETWEEN CP AND THC



or substituted toluenes or metathesis products. Unfortunately, facilities to carry out GLC-mass spectroscopy analysis were not available and because the complexity of the product mixture, detailed analysis was not possible.

In order to simplify the system, a similar reaction using a reactant that cannot undergo metathesis was carried out.

(b) REACTION BETWEEN TUNGSTEN HEXACHLORIDE AND CYCLOHEXENE

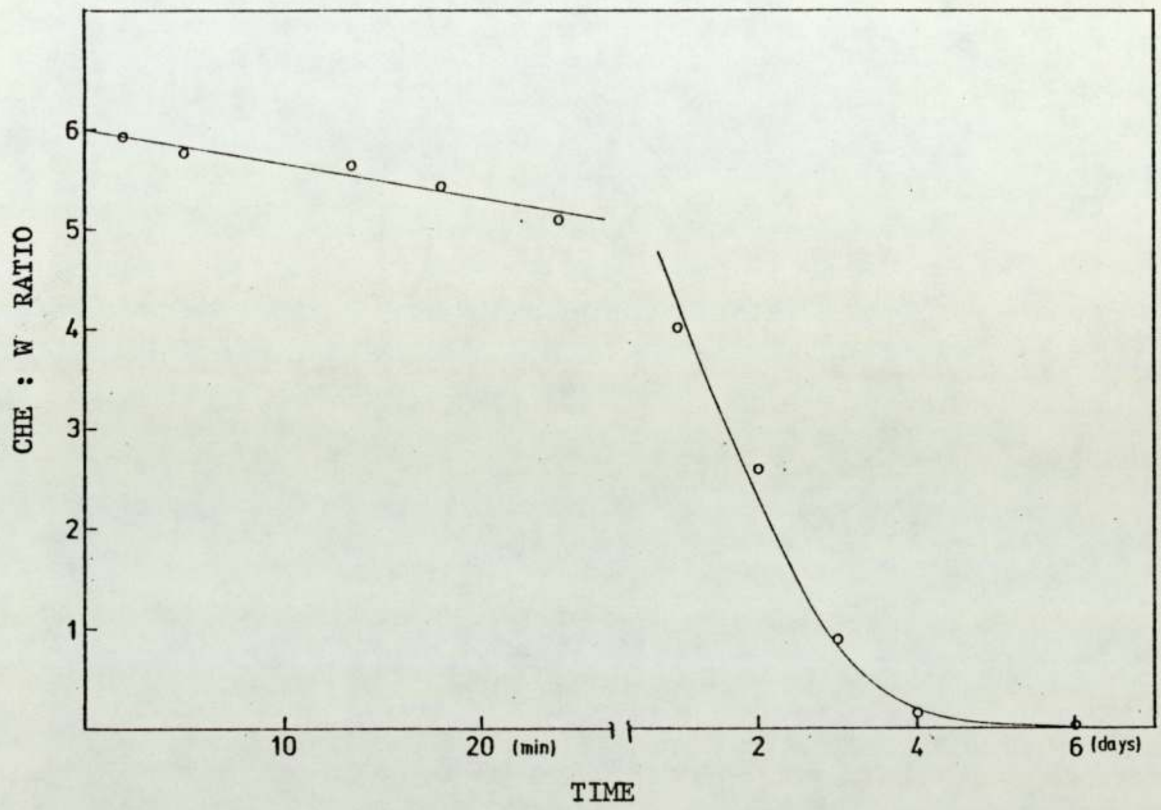
A reaction between THC and CHE was carried out following the procedure described in Section II,5,b,ii, using 15 ml of a THC solution ([THC] = 7.2×10^{-2} mol dm^{-3}) and a CP : THC initial molar ratio of 6 : 1. The change of CHE : W molar ratio with time is shown in Fig IV.12.

In this case, unlike the reaction of THC with CP, no CHE was quickly consumed after mixing of the solutions but a slow decrease in the concentration of CHE was observed. These results could probably be associated with the chlorination reaction of CHE by THC described by San Filippo et al(29).

(c) PRODUCTION OF HYDROGEN CHLORIDE

During the course of the studies described in the previous section and other work carried out in these laboratories, it was apparent that the reactions described were accompanied by the

Fig IV.12 REACTION BETWEEN CHE AND THC; CHANGE IN CHE : W RATIO WITH TIME



production of hydrogen chloride. Initially, the production of HCl was interpreted as a by product of hydrolysis but the quantities of HCl produced were suspected to exceed those expected from hydrolysis.

The evolution of HCl from the reaction between THC and olefins was measured following the procedure described in Section II,5,b,iii. The reaction was carried out using 15 ml of a THC solution ([THC] = 7.2×10^{-2} mol dm^{-3}) and enough CP to produce a CP : THC molar ratio of 6 : 1. The amount of HCl produced corresponded to 1.61 moles of HCl per mole of THC after 48 h.

A similar experiment was carried out using CHE and following the procedure described in Section II,5,b,iv. The initial CHE : THC molar ratio being 6 : 1. From an initial 1.29 mmol of THC, 1.92 m mol of CHE were consumed and 1.02 mmol of HCL were produced after 24 h. It can be suggested with hesitation that $\frac{1}{2}$ mole of HCl was produced per mole of CHE consumed.

CHAPTER V

DISCUSSION

The kinetic results show that the polymerisation of CP initiated by THC / 2ATB is by no means simple, since none of the schemes that normally apply to typical polymerisation reactions can be used even with modifications, to explain the kinetic behaviour of the system. One possible explanation that could account for the complicated nature of the polymerisation system is the presence of more than one active species in the reaction. In order to investigate this possibility, it was thought that a study of the initial stages of the initiation process, ie the reactions between THC and olefins, could provide some answers to this particular problem. What was believed to be a simple reaction turned out to be at least as complex as the polymerisation itself.

There is evidence in the literature that THC can react with cyclic alkenes to produce chlorinated compounds(29) and it has been shown also(30,133) that the mean oxidation state of tungsten in solution decreases when THC is allowed to react with CP.

The spectroscopic results as well as the GLC analyses of the CP / THC solutions indicate that the THC cannot exist as such in solution when olefins are present because it has been shown that THC reacts immediately with one mole of CP to produce a completely new species which it is suspected is not in equilibrium with THC. This new species is itself not stable in solution if more CP is present but reacts or decomposes in a first order manner to produce another species.

The results tend to suggest that a series of reactions takes place between THC and CP and that at least two different species maybe more, could be present in the system prior to the cocatalyst addition. This is additionally supported by the results obtained by Amass(30) for the changes in the oxidation state of tungsten when THC was reacted with CP (Table I.1). It was reported that the mean oxidation state of tungsten after 20 minutes of reaction between THC and CP was 4.3. This suggests that a mixture of W(VI) and W(IV) is present in the reaction and maybe W(V) also. If one additionally considers the possible changes in the ligands that can take place, the possibility of several species being present at the same time is greatly increased.

Although it seems plausible therefore that a series of reactions takes place between THC and CP, the species formed in this system require the addition of ATB in order to create activity. It could be argued that the addition of ATB could lead to a series of scrambling reactions that would result in the production of only one type of complex in solution. The spectroscopic evidence however discounts this possibility because the UV/visible spectrum of the system, THC + CP + ATB, when the THC / CP is aged for one hour, is significantly different from the spectrum obtained when the ageing time is short. Accordingly, if a series of intermediates is assumed to be present before the addition of ATB, then it is quite likely that the addition of ATB will lead to a number of complexes of varying structures and activities.

Proof that different complexes may not show the same kinetic behaviour can be drawn from a comparison of the results obtained with a premix THC / 2ATB catalyst and those for an aged system. Although both these systems are active towards metathesis, the premix system forms a catalyst that produces only low molecular weight oligomers at a very fast rate and terminating rapidly, whereas the aged system produces a material with the normal bimodal molecular weight distribution. Then it is reasonable to assume that after THC is allowed to react with CP, species are formed that when reacted with ATB, form different active species that can have different rates of propagation, termination and transfer, hence producing mainly high or mainly low molecular weight materials.

