To my parents
for their invaluable encouragement
and support throughout all
my studies

METATHETIC POLYMERISATION OF CYCLIC ALKENES

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SUMMARY

The monometallic initiation of the ring opening polymerisation of cyclopentene as a solution in toluene or chlorobenzene has been investigated by dilatometric and calorimetric techniques using WCl_6 or WCl_6/O_2 as the catalyst.

These studies indicated the occurrence of a series of reactions between cyclopentene and tungsten hexachloride and that the kinetic behaviour of the system and the products of the reaction depended on the solvent used. The kinetic behaviour of WCl_6/cyclopentene system in toluene was complex; the dependence of the rate of polymerisation on the concentration of tungsten hexachloride showed a maximum. Deviations from simple kinetics were associated with the slow formation of an oily precipitate. In the chlorobenzene system the products of the reactions remained soluble and the kinetics of the polymerisation have been interpreted in terms of one of the intermediate products of the series of reactions acting as active species for the metathesis polymerisation of cyclopentene.

Spectrophotometric studies have been used in chlorobenzene to elucidate the kinetic nature of the reaction involved in the system. Based on this technique and by use of computer simulation a kinetic scheme has been postulated and the rate constants obtained from these studies have been applied to dilatometric results to explain many of the features of the polymerisation. According to this kinetic scheme the active species is most likely removed from the system by a bimolecular termination reaction.

It was found that oxygen could only have a very effective cocatalyst activity if the system was heterogeneous where the source of activity before the addition of oxygen could remain dormant and the active centres produced on the addition of oxygen to the system insoluble.

Polymerisation of n-butyl vinyl ether initiated by a metathesis active species indicated that the metathetically active species could be ionic in nature.

KEY WORDS :

METATHESIS, RING-OPENING POLYMERISATION, CYCLOPENTENE,
TUNGSTEN HEXACHLORIDE, OXYGEN.

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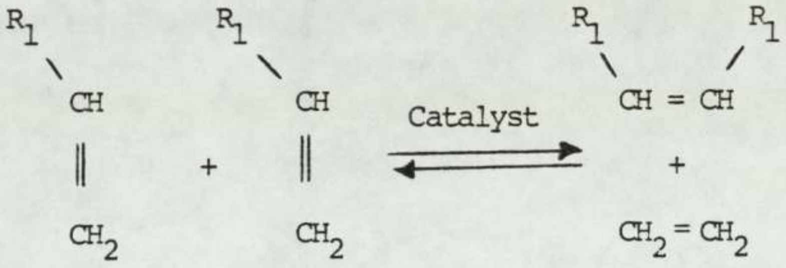
CHAPTER 1

LITERATURE SURVEY

1.1 INTRODUCTION

The subject of olefin metathesis, discovered by Banks and Bailey$^{(1)}$ in 1964, has drawn considerable attention towards the development and study of one of the most intriguing fields of chemistry ever known with the application ranging from the production of high molecular weight polymers from the ring opening of cyclic alkenes, to the preparation of new alkenes by the metathesis of acyclic olefins.

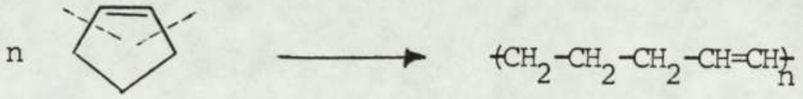
The metathesis of olefins and ring opening polymerisation of cyclic alkenes is a catalytic reaction involving the making and breaking of carbon-carbon double bonds, an example of which might be:



A non-catalytic counterpart of this reaction was observed in 1931 by Schneider and Frohlich$^{(2)}$ while studying the mechanism of formation of aromatics from aliphatic hydrocarbons. They reported that Propylene could be converted by heating at 725°C to ethylene and butene. 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.$^{(3)}$

It was not until the discovery of heterogeneous and homogeneous catalysts, which could promote the reaction at much lower temperatures and minimise side reactions, that the potential of the metathesis reaction could be realised. The catalysis of the reaction was first mentioned by Banks and Bailey (1) who reported that an acyclic olefin could more readily and selectively give rise to roughly equimolar amounts of the higher and lower molecular weight homologues when contacted with heterogeneous catalysts prepared from molybdenum or tungsten hexacarbonyls supported on alumina.

Prior to Banks and Bailey's discovery, (1) the polymerisation of cyclic alkenes by both heterogeneous (4) and homogeneous catalysts (5-7) had been reported, but its similarity to the olefin metathesis reaction was not recognised at the time. The mechanism suggested by Natta (6) for the ring opening polymerisation reaction involved cleavage of a carbon-carbon single bond adjacent to the double bond.



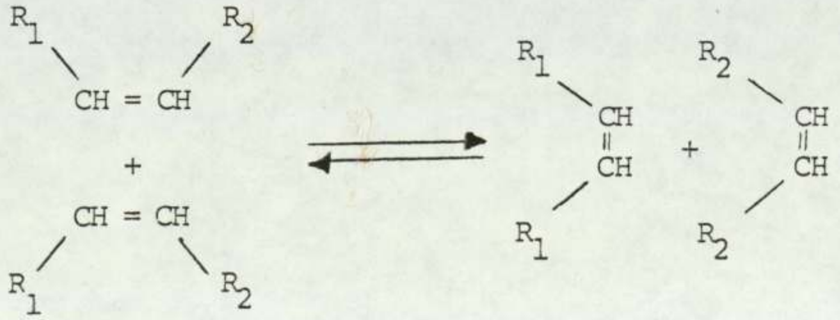
Calderon and co-workers (8-10) were the first to report the homogeneous catalysis of linear olefin metathesis using WCl_6-EtOH-$EtAlCl_2$ as a catalyst mixture and to recognise the similarity between the reactions of cyclic and acyclic alkenes. They also suggested that both reactions should be explained by an exchange of alkylidene groups.

The determination of the nature of the catalyst responsible for the olefin metathesis and the ring opening polymerisation of cyclic alkenes is difficult. In most cases the catalyst is generated by the interaction of a transition metal compound of group IV or VI with an organometallic species of groups I to III. The catalyst systems are very sensitive to oxygen; traces of oxygen appear to activate the catalyst (11,12) while large amounts destroy the catalytic activity of the species.

Since the initial discovery of olefin metathesis attempts have been made to apply this reaction to a range of substrates, many of which have functional groups, or in more recent work are alkynes. Despite the large research interest in this field, few successful industrial applications have been reported, the most notable of which is probably the "Phillips Triolefin Process". (13)

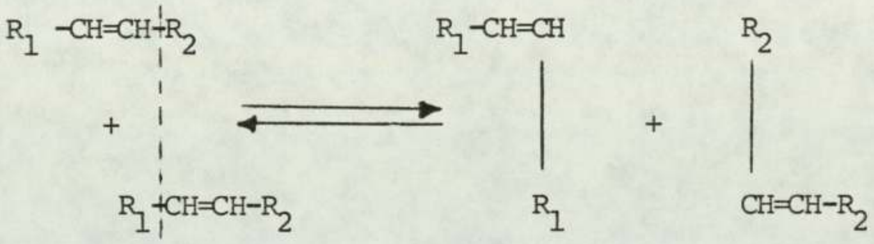
1.2 GENERAL ASPECTS OF OLEFIN METATHESIS

The general metathesis reaction by which olefins are converted to product olefins can be represented by :



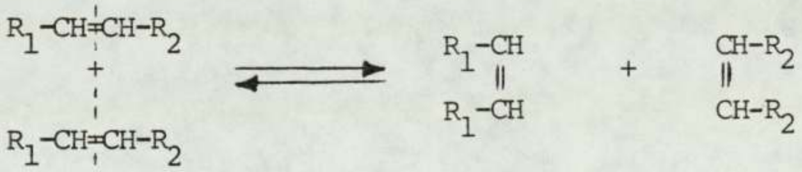
Two schemes which could restrict the product mixture to that observed were visualised as possible routes for such a reaction:

(i) Transalkylation which involves the interchange of alkyl groups via cleavage of a carbon-carbon single bond adjacent to the double bond, and is generally analogous to the mechanism proposed by Natta(6) i.e.

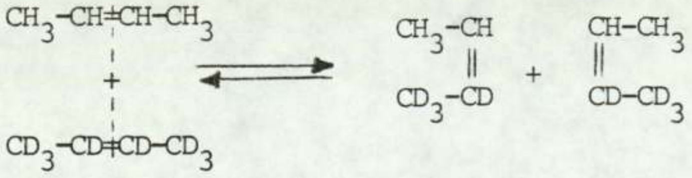


and (ii) Transalkylidenation which involves the cleavage of the double bond itself as a means of redistributing the alkylidene species;

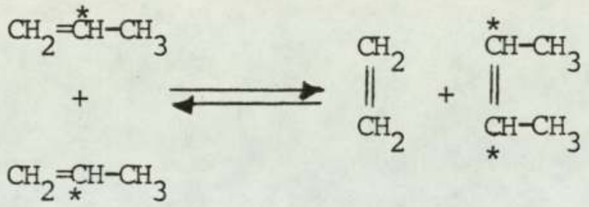
thus:



To distinguish between these two possibilities Calderon and co-workers(9) analysed the products formed in the reaction of a deuterated olefin with the analogous normal olefin using the homogeneous system WCl_6-EtOH-$EtAlCl_2$. In the reaction between 2-butene and 2-butene-d_8, the only new product was 2-butene-d_4. They concluded that a transalkylidenation reaction had taken place.



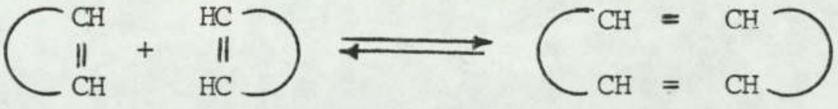
Mol et al (14) obtained analogous results in the heterogeneously catalysed metathesis of propene labelled with ^{14}C. In experiments with 2-^{14}C propene in the presence of Re_2O_7-Al_2O_3 catalyst, the ethylene formed showed no radioactivity while the 2-butene showed a molar radioactivity twice as high as that of the starting material. This result also excludes the transalkylation reaction and reinforces the transalkylidenation scheme for the metathesis reaction.



$$CH_2{=}\overset{*}{C}H{-}CH_3 + CH_2{=}\underset{*}{C}H{-}CH_3 \rightleftharpoons CH_2{=}CH_2 + CH_3{-}\overset{*}{C}H{=}\overset{*}{C}H{-}CH_3$$

Further experiments with 1-^{14}C propene and 3-^{14}C propene showed that the methyl groups of the respective propenes retain their identities throughout the metathesis reaction thereby excluding the formation of any π-allylic intermediate in providing a pathway for double bond migration. Similar results were obtained by Clark and Cook (15) in experiments with radioactive propene on a MoO_3-CoO-Al_2O_3 catalyst.

Calderon et al (10) and Wasserman et al (16) were the first to realise that the ring opening polymerisation which had been known for several years might be a special case of the metathesis reaction. In contrast with Natta (6) who had proposed earlier that the ring opening polymerisation proceeds by cleavage of a carbon-carbon single bond adjacent to the double bond, they suggested a transalkylidenation mechanism.



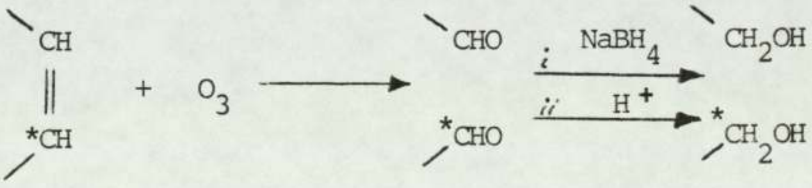
Direct experimental evidence for the transalkylidenation mechanism in the case of ring opening polymerisation of cyclic alkenes was shown by Dall'Asta and Motroni$^{(17,18)}$ who copolymerised cyclooctene with cyclopentene, which was ^{14}C labelled at the double bond; the catalyst system consisted of $WOCl_4/EtAlCl_2$/benzoyl peroxide. From an analysis of the distribution of radioactivity in the random copolymer the site of ring opening could be located. The distribution of radioactivity in the case of α-single bond cleavage would be as follows:

$$\sim\sim -CH{=}CH-(CH_2)_6-\overset{*}{C}H{=}\overset{*}{C}H-(CH_2)_3-CH{=}CH-(CH_2)_6- \sim\sim$$

Cleavage of the double bond would lead to a different distribution:

$$\sim\sim {=}CH-(CH_2)_6-CH{=}\overset{*}{C}H-(CH_2)_3-\overset{*}{C}H{=}CH-(CH_2)_6-CH{=} \sim\sim$$

When the copolymer was ozonised and reduced it was found that all the radioactivity was present in the C_5 diol.



Thus the products of the reaction were:

$HOCH_2-(CH_2)_6-CH_2OH$	1,8 - octanediol
$HO\overset{*}{C}H_2-(CH_2)_3-\overset{*}{C}H_2OH$	1,5 - pentanediol

It was therefore concluded that the metathesis reaction of cyclic and acyclic alkenes indeed proceeds via the rupture and formation of carbon-carbon double bonds.

1.3 CATALYST SYSTEMS:

A wide variety of metallic derivatives have been reported to activate the metathesis of olefins and the ring opening polymerisation of cyclic alkenes. The majority of these catalysts contain either tungsten or molybdenum as the transition metal. Other transition metals that show metathesis activity include Ta, Nb, Ru and Re. The catalysts can be classified into two main categories.

(i) Heterogeneous Catalysts: Heterogeneous catalysts are normally composed of a transition metal oxide or carbonyl promoter deposited on a high surface area support such as alumina or silica, and in certain cases combine with a co-catalyst.

(ii) Homogeneous Catalysts: Homogeneous catalysts generally contain a transition metal salt or coordination compound in combination with a selected organometallic derivative or a Lewis acid. Muetterties and Busch(19) have reported that some of the catalysts prepared from soluble precursors could in fact be heterogeneous due to formation of a solid which is active towards the metathesis reaction.

Complexes of W(VI) as well as W(0) are active precursors for both types and the co-catalyst used to activate the system may also range from Lewis acids, such as $AlCl_3$ or $AlBr_3$ to strong reducing agents like LiBu or $LiAlH_4$. Monometallic systems have also been reported to promote the metathesis reaction.(20-24)

Therefore every catalyst system must be treated independently with the hope of producing an overall mechanism for the olefin metathesis reaction, but with such a wide range of catalyst combination available the exact nature of the active site is difficult to describe

1.3.1 HETEROGENEOUS CATALYSTS :

Supported heterogeneous catalysts for the metathesis reaction are mainly transition metal oxides, carbonyls or sulphides deposited on high surface area supports. Catalysts derived from the oxides and carbonyls of molybdenum, tungsten and rhenium show the greatest activity for olefin metathesis.(1,25-27) Silica and alumina have been found to be the most effective supports and are the most widely used. Heterogeneous catalysts based on rhenium oxide have high activity and selectivity characteristics at temperatures as low as 25°C.(28)

The exact role of each component in a catalytic system is not easily distinguished. In fact MoS_2 alone has been reported to be effective for olefin metathesis after evacuation at about 450°C for several hours.(22) On the other hand alumina has been observed to promote the metathesis of propene in the absence of any promoter(20), as has magnesium oxide(21), although their activities are very low.

1.3.1.1. PREPARATION AND ACTIVATION :

Activation of heterogeneous catalyst systems before use is necessary, probably to remove catalyst poisons such as water and other polar compounds from the surface of the catalyst. High temperature activation may also provide some chemical interaction between the promoter and the support.

A typical supported metal oxide catalyst is prepared by impregnating the alumina support with an aqueous solution of ammonium metatungstate. The suspension is then dried by rotary evaporation and activated at 500°-600°C for about 5 hours, when the metatungstate decomposes to tungsten oxide on the surface of the support.

The high temperature activation of transition metal oxides can be carried out in air while high vacuum condition or an inert atmosphere is necessary for activation of transition metal carbonyls, due to their high sensitivities to air. These can be prepared by impregnating pre-activated alumina under vacuum with hexacarbonyl-cyclohexane solution at about 65°C. Cyclohexane is then removed under vacuum at 120°-140°C.

Infra-red spectroscopy results established by Kemball and co-workers(29,30) show that 2 or 3 moles of carbon monoxide are evolved during the activation of $Mo(CO)_6$-Al_2O_3 catalyst. However it has been shown subsequently that $Mo(CO)_4$ is not an active species and therefore an active site completely free of CO or even oxidised was suggested for supported metal carbonyl catalysts.(31,32)

The activity of supported metal oxide type catalysts can be regained by repeating the activation procedure using a controlled amount of oxygen to burn off accumulated coke.(25,33) Indeed regeneration of WO_3-Al_2O_3 for 110 times over a period of one year has been reported.(33)

1.3.1.2. ENHANCEMENT OF CATALYTIC ACTIVITY :

Side reactions such as a double bond isomerisation which lower the selectivity could largely be reduced by treating the catalyst with various metal ions.(34-36) Bradshaw and co-workers increased the selectivity of the catalyst by poisoning the isomerisation sites with sodium ions.(34) Incorporation of cobalt oxide to the catalyst system has been reported to reduce the coke formation.(1)

A controlled treatment of oxide based catalysts with gases such as carbon monoxide and hydrogen can increase the activity and selectivity of the catalyst although prolonged treatment causes deactivation.(25,27,33,37)

The activity of supported metal carbonyls could also be increased by pretreatment of the catalyst. Kemball and co-workers(38) showed that the activity of $Mo(CO)_6$-Al_2O_3 is enhanced by treating the catalyst with halogenated alkenes before admission of reactants. The inclusion of various additives in the olefin feed can also have remarkable effect on activity and selectivity of the catalyst(39-41) Addition of tributyl phosphine has been reported to increase the conversion of 2-pentene catalysed by WO_3-SiO_2(39) as triethyl aluminium has for increasing the activity of supported metal oxide catalysts.(40)

1.3.2 HOMOGENEOUS CATALYSTS :

The olefin metathesis can be performed in the homogeneous phase with complexes of tungsten, molybdenum or rhenium associated with various co-catalysts such as alkyl aluminium compounds, butyl lithium, Grignard compounds or alkyl and aryl tins. In fact the first homogeneous system for the olefin metathesis has been reported by Natta and co-workers(6) who polymerised cyclopentene through ring opening using WCl_6-$Al(C_2H_5)_3$ as catalyst system.

Significantly, Ivin and co-workers (24) have shown that $EtAlCl_2$ alone under certain conditions catalyses the ring opening polymerisation of norbornene. Amass and co-workers(23) on the other hand, have reported the metathesis polymerisation of cyclopentene using WCl_6 alone as the catalyst. This could perhaps indicate the involvement of aluminium along with the transition metal in the active site.

There are three main factors affecting the reactivity of the homogeneous catalysts towards the metathesis of any given olefin substrate, namely:

(i) the combination of catalyst components
(ii) the molar ratio of the respective components
and (iii) the order of mixing of catalyst components

1.3.2.1 COMBINATION OF CATALYST COMPONENTS :

Most of the catalyst systems able to metathesise both acyclic internal olefins and cyclic alkenes are based on WCl_6.(9,42)

Calderon and co-workers were first to introduce a homogeneous catalyst for the acyclic olefin metathesis reaction.(8) They used WCl_6-$EtAlCl_2$-EtOH to convert 2-pentene into 2-butene and 3-hexene. This catalyst is also very effective in the metathetic polymerisation of a variety of cyclic alkenes.(42)

The activity of the catalyst for polymerisation of cyclopentene has been reported to improve significantly by slight modification of the catalyst, where a chlorinated alcohol is employed in place of ethanol.(43)

Homogeneous catalysts suitable for the metathesis of α-olefins may be derived from dichlorodinitrosyl molybdenum (II) or tungsten (II) complexes in combination with an organoaluminium halide.(44, 45) Zuech et al have reported that $MoCl_2(Py)_2(NO)_2$-$(CH_3)_3Al_2Cl_3$ is an active catalyst towards the metathesis of 1-octene.(44)

Catalyst systems based on $MoCl_5$ are essentially inactive on internal or terminal acyclic olefins but a fair catalytic activity towards the ring opening polymerisation of cyclobutene and cyclopentene has been reported for the catalyst system $MoCl_5$-R_3Al.(5,6)

1.3.2.2. MOLAR RATIO OF CATALYST COMPONENTS :

The molar ratio of the catalyst components is one of the main factors governing the activity of the catalyst. Wang and Menapace(46) observed a sharp dependency of the conversion on the ratio Li/W while studying the metathesis of 2-pentene using WCl_6-nBuLi. Only at Li/W=2 were good results obtained, suggesting a W^{IV} catalytic intermediate for the reaction.

Using WCl_6-$EtAlCl_2$ as catalyst for the ring opening polymerisation of cyclooctene and 3-methyl cyclooctene a maximum catalytic activity has been observed with Al:W=4.(47) Significantly, studies on zerovalent tungsten complexes give the same results.

Korda et al (48) have studied the influence of the Al:W molar ratio on the metathesis of 3-heptene using (mesitylene)$W(CO)_3$-$EtAlCl_2$ system and found that the highest activity could be obtained with Al:W=4.

These observations explain the complexity of the active catalyst and why the exact role of cocatalyst is still unclear.

1.3.2.3. - EFFECT OF ORDER OF MIXING :

The activity of the catalyst can be greatly influenced by the way the reaction components are mixed. Addition of catalyst to the olefin solution followed by incorporation of cocatalyst and activator is known as the conventional method.

Addition of 2-pentene to a premixed system of WCl_6-$EtAlCl_2$ in toluene has been reported to produce a rapid Friedel-Crafts alkylation almost exclusively, whereas preparation of the catalyst in the presence of the olefin results in a rapid metathesis reaction.(49)

Amass and Tuck(50) have reported that the rate of polymerisation of cyclopentene greatly depends on the time delay between the addition of WCl_6 and $Al(iBu)_3$ to the monomer solution. They introduced a t_{max} term at which the polymerisation rate was at its maximum and found that this had a reciprocal proportionality to the initial monomer concentration.

Menapace and co-workers$^{(51)}$ have studied the influence of the order of mixing of reagents on the metathesis of 2-pentene using WCl_6-$PhNH_2$-$Et_3Al_2Cl_3$ and found that the poorest selectivity was observed when $Et_3Al_2Cl_3$ had reacted with WCl_6 before the addition of aniline and olefin. Earlier reports by the same group$^{(52)}$ showed a decrease in selectivity when the binary catalyst system WCl_6 and nBuLi were premixed in the absence of the 2-pentene, but in the presence of $AlCl_3$ or $AlBr_3$ as activator both conversion and selectivity were improved only when WCl_6 and n-BuLi were premixed prior to the addition of the olefin and aluminium compound.

1.3.2.4 ENHANCEMENT OF CATALYST ACTIVITY :

The catalyst activity of WCl_6 based catalyst may be increased by controlled treatment of the tungsten complex with protic substances such as ethanol, prior to the addition of the organoaluminium compound$^{(8)}$. It is believed that species such as WCl_5OEt are formed and the reaction is accompanied by the evolution of stoichiometric amount of hydrogen chloride.$^{(53)}$ Höcker and Jones have reported that the formation of WCl_5OEt is in fact a two-step process.$^{(54)}$

$$WCl_6 + 2C_2H_5OH \xrightarrow{-HCl} (C_2H_5O)_2\,WCl_4$$

$$(C_2H_5O)_2WCl_4 + WCl_6 \longrightarrow 2\ C_2H_5OWCl_5$$

Wang et al$^{(52)}$ have studied the effect of aluminium halide on the metathesis of 2-pentene by a binary catalyst system of WCl_6-nBuLi and found that the activity of this system increases considerably by introducing $AlCl_3$ or $AlBr_3$ to the catalyst system.

It has been reported that under an atmosphere of carbon monoxide the activity of metathesis catalysts derived from group VI metal halide complexes increases considerably compared with an argon atmosphere; formation of metal carbonyl derivatives may well have taken place.(55) Carbon monoxide not only increases the activity but also has a marked effect on the selectivity of the catalyst system, especially when a terminal olefin is used. Bencze and Marko reported (55) that under carbon monoxide atmosphere the catalyst system obtained from $W\left[C_2H_4(PPh_2)_2\right]_2\text{-}Cl_3$ and $EtAlCl_2$ could transform 90% of the initial 1-pentene to a mixture composed of about equal quantities of 2-pentene, hexenes, heptenes and octenes, whereas similar experiments under argon showed a metathesis conversion of 2% for 1-pentene.

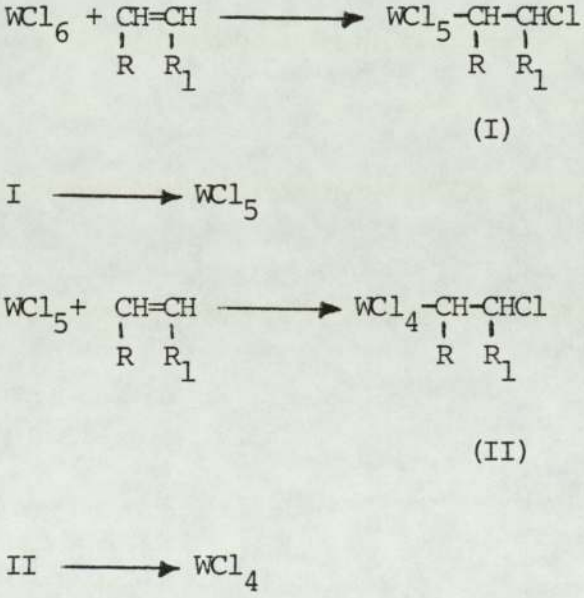
Nitric oxide is also capable of increasing the catalyst activity of a number of molybdenum systems, presumably through formation of molybdenum nitrosyl species. Treatment of $MoCl_3(PhCO_2)_2$ with nitric oxide prior to the addition of $Me_3Al_2Cl_3$ results in a catalyst which gives a 60% yield of 4-octene from 1-pentene after 17 minutes. Without NO treatment this catalyst gave only 0.8% conversion after 1 hour.(56)

Oxygen has been reported to have a rate increasing effect on the metathesis reaction.(48, 57) The catalyst activity of (mesitylene)$W(CO)_3\text{-}EtAlCl_2$ increases by introducing molecular oxygen into the system.(48) Amass and Zurimendi have suggested that the rate-increasing effect of oxygen is probably due to re-oxidation of consumed catalyst back to its original active oxidation state.(57)

1.3.2.5. REACTION OF TRANSITION METAL COMPOUND WITH OLEFIN

Although the olefin metathesis reaction has been the subject of intensive investigations in recent years, only few reports have been found in the literature on the initial interaction between transition metal compounds and the olefin.(50, 58, 59)

Based on the report by Brown and McCann (60) investigating the reduction of tungsten hexachloride by tetrachloroethylene, Amass (58) proposed the following reactions as the initial interaction involved in the olefin metathesis reaction:



$$WCl_6 + \underset{R}{CH}{=}\underset{R_1}{CH} \longrightarrow WCl_5{-}\underset{R}{CH}{-}\underset{R_1}{C}HCl$$

(I)

$$I \longrightarrow WCl_5$$

$$WCl_5 + \underset{R}{CH}{=}\underset{R_1}{CH} \longrightarrow WCl_4{-}\underset{R}{CH}{-}\underset{R_1}{C}HCl$$

(II)

$$II \longrightarrow WCl_4$$

Table 1-1 shows the changes in the oxidation state, determined by ceric sulphate titration, of the tungsten atom during the reactions involved in the polymerisation of cyclopentene.(58)

TABLE 1-1 CHANGES IN THE MEAN OXIDATION STATE OF TUNGSTEN DURING THE REACTIONS INVOLVED IN THE POLYMERISATION OF CYCLOPENTENE.(58)

REACTION CONDITIONS	MEAN OXIDATION STATE
1) WCl_6 Solution	6.0
2) WCl_6+CP after 1 minute	5.1
3) WCl_6+CP after 20 minutes	4.3
4) (3)+$AliBu_2OiBu$	4.3
5) (4) after 2 hours	4.4

Filippo and co-workers(61) have reported the reaction of $MoCl_5$ or WCl_6 with olefins as a potentially useful procedure for the stereoselective chlorination of carbon-carbon double bonds. In the reaction of $MoCl_5$ with cyclopentene, a 66% yield of cis 1,2 dichlorocyclopentane and no trans (less than 1%) was observed.

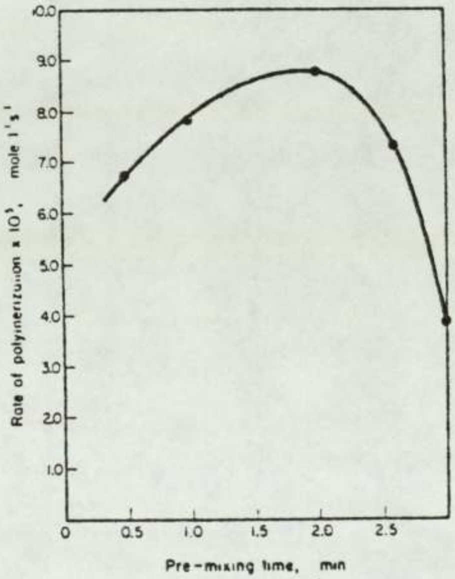
Addition of WCl_6 to the solution of cyclopentene in toluene prior to the incorporation of $AliBu_3$ in the ring opening polymerisation has been reported to be accompanied by colour changes, suggesting that the WCl_6 reacts with cyclopentene in some ways to change the nature of the ligands surrounding the tungsten atom.(50) In fact ultraviolet/visible spectrophotometric studies by Amass and Zurimendi(57) indicate the possibility of the immediate formation of a 1:1 complex between WCl_6 and cyclopentene followed by reaction of this complex with another cyclopentene molecule.

Such reactions can help to explain the activity of the $WCl_6/AliBu_3$ catalyst system for the polymerisation of cyclopentene. The strong dependence of the rate of polymerisation on the time delay between the addition of WCl_6 and $AliBu_3$ to the cyclopentene solution as shown in fig. 1-1, was explained by a series of reactions between WCl_6 and monomer$^{(50)}$:

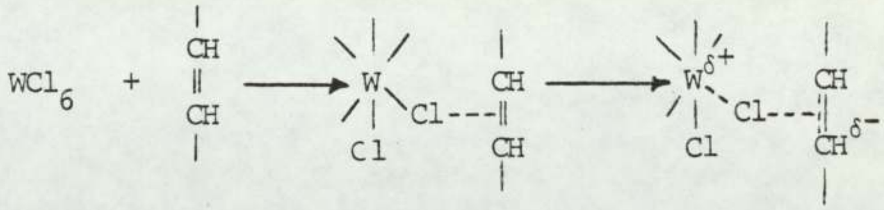
$$WCl_6 + CP \longrightarrow W^* \xrightarrow{2AliBu_3} W^*/Al_2$$

$$W^* + CP \longrightarrow W^{**} \xrightarrow{AliBu_3} W^{**}/Al_x$$

Fig. 1-1 Dependence of the rate of cyclopentene polymerisation on pre-mixing time$^{(50)}$.



Furthermore, studies on polymer degradation by olefin metathesis using WCl_6-$Sn(Me)_4$ catalyst system led Hummel et al$^{(59)}$ to suggest a complex formation between WCl_6 and the double bond of the olefin or the polymer:



Significantly WCl_6 alone has been reported to polymerise cycloolefins by the ring opening mechanism(23) and reactions of this type, between the transition metal halide and cyclopentene, must be considered.

1.3.2.6 ROLE OF COCATALYST :

It was initially believed that the organometallic component acts as reducing agent in the olefin metathesis reaction. Wang and Menapace(46) have suggested that the function of BuLi in the binary catalyst system WCl_6- nBuLi could be to reduce W(VI) to W (IV) since the W:Li molar ratio 1:2 was observed to give the maximum catalyst activity and proposed the following reactions :

$$WCl_6 + 2BuLi \xrightarrow{-2LiCl} \overset{VI}{WCl_4(Bu)_2} \xrightarrow{-2Bu.} \overset{IV}{WCl_4}$$

$$WCl_4 + 2Olefin \rightleftharpoons WCl_4\ (olefin)_2$$

However, treatment of WCl_6 with reducing agent such as zinc, magnesium or sodium amalgam, which should produce WCl_4, does not lead to catalytically active species(62). Furthermore the cocatalyst activity of $EtAlCl_2$ in systems containing zerovalent tungsten complexes such as (mesitylene) W $(CO)_3$(48) indicates that the reducing property of the organometallic compound should not be considered as the only function involved.

The combination of WCl_6 with the non-reducing cocatalyst $AlBr_3$ is indeed a very active catalyst for the ring opening polymerisation of cyclic alkenes.(63) Two possible explanations have been presented for the role of aluminium halide in this system, both taking account of the Lewis acidity of the AlX_3(X = halide).
It has been suggested that the inactive trans bisolefin complex, $(\text{olefin})_2WCl_4$, formed by the olefin-induced reduction of WCl_6, is isomerised rapidly by the Lewis acid AlX_3. The scheme presented by Wang et al(52) is shown below :

$$\begin{tikzcd}
\mathrm{WCl_6} + \text{Olefin} \arrow[r] & \text{trans-}\left[\mathrm{WCl_4(olefin)_2}\right] \arrow[d, shift left] \arrow[d, phantom, "\mathrm{AlCl_3}"' near start, shift right=3] \\
\text{cis-}\left[\mathrm{WCl_4(olefin)_2}\right] \arrow[r, shift right] & \left[\mathrm{WCl_3\ (olefin)_2}\right]^+ \left[\mathrm{AlCl_4}\right]^- \arrow[u, shift left] \arrow[l, shift right, "-\mathrm{AlCl_3}"']
\end{tikzcd}$$

Calderon has suggested that the aluminium halide may function as a Lewis acid, reacting with the transition metal compound in an acid-base type equilibrium providing coordination site for the reacting olefin.(53)

$$\mathrm{WCl_x} + \mathrm{AlCl_3} \rightleftarrows \left[\mathrm{WCl_{x-1}}\right]^+ + \left[\mathrm{AlCl_4}\right]^-$$

The following interpretations have also been made of the role of cocatalyst (53) :

(i) - alkylating agent

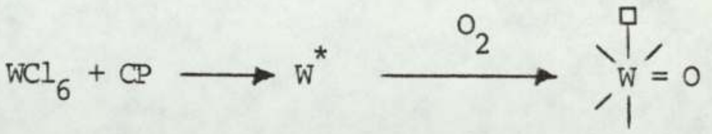
(ii) - complexing agent

These will be discussed in greater detail in a later section.

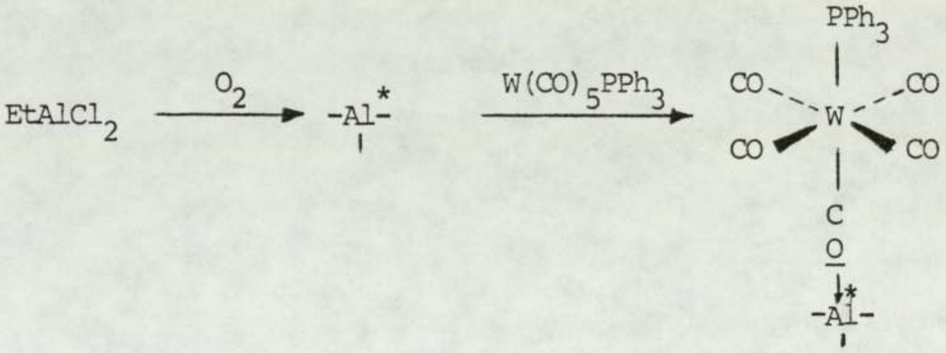
1.3.2.7 EFFECT OF OXYGEN :

Muetterties and co-workers found that under completely oxygen-free conditions WCl_6 based catalyst systems were inactive towards the metathesis reaction at least for acyclic internal olefins.(64) Activation of the system, according to this report is caused by the syringe-septum technique used which provides good but not total exclusion of atmospheric oxygen and water. They demonstrated that $WOCl_4$ was an active catalyst precursor under conditions in which oxygen and water were rigorously excluded and that the catalyst ligand requirements in tungsten (VI) based systems included both chlorine and oxygen atoms in the reagent mixture. Although $W(OCH_3)_6$ is metathetically active in the presence of $EtAlCl_2$, it does not form an active catalyst when in combination with either BuLi or $Al(CH_3)_3$.

Studies on the monometallic initiation of the metathesis polymerisation of cyclopentene by Amass and McGourty(11) indicated that an active catalyst is produced on the addition of oxygen into the WCl_6/cyclopentene system. The activity of this catalyst system sharply depends on the premixing time between WCl_6 and cyclopentene prior to the addition of oxygen, suggesting that the active species results from the oily precipitate obtained during this reaction. The following mechanism was proposed for the activation of the system.



The effect of oxygen on the metathesis of 2-pentene by a binary catalyst system of $W(CO)_5PPh_3$ - $EtAlCl_2$ has been studied by Basset and co-workers.(65) They reported a drastic change in the catalytic activity after introduction of molecular oxygen to the system and suggested that the promoting effect of oxygen was due to an increase in the Lewis acidity of the alkyl aluminium compound by producing an intermediate $-\underset{|}{Al}^*-$ during the oxidation of $EtAlCl_2$ to $Et-OAlCl_2$, which would probably react with the tungsten complex through the terminal oxygen of the carbonyl group trans to the PPh_3 ligand.



Finally, studies by Korda et al (48) showed that in contrast to the arene complexes of tungsten, the catalyst system $W(CO)_6$-$EtAlCl_2$ is unable to form catalytically active species for the metathesis of 3-heptene in the absence of oxygen.

1.3.2.8 HETEROGENEOUS NATURE OF SOLUBLE CATALYSTS :

Muetterties and Busch have reported that some and perhaps all WCl_6-based catalyst systems are insoluble in the reaction media and therefore should be considered as heterogeneous systems.(19) They demonstrated that the colourless filtrate from an active WCl_6-BuLi system yielded no metathesis products when 2-pentene was added; on the other hand the solids showed a catalytic activity nearly as high as the standard unfiltered reaction system. In contrast, Wolovsky and Nir(66) have reported that for the catalyst system WCl_6 - $EtAlCl_2$, the total metathetic activity has been found to reside in the soluble fraction of the catalyst while no metathetic activity was observed with the insoluble part.

Basset and co-workers(67) suggested that the stereochemical studies of the products in the early stages of the metathesis reaction gives a clear distinction between homogeneous and heterogeneous systems. They found that the stereoselectivity of the metathesis of cis 2-pentene using various tungsten based homogeneous systems was independent of steric environment of the transition metal producing high trans/cis 2-butene ratios.

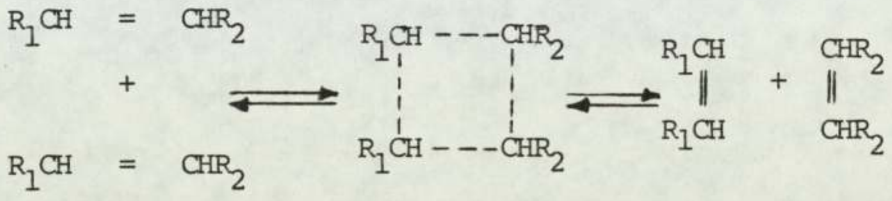
1.4 MECHANISMS :

The olefin metathesis reaction has provided one of the most challenging mechanistic problems in organometallic chemistry. Model and theoretical studies have provided evidence for the following mechanisms:

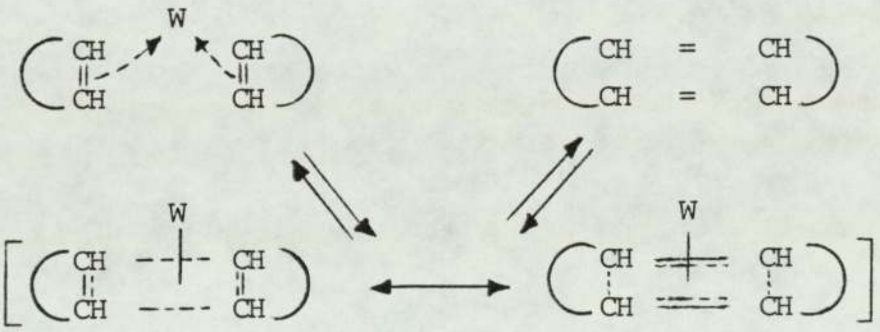
i - Quasicyclobutane transition state
ii - Tetramethylene - metal complex
iii - Metallocyclopentane transition state
iv - Metallocarbene - metallocyclobutane scheme

1.4.1 QUASICYCLOBUTANE TRANSITION STATE :

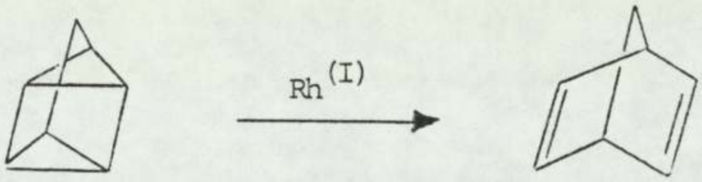
Bradshaw et al (34) were the first to suggest that the quasicyclobutane intermediate, involved in the olefin metathesis reaction, was compatible with a transalkylidenation scheme :



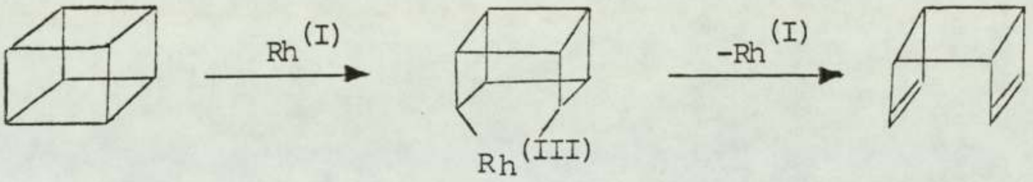
With regard to the ring opening polymerisation, Calderon and co-workers (10), on the basis of the observation of macrocyclic species postulated the same intermediate :



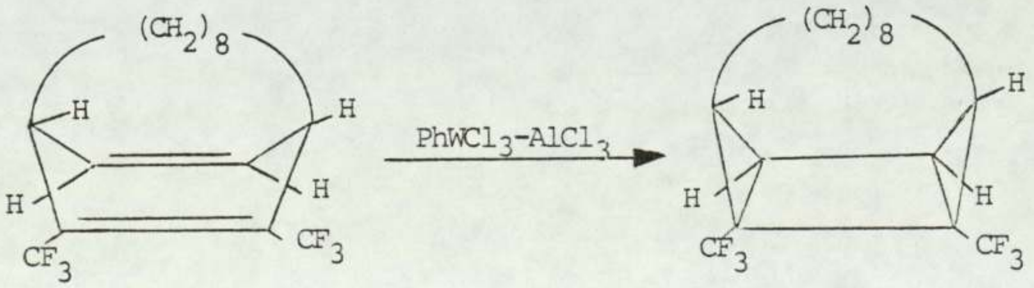
Since a mechanism involving such a concerted molecular transformation in the metal-free system is strictly forbidden by the Woodward-Hoffmann rules (68), the presence of transition metal was thought to provide an allowed reaction pathway through interaction with the metal d orbitals. (69,70) The valence isomerisation of quadricyclene to norbornadiene in the presence of a Rh$^{(I)}$ catalyst is the best example for such a forbidden-to-allowed process (71) :



However, this apparently synchronous isomerisation now appears to proceed through the non-concerted oxidative addition mechanism(72) :



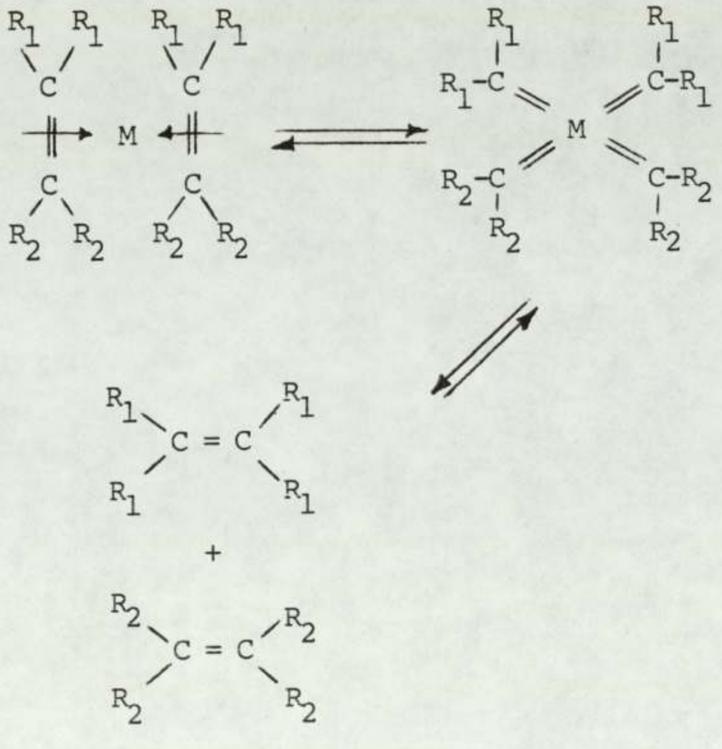
The quasicyclobutane intermediate, proposed by Bradshaw(34), is open to criticism on a number of counts but mainly because the isolation of cyclobutane from ethylene is impossible even in the presence of a known metathesis catalyst.(73) However, Gassman and Johnson's report(74) in support of the quasicyclobutane intermediate discloses the conversion of two non-conjugated olefinic groups into cyclobutane by a commonly accepted metathesis catalyst :



These results do not parallel those reported by Feast and Wilson(75) in which ring opening polymerisation of bicyclic dienes initiated by WCl_6 based metathesis catalyst were mentioned.