It has been shown that the initial rate of monomer consumption, determined calorimetrically is proportional to the initial THC concentration at constant concentration of CP and ageing time. However, any attempt to find a kinetic scheme that could explain all the results seemed quite impossible. It looks feasible that a model similar to that proposed by Amass and Tuck would apply to the initiation part of the system, however, some modifications have to be made. The kinetic mechanism involved a slow reaction between THC and CP in solution, this can be quite categorically discounted. However, if the THC is substituted in that scheme by the rapidly created species, THC / CP, there is no reason why a similar kinetic scheme could not be applied to the reaction.

It is very significant that the dependence on ageing time of the dilatometrically determined initial rate is different from that of the calorimetrically determined rate. The dilatometric results show a strong dependence of the initial rate of polymerisation on ageing time and it is suggested that the ability of the system to produce high molecular weight material changes rather than the overall ability to consume monomer which is measured by calorimetry. Additional evidence for this proposal can be drawn from the GPC analyses of the polymerisation products. These results showed that the ratio of high to low molecular weight materials, and hence their rates of production, depended on the ageing time of the catalyst in a manner similar to the dependence of dilatometric rates.

It can therefore be suggested that the following expression would be more representative of the reaction under study:

$$\text{Rate of reaction} = \frac{d[CP]}{dt} = [CP] \, \Sigma \, kp_i \, [W_i^*] \qquad \ldots(1)$$

where $[CP]$ is concentration of CP

$W_i{}^*$ is any active species (i) and

kp_i is the propagation rate constant for the active species W_i^*.

If the concentration of W_i^* depends on the initial concentration of CP and ageing time, a very complicated kinetic system is produced. It is important to note that if a similar catalyst system is used for the metathesis of linear olefins, large differences would not be apparent with different ageing times.

One aspect that the experimental evidence has proved without any doubt is the presence in the system of termination. It has been shown that the reaction followed either calorimetrically or dilatometrically reached a state of zero rate that did not represent the monomer-oligomer-polymer equilibrium because the addition of fresh monomer solution did not produce any effect whereas the addition of oxygen produced a catalyst capable of taking the reaction to equilibrium.

It is possible to suggest that a second order termination reaction is the best way of explaining the results obtained. However, the system is once more, more complicated than a simple second order termination for only one active species.

It can be suggested that the deviation from linearity in some of the plots of [CP] / Rp against time could be due to the fact that inactive species produced during termination could once more participate in termination reactions that might be described by:

$$W^* + W^* \xrightarrow{k_1} 2\,W_{inactive}$$

$$W^* + W_{inactive} \xrightarrow{k_2} 2\,W_{inactive}$$

Then the rate of consumption of active species can be written as:

$$\frac{-d[W^*]}{dt} = k_1 [W^*]^2 + k_2 [W^*][W_{in}] \qquad \ldots(2)$$

if $[W^*] = a[W^*]_o$ (where $0 < a < 1$)

and $[W_{in}] = (1-a)[W^*]_o$

then $\frac{-da}{dt} = (k_1 a^2 + k_2 a(1-a))[W^*]_o$

Resolution of the differential equation gives:

$$a = \frac{k_2}{(k_2-k_1) + k_1 \exp(k_2[W^*]_o t)} \qquad \ldots(3)$$

If only one active species W* is considered to catalyse the reaction then:

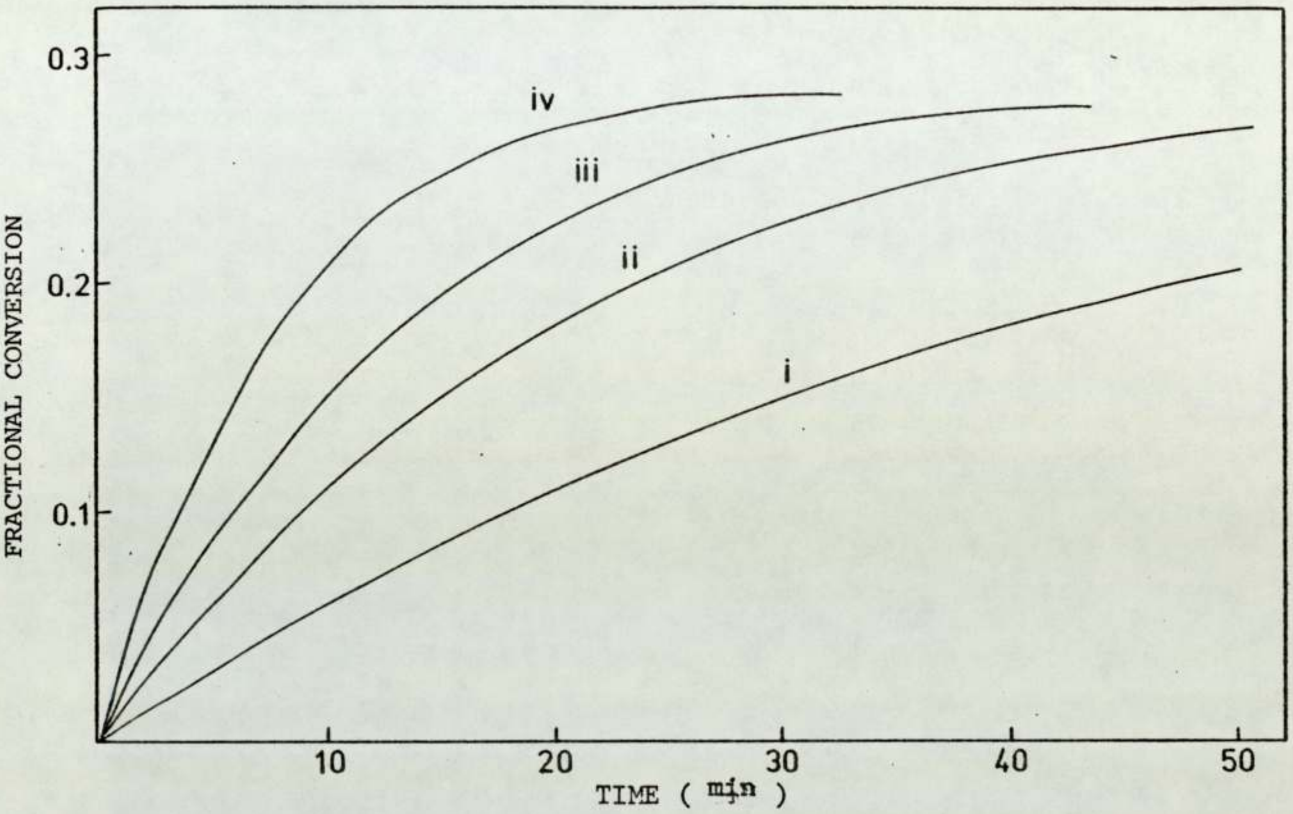
$$Rp = \frac{d[CP]}{dt} = kp[CP][W^*] = kp[CP][W^*]_o\, a \qquad \ldots(4)$$

Substituting (3) in (4) and solving the differential equation gives:

$$\frac{[CP]_o-[CP]}{[CP]_o} = 1-\exp\left(\frac{kp}{k_2-k_1}\left(k_2[W^*]_o t-\ln\left(1-\frac{k_1}{k_2}(1-\exp(k_2[W^*]_o))\right)\right)\right) \qquad \ldots(5)$$

Equation (5) was used to simulate the system by means of a computer programme into which was fed values of the constants k_1, k_2, kp and $[W^*]_o$, that were estimated from the dilatometric results. These values were then refined to give the conversion time curves as shown in Fig V.1, a series of simulated curves for different initial concentrations of active species ($[W^*]_o$).

Fig V.1 SIMULATED POLYMERISATION CURVES FOR ONLY ONE ACTIVE SPECIES



(Rate constants ($dm^3 mol^{-1} s^{-1}$) - $k_1 = 20$, $k_2 = 50$, kp = 11.
Active site concentration ($mol\ dm^{-3} \times 10^5$) - [W*] - i = 1, ii = 2, iii = 3, iv = 5)

If the shapes of these curves are compared with the conversion-time curves obtained by dilatometry (for example, Fig III.5) they show a remarkable similarity. This suggests that a kinetically similar system can apply to the polymerisation reaction. However, it was impossible to accommodate the results obtained calorimetrically within this kinetic scheme. The difference in the results obtained for similar reactions followed dilatometrically or calorimetrically could be explained on the basis of the presence of more than one active species. Dilatometry was not able to measure the participation in the system of any active site that could only produce low molecular weight material. Based on this assumption, inherent in equation (1) a kinetic scheme is proposed involving a second active species (W**) that can produce only low molecular weight material at a very fast rate terminating rapidly in a second order manner. Then the concentration of the second active species can be expressed as:

$$[W^{**}] = \frac{[W^{**}]_o}{[W^{**}]_o\, k_3 t + 1} \qquad \ldots(6)$$

where k_3 is the rate constant for the second order termination of W**.

If the rate of monomer consumption is expressed as:

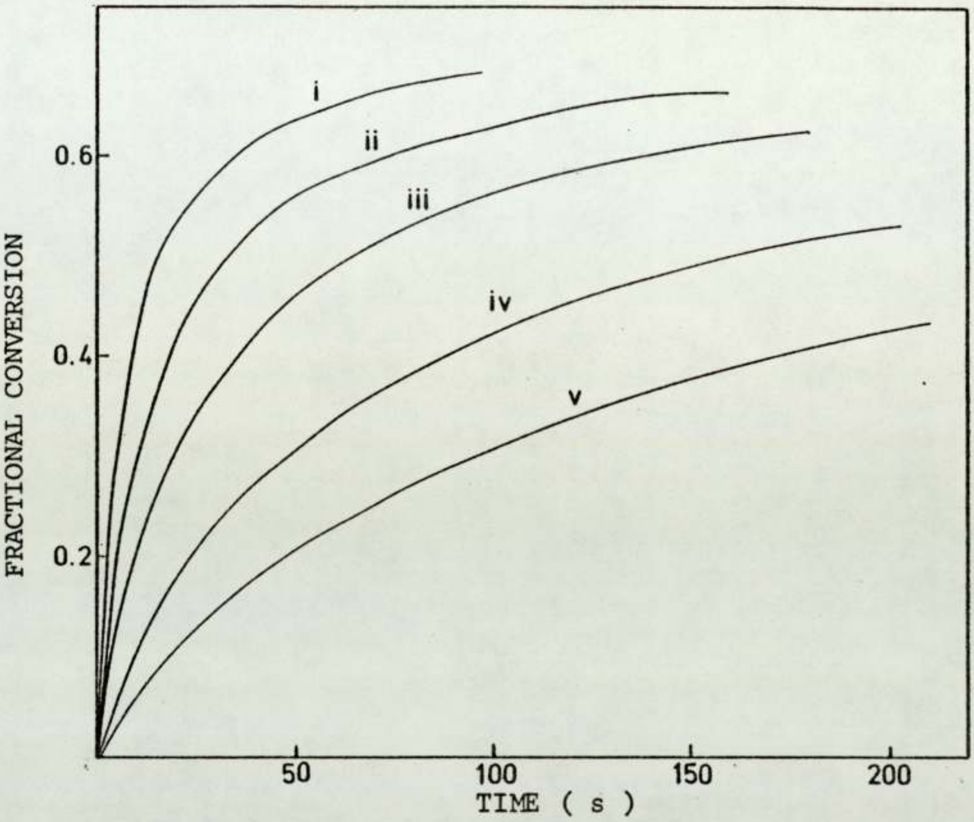
$$Rp = \frac{-d[CP]}{dt} = kp_1\ [CP][W^*] + kp_2\ [CP][W^{**}] \qquad \ldots(7)$$

Substitution of (3) and (6) in (7) will integrate to:

$$\frac{[CP]_o - [CP]}{[CP]_o} = 1\text{-}\exp\left(\frac{kp_1}{k_1 - k_2}(k_2[W^*]_o t - \ln(1 - \frac{k_1}{k_2}(1 - \exp(k_2[W^*]_o t))))\right.$$
$$\left. - \frac{kp_2}{k_3}\ \ln(k_3[W^{**}]_o t + 1)\right) \qquad \ldots(8)$$

The evaluation of equation (8) in a manner similar to that used for equation (5) leads eventually to the curves shown in Fig V.2.

Fig V.2 SIMULATED POLYMERISATION CURVES FOR TWO ACTIVE SPECIES



(Rate constants ($dm^3 mol^{-1} s^{-1}$)- k_1 = 20, k_2 = 50, k_3 = 1000, kp = 11, kp_2 = 250. Active sites concentrations (mol $dm^{-3} \times 10^4$), $[W^*]_o$ = $2[W^{**}]_o$ - i = 10, ii = 5, iii = 2.5, iv = 1, v = 0.5)

The shapes of this family of curves are similar to those obtained by calorimetry (Fig III.10). Comparison of Figs III.5 and III.10 show a difference in shape in the initial stages of the reaction. The significant feature of the treatment proposed is that, using values of kp_1, kp_2, k_1, k_2 and k_3 estimated from these figures, the difference between the curves can be predicted.

It has been shown that oxygen can convert an inactive catalyst into an active one that would not terminate in the same manner but that takes the reaction to equilibrium.

In order to try to identify the nature of the bonds formed when oxygen was added to the system, experiments were carried out with catalyst already containing oxygen. The catalysts chosen were THC / ETOH and TOC because they possess a single metal-oxygen bond and a double metal oxygen bond respectively.

The system containing THC / ETOH cocatalysed by either ATB or AEDC showed a fast initial rate of reaction followed immediately by a steady consumption of monomer, leading the system eventually to equilibrium. The reactions catalysed by TOC showed a rapid polymerisation followed by a rapid termination in a manner very similar to that observed for the THC / 2ATB system.

These results tend to suggest that the bonds formed by the reaction of the 'dead' species with oxygen would be similar in nature to the bonds formed from the reaction between THC and ETOH that has been suggested(35) to be W-O-R rather than W=O as in TOC.

It can be suggested that hydroperoxides and epoxides (well known activators) would form a W-O-R species and for this reason do not have associated with them the same sort of termination as the THC / 2ATB system.

CHAPTER VI

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

(1) GENERAL CONCLUSIONS

The studies of the initial stages of the reaction showed that WCl_6 reacts with cyclopentene to produce at least two species that when reacted with $AliBu_3$ formed different catalytically active sites capable of metathesising cyclopentene. It was shown that WCl_6 does not exist as such in solution in the presence of an olefin such as cyclopentene but a new species WCl_6 / olefin is instantaneously formed which probably subsequently reacts with more olefin in a first order manner.

The studies of the dependence of the initial rate of polymerisation on ageing time showed that the ageing time at which a maximum rate of polymerisation is obtained does not depend upon the initial concentration of WCl_6 but only on the concentration of cyclopentene. This tends to confirm the kinetic scheme proposed originally by Amass and Tuck$^{(25)}$.

The kinetic evidence supports the presence of more than one active species in the system. Based on the dilatometric, calorimetric and molecular weight determination studies the following equation was suggested to represent the kinetics of the reaction under study.

$$Rp = \frac{-d[CP]}{dt} = [CP] \Sigma kp_i [W_i^*]$$

where:

[CP] is the concentration of cyclopentene

W_i^* is any active species (i) and

kp_i is the propagation rate constant for the active species W_i^*.