1.4.2 - TETRAMETHYLENE - METAL COMPLEX :

On the grounds that negligible quantities of cyclobutane were obtained from the reaction of ethylene with an active metathesis catalyst, Lewandos and Pettit suggested an alternative concerted pairwise exchange mechanism in which the carbon-carbon σ bonds of the initial olefins are ruptured concurrently with the π bonds, so that no genuine cyclobutane molecule is ever formed along the reaction coordination(73) :

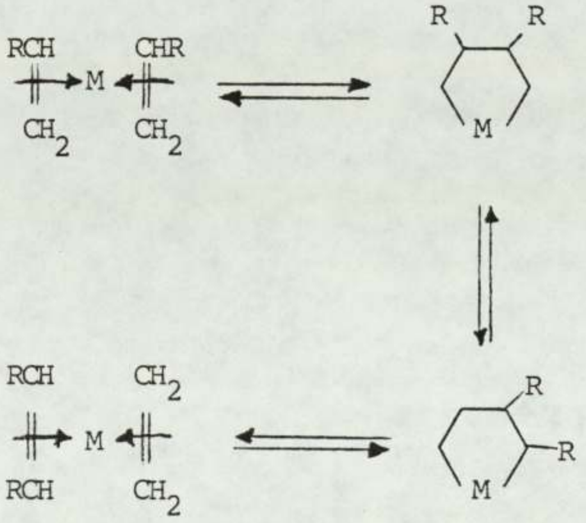


Molecular-orbital considerations indicate that the mechanism is symmetry allowed.

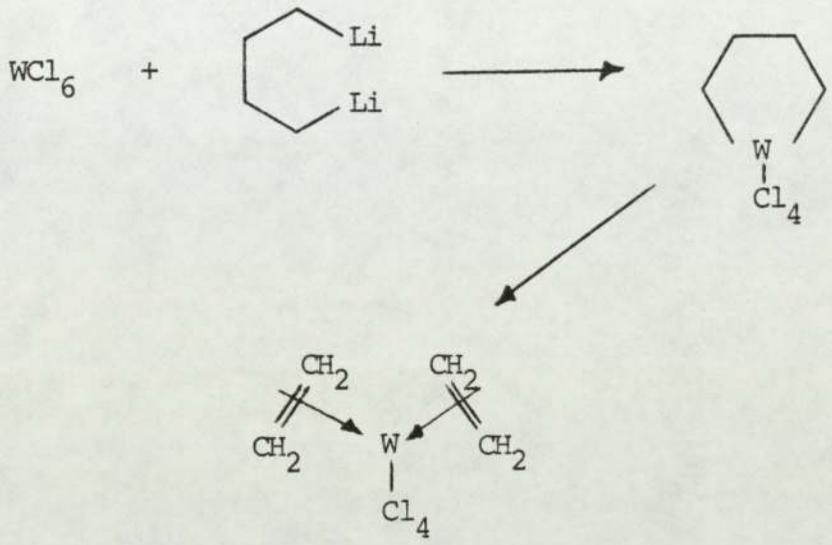
In support of Pettit's mechanism, O'Neill and Rooney (76) reported the decomposition of diazomethane into ethylene and N_2 using a $CoO-MoO_3$ supported catalyst which is active in the metathesis of propene and suggested that the same sites that are active in metathesis also selectively convert adsorbed methylene into ethylene.

1.4.3 METALLOCYCLOPENTANE TRANSITION STATE :

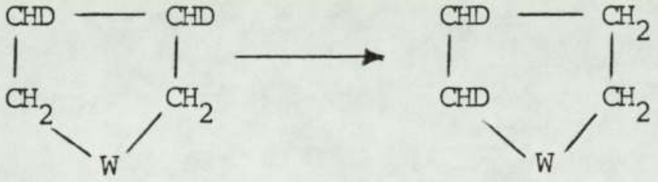
The non-concerted pathway involved in symmetry restricted reactions of cubane and its derivatives catalysed by Rh(I) led Cassar et al (72) to suggest that the same scheme could be involved in the olefin metathesis reaction. Grubbs and Brunck suggested a non-concerted, pairwise exchange of alkylidene groups through a metallocyclopentane intermediate (77) :



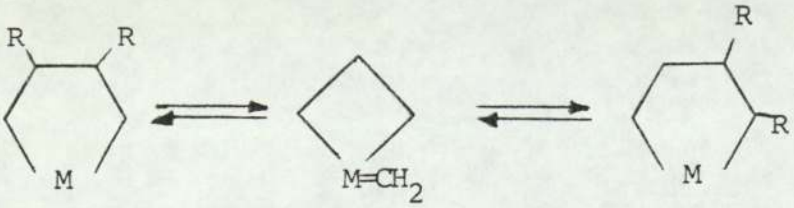
This proposal was largely based on the formation of ethylene from 1,4 dilithiobutane in the presence of WCl_6 :



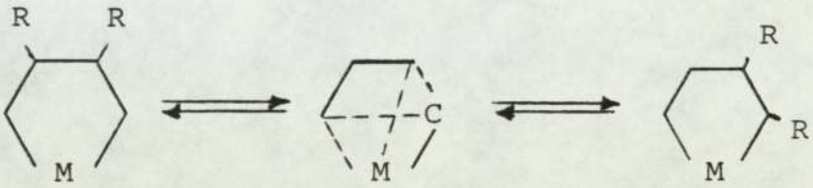
Extending the investigation further by using 1,4 dilithio, 2,3 dideuteriobutanes, Grubbs and Brunck, based on the observed products C_2H_3D $C_2H_2D_2$ and C_2H_4, concluded that their metallocycle intermediate can rearrange and thus provide a pathway for alkylidene scrambling:



Two possible routes were proposed (78) for such a rearrangement of the metallocyclopentane intermediate: one involves a carbene metallocycle pathway, thus :



and the other involves a concerted route :

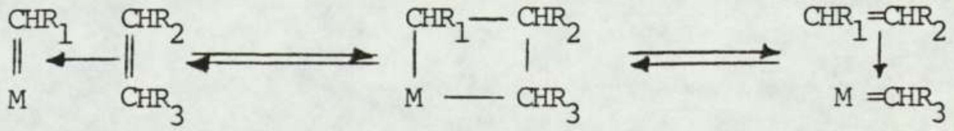


This scheme leaves several questions unanswered. There appears to be no reason why the rearrangement of metallocycle intermediate should occur or why it should be rapid.

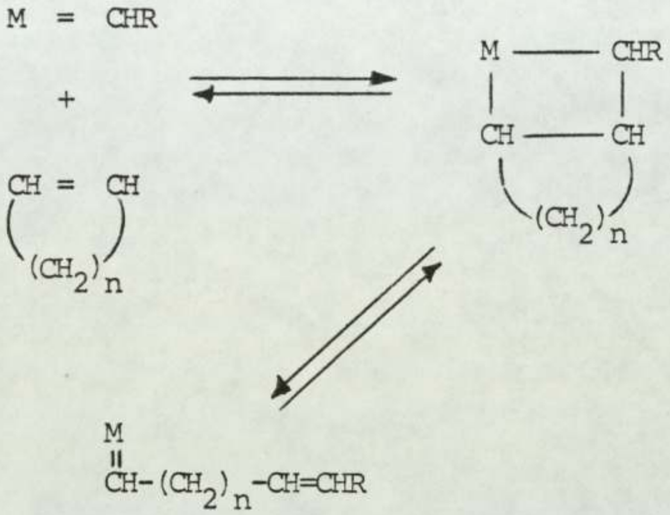
1.4.4 METALLOCARBENE - METALLOCYCLOBUTANE SCHEME :

Despite the limited application of other individual mechanisms, the mechanism for the metathesis reaction which enjoys most success is that based on the metallocarbene intermediate.

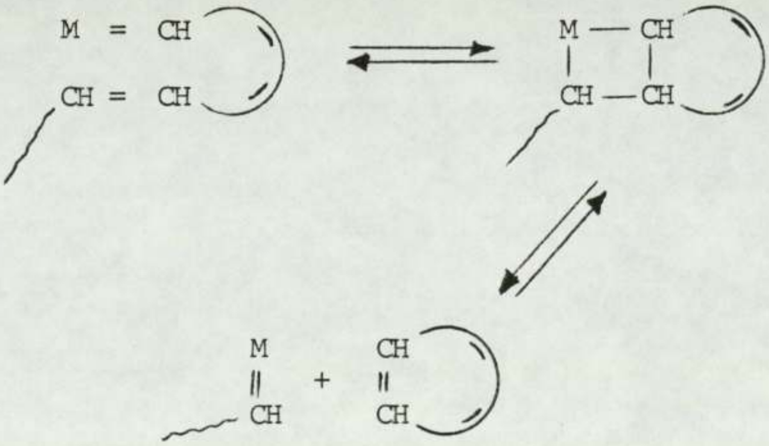
Herisson and Chauvin (79) were the first to propose a non-concerted, non-pairwise mechanism in which metallocarbenes reversibly react with alkenes to give metallocyclobutane intermediates :



When applied to cyclic alkenes, the carbene mechanism is consistent with a ring opening polymerisation by chain end growth and a kinetic chain process can be used to explain the propagation reaction:

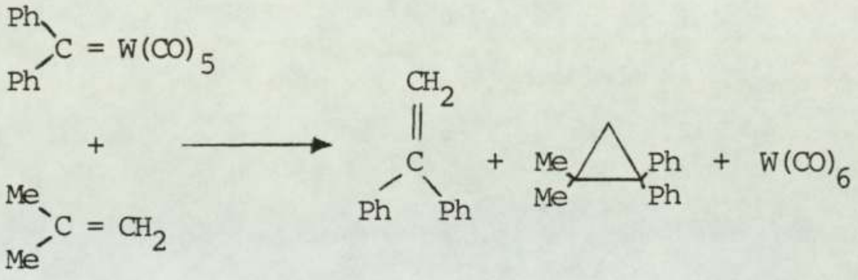


The macrocyclic oligomer formation during the polymerisation is accomplished by the intramolecular 'back-biting' transalkylidenation of the growing metal-carbene chain end with any internal double bond of the same chain:

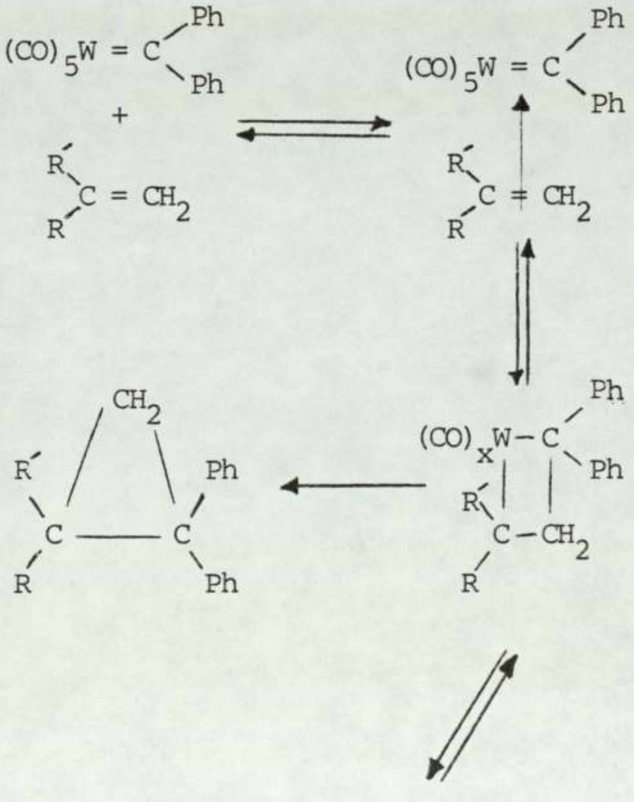


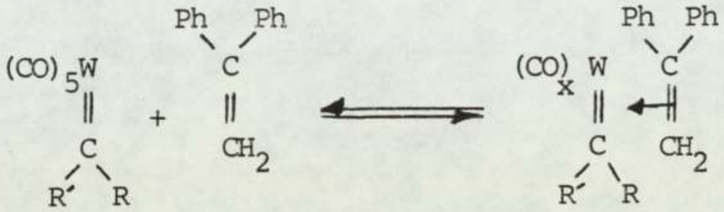
Dolgoplosk and co-workers found that even small amounts of phenyldiazomethane in the presence of WCl_6 or $MoCl_5$ initiated the ring opening polymerisation of cyclopentene, the occurrence of which was considered as direct proof of carbene initiation.(80,81)

The major breakthrough in support of the metallocyclobutane was the use of transition metal carbene complexes as model compounds in reactions with alkenes. Casey and Burkhardt$^{(82)}$ prepared and isolated diphenyl carbene pentacarbonyl tungsten(0), $Ph_2C{=}W(CO)_5$, a complex which upon heating reacted with isobutylene to undergo the following reaction :



The metallocyclobutane scheme proposed for this reaction accommodates both alkylidene transfer reactions and the formation of cyclopropane:





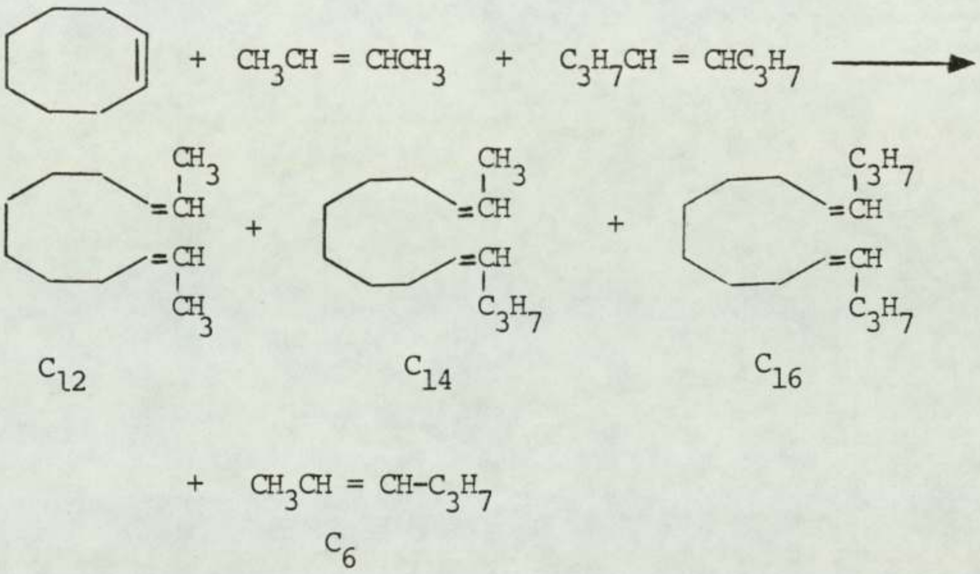
Further support for the carbene mechanism was provided by Kelly and Calderon(83) who found that the ratio of macrocycle oligomers $C_{12} : C_{16}$, $C_{20} : C_{16}$, $C_{24} : C_{16}$, $C_{28} : C_{16}$ and $C_{32} : C_{16}$ were essentially constant throughout the ring opening polymerisation of 1,5 cyclooctadiene using WCl_6-$EtAlCl_2$-EtOH catalyst system. The constancy of $C_{12} : C_{16}$ was considered as the key point since the formation of C_{12} according to the pairwise mechanism requires cross metathesis of the cyclooctadiene with cyclobutene and the formation of the latter is unlikely.

1.4.4.1 EVIDENCE SUPPORTING THE CARBENE MECHANISM :

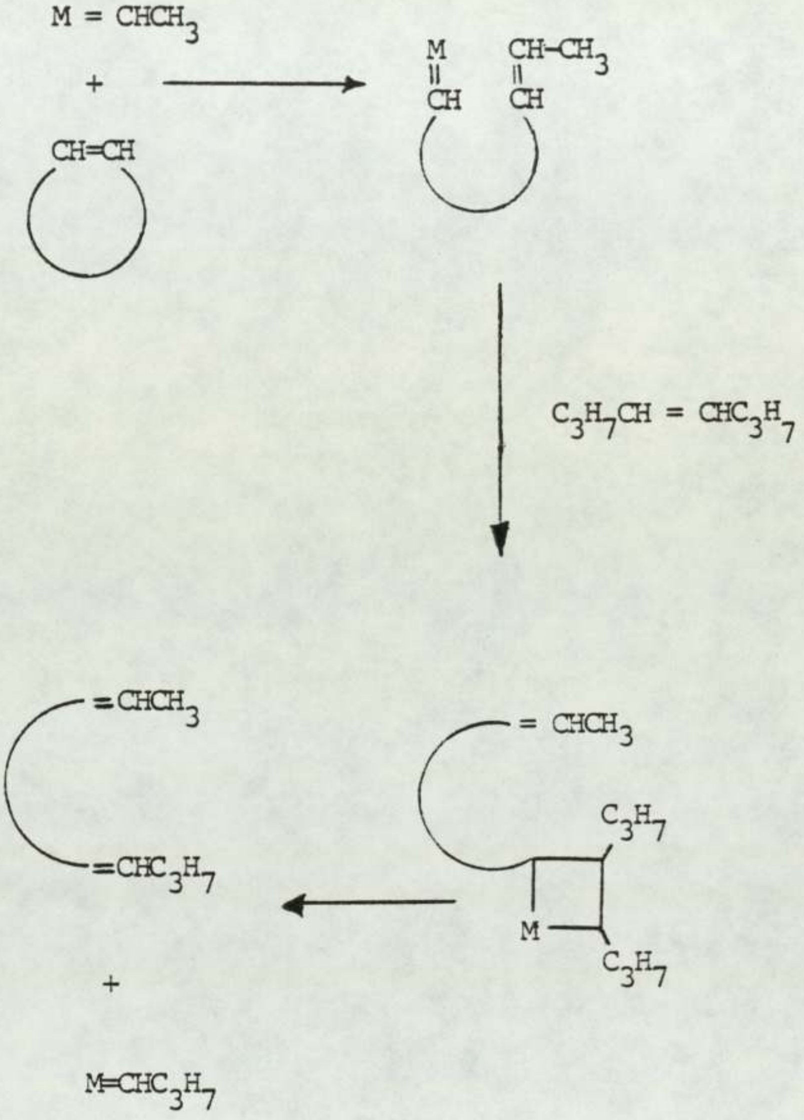
There is a growing consensus in the literature that metallocarbenes and metallocyclobutane complexes are key components in olefin metathesis and the ring opening polymerisation of cyclic alkenes. This concept is mainly supported by (a) kinetic studies (b) studies concerning the first formed products and (c) studies using metal-carbene complexes.

(a) - Kinetic Studies :

To differentiate between the pairwise and the non-pairwise mechanism, Katz and McGinnis$^{(84)}$ studied the metathesis of cyclooctene with a mixture of 2-butene and 4-octene:

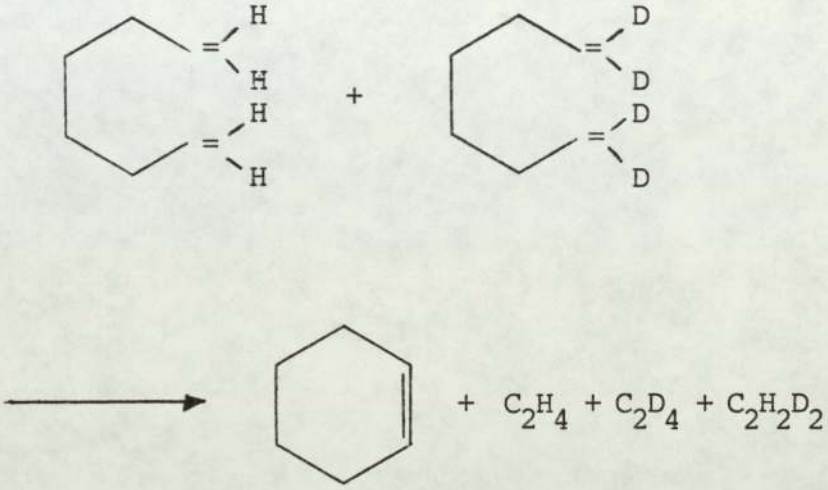


For a pairwise mechanism to operate in this system the C_{14} diene would not be a "first" product of the reaction, it would of necessity have to be formed from the reaction of cyclooctene with 2-hexene, itself a product of the initial metathesis. Extrapolation of the C_{14}/C_{12} or C_{14}/C_{16} molar ratio to zero reaction time should lead to zero for either ratio. However, such extrapolations indicate that C_{14} diene is a major "first" product of metathesis, which can only occur if a non-pairwise chain operates:



However, this experiment cannot rule out the possibility of the pairwise scheme if the exchange step is the rate-determining step.

Additional experimental evidence for the metallocarbene involvement in olefin metathesis reaction has been provided by Grubbs and co-workers (85) who studied the metathesis of 1,7 octadiene with 1,7 octadiene 1,1,8,8d_4.

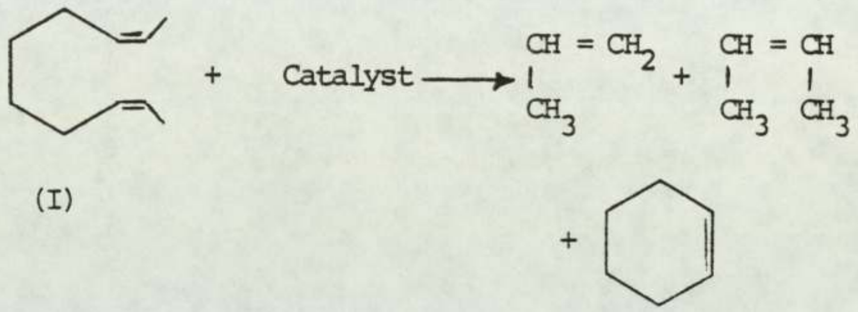


Since cyclohexene does not undergo any further reaction, the ratio of ethylene $d_4:d_2:d_o$ can be calculated exactly for both pairwise and non pairwise mechanisms under non-equilibrating conditions. A calculation of $d_4:d_2:d_o$ ratio based on the pairwise mechanism predicts a maximum ratio of $d_4:d_2:d_o$ of 1:1.6:1 whereas carbene mechanism requires the production of a statistical distribution of ethylene giving $d_4:d_2:d_o$ of 1:2:1.

The metathesis of 1:1 mixture of the d_4 and d_o 1,7 octadiene with two different catalysts, one heterogeneous and alkyl activated the other homogeneous and non alkyl activated, suggested that the olefin metathesis reaction proceeded through a non pairwise interchange of carbons between two olefins.

(b) - <u>Studies on the First Formed Products</u> :

Depending upon the structure of the initial carbene, the first formed olefins can be different from the normal metathesis products, therefore an insight into the mechanism of the metathesis reaction can be provided from a study of these products. Grubbs and Hoppin observed that addition of 2,8 decadiene (I) to the premixed catalyst $WCl_6/Sn(CH_3)_4$ results in the initial formation of propylene followed by the production of the usual metathesis products.(86)



(I)

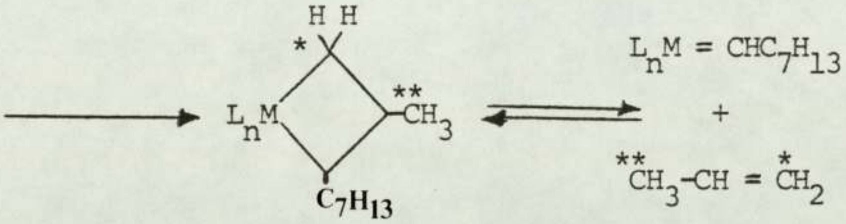
Table 1-2 summarises the composition of propylene produced in deuterium-labelling experiments involving $Sn(CD_3)_4$ and $\left[1,1,1,10,10,10,d_6\right]$ 2,8 decadiene (II).

TABLE 1-2 DEPENDENCE OF COMPOSITION OF PROPYLENE ON THE OLEFIN AND THE CATALYST USED.(86)

Olefin	Catalyst	Propylene
II	$WCl_6/Sn(CH_3)_4$	$CH_2{=}CH{-}CD_3$
I	$WCl_6/Sn(CD_3)_4$	$CD_2{=}CH{-}CH_3$
II	$WCl_6/Sn(CD_3)_4$	$CD_2{=}CH{-}CD_3$

These results led the authors to suggest the following scheme for the reaction$^{(86)}$:

$$L_nM = \overset{*}{C}H_2 \quad + \quad \overset{**}{C}H_3\text{-}CH = CH\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}CH_3$$



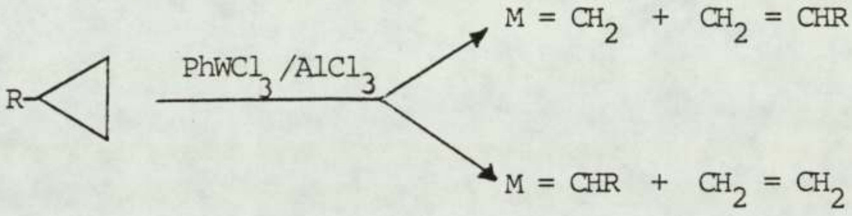
(c) - Metathesis Induced by Metal Carbenes :

Katz and co-workers have reported that (diphenyl carbene) pentacarbonyl tungsten, $(CO)_5W{=}CPh_2$, initiates the ring opening polymerisation of cyclic alkenes producing high molecular weight polyalkenamer with largely cis stereochemistry.$^{(87)}$ Isolated metal carbenes have been also used to initiate the metathesis of acyclic olefins. It has been reported that 2-pentene reacts with $(CO)_5W{=}CPh_2$ to produce 2-butene and 3-hexene.$^{(88)}$

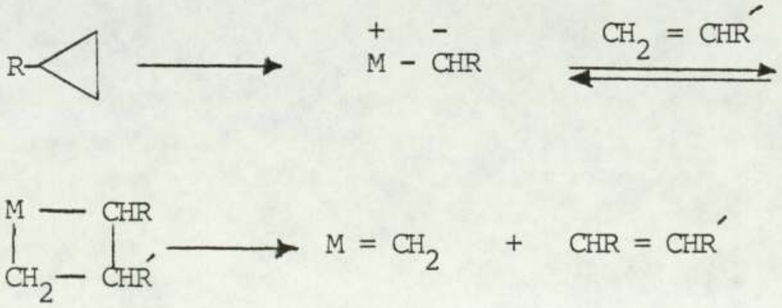
1.4.4.2 NATURE OF CHAIN CARRIER :

Although substantial supportive evidence exists for metallocarbene intermediate, relatively little is known about the origin and the nature of this crucial chain carrying species. According to numerous data from many studies the chain carrier in the degenerate metathesis of terminal olefins and in cross-metathesis of cyclic alkenes with 1-alkenes is either nucleophilic or electrophilic in nature. The important question as to which is the predominant has never been resolved. Experimental evidence for the contention that metathesis carbenes are nucleophilic was offered by Gassman and Johnson in a series of trapping tests utilizing Michael acceptors as carbene traps.(89,90) They reported that ethylidene carbene generated from 2-butene was trapped by ethyl acrylate to yield the expected ethyl cyclopropyl ester.

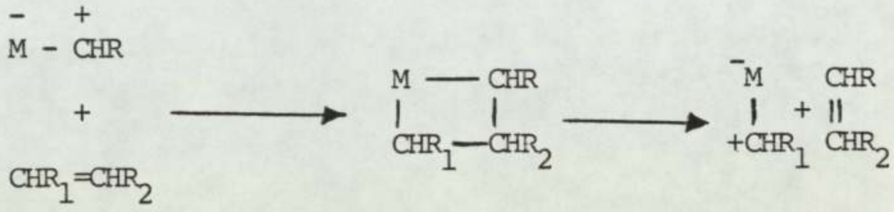
Additionally, Gassman and Johnson, in a later publication,(91) reported that the catalyst system $PhWCl_3/AlCl_3$, which is known to promote retro-carbene addition(92), could offer an attractive possibility for the generation of C-alkyl substituted tungsten carbene complexes according to the following reaction :



Based on these results they analysed the products obtained from the reaction of ethyl cyclopropane and a terminal olefin using the catalyst system $PhWCl_3$-$AlCl_3$ and found that olefins of the type $RCH = CHR'$ were obtained in large amounts suggesting the following scheme for the reaction(91) :



In contrast, Katz and McGinnis (84) suggested an electrophilic character for the active carbon centre attached to the metal :

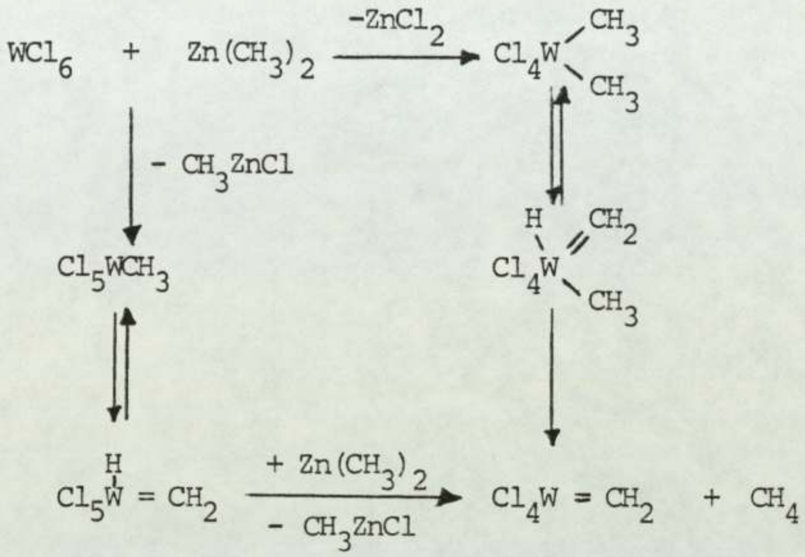


$$\overset{-}{M}-\overset{+}{C}HR + CHR_1{=}CHR_2 \longrightarrow \begin{array}{ccc} M & - & CHR \\ | & & | \\ CHR_1 & - & CHR_2 \end{array} \longrightarrow \begin{array}{ccc} \overset{-}{M} & & CHR \\ | & + & \| \\ {}^{+}CHR_1 & & CHR_2 \end{array}$$

A comprehensive work has been recently provided by Bencze et al (93) in support of the electrophilic nature of the chain carrier in the metathesis reaction. They analysed the minor products from cross-metathesis of norbornadiene with 1-hexene and found that the complex alkylidene $Bu\overset{\delta+}{C}H = \overset{\delta-}{M}$ was the major chain carrier.

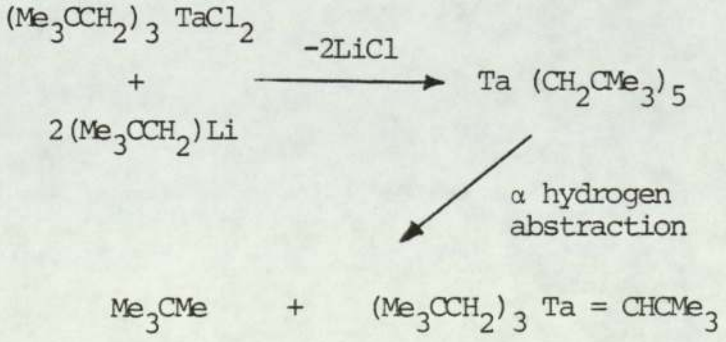
1.4.4.3 INITIAL CARBENE FORMATION :

Although the metallocarbene involvement in the olefin metathesis reaction is well established, the mechanism of their initial formation is a key question. Based on the role of cocatalyst as an alkylating agent, Muetterties suggested that α-hydrogen migration from the σ bonded alkyl group to the transition metal could be the source of carbene-metal generation. (94) This suggestion was based on the generation of methane observed in the reaction of WCl_6 with $(CH_3)_2Zn$:

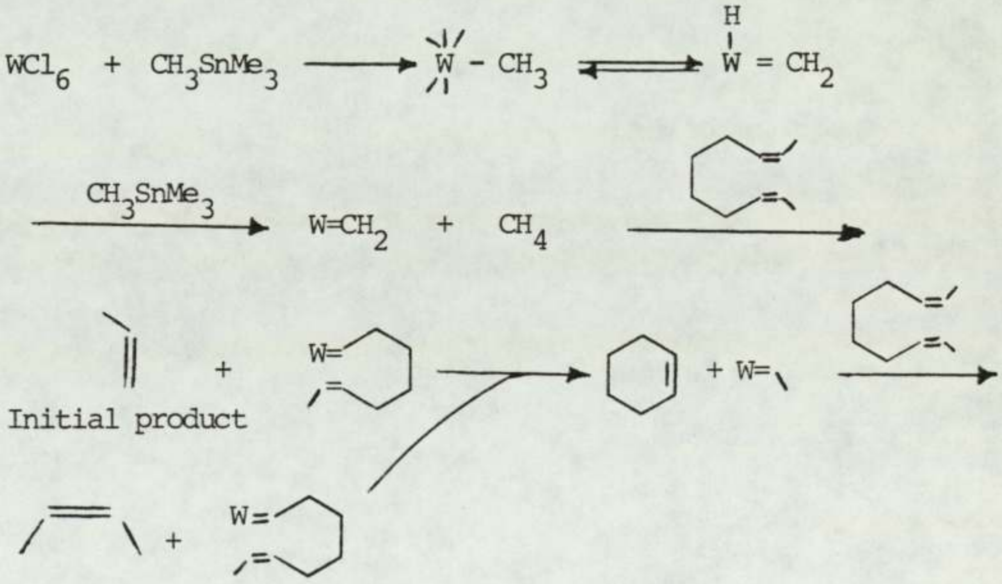


Such a $CH_3\text{-}W \rightleftharpoons CH_2\text{=}W\text{-}H$ equilibrium has been demonstrated by Cooper and Green(95) and could be considered as support for the Muetterties mechanism.

Experimental evidence for such a proposal is reported by Schrock(96) who showed that tantalum alkylidene complexes can be formed through α-hydrogen abstraction in the reaction of tantalum halides with alkyl lithium reagents :

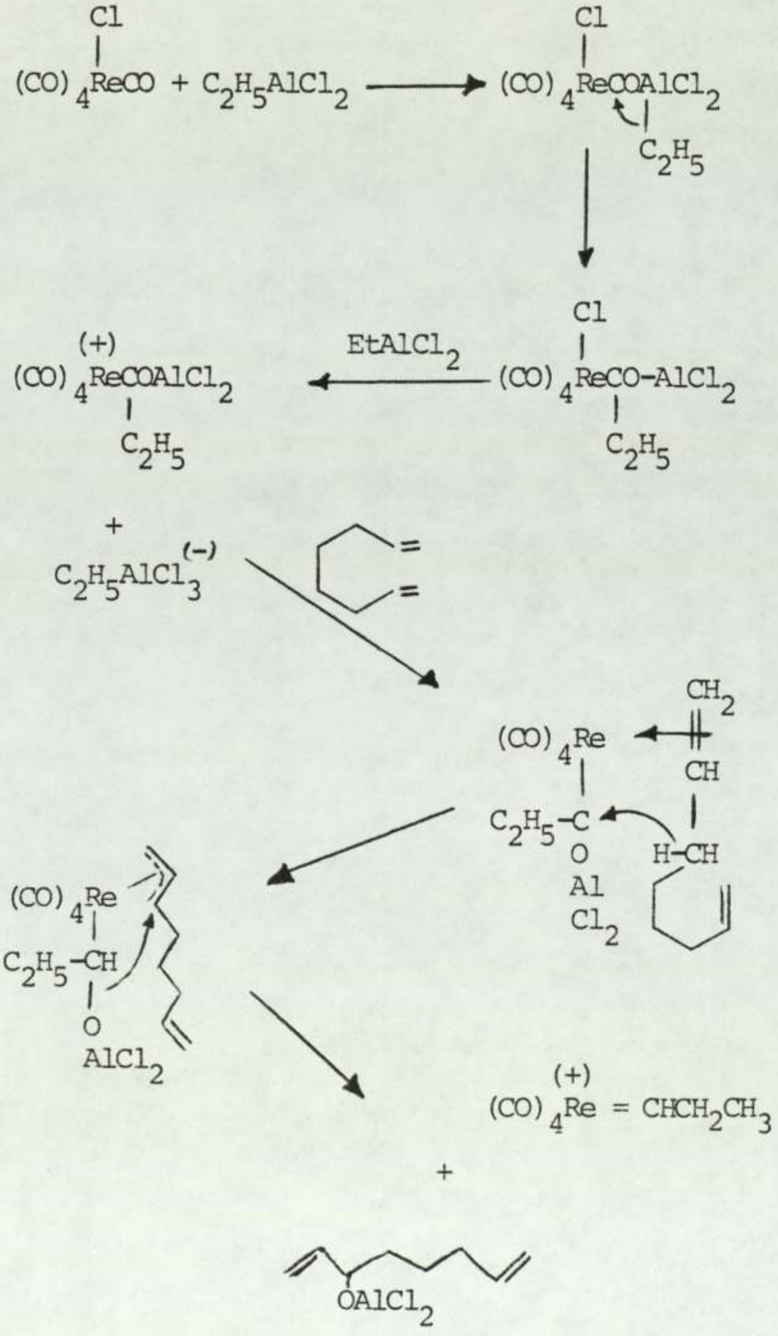


Additional evidence for the generation of a carbene-metal initiating species from the alkyl group transferred from the cocatalyst has been provided by work described in section 1.4.4.1(b). Grubbs and Hoppin (86), who studied the metathesis of 2,8 decadiene using the $WCl_6/Sn(Me)_4$ catalyst system, observed that methane was produced when the catalyst components were allowed to react prior to addition of an olefin. Addition of 2,8 decadiene to the prepared catalyst was accompanied by the initial production of propylene after which the expected metathesis products were produced as shown in the following scheme :



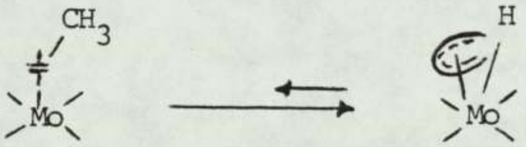
Deuterium-labelling experiments involving $Sn(CD_3)_4$ and $[1,1,1,10,10,10,d_6]$ 2,8 decadiene confirmed that propylene is indeed the first olefin formed and its structure, as shown in table 1-2, indicated that the methylidene and ethylidene moieties originated from $Sn(CH_3)_4$ and 2,8 decadiene respectively.

Greenlee and Farona (97) proposed an alternative route to carbene formation based on their gas evolution studies of the metathesis of 1,7 octadiene using the $Re(CO)_5Cl$-$EtAlCl_2$ catalyst system. The key step in this scheme is insertion of the CO ligand into -C-Al bond of $EtAlCl_2$ according to the following mechanism :

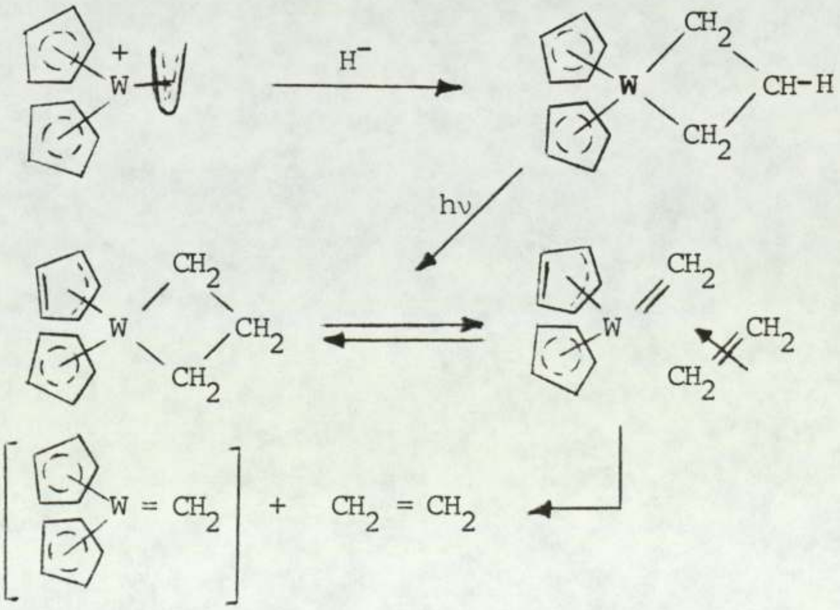


The proposed scheme, however, does not clearly illustrate the electronic configuration of each individual step.

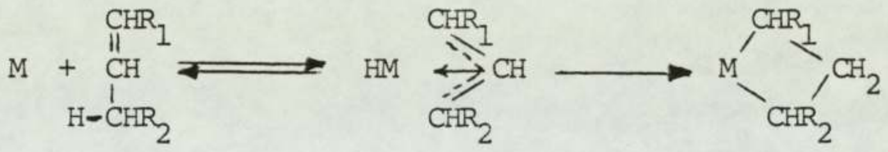
To explain the formation of carbene in the systems where cocatalysts containing alkyl groups are absent, one could refer to reports presented by Osborn (98) and Green. (99, 100) Osborn et al (98) demonstrated that a stable π allyl hydride complex is observed on treatment of $MoCl_3(THF)_3$ with Na-Hg under propylene in the presence of $Ph_2PCH_2CH_2PPh_2$, suggesting the following equilibrium :



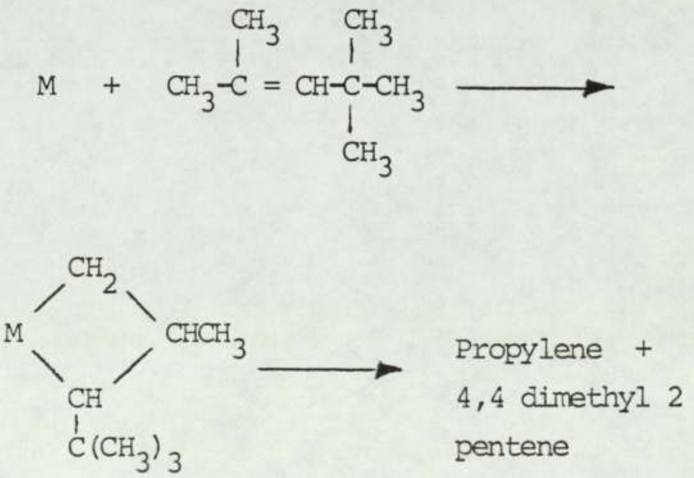
Green and co-workers revealed that stable metallocyclobutane can be produced by H^- nucleophilic attack on the central carbon atom of a η^3-allylic ligand (99), which under irradiation produced ethylene.(100)



Osborn and Green's results, if relevant to the olefin metathesis reaction, provide the initial experimental evidence for exclusion of a reaction of olefin with the transition metal compound presumably to produce the initiating carbene-metal complex simply by a sequence of π complexation followed by a hydride shift to form a π-allyl metal hydride which then rearranges into a metallocyclobutane via a nucleophilic attack of the hydride on the central atom of the π-allyl species.



Indeed, experimental support for such a mechanism based on Green's Studies has recently been provided by Farona and Tucker (101) who studied the metathesis of 2,4,4 trimethyl 2-pentene using $Mo(CO)_6$ on alumina and found that the initial olefins formed were in line with such a mechanism.

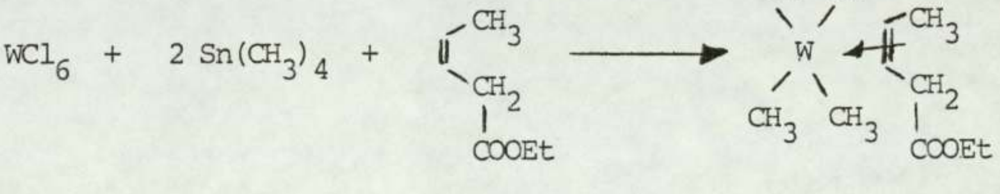


4,4 dimethyl 1-pentene is also formed in the reaction which is due to the isomerisation of the starting olefin to 1-ene.

The necessary presence of an allylic hydrogen in the olefin, in order for the mechanism to be operative, can be considered as an alternative in studying such a mechanism in detail. According to this scheme ethylene should be inert to self-metathesis due to the inability to generate the starting metallocycles.

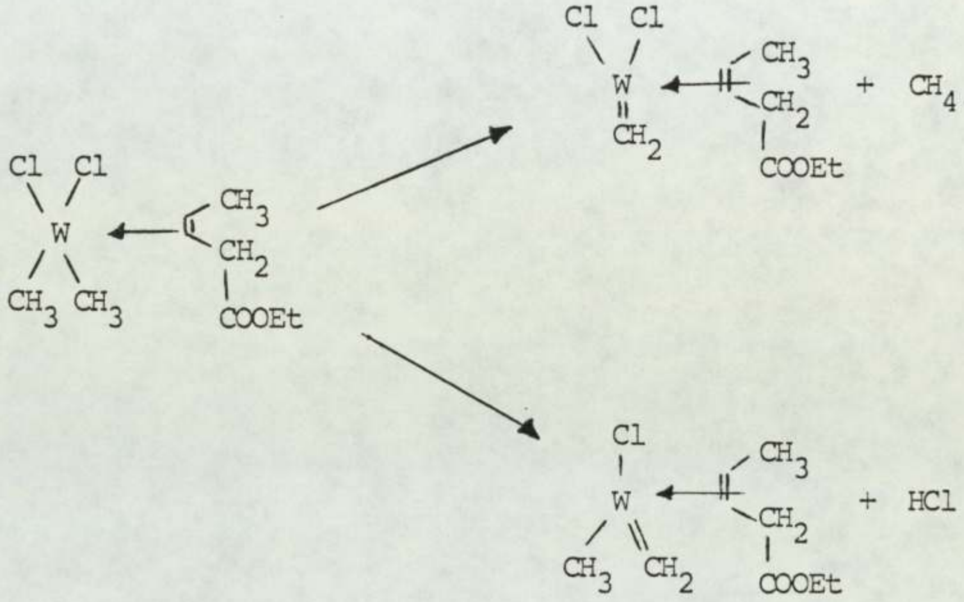
Indeed Olslhoorn and Boelhouwer (102) found that it was necessary to pre-expose the catalyst system Re_2O_7/Al_2O_3 to higher olefin such as propylene or 1-butene before they could appreciably metathesise C_2H_4 with C_2D_4.