The kinetic studies clearly showed the presence of termination for the system WCl_6 / $AliBu_3$ / cyclopentene. It was suggested that inactive species produced during termination could once more participate in termination reactions, so that termination might be described by:

$$W^* + W^* \xrightarrow{k_1} 2\ W_{inactive}$$

$$W^* + W_{inactive} \xrightarrow{k_2} 2\ W_{inactive}$$

When this equation is included in the kinetic treatment for the rate of propagation, the following equation is obtained:

$$\frac{[CP]_o - [CP]}{[CP]_o} = 1\text{-}\exp\left(\frac{kp}{k_2 - k_1}\left(k_2[W^*]_o t - \ln\left(1 - \frac{k_1}{k_2}\left(1 - \exp(k_2[W^*]_o t)\right)\right)\right)\right)$$

This equation was used to simulate the kinetic behaviour of the system and the dilatometric results were perfectly accommodated under the scheme. However, the calorimetric curves showed behaviour different to that predicted. Therefore, another active species was introduced which would represent a catalyst capable of producing only low molecular weight materials. If a second order termination is assumed, the equation representing the system could be expressed as follows:

$$\frac{[CP]_o-[CP]}{[CP]_o} = 1-\exp\left(\frac{kp_1}{k_1-k_2}\left(k_2[W^*]_o t-\ln\left(1-\frac{k_1}{k_2}\left(1-\exp(k_2[W^*]_o t)\right)\right)\right) - \frac{kp_2}{k_3}\ln\left(k_3[W^{**}]_o t + 1\right)\right)$$

This equation could simulate the kinetic behaviour of the calorimetric system confirming the presence of at least two kinetically active species.

The addition of oxygen to a terminated system led to the regeneration of catalyst activity. The subsequent behaviour of the polymerisation was similar to the behaviour shown by the WCl_6 / EtOH system rather than $WOCl_4$ which tends to suggest that the role of oxygen is to create a W-O-R species.

(2) SUGGESTIONS FOR FURTHER WORK

Although all the experimental evidence tends to support the kinetic mechanisms suggested in this project, there is a series of experiments that could add to the understanding of the system.

(i) Detailed molecular weight determinations could be undertaken at different monomer and catalyst concentrations using the system WCl_6 / $AliBu_3$ and WCl_6 / EtOH / $AliBu_3$ and the results compared.

(ii) Kinetic studies of the WCl_6 / EtOH / $AliBu_3$ system could be carried out and the dependence of t_{max} on the initial monomer concentration studied.

(iii) The nature of the products of reaction between WCl_6 and the olefin would lead to a better understanding of the initiation reaction. These reactions should then be compared with the reactions of the WCl_6 / EtOH system.

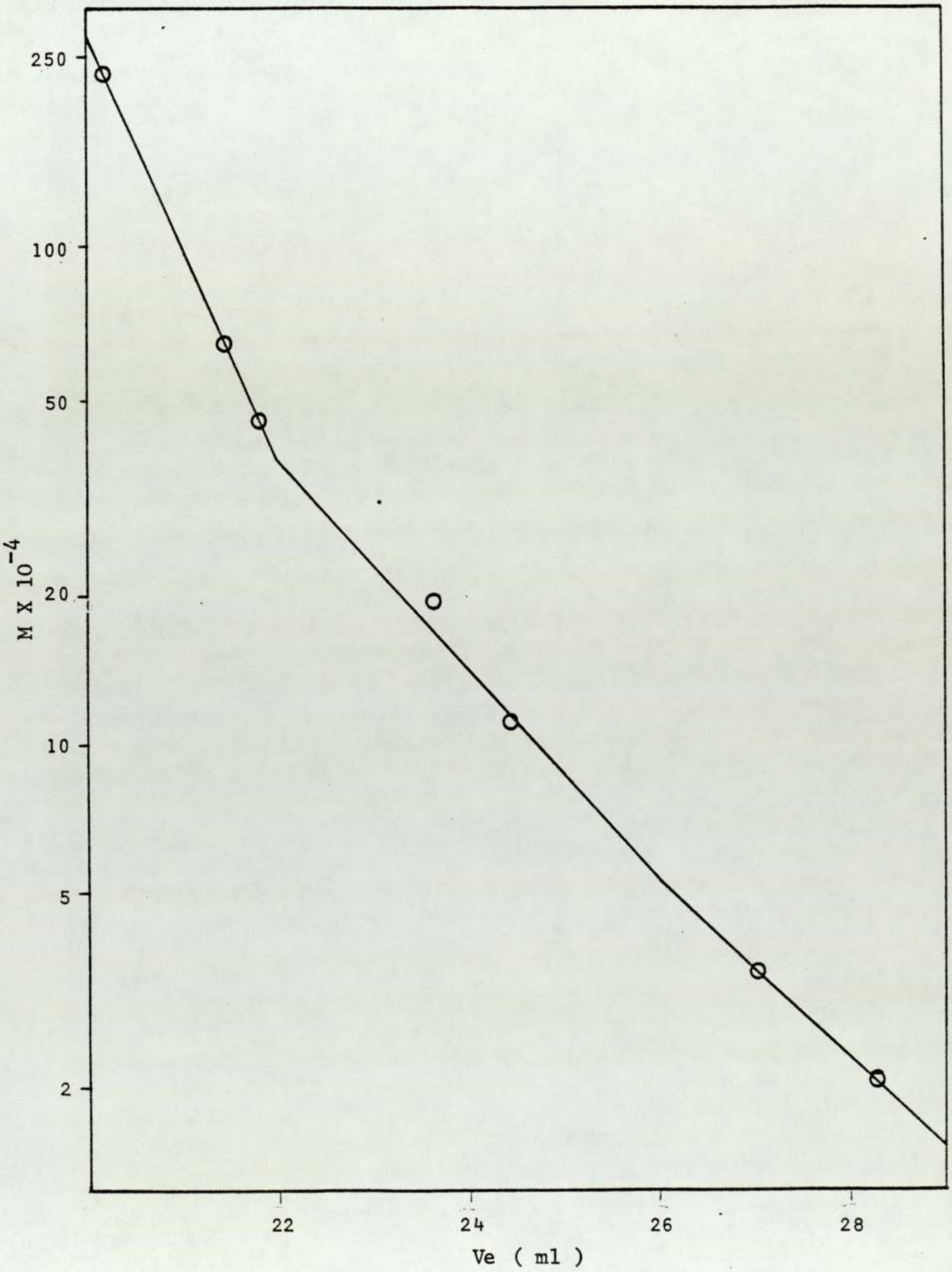
(iv) The role of the metal alkyl cocatalyst should be studied in greater detail.

(v) The origin of hydrogen chloride, produced in reaction between WCl_6 and cyclopentene, should be determined.