Recent mechanisms which take into account both olefin and the cocatalyst for the initial formation of carbene metal complexes are those presented by Otton and Hummel. Otton et al (103) used $WCl_6/Sn(CH_3)_4$ catalyst system for the metathesis of ethylenic esters and suggested the following scheme :

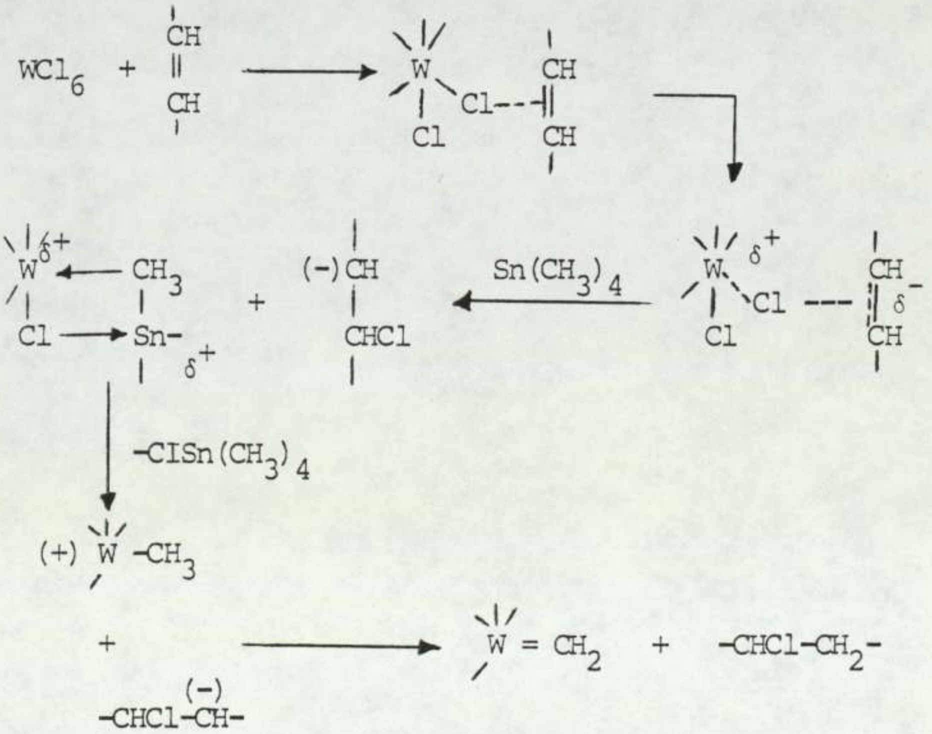


The two chlorine atoms might have been removed by $Sn(CH_3)_4$ or by the olefin acting as a reducing agent in order to accommodate the incoming olefin.

The active species initially formed would then form the metal carbene through α-hydrogen-abstraction.



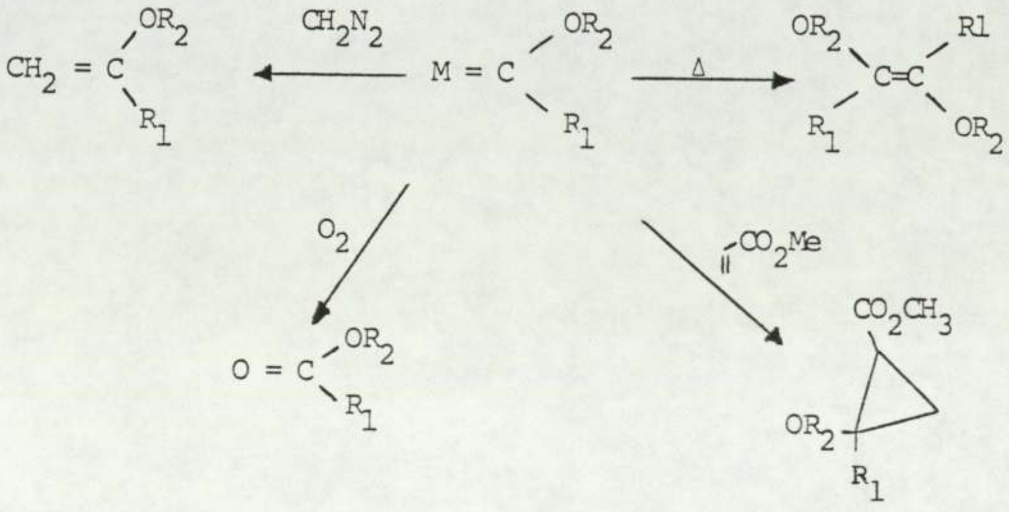
Hummel et al (59) based on observations during degradation of 1,4 polybutadiene using $WCl_6/Sn(CH_3)_4$ proposed the following mechanism for the formation of the carbene :



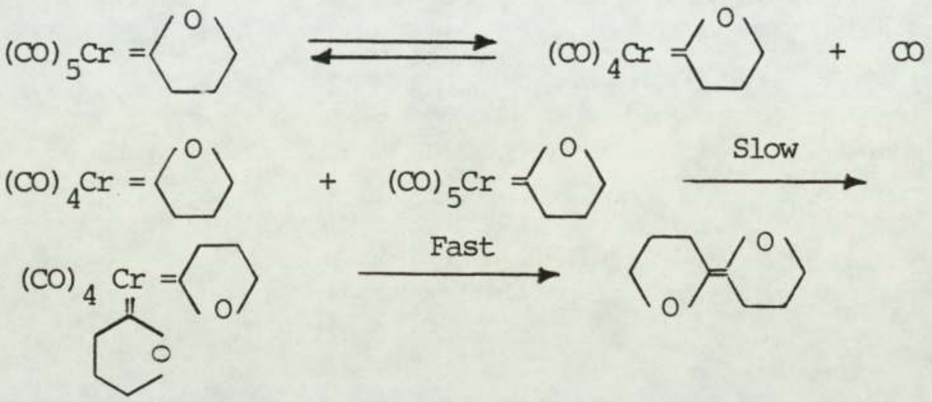
1.4.4.4 METAL CARBENE TERMINATION REACTIONS :

The olefin metathesis and ring opening polymerisation of cyclic alkenes have been described as chain reactions that initiate and propagate via metal carbenes and metallocyclobutane intermediates and must like any other chain reactions involve a termination step. In spite of the fact that the lifetime of most active catalysts is short, only a few reports in the literature cover the termination reaction in olefin metathesis. Muetterties (94) suggested that the most active catalyst available is $WCl_6/EtOH/EtAlCl_2$ and reported a life-time of 10-25 minutes, when operating at 25°C, for this system.

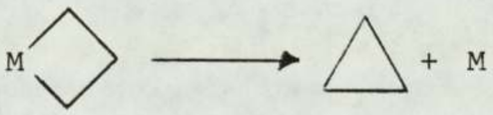
Termination reactions that destroy the catalytic intermediates involve either impurities such as oxygen, water and organic molecules containing polar groups. Disadvantageous side reactions of the metal carbene and metallocyclobutane can also account for the deactivation of the active intermediates. Casey (104) demonstrated the following reactions for releasing the carbene ligand from a metal complex:



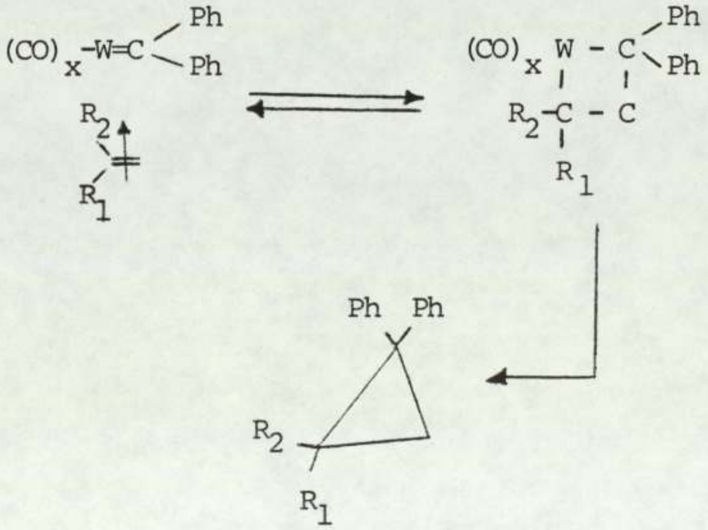
It has been reported that dimerisation is predominant in the carbene thermal decomposition, suggesting the following scheme$^{(105)}$:



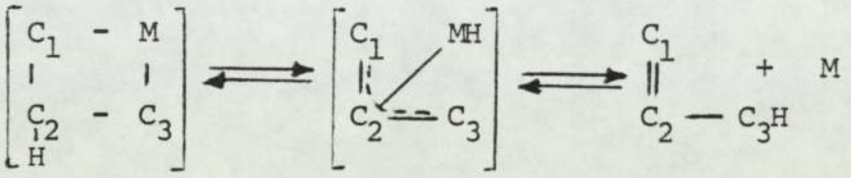
There are a number of reasonable side reactions for the metallocyclobutane intermediate. The most important one is the reductive elimination reaction of cyclopropane.



Casey and Burkhardt reported that reaction of diphenyl carbene pentacarbonyl tungsten (O), $(CO)_5W = CPh_2$, with isobutylene produced tetrasubstituted cyclopropane as a minor product.$^{(82)}$

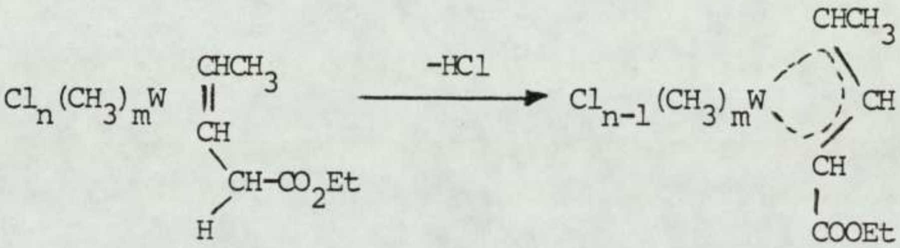


Additionally, metallocyclobutanes have been observed to interconvert to propylene derivatives by way of β-hydrogen transfer reaction.(106)



Thus reactions affording either cyclopropane or propylene would most likely represent forms of termination of metathesis activity.

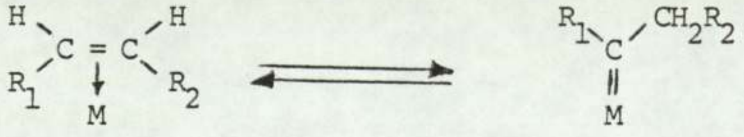
Otton et al(103) studied the metathesis of ethylenic esters using $WCl_6/Sn(CH_3)_4$ catalyst system and suggested the following scheme for the termination step :



Carbene termination reactions via bimolecular methylene decomposition has been suggested by Grubbs and Hoppin (86) as a source of ethylene in the reaction of WCl_6 with $Sn(CH_3)_4$.

$$2\ L_nM = \overset{*}{C}H_2 \longrightarrow \overset{*}{C}H_2 = \overset{*}{C}H_2$$

Probably the more appropriate mechanism for chain termination is direct and reversible conversion of coordinated olefin to carbene in one step via 1, 2 hydride shift :



The possibility, in principle, of the occurrence of this reaction was demonstrated by Fischer and Held using model compounds.(107)

A recent report by Amass and Zurimendi(108) gives evidence for the occurrence of termination reactions in the polymerisation of cyclopentene initiated by $WCl_6/AliBu_3$. They suggested the following bimolecular reaction responsible for catalyst deactivation :

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

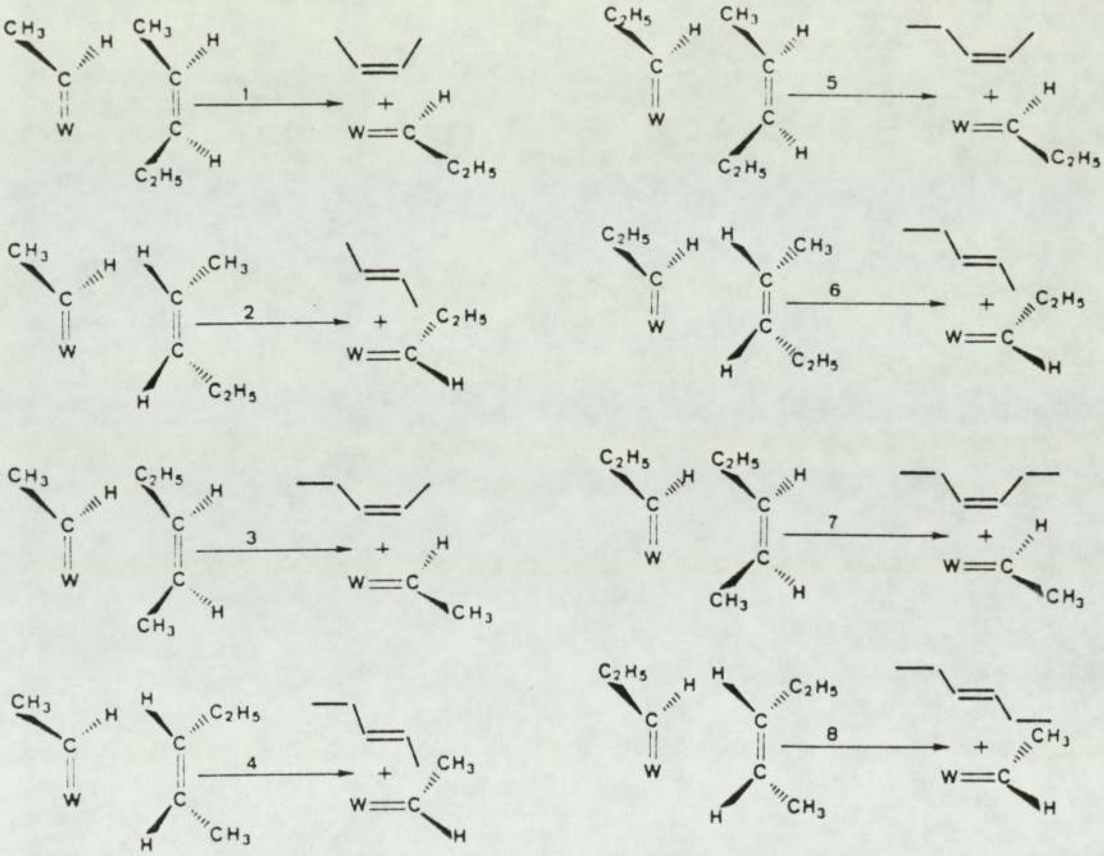
$$W^* + W_{inactive} \longrightarrow 2\,W_{inactive}$$

where W^* is the active species and $W_{inactive}$ the product of the termination reaction. They also showed that addition of dry oxygen to the dead system resulted in a steady increase in the rate of polymerisation indicating that $W_{inactive}$ may be in a lower oxidation state than W^*.

1.5 STEREOCHEMISTRY :

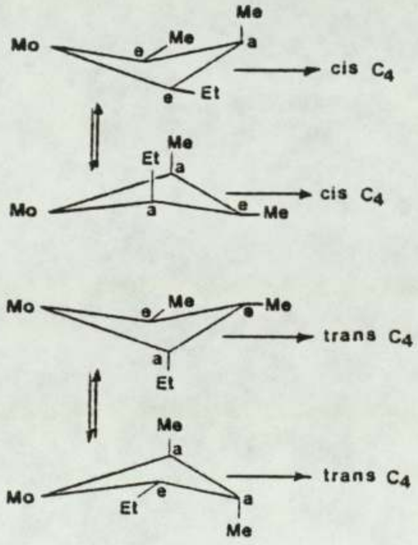
Olefin metathesis is usually accompanied by cis-trans isomerisation of the starting olefin and of the products. Various stereochemical studies seem to indicate that this geometric isomerisation proceeds according to a metathetic mechanism.(9, 109)

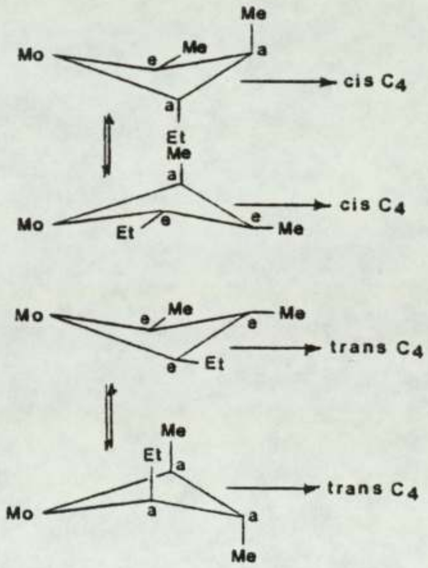
To account for cis-trans isomerisation of the starting olefin as a probable alternative route to the metathesis reaction, Basset and co-workers (110) proposed a model in which the stereochemistry was only determined by the geometry of the approach of the olefin. For the metathesis of cis-2 pentene they outlined the following scheme as the only possible coordinations open to the olefin :



The mathematical equation derived from this kinetic model when applied to the initial stages of cis 2-pentene metathesis indicated that a linear relationship could be observed by plotting trans/cis 2-butene against trans/cis 2-pentene which was in good agreement with the experimental results.(110)

The cis, trans nature of the starting olefin plays a role in the distribution of the geometric isomers in the products.(67) In most cases a cis olefin gives preferentially a cis olefin and a trans olefin, a trans product. Leconte and Basset(111) suggested that the retention of configuration of starting olefin could be due to the possible conformations of the metallocyclobutane transition state. They outlined the following possible metallocyclobutanes involved in the metathesis of cis 2-pentene (left) and trans 2-pentene (right) :





This model shows that the following interactions could be present in a metallocyclobutane intermediate :

(i) 1-2 equatorial-axial or axial-equatorial interactions

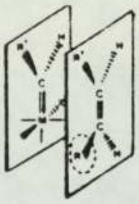
(ii) 2-4 repulsive interaction between an axial substituent in the 2 position and the transition metal or its ligands.

(iii) 3-4 interactions

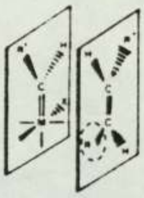
and (iv) 1-3 diaxial interactions

among which only 1-3 or 3-4 interactions are able to give a satisfactory explanation for the retention of configuration.

The possible 3-4 interaction could account for the retention of configuration if an asymmetric ligand distribution around the metallocarbene is proposed :



cis favoured coordination of a cis olefin



trans favoured coordination of a trans olefin

However, according to this interaction, by increasing the size of R group of a cis or trans olefin $RCH{=}R'CH$ one should progressively increase the stereoselectivity, but unexpectedly, increasing the size of R group above a certain value decreases the stereoselectivity which rules out the model of asymmetric ligand arrangements as being responsible for the retention of configuration.(111,112)

Taking into account the 1-3 diaxial interaction, it appears that for cis 2-pentene the most favoured metallocyclobutane is the one with groups in 1-3 diequatorial position leading to cis 2-butene. In the case of trans 2-pentene, the most favoured transition state is the one with three substituents in 1-2-3 triequatorial position leading to trans 2-butene.

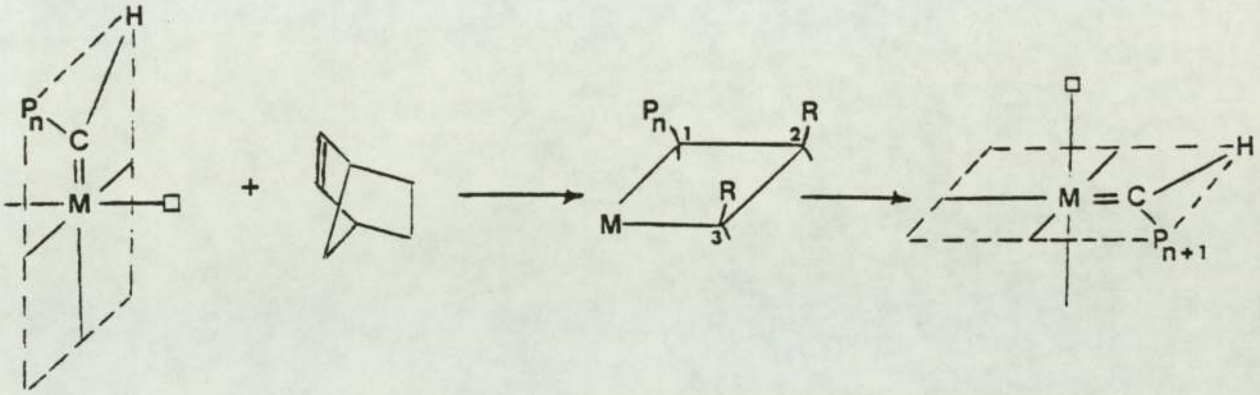
Therefore with cis olefins, the 1-3 diaxial interaction will be more effective than 1-2 interaction, whereas with trans olefins the two simultaneous interactions will favour the formation of trans products.

The consideration of the minimized 1-3 diaxial interaction was also considered by Katz and Hersh (88) using $(C_6H_5)_2C{=}W(CO)_5$ as catalyst in the metathesis of cis 2-pentene.

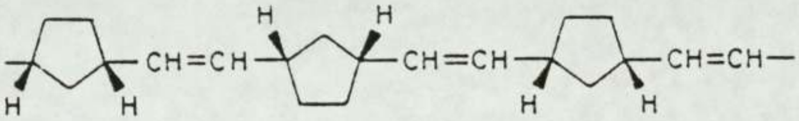
The influence of the nature of transition metal on the stereoselectivity of metathesis has also been studied by Leconte and Basset.(111) Using various Cr, Mo and W complexes for the metathesis of cis and trans 2-pentene they found that the stereoselectivity decreased in the order of Cr> Mo>>W; suggesting that an increase in bond length $M-C_1$ and $M-C_3$ from Cr to W decreases the 1-3 repulsive interaction in the metallocyclobutane intermediate, therefore loosing the stereoselectivity.

Ivin et al(113) have suggested a Cossee type active centre for the double bond propagation in the ring opening polymerisation of norbornene. Coordination of monomer to the active centre could result in either cis or trans double bonds depending on the catalyst system.

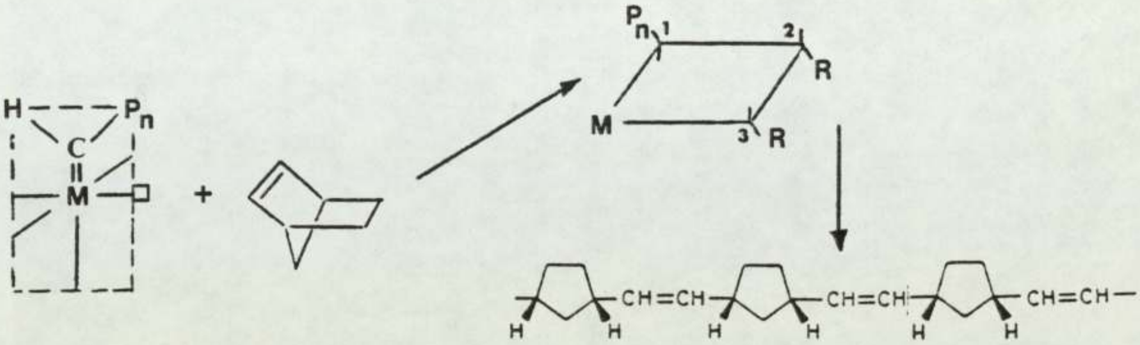
Coordination in a cis manner leads to a metallocyclobutane in which the substituents at carbons 1 and 2 are cis giving polymer chains with cis double bond. In this case the metallocarbene formed is a mirror image of starting carbene.



This inversion of stereochemistry of the metallocarbene leads to a syndiotactic arrangement of cyclopentane rings in the polymer chain.



Coordination in a trans manner leads to a metallocyclobutane in which the substituents at carbons 1 and 2 are trans giving polymer chains with trans double bond. In this case the metallocarbene regenerates itself therefore resulting in retention of stereochemistry of the metal-carbene giving polymer chains with isotactic cyclopentane rings.



Using $ReCl_5$ catalyst they obtained all-cis polymer where the adjacent rings had syndiotactic dyad relationship. On the other hand the catalyst system WCl_6/nBu_4Sn gave a polymer with blocky cis, trans distribution where cis double bonds were associated with syndiotactic and trans with isotactic dyads, indicating the presence of two kinetically distinct species, one giving cis double bonds the other giving trans.

That the blockiness of such a polymer cannot be determined leads to an alternative explanation for the cis, trans distribution of double bonds. The new double bond incorporated into polymer chain could still be coordinated to the transition metal. The way in which such a double bond is coordinated could force the incoming monomer to coordinate in either cis or trans manner.

Significantly, Taghizadeh et al (114) observed a random coordination of the norbornene to the metallocarbene initiating species, regardless of transition metal used, the ligands coordinated to the precursor complex and the cocatalyst employed.

These results contrasted sharply with those obtained with acyclic olefins using the same or similar catalysts. Based on the energy levels of the coordinated olefin and of the metallocyclobutane intermediates, they suggested that in the case of acyclic alkenes the coordinated olefin has an energy smaller than that of the cis and trans directing metallocyclobutanes therefore the resulting stereoselectivity is governed by the energy levels of the two metallocycles. Whereas in the case of norbornene this energy is higher than that of two metallocyclobutanes, therefore the system looses its stereoselectivity.

Finally, the recent report by Grubbs (115) in which a planar metallocyclobutane intermediate has been suggested for olefin metathesis, rules out the repulsive interactions held responsible for the stereoselectivity of the reaction, giving a new direction to the stereochemical studies of olefin metathesis.

1.6 THERMODYNAMICS:

The thermodynamic considerations involved in cyclic alkene metathesis are quite different from those of acyclic olefins owing to the occurrence of the ring strain and also to the drastic decrease in the total number of molecules as a result of the ring opening polymerisation. These thermodynamic differences lead to a random distribution of alkylidene groups for acyclic olefins and a non-random distribution of alkylidene groups for cyclic alkene polymerisation.

1.6.1 THERMODYNAMICS OF ACYCLIC OLEFINS :

A remarkable feature of the metathesis of acyclic olefins is that the difference between the enthalpy of products and reactants is virtually zero, because the total number and the types of chemical bonds remain unchanged. Therefore, ideally, such a reaction is determined by the entropy of the system and the product distribution at equilibrium corresponds to a random distribution of the alkylidene moieties. The metathesis of 2-pentene with the catalyst system $WCl_6/EtOH/EtAlCl_2$ (8) is a typical example of such an entropy controlled reaction where the molar ratio of 2-butene: 2-pentene: 3-hexene at equilibrium has been shown to be 1:2:1 which corresponds exactly to a random distribution of the two alkylidene moieties of 2-pentene. Equilibrium can be approached from either direction i.e. an equimolar mixture of 2-butene and 3-hexene leads to the same distribution.

1.6.2 THERMODYNAMICS OF CYCLIC ALKENES :

Ring opening polymerisations are favoured by enthalpy and in many cases, also by entropy changes. The enthalpy term derives mainly from the release of ring strain which is high for 4 and 5 membered rings but relatively small for higher rings. Cyclohexene is a strain-free ring and inert towards metathesis polymerisation. The entropy change derives from structural changes in the polymerisation. The negative translational entropy resulting from incorporation of monomer into a polymer chain is offset by the positive torsional and vibrational entropy changes. On this basis the change in entropy involved in cyclic alkene polymerisation appears to be negative for small rings up to cyclohexene and positive for eight or higher membered rings. As a result of ring opening polymerisation the ring strain energy is released and the high molecular weight polymer produced can assume many conformations balancing the decrease in the entropy caused by the drastic drop in the number of monomer molecules.

The magnitude of the equilibrium monomer concentration ($\left[M\right]_e$) at a given temperature can be used as a measure of monomer polymerisability at that temperature (116) since :

$$\Delta G = -RT\ln K_e \quad \text{and since} \quad K_e = \left[M\right]_e^{-1}$$

$$\Delta G = RT\ln\left[M\right]_e$$

Accordingly the more readily a monomer polymerises the lower will be the concentration of monomer at equilibrium.

Ofstead and Calderon(42) studied the equilibrium polymerisation of cyclopentene initiated by $WCl_6/EtOH/EtAlCl_2$ at different temperatures, the results of which are given in table 1-3.

TABLE 1-3 TEMPERATURE DEPENDENCE OF EQUILIBRIUM CYCLOPENTENE CONCENTRATION.(42)

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

They calculated the enthalpy, entropy and ceiling temperature of the polymerisation to be -4.4 Kcal.mol^{-1}, -14.9 cal.mol.$^{-1}$ deg.$^{-1}$ and 150°C respectively, by plotting $\ln[M]_e$ against T^{-1} based on the following equation :

$$\ln\left[M\right]_e = \frac{\Delta Hp}{RT} - \frac{\Delta S^{o}p}{R}$$

where $\left[M\right]_e$ = equilibrium monomer concentration

ΔHp = enthalpy change during polymerisation

$\Delta S^{o}p$ = the standard entropy change for $a\left[M\right] = 1$ mol.dm^{-3}

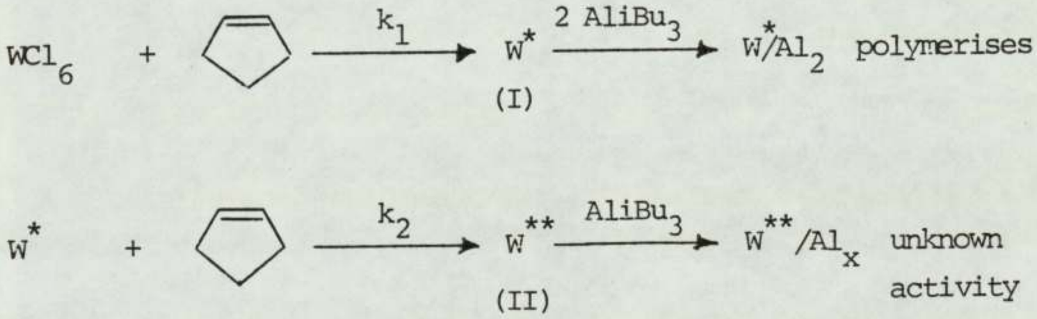
The enthalpy of polymerisation calculated by Ofstead and Calderon$^{(42)}$ was close to the ring strain value for cyclopentene (4.9 Kcal mol^{-1}) reported by Cox.$^{(117)}$

1.7 KINETICS OF METATHESIS POLYMERISATION :

The kinetic studies of ring opening polymerisation of cyclic alkenes have provided additional support for carbene initiation reaction.$^{(83)}$ Dolgoplosk and co-workers$^{(118)}$, using a dilatometry technique, studied the kinetics of cyclopentene polymerisation under the action of the homogeneous system $MoCl_3(C_{17}H_{35}COO)_2$-$Et_2AlCl$ and observed a linear relationship between the initial rate of polymerisation and the initial monomer concentration, giving an equilibrium monomer concentration of 0.6 mol dm^{-3} at 2.7°C. Their results indicated an order of reaction close to 0.6

with respect to the catalyst and first order with respect to the monomer concentration.

Amass and Tuck(50) investigated the polymerisation of cyclopentene with $WCl_6/AliBu_3$ and reported a strong dependence of the rate of polymerisation on the time delay between the addition of WCl_6 and $AliBu_3$ to the cyclopentene solution, suggesting the following reactions :



They introduced a t_{max} term which was the premixing time of WCl_6 with cyclopentene that produced the maximum rate of polymerisation when $AliBu_3$ was added. The kinetic studies revealed a reciprocal proportionality of the t_{max} to the initial monomer concentration :

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

Based on these results authors reported a first order reaction with respect to monomer and first order with respect to catalyst concentration.

In a recent publication, Amass and Zurimendi (108) reported the occurrence of termination reaction in the ring opening polymerisation of cyclopentene initiated by $WCl_6/AliBu_3$ and suggested the following kinetics for the reaction :

$$W^* + W^* \xrightarrow{k_{t_1}} 2\,W_{inact.}$$

$$W^* + W_{inact.} \xrightarrow{k_{t_2}} 2\,W_{inact.}$$

where W^* = active species

$W_{inact.}$ = the product of termination reaction

Therefore, the rate of decay of active species is given by :

$$\frac{-d\left[W^*\right]}{dt} = k_{t_1}\left[W^*\right]^2 + k_{t_2}\left[W^*\right]\left[W_{inact}\right]$$

If the initial concentration of active species is $\left[W^*\right]_o$ and at any time (t) the fraction of species remaining is α then :

$$\left[W^*\right] = \left[W^*\right]_o \alpha$$

$$\frac{-d\left[W^*\right]}{dt} = \left[W^*\right]_o^2 \left\{k_{t_1}\alpha^2 + k_{t_2}\alpha\,(1-\alpha)\right\}$$

Resolution of the differential equation gives :

$$\alpha = \frac{k_{t_2}}{k_{t_2} - k_{t_1} (1 - \exp k_{t_2} \left[W^*\right]_o t)}$$

Considering the propagation reaction as a simple bimolecular reaction then :

$$Rp = k_p \left[M\right]\left[W^*\right] = k_p \left[M\right]\left[W^*\right]_o \alpha$$

Therefore :

$$Rp = \frac{k_p \left[M\right] \left[W^*\right]_o k_{t_2}}{k_{t_2} - k_{t_1} (1 - \exp k_{t_2} \left[W^*\right]_o t)}$$

This equation predicts that the rate of polymerisation at any time during the course of a polymerisation decreases in a complex exponential manner.

1.8 - SCOPE OF THIS WORK :

Assuming that monometallic initiation of cyclopentene polymerisation would not be as complex as bimetallic catalyst systems attempts were made in this project to characterise the nature of the active species and to study the kinetics of the reaction in order to elucidate the mechanism involved and to compare the data with that obtained for bimetallic systems which in turn might illustrate the role of the cocatalyst in the metathesis reaction.

CHAPTER 2

EXPERIMENTAL WORK

2.1 GENERAL TECHNIQUES :

Tungsten hexachloride and the catalyst derived therefrom are very sensitive to the traces of impurities such as moisture and oxygen; therefore all the purifications, catalyst preparations and the metathesis reactions were carried out under high vacuum.

2.1.1 THE HIGH VACUUM LINE :

The high vacuum line shown in fig. 2-1 consisted of a manifold (A) where high vacuum distillation could be carried out. The manifold was evacuated using an Edwards rotary vacuum pump (B) assisted by a mercury diffusion pump (C). To condense any vapour coming from the manifold and/or from the diffusion pump, two liquid nitrogen traps were used (D and E). Reading on the fixed vacustat (F) indicated the attainment of a pressure of the order of 10^{-5}mmHg using this technique.

2.1.2 DEGASSING PROCESS :

The degassing of the liquids prior to distillation was carried out by immersing the flask attached to the manifold into the liquid nitrogen, keeping the main tap G closed. When frozen, the appropriate taps were opened and the system was evacuated. In order to pass any dissolved gases into the manifold, the flask was then immersed in methanol with the tap G closed. The system was then evacuated after re-freezing the liquid and opening the main tap.

This procedure was repeated until no gas bubbles escaped from the liquid on warming to room temperature.

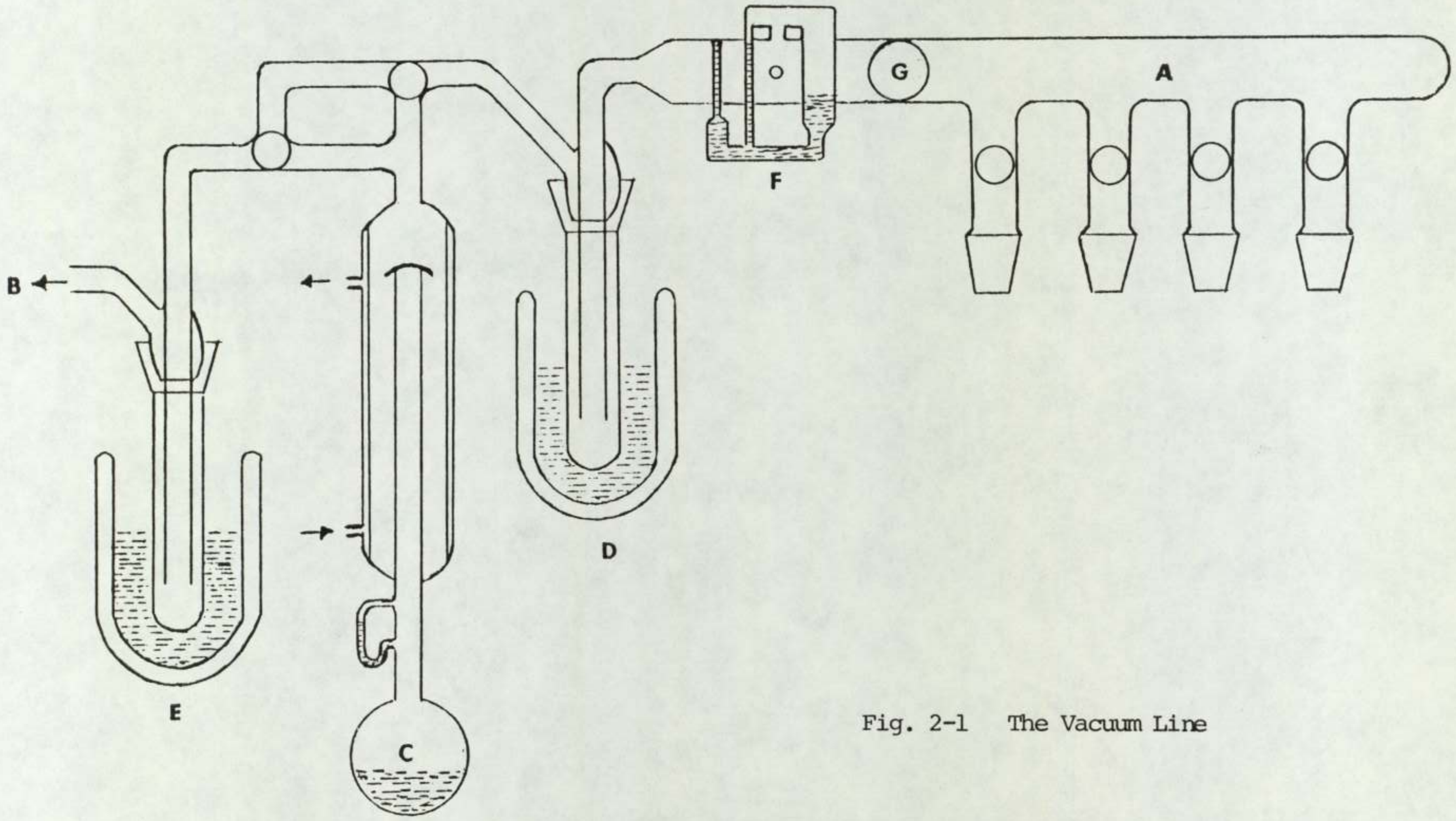


Fig. 2-1 The Vacuum Line

2.1.3 TRAP TO TRAP DISTILLATION :

The degassed monomer or solvent could be transferred to another flask by high vacuum distillation. In this process the empty flask was evacuated and then immersed into liquid nitrogen. After closing the main tap G and opening the appropriate taps, the liquid distilled into the second flask.

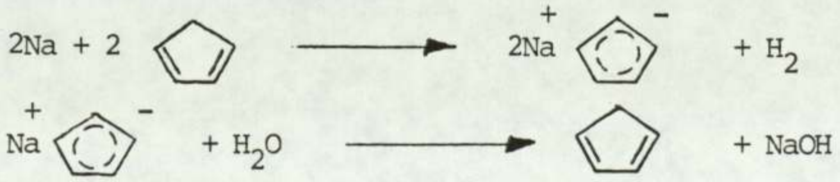
2.1.4 TREATMENT OF GLASSWARE :

All the glassware used in this work was treated with concentrated sodium hydroxide solution and/or chromic acid, then rinsed thoroughly with water and dried in an oven when possible. The apparatus was then attached to the vacuum line and flame dried in order to remove any moisture remaining on the walls.

2.2 PURIFICATION AND DRYING PROCEDURE :

2.2.1 CYCLOPENTENE :

Traces of cyclopentadiene and water, normally present in cyclopentene, deactivate the catalyst towards polymerisation and had to be removed before use. In order to purify and dry the monomer, fine slices of sodium metal were added to cyclopentene, producing cyclopentadienyl sodium which is a very efficient drying agent reacting with water to regenerate cyclopentadiene :



It was apparent that the cyclopentene was dry and pure when the sodium metal had become coated with a brownish solid. The monomer was either stored under high vacuum and vacuum-distilled when required or after 48 hours it was distilled into another vessel containing fresh sodium and kept under vacuum.

2.2.2 TOLUENE :

Toluene was first fractionally distilled from a flask containing sodium through a 2m column packed with glass beads. The middle fraction was removed and partially dried using fine slices of sodium metal. After a period of 24 hours, the toluene was degassed and vacuum-distilled over sodium metal and small amount of benzophenone where sufficient drying takes place on standing for 2 days. In order to remove any olefin present in the solvent, the toluene was then vacuum-distilled into another flask containing pure tungsten hexachloride. Both olefins and water could react with the tungsten compound leaving a pure and dry solvent. The toluene was then vacuum-distilled over sodium metal and some benzophenone and stored under vacuum.

2.2.3 CHLOROBENZENE :

Chlorobenzene was partially dried by standing over P_2O_5 under vacuum for 24 hours, then vacuum-distilled into another flask containg pure tungsten hexachloride in order to obtain efficiently dry solvent free from olefins. After a period of 2 days the chlorobenzene was vacuum-distilled over more WCl_6 and stored under vacuum. Sodium was used as a drying agent on a number of occasions but its use was discontinued when the contents of one flask erupted.

2.2.4 ETHANOL

Ethanol was dried by refluxing 10 ml of the alcohol, under nitrogen, over one gram of pure magnesium coupled with small amount of iodine, in order to convert all the metal into the ethoxide. At this stage an extra 140 ml of ethanol was added to the system and the mixture was allowed to reflux for a further 30 minutes.

$$Mg + 2CH_3CH_2OH \longrightarrow H_2 + Mg(OC_2H_5)_2$$

$$Mg(OC_2H_5)_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2C_2H_5OH$$

The alcohol was then distilled under nitrogen, into another flask containing activated molecular sieves, followed by degassing and storage under vacuum.

2.2.5 TUNGSTEN HEXACHLORIDE :

Although commercial tungsten hexachloride was nominally 99% pure, it was apparent that further purification was necessary in order to remove the impurities, mainly $WOCl_4$ and WO_2Cl_2.

A high vacuum sublimation technique was employed where the apparatus shown in fig.2-2 was immersed in an oil bath of 120°C while attached to the vacuum line. Using a hot finger maintained at a temperature between 75 and 80°C, the impurities $WOCl_4$ and WO_2Cl_2 could only sublime to the walls of the apparatus above the oil level and away from the hot finger on to which pure WCl_6 could sublime.

The purified tungsten hexachloride was then transferred from the finger into ampoules which were sealed off under vacuum while immersed in a water bath of 80°C.

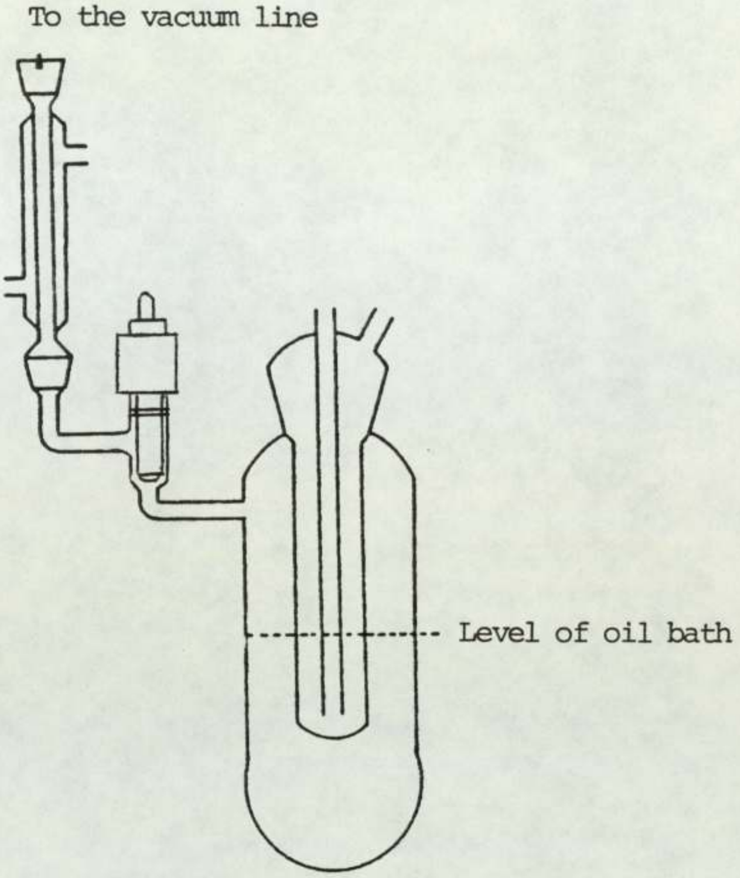


Fig. 2-2 Apparatus used for purification of tungsten hexachloride

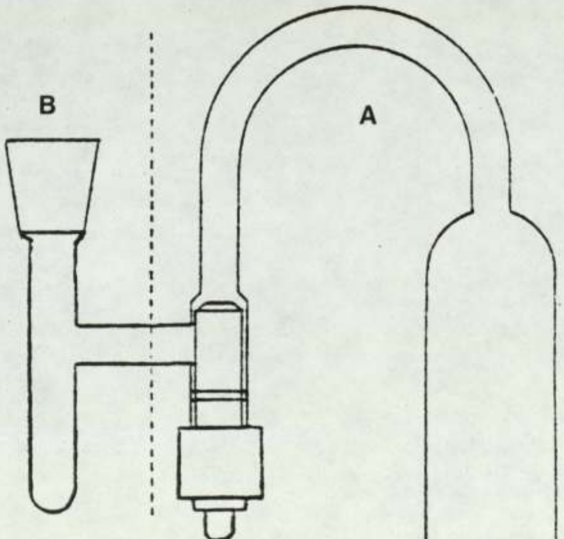


Fig. 2-3 Apparatus used for storage of catalyst solutions

2.2.6 CYCLOHEXENE :

Cyclohexene was distilled and partially dried over slices of sodium. After a period of 24 hours the cyclohexene was vacuum-distilled over fresh sodium and a small amount of benzophenone and stored under vacuum until required.

2.2.7 n-BUTYL VINYL ETHER :

n-Butyl vinyl ether was repeatedly washed with water, made slightly alkaline using sodium hydroxide. It was then fractionally distilled and middle fraction was collected over slices of sodium. The system was degassed and kept under vacuum for a period of 24 hours after which it was vacuum-distilled over fresh sodium and stored under vacuum.