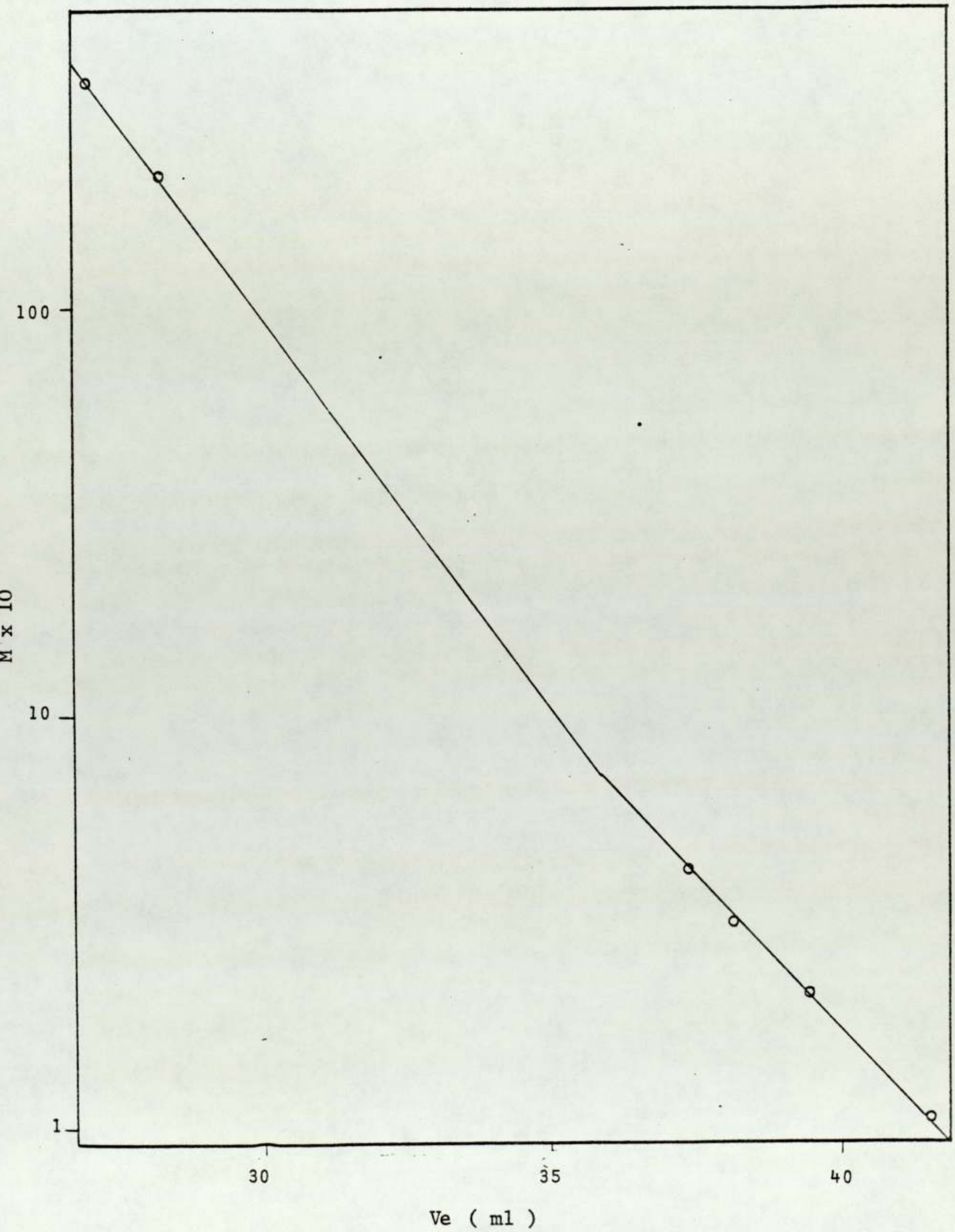
APPENDIX I

GPC CALIBRATION CURVES

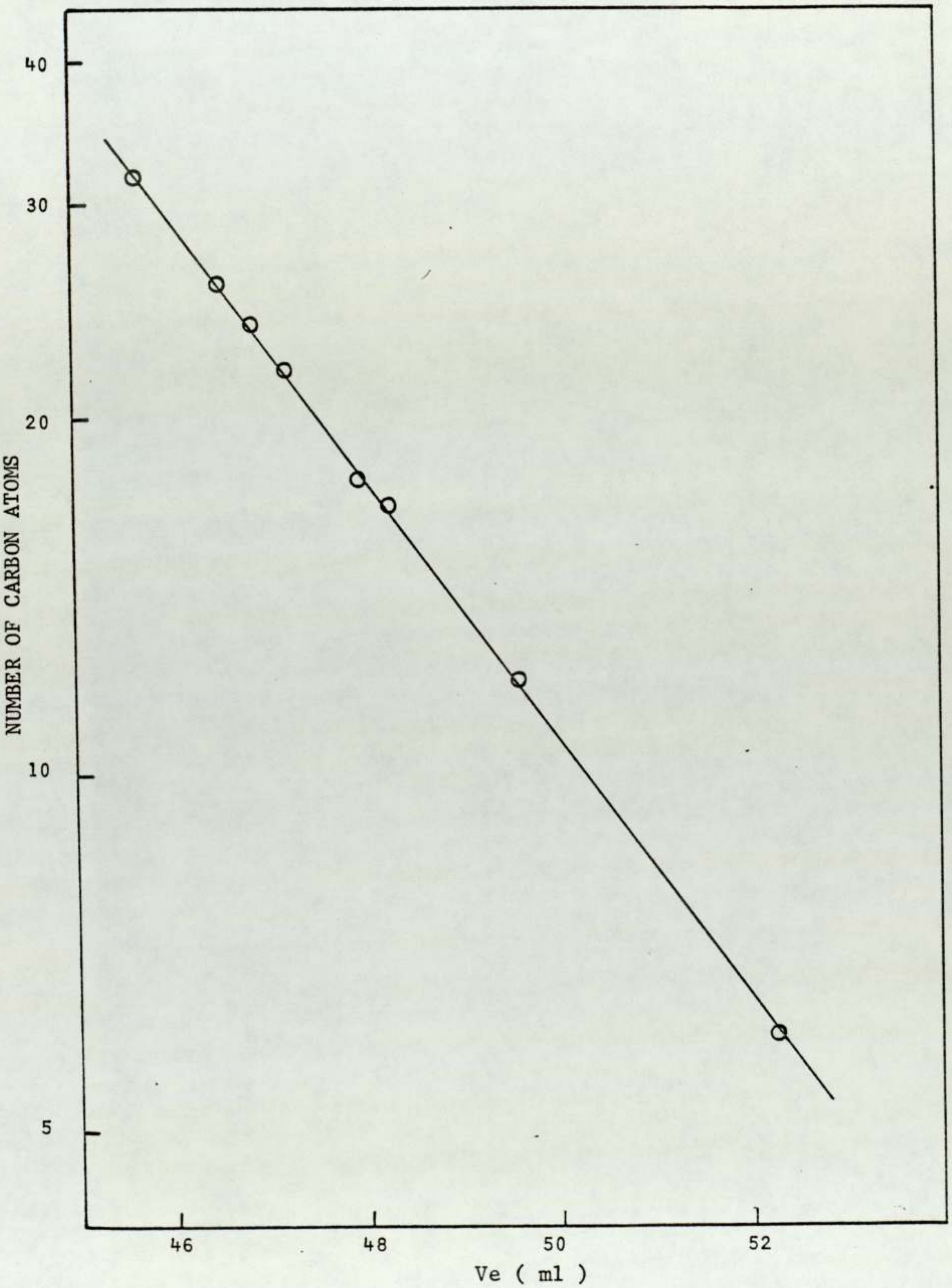
GPC CALIBRATION CURVE FOR HIGH MOLECULAR WEIGHT POLYSTYRENE



GPC CALIBRATION CURVE FOR MEDIUM AND LOW MOLECULAR WEIGHT POLYSTYRENE



GPC CALIBRATION CURVE FOR LINEAR ALKANES



APPENDIX II

PUBLICATION

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THE KINETICS OF THE METATHESIS POLYMERISATION OF CYCLOPENTENE INITIATED BY $WCl_6/AliBu_3$ COMPLEXES

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Summary

In a recent publication it was disclosed that catalysts derived from $WCl_6/AliBu_3$ display complex kinetic behaviour. Evidence was presented to suggest that a series of reactions takes place between WCl_6 and cyclopentene to produce a number of tungsten species which may subsequently react with $Al(iBu)_3$ to produce methathesis catalysts of varying activities. A significant observation was that the rate of polymerisation under a given set of conditions depends on the time that elapses between the addition of WCl_6 and $Al(iBu)_3$ to the solution of cyclopentene.

More recent investigations substantiate the fact that the catalyst produced from WCl_6 and $Al(iBu)_3$ is not a living system. During the course of polymerisation the rate of polymerisation decreases at a rate faster than can be accounted for by consumption of monomer alone. The decrease in the rate of polymerisation as observed by dilatometry is a reaction that is second order in the concentration of active species. Frequently the polymerisation of monomer to high molecular weight polymer did not proceed to equilibrium concentration of monomer; upon the further addition of catalyst components the polymerisation proceeded at a higher rate. The kinetics of termination show similarities with the bimolecular termination reaction that occurs in the Ziegler–Natta polymerisation of linear olefins, and support is given to the proposal by Ivin *et al.* for a mechanism common to both the metathesis polymerisation of cyclopentene and the addition polymerisation of α-olefins.