2.3 PREPARATION OF SOLUTIONS :

2.3.1 TUNGSTEN HEXACHLORIDE :

For the preparation of the catalyst solution a weighed amount of tungsten hexachloride was introduced, under nitrogen, into the apparatus shown in fig. 2-3. The apparatus was then attached to the vacuum line and the required amount of solvent was distilled into the system after which the greaseless tap was securely closed and the apparatus was removed from the vacuum line.

For polymerisation studies the solution of tungsten hexachloride was transferred to a series of breakseals. The part 'B' of the apparatus was fitted with a rubber septum, under nitrogen; the greaseless tap was opened and the side tube was filled with the solution. After closing the tap the required volume of the solution was transferred into the nitrogen-filled breakseals by syringe. The breakseals were then sealed off under high vacuum.

2.3.2 TUNGSTEN HEXACHLORIDE - ETHANOL :

Under a stream of nitrogen, a calculated volume of ethanol was added to the solution of tungsten hexachloride, contained in the flask shown in fig. 2-3, so that the molar ratio of the tungsten hexachloride to ethanol was 1:1. The solution was then stored under dry nitrogen for use.

2.4 EXPERIMENTAL TECHNIQUES :

2.4.1 DILATOMETRY STUDIES :

2.4.1.1 PRINCIPLES OF THE DILATOMETRIC TECHNIQUE :

The overall polymerisation rate ($-d\left[CP\right]/dt$) can be monitored through the change in a physical or chemical property of the system. The density of the polymer is normally greater than that of the monomer and this provides a method for the continuous determination of the conversion of monomer to high molecular weight polymer using a dilatometric technique. The contraction in volume on polymerisation can be monitored continuously as a decrease in height of the meniscus in the capillary tube of the dilatometer, shown in fig.2-4. If the meniscus moves from point A to point B, the decrease in volume (ΔV) would be :

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

where Δh = distance from A to B

r = radius of the capillary

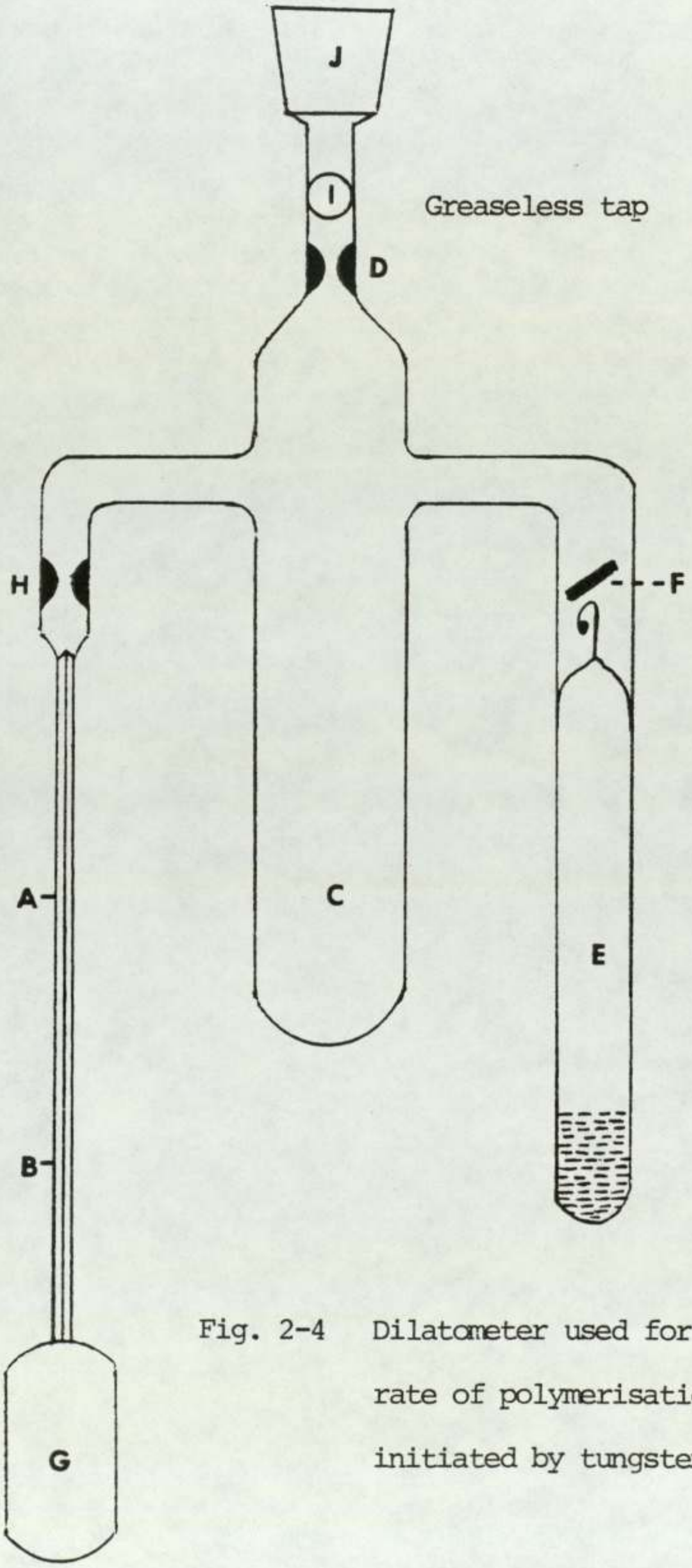


Fig. 2-4 Dilatometer used for determination of rate of polymerisation of CP initiated by tungsten hexachloride

If m grams of monomer completely polymerise, then m grams of polymer are produced and the volume contraction would be :

$$\Delta V = V_p - V_m$$

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

where V_p = volume of polymer

V_m = volume of monomer

ρ_p = density of polymer

ρ_m = density of monomer

If the number of moles of monomer polymerised is designated as ΔM then :

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

M_m being the molecular weight of monomer. Therefore the number of monomer moles polymerised would be :

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

Assuming the volume of the dilatometer (V) is much greater than the total volume change (ΔV) then any change in concentration of monomer $\Delta[M]$ can be written as :

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

Since $\Delta V = \pi r^2 \Delta h$ then :

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

which indicates that the rate of polymerisation is proportional to $\Delta h/\Delta t$ since :

$$R_p = -\frac{d[M]}{dt} = \frac{\Delta h}{\Delta t} \times K$$

where $K = \frac{\pi r^2}{VM_m} \left(\frac{\rho_p \rho_m}{\rho_m - \rho_p} \right)$

In order to avoid thermal fluctuation in the meniscus the experiments are usually carried out in a constant temperature bath.

2.4.1.2 DILATOMETRY EXPERIMENTS :

(a) Tungsten compound alone as catalyst :

A typical dilatometer used in this work is shown in fig.2-4 and contained an ampoule of catalyst solution sealed directly to the apparatus.

The required amounts of cyclopentene and solvent were distilled into the bulb C and while the solution was still frozen the apparatus was sealed off at point D. When thermal equilibrium was reached on warming up the system to room temperature, the breakseal E was broken using the glass rod F, allowing the tungsten hexachloride solution to mix with the cyclopentene solution after which the dilatometer G was immediately filled and then sealed off at H. The dilatometer was placed in a water bath held at constant temperature and the decrease in the height of the meniscus in the capillary tube was followed using a cathetometer.

When WCl_6-EtOH was used as the catalyst, the dilatometer shown in fig. 2-5 was employed. The only difference between the two dilatometers lies in the way the catalyst was introduced into the cyclopentene solution. In the latter case, the catalyst was added to the solution by a syringe through the rubber septum E.

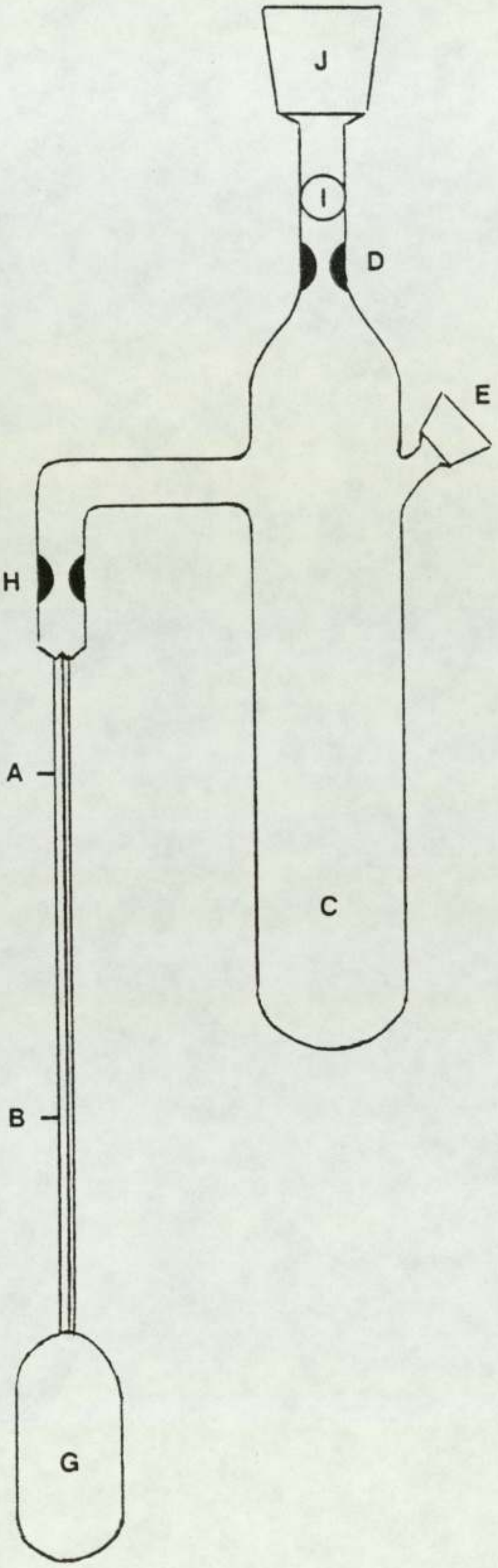


Fig. 2-5 Dilatometer used for determination of rate of polymerisation of cyclopentene initiated by WCl_6/EtOH catalyst system

(b) Oxygen as cocatalyst :

The required volumes of cyclopentene and toluene were first vacuum-distilled into the apparatus shown in fig. 2-6 and the system was warmed to room temperature. The catalyst was mixed with the cyclopentene solution by breaking the breakseal B using the glass rod C. The apparatus was then connected to another apparatus shown in fig. 2-7 through E and F and the whole system was attached to the vacuum line through G.

Keeping taps D and M closed, the system was evacuated by opening taps H, I and J. The solution was then transferred into the bulb K by closing taps H and J and opening tap D. After various periods of time, dry oxygen was introduced into the system through F and I. The bulb L was filled immediately with the solution through tap J which was then closed. The apparatus was placed in a water bath of constant temperature where the decrease in the height of the meniscus of capillary tube was followed using a cathetometer.

2.4.2 CALORIMETRY STUDIES :

As the ring opening polymerisation of cyclopentene is an exothermic reaction ($\Delta H = -4.4$ Kcal.mol.$^{-1}$ (42)) an alternative method for the determination of the rate of polymerisation is the measurement of the heat of polymerisation using a calorimetry technique where the change in temperature in an adiabatic system could be recorded as a function of time.

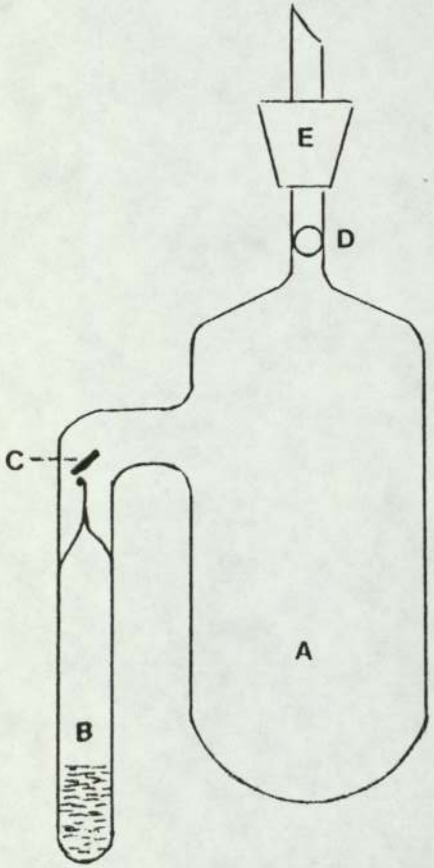
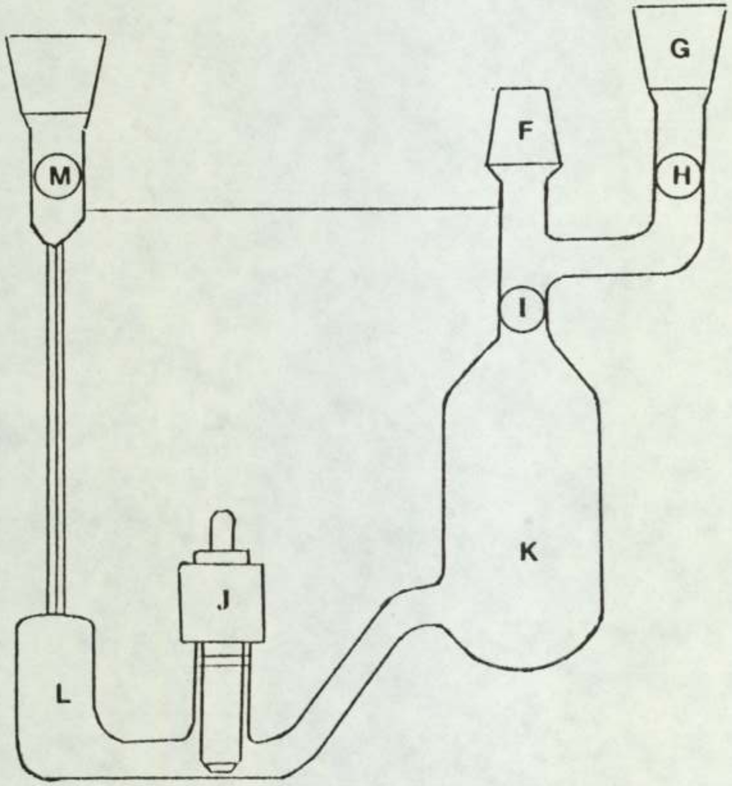


Fig. 2-6 Pre-reaction vessel

Fig. 2-7 Dilatometer used for determination of rate of Polymerisation of toluene solutions of CP initiated by WCl_6/O_2



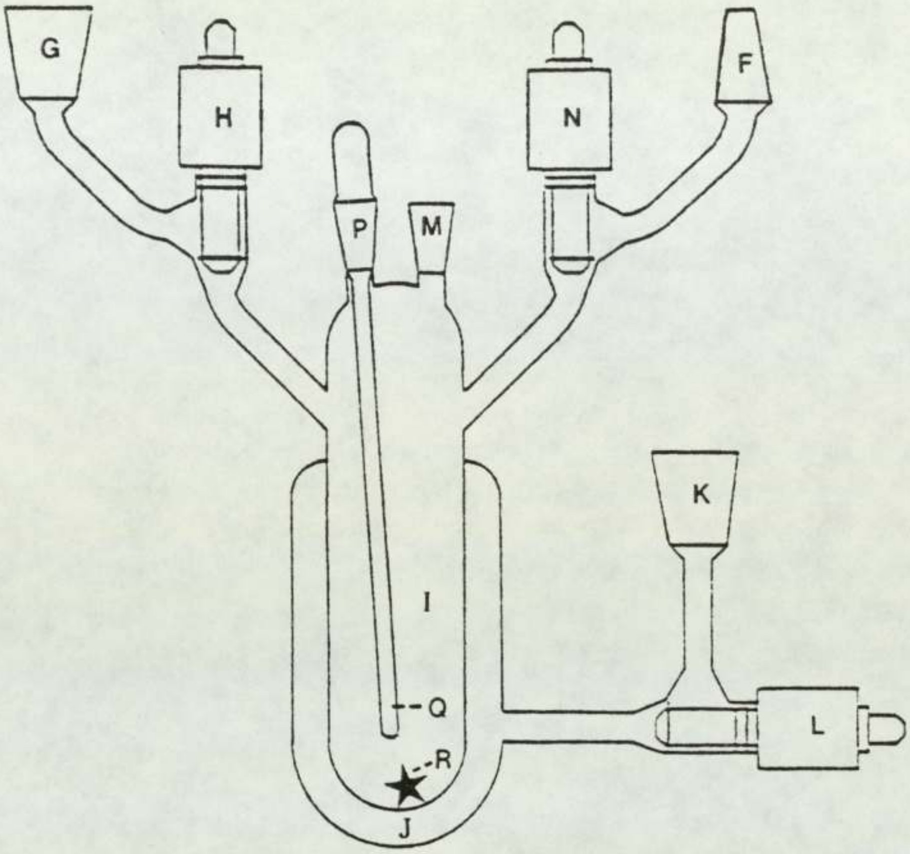
2.4.2.1 CALORIMETER :

A slight modification of the technique adopted by Biddulph and Plesch (119) was used. The temperature sensing device was a thermistor of 2KΩ (GL23, RS Components Limited), incorporated, as a part of Wheatstone Bridge, to a Knauer auto-potentiometer bridge adapted with a Servoscribe IS recorder. The deflection in the measuring system was calibrated by comparison of the changes in the temperature of the system, using a thermometer, with the deflection in the measuring system so that the deflection from the null point could be used to determine the heat changes and hence the extent of the reaction over a period of time.

2.4.2.2. CALORIMETRY EXPERIMENTS

(a) Calorimeter A :

After distilling the required amounts of cyclopentene and toluene into the apparatus shown in fig. 2-6 and allowing the polymerisation to proceed by breaking the breakseal B containing the catalyst solution, the apparatus was connected to the calorimeter shown in fig. 2-8 through E and F. The whole system was attached to the vacuum line through G and evacuated by opening the appropriate taps. Tap H was then closed and the solution was transferred into the bulb I by opening the tap D. After closing all the greaseless taps the calorimeter was removed from the vacuum line in order to evacuate the double jacket J through K and L. A stream of dry nitrogen was then introduced into the system through M in order to prevent oxygen getting into the system. After a period of 24 hours, the calorimeter was placed on a magnetic stirrer and thermistor was connected to the balancing bridge. When a stable base line was obtained, dry oxygen



F, G, K - glass joints

H, L, N - greaseless taps

I - reaction vessel

J - double Jacket

M - rubber septum

P - greaseless joint

Q - thermistor

R - magnetic follower

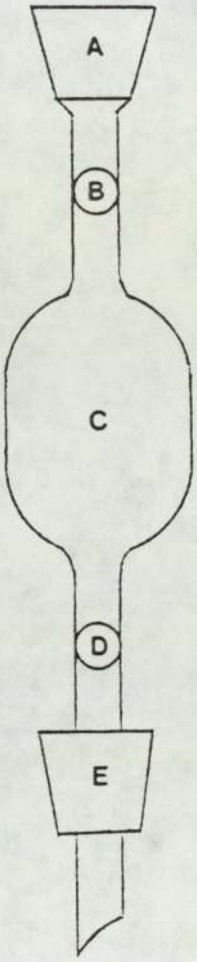
Fig. 2-8 Calorimeter A used for determination of rate of polymerisation of toluene solutions of cyclopentene initiated by tungsten hexachloride/oxygen system was introduced into the system through G using the apparatus shown in fig. 2-9. The change in temperature was automatically recorded as a function of time.

(b) Calorimeter B :

The required amounts of cyclopentene and chlorobenzene were distilled into the apparatus shown in fig. 2-6. By mixing the catalyst with cyclopentene solution the polymerisation was allowed to proceed for a required period of time after which the apparatus was connected to the calorimeter shown in fig. 2-10 through E and F. The whole system was then attached to the vacuum line through G and evacuated by opening the appropriate taps. By closing tap H and opening tap D, the solution was allowed to transfer into the calorimeter. After closing tap I, the system was removed from the vacuum line and the double jacket J was then evacuated through K and L. After placing the apparatus on a magnetic stirrer and connecting the thermistor to the balancing bridge, the system was allowed to produce a stable base line after which dry oxygen was introduced into the system through G using the apparatus shown in fig. 2-9. The change in temperature was automatically recorded as a function of time.