Substantial spectroscopic evidence is to be produced to show the presence of a number of species in the reaction system, the presence of these being used to account for the reactions that occur between cyclopentene, WCl_6 and subsequently $Al(iBu)_3$.

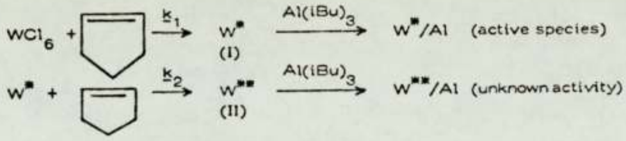
Introduction

In a previous publication [1], the kinetics of the polymerisation of cyclopentene were described when WCl_6 was used in conjunction with $Al(iBu)_3$ as a catalyst/initiator for the polymerisation. The principal characteristic of this system is its complex kinetic nature. The initial studies of the rate of polymerisation were fraught with difficulties because of the irreproducibility of the rates under apparently identical conditions. In summary it was found that:

(i) the rate of polymerisation depended on the time that elapsed between the addition of the catalyst components WCl_6 and $AliBu_3$ to a solution of cyclopentene (*i.e.*, the premixing time of WCl_6 with cyclopentene);

(ii) a time t_{max} was described which was the premixing time of WCl_6 with cyclopentene that produced the maximum rate of polymerisation (when $Al(iBu)_3$ was added) at a given concentration of monomer and initiator;

(iii) t_{max} depended upon the concentration of monomer. A simple kinetic scheme was drawn up that agreed with the observation that t_{max} was proportional to the reciprocal concentration of the monomer, *i.e.*



According to this kinetic scheme,

$$t_{max} = \frac{1}{[CP]_0}\left(\frac{1}{k_1 - k_2}\right) \ln \frac{k_1}{k_2} \qquad (1)$$

The present studies have been directed towards the verification of this scheme and the establishment of the presence of a number of intermediates that could be catalytically active.

Experimental

Purification of solvents, monomer and catalyst components

Rigorous purification procedures were adopted, which have been adequately described elsewhere [1].

Measurement of rate of polymerisation

(i) By dilatometry

For the design of the dilatometer used and the procedure adopted, reference should be made to a previous publication [1].

(ii) By measurement of the heat of polymerisation

A slight modification of the techniques described originally by Plesch and Biddulph [2] has been used. The apparatus is shown in Fig. 1, in which the temperature sensing device was a thermistor which was part of a Wheatstone Bridge circuit. The apparatus was calibrated over the temperature used

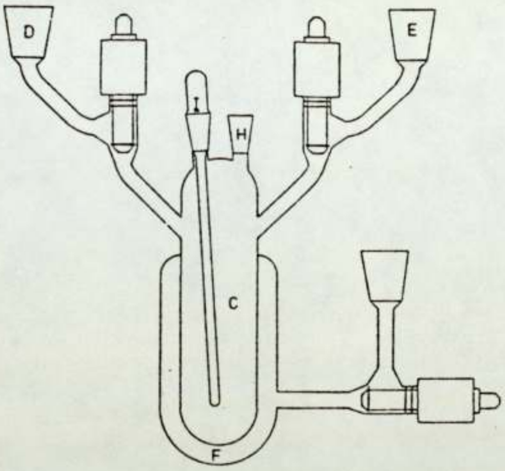


Fig. 1. Apparatus for calorimetric studies.

using a Knauer bridge and the deflection from the null point could be used to determine the temperature and enthalpy changes and hence the extent of reaction over a period of time.

UV spectrophotometric studies

A simple device was used for these studies consisting of a 0.1 cm cell that could be filled anaerobically and to which solutions of either cyclopentene, WCl_6 or $Al(iBu)_3$ could be added by syringe or by distillation. The UV/visible spectra in this series were recorded using a Unicam SP800 spectrophotometer.

Results and discussion

The previously described kinetic scheme postulated that a series of intermediates arises out of the reaction between WCl_6 and cyclopentene, one or more of which may be converted rapidly into an active catalyst for the polymerisation of cyclopentene upon the addition of $Al(iBu)_3$. The initial rate of polymerisation (Rp_0) could be described by the simple kinetic equation:

$$Rp_0 = kp[W^*/Al]_0[CP]_0 \tag{2}$$

and $[W^*/Al]_0$ was identical to [I] when $Al(iBu)_3$ was added and any I present in the system was 'frozen out' as active catalyst upon the addition of $Al(iBu)_3$. If this is so, the rate of polymerisation may be used as a measure of $[W^*/Al]$ at any time.

A typical curve for the determination of the rate of polymerisation of cyclopentene, as determined by dilatometry, is shown in Fig. 2, from which it can be seen that the rate of polymerisation decreased as a function of con-

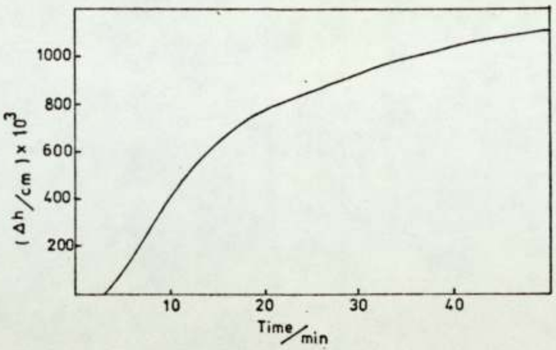


Fig. 2. Typical conversion–time curve determined by dilatometry.

version. If eqn. (2) applies to this system, the observed decrease in the rate of polymerisation can be ascribed either to a decrease in the concentration of monomer or to a decrease in the concentration of the active species for the polymerisation. The decrease in concentration of monomer that occurred during the course of the above polymerisation can be estimated from the ratio

$$\frac{h_0 - h_t}{h_0 - h_\infty}$$

to be of the order of 12% so that the decrease in concentration of monomer alone cannot be used to describe such a large decrease in the rate of polymerisation. Furthermore, if the monomer is consumed in a first order manner, a plot of log [monomer] against time should be linear. Such a plot is shown in Fig. 3 where a large deviation from linearity may be observed. This plot is typical of many similar dilatometric determinations of rates of polymerisation.

The failure to ascribe the decrease in the rate of propagation to the decrease in concentration of monomer led us to suspect that the decrease was

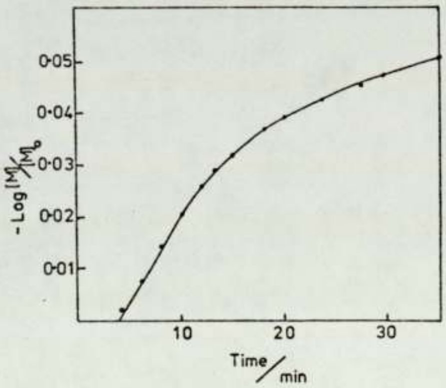


Fig. 3. Dependence of log[monomer] upon reaction time.

due to a consumption of the propagating centre. It has been stated earlier that the initial rate of polymerisation could be used as a method of determination of the concentration of active sites and so the rate of polymerisation, as determined by the slope of the curve at any time *t*, could be used as a measure of the concentration of active species at that time. When the conversion–time curve is analysed by such techniques, it is apparent that the decrease in the rate of polymerisation can be accounted for by a second order consumption of the propagating species. In agreement with such an observation is that the reciprocal rate of polymerisation and hence concentration of propagating species is a linear function of time as shown in Fig. 4.

Further evidence for the consumption of propagating species can be obtained from Fig. 5. This represents the course of the polymerisation of cyclopentene when $WCl_6/Al(iBu)_3$ is acting as initiator. From A to B represents the polymerisation initiated by the initial injection of catalyst components; at point B a further injection of catalyst, identical in amounts to the original injection, was performed and the rate of polymerisation was subsequently much higher, commensurate with the presence of a high concentration of propagating species. With this particular catalyst system, it would appear

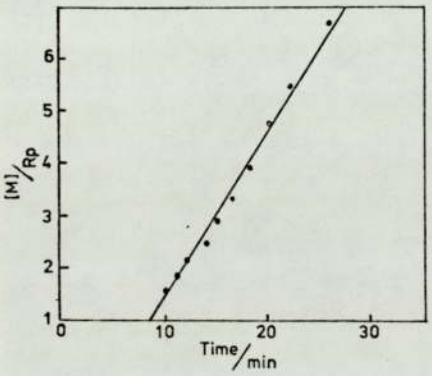


Fig. 4. Dependence of [M]/*Rp* upon reaction time.

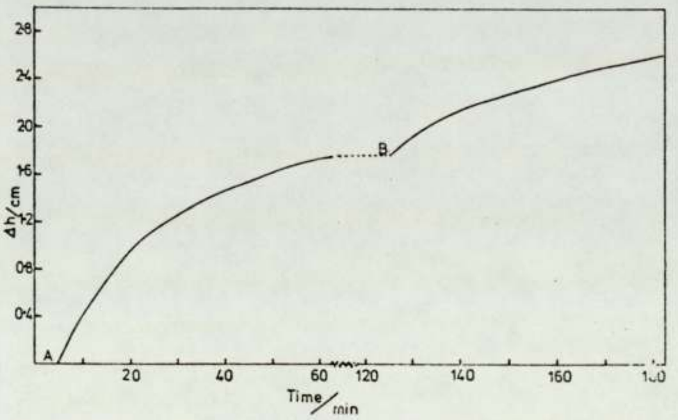


Fig. 5. Effect of separate additions of catalyst on the polymerisation of cyclopentene.

likely therefore that account has to be taken of the presence of a termination reaction. The depletion of catalyst species and the kinetic behaviour of this depletion would suggest that such a termination reaction should be second order in nature and it is proposed that the bimolecular termination reaction,

$$W^* + W^* \longrightarrow \text{Polymer}$$

is present. During this reaction, the activity of the propagating centre is destroyed and this does not represent any form of transfer reaction.

The measurement of the rate of polymerisation using a calorimetric technique

12 ml of a 1.9 M solution of cyclopentene in toluene were introduced into the reactor vessel (C) shown in Fig. 1, through tap D whilst the apparatus was evacuated through tap E. The apparatus was then filled with argon, and removed from the vacuum line. The silvered jacket (F) was then evacuated through tap G and the whole apparatus was thermally insulated from the surroundings. When the temperature of the apparatus was stable, 0.35 ml of 5×10^{-4} M solution of WCl_6 were added through the suba-seal (H) followed after 4 min by 0.35 ml of 1×10^{-3} M solution of $Al(iBu)_3$. The subsequent temperature change was recorded by the thermistor (I) as described earlier.

Figure 6 summarises a number of studies carried out with this system. The curve from the origin to (J) represents the temperature change recorded in the above experiment. It is assumed that in this system a measure is made of the amount of cyclopentene consumed in all reactions. If a comparison is made between this curve and that shown in Fig. 2, wherein the experiment was carried out under a similar set of conditions, the initial rate of consumption of monomer is maintained for a prolonged period. One can tentatively assume that the dilatometer is not therefore able to measure the rate of con-

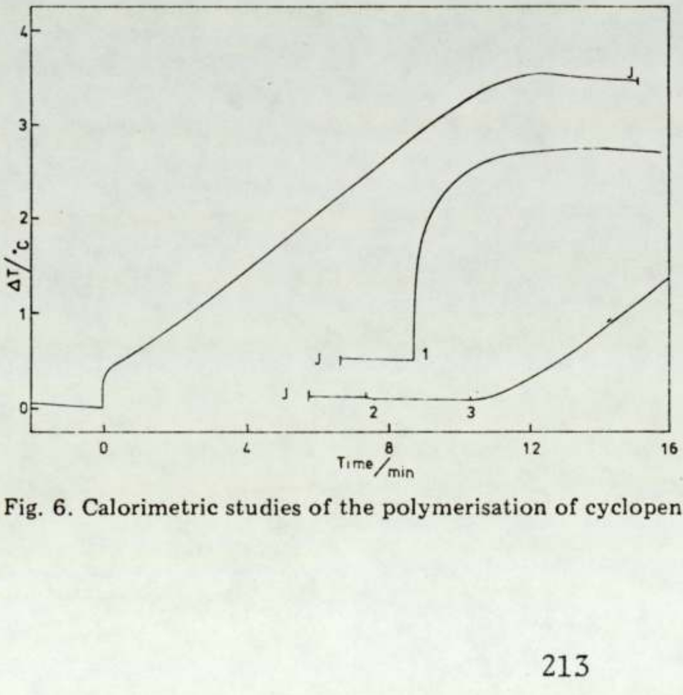


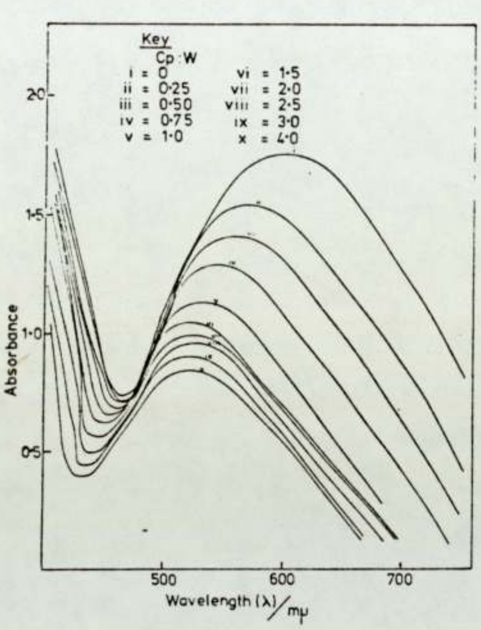
Fig. 6. Calorimetric studies of the polymerisation of cyclopentene.

sumption of monomer, only the rate of production of polymer of a sufficiently high molecular weight to cause the volume of the system to contract. The calorimetric curve however would suggest that cyclopentene is also consumed in a reaction that leads to the production of thermally more stable products but which are of similar density to that of cyclopentene. An analysis of the curves has not been carried out to apportion the contributions of the rates of production of polymer and oligomers in the above case. However, it is again established in this system that there is a termination reaction to be considered, for Fig. 6 also shows that if more WCl_6 is added (at point (1)) further consumption of cyclopentene ensues, whereas if more cyclopentene is added (point (2)) no reaction takes place. Point (3) on Fig. 6 shows the effect of introducing air into the apparatus which most likely causes an oxidation of the consumed catalyst back to its original active oxidation state. The initial rise in temperature on the addition of $Al(iBu)_3$ shown in Fig. 6 at zero time is probably due to complex formation between the $Al(iBu)_3$ and the tungsten compound. The reaction of WCl_6 with $AliBu_3$ in the absence of any monomer gives rise to a similar temperature rise.

UV/visible spectrophotometric study

The reaction between WCl_6 and cyclopentene has associated with it many colour changes. For this reason an attempt has been made to study the changes that take place in the UV/visible spectrum at all stages of the reaction. These studies were found to be extremely difficult to perform with any degree of reproducibility, principally because it was felt that the solvents used contained traces of impurities, and WCl_6 is such a powerful chromophor that dilute solutions of WCl_6, which could have led to high impurity: WCl_6 molar ratios had to be used. Spectrum (i) in Fig. 7 shows the visible absorption spectrum of WCl_6 in toluene; λ_{max} occurs at approximately 600 mμ. The solvent used in these studies was purified by successive distillations from WCl_6 until λ_{max} was constant. Samples of cyclopentene were then added to the solution of WCl_6 and the visible spectrum recorded after each addition until the molar ratio CP : WCl_6 was 4:1. These spectra are shown as (ii)-(x) in Fig. 7. It appeared initially that there was a gradual shift in λ_{max} as the addition of cyclopentene took place. However, on further investigation it would appear that curves (ii)-(iv) are in fact the resultants of the appropriate proportional additions of curves (i) and (v)(λ_{max} = 520 mμ).

The change from (i) to (ii) or any of the other spectra in the series was instantaneous at room temperature and, with hesitation, it is suggested that spectrum (v) may represent the presence of a simple coordination complex between WCl_6 and the olefin, most probably in a simple molar ratio CP : WCl_6. Closer examination of the spectra shown in Fig. 7 reveals that it is likely that a 1:1 complex of WCl_6 and cyclopentene is formed. Figure 8 shows the dependence of the absorption at 600 mμ on the cyclopentene : WCl_6 molar ratio when allowance is made for the dilution that occurs on the addition of cyclopentene.



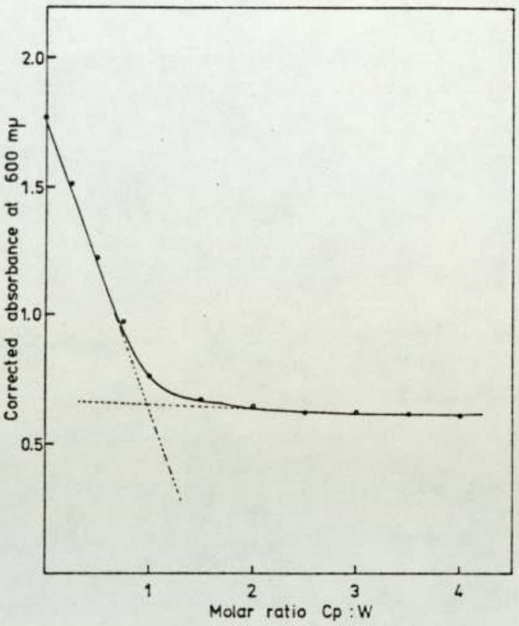


Fig. 7. Spectrophotometric studies of the reaction between WCl_6 and cyclopentene (CP).

Fig. 8. Effect of the CP:W molar ratio on absorbance at 600 mμ.

Whatever the structure of this species, it is not stable, for there is a further change in the absorption spectrum of the system if (x) is allowed to stand. Figure 9 shows the change that takes place in the absorbance at 520 mμ if the products of the reaction between WCl_6 and cyclopentene are allowed to stand. The disappearance of the peak at 520 mμ occurs in a first order manner with respect to the species giving rise to this peak, since a plot of log (absorbance) against time, shown in Fig. 10, is linear. It is not yet clear whether this reaction involves another molecule of cyclopentene but it

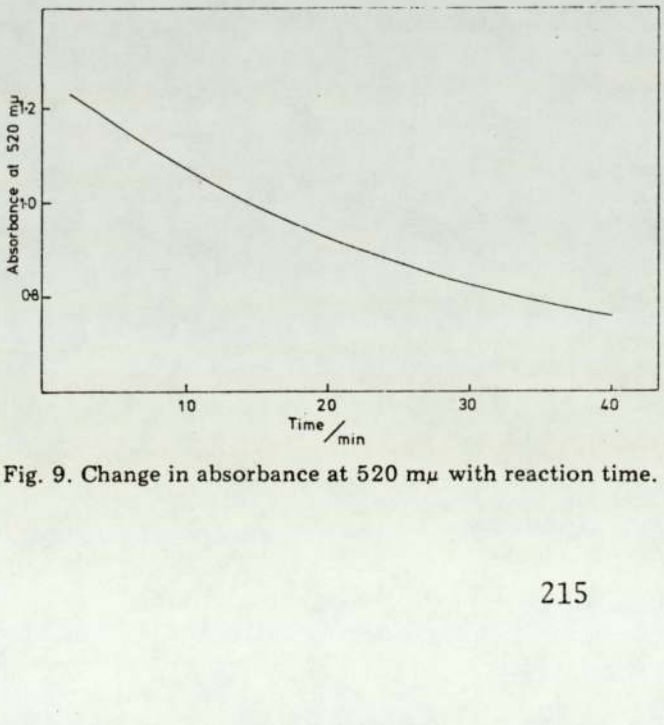


Fig. 9. Change in absorbance at 520 mμ with reaction time.

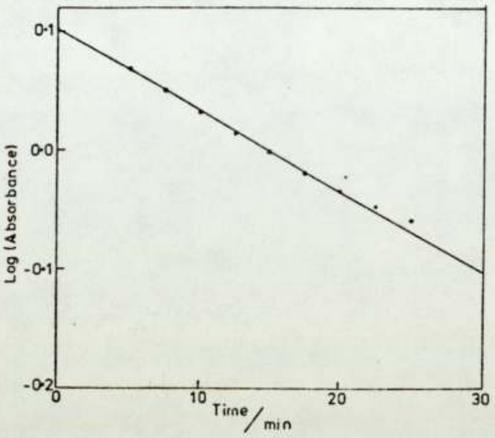


Fig. 10. Dependence of log[abs_{520}] on reaction time.

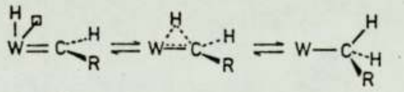
is highly likely that such a reaction could account for the deviation from linearity at long reaction times. The disappearance of the peak at 520 mμ is also commensurate with the change in catalytic activity as the time of premixing of cyclopentene with WCl_6 was changed in the dilatometric studies [1]. It is not easy to assign direct comparisons between these studies and those of the dependence of premixing time of WCl_6 and cyclopentene on the rate of polymerisation because the concentrations of materials are so substantially different.

Although the nature of the reaction products is unknown it is obvious that any mechanism proposed for the metathesis reaction using WCl_6 will have to take account of more than one intermediate that can react with $Al(iBu)_3$ to form a catalyst.

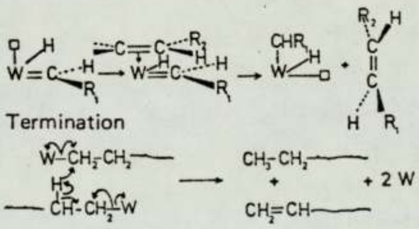
Conclusions

The spectroscopic evidence presented here suggests that there is a series of reactions that can take place between cyclopentene and tungsten hexachloride, the first product of which involves the reactant in a 1:1 molar ratio to give rise to a species that has an absorption maximum at 520 mμ. Furthermore, the product subsequently changes to some other species. The absorption curves for the addition of $Al(iBu)_3$ have not yet been resolved and are not presented at this time because they are complex and depend upon many factors including the molar ratios of WCl_6:Cl and W : Al and the time of reaction of cyclopentene with WCl_6. It is hoped that these will be included in a subsequent publication.

The presence of more than one species can be used to account for the comparative shapes of the dilatometric and calorimetric curves. As the rate of formation of high polymer decreases, the overall rate of consumption of monomer remains constant for a long period. It is possible that another species, as suggested to be present in a previous publication, gives rise to the difference in the consumptions of monomer and forms oligomeric material. Whatever the explanation for the overall consumption of monomer, the one or more catalytically active species present are undoubtedly involved in a termination reaction. When the consumption of monomer has ceased, the concentration of cyclopentene has not reached the equilibrium concentration because the addition of more monomer does not result in further reaction whereas the addition of more catalyst promotes further reaction. The decay in the rate of production of high polymer suggests a second order termination reaction, which of course is in agreement with the suggestion by Green *et al.* [3] that the Ziegler–Natta polymerisation of linear olefins and the ring-opening polymerisation of cyclic olefins are the same class of catalysis. Henrici-Olivé and Olivé [4] have proposed a second order termination reaction, involving a β hydrogen atom for the polymerisation of linear olefins. It is now tentatively suggested that the structure of the propagating species in this reaction could be:



where $\overset{H}{W\!=\!C}$ represents a type of π bridging bond that the propagation takes place by the following series using olefin metathesis as an example accounting also for the stereochemistry of the reaction:



Suitable molecular orbital diagrams can be drawn to validate this type of mechanism and also to account for the Cossee [5] monometallic propagation without flip-back.

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