2.4.3 NORMAL POLYMERISATION :

The required amounts of cyclopentene and chlorobenzene were first vacuum-distilled into the bulb A of the apparatus shown in fig. 2-11 followed by the injection of the catalyst solution into the system through the rubber septum B. The apparatus was then connected to the vessel shown in fig. 2-12 through D and E. Keeping the greaseless tap C closed, the whole system was evacuated by attaching the apparatus to the vacuum line through H. By closing tap I and



A - glass joint

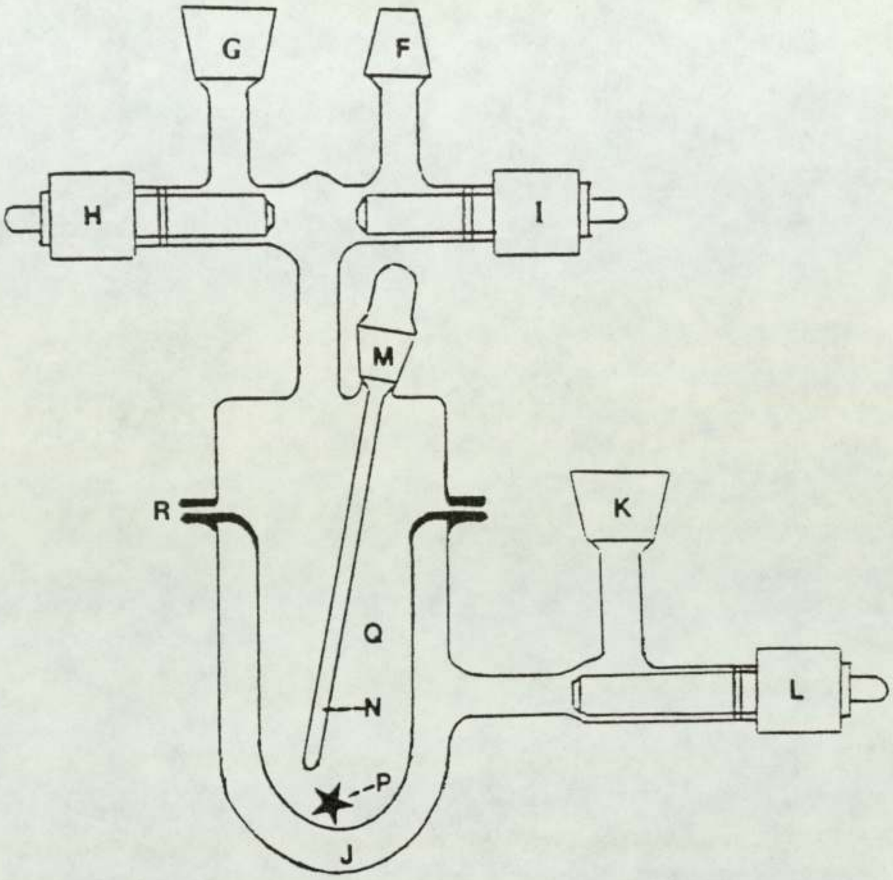
B - greaseless tap

C - calibrated oxygen bulb

D - greaseless tap

E - glass joint

Fig. 2-9 Apparatus used for introduction of oxygen into the system under study



F, G, K - glass joints

H, I, L - greaseless taps

J - double jacket

M - greaseless joint

N - thermistor

P - magnetic follower

Q - reaction flask

R - flange joint

Fig. 2-10 Calorimeter B used for determination of rate of polymerisation of chlorobenzene solutions of cyclopentene initiated by tungsten hexachloride/oxygen system

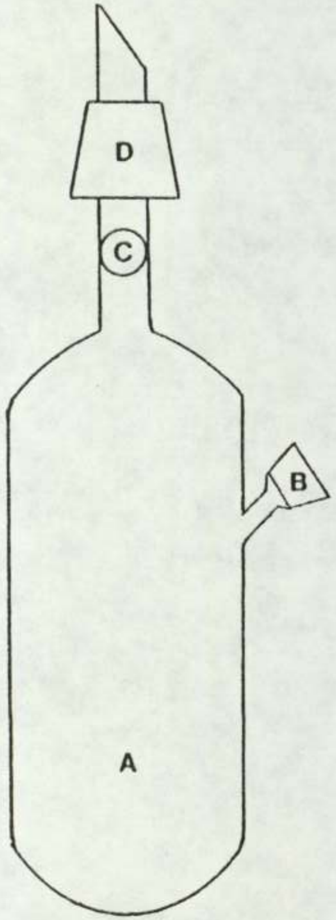
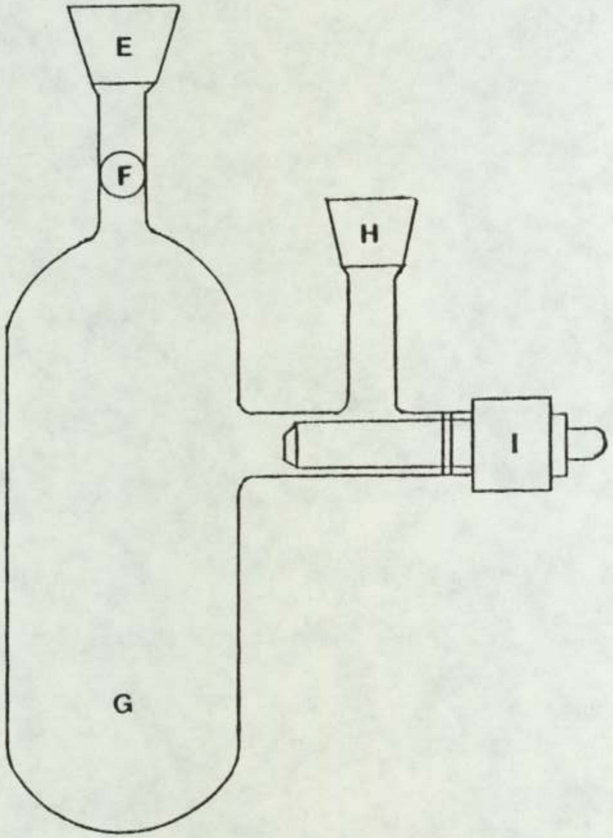


Fig. 2-11 Mixing vessel

Fig. 2-12 Reaction vessel used for normal polymerisation

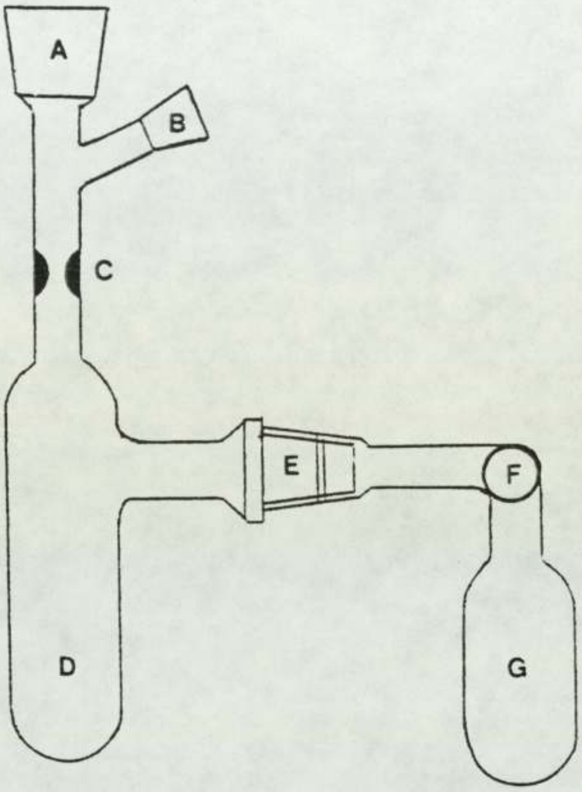


opening tap C, the solution was transferred into the bulb G where it could be kept for a required period after which the solution was allowed to react with dry oxygen using the apparatus shown in fig. 2-9. The polymer was then obtained by precipitation of the polymerisate in methanol and purified by successive precipitations in methanol from chloroform solutions after which it was dried and weighed.

2.4.4 REACTION OF TUNGSTEN HEXACHLORIDE WITH CYCLIC ALKENES :

2.4.4.1 FORMATION OF HYDROGEN CHLORIDE :

The reaction of tungsten hexachloride with cyclopentene was accompanied by the evolution of HCl and the apparatus shown in fig. 2-13 was used to investigate its formation. The experiment was based on the absorption of HCl by polyvinylpyridine cross-linked with 2% divinyl benzene. A known amount of this polymer was placed in bulb G and the apparatus was evacuated until a constant weight was obtained. Tap F was then closed and, under a stream of nitrogen, a known amount of tungsten hexachloride was introduced into the bulb D through B. After distilling the required amounts of cyclopentene and toluene into the system, the apparatus was sealed off at point C while the solution was still frozen. Tap F was then opened and the system was allowed to stand for 2 days in the dark. After this period the tap F was closed and the two parts of the apparatus were separated at the greaseless joint E. The bulb G was evacuated and weighed until a constant weight was obtained. The amount of HCl absorbed by the polyvinylpyridine was then calculated.



A - glass joint

B - rubber septum

C - sealing-off point

D - reaction bulb

E - greaseless joint

F - greaseless tap

G - absorber bulb

Fig. 2-13 Apparatus used for investigation of hydrogen chloride formation

2.4.4.2 FORMATION OF PRECIPITATE :

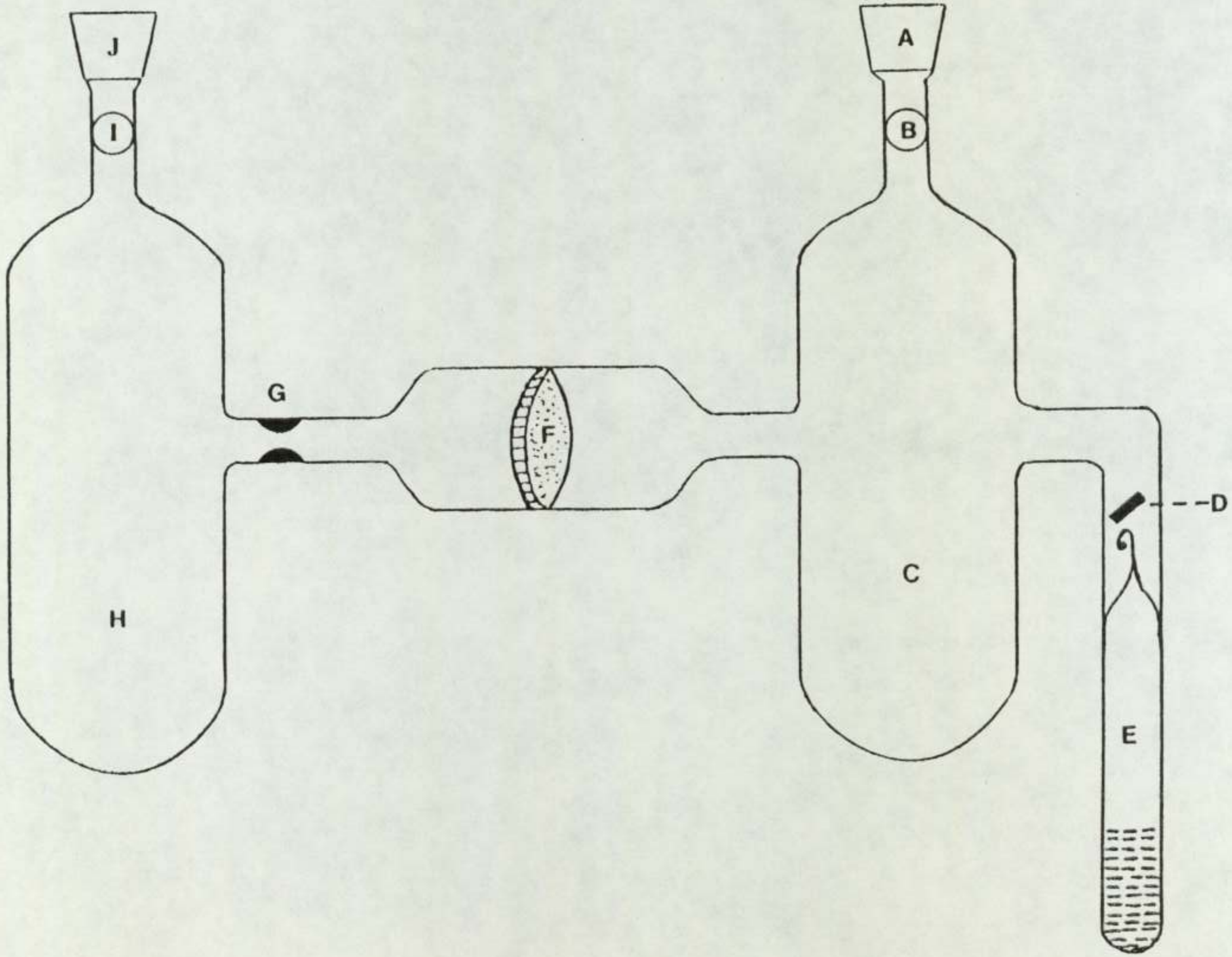
The reaction of tungsten hexachloride with cyclopentene (or cyclohexene) was always accompanied, when toluene was used as solvent, by the appearance of an oily precipitate. In order to separate this precipitate from the solution the apparatus shown in fig. 2-14 was used. In this experiment the required amounts of cycloolefin and toluene were vacuum-distilled into the bulb C of the apparatus. Following this, the catalyst was allowed to mix with the solution by breaking the breakseal E using the glass rod D. After a period of 24 hours the clear solution was transferred into the bulb H through the glass filter F; and the oily precipitate was repeatedly washed by forward vacuum distillation of the clear solution before the apparatus was sealed off at point G. Fresh cyclopentene was distilled into the bulb C and allowed to be in contact with the precipitate for a period of one hour after which dry oxygen was admitted through A using the apparatus shown in fig. 2-9 to control the quantity of gas added. The polymer was then obtained by precipitating the polymerisate in methanol. The clear solution in bulb H was allowed to stand for a further period of 24 hours after which dry oxygen was introduced into the system through J by following a similar procedure.

2.4.5 ULTRAVIOLET/VISIBLE SPECTROSCOPY :

2.4.5.1 THE PRINCIPLES OF THE U.V/VISIBLE SPECTROSCOPY :

When a beam of electromagnetic radiation is passed through a substance the radiation can be either absorbed or transmitted depending on its frequency and the structure of molecules it encounters.

Fig. 2-14 Apparatus used for separation of the oily precipitate



When a molecule absorbs radiation it gains energy the value of which depends on the frequency of the radiation. The higher the frequency the greater the quantum gain in energy. This energy absorbed by the molecule may bring about increased vibration or rotation of the atoms or may raise the electrons to higher energy levels.

The visible and ultraviolet spectra are associated with transitions between electronic energy levels. The transitions are generally between a bonding or lone pair orbital and an unfilled non-bonding or antibonding orbital. The wavelength of any absorption is therefore a measure of the separation of these energy levels which is unique for each kind of species. The absorbance at any fixed wavelength is proportional to the molar concentration of the absorbing substance and the optical path length of the cell containing the substance. This is known as Beer-Lambert law, a law that governs the absorption of all types of electromagnetic radiations.

$$\log I_o/I = A = \varepsilon lc$$

where I_o = the intensity of incident radiation

I = the intensity of transmitted radiation

A = the absorbance

ε = the extinction coefficient

c = the concentration of absorbent

l = the pathway length of the cell

2.4.5.2 INSTRUMENTATION :

The instrument used for recording the u.v./visible spectra was Unicam SP 800 B ultraviolet spectrophotometer.

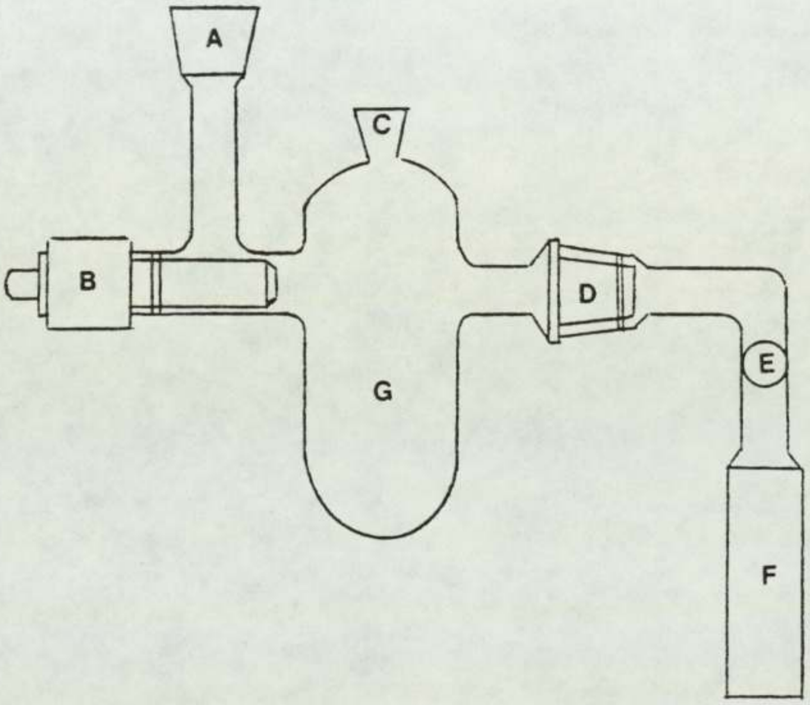
2.4.5.3 ULTRAVIOLET/VISIBLE EXPERIMENTS :

The apparatus shown in fig. 2-15 was used to follow the u.v/visible spectral changes taking place in the reaction of tungsten hexachloride with cyclopentene.

The system was first evacuated by attaching the apparatus to the vacuum line through A after which the tap B was closed and the required amounts of tungsten hexachloride, chlorobenzene and cyclopentene were injected into the bulb G through the rubber septum C. The cell F was then filled and removed from the mixing bulb G by dismantling the apparatus through the greaseless joint D. Using chlorobenzene as reference, the u.v/visible spectrum of the reaction was recorded.

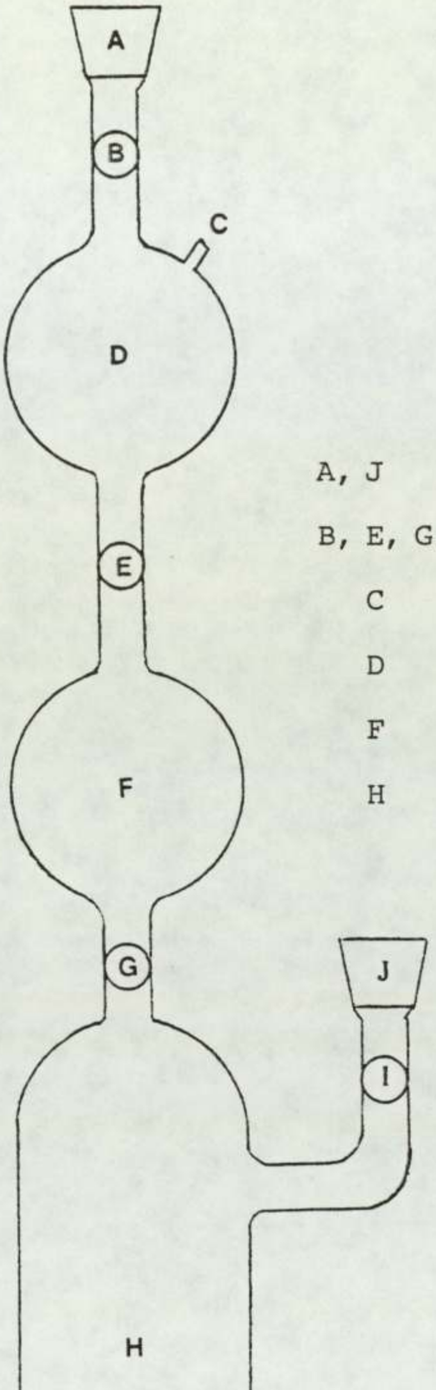
In some experiments, after a predetermined reaction time between the catalyst and cyclopentene, the effect of oxygen was also studied by introducing air into the system for short period of time through D and E. The spectral changes were then followed using chlorobenzene as reference.

To investigate whether the species giving rise to such spectral changes is active towards the metathesis polymerisation of cyclopentene, the following procedure was carried out. The required amounts of tungsten hexachloride, chlorobenzene and cyclopentene were injected through the rubber septum C into the bulb D of the apparatus shown in fig. 2-16. The solution was then transferred into the bulb F by opening the tap E and stored for a predetermined time. In the meanwhile, the required amount



A - glass joint	E - greaseless tap
B - greaseless tap	F - 1 mm quartz cell
C - rubber septum	G - mixing bulb
D - greaseless joint	

Fig. 2-15 Apparatus used for u.v/visible spectroscopic studies



A, J - glass joints

B, E, G, I - greaseless taps

C - rubber septum

D - mixing bulb

F - reaction bulb

H - polymerisation bulb

Fig. 2-16 Apparatus used for investigation of metathesis activity of CP+WCl_6/O_2 system when $\left[CP\right]_o < \left[CP\right]_e$

of cyclopentene was vacuum-distilled into the bulb H through J. Oxygen was then introduced into the bulb F and allowed to react for a predetermined time after which the mixture was transferred into the bulb H through tap G and kept for a required period of time. The polymer was then collected by precipitating the polymerisate in methanol and purified by successive precipitations in methanol from chloroform solutions.

2.4.6 REACTION OF n-BUTYL VINYL ETHER :

According to the literature vinyl ethers do not react metathetically (120). Based on this statement the following reactions were carried out in order to determine the nature of the metathetical active species since cationic nature of the active centre would lead to the polymerisation of n-butyl vinyl ether.

The apparatus used in this work is shown in fig. 2-17. After the evacuation of the apparatus through A, the required amounts of cyclopentene and chlorobenzene were distilled into the bulb E. Tap D was closed and required amount of n-butyl vinyl ether was then distilled into the bulb C. The catalyst was mixed with cyclopentene in the bulb E by breaking the breakseal G using glass rod F. After a period of 10 minutes the tap D was opened and n-butyl vinyl ether was transferred into the bulb E and allowed to stand for a period of 30 minutes after which the solution was analysed.

When the presence of proton sponge was required, the known amount of 1,8 bis (dimethyl amino) naphthalene was transferred into the

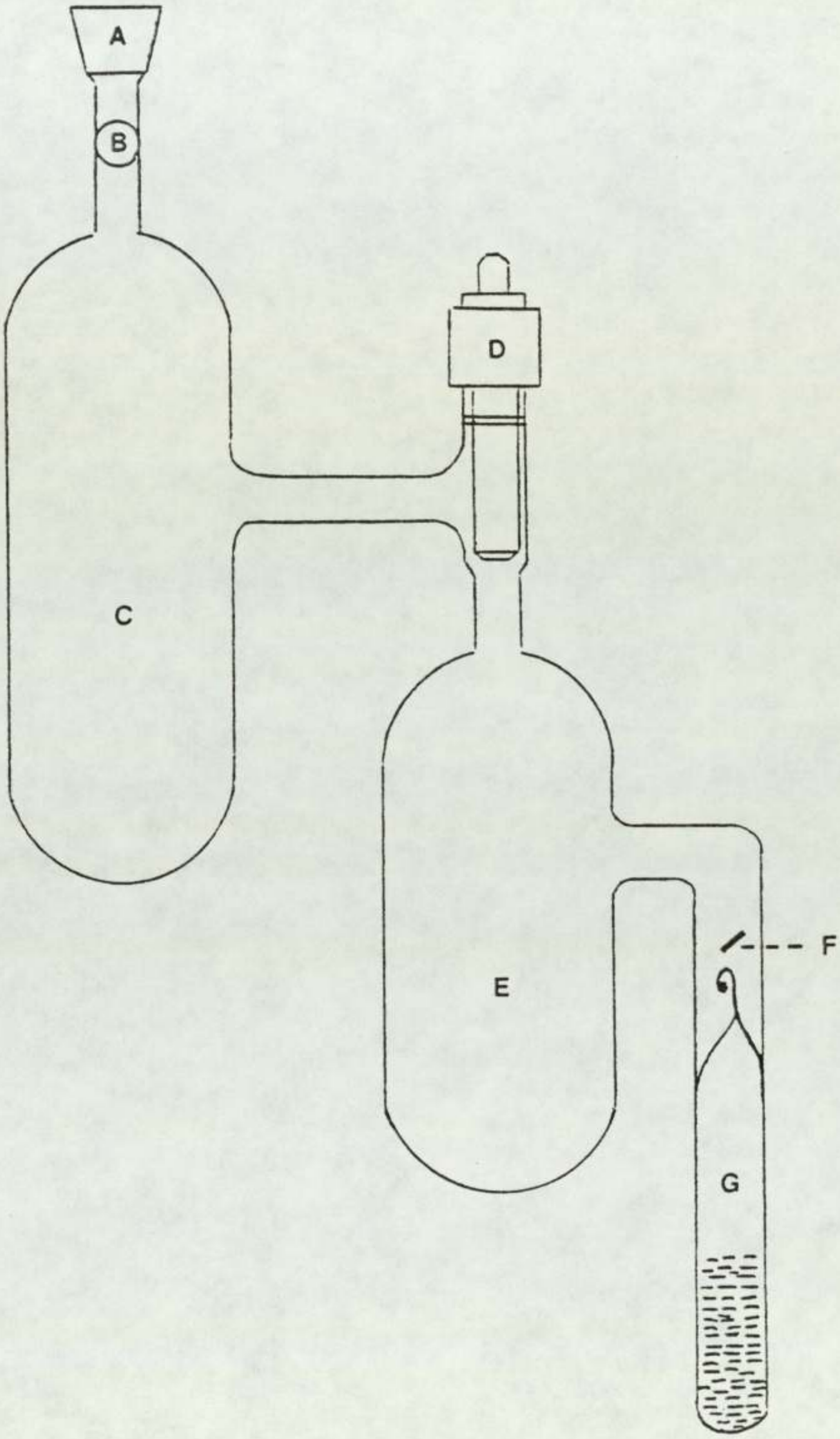


Fig. 2-17 Apparatus used for reactions of n-butyl vinyl ether with the species responsible for the metathesis polymerisation of cyclopentene

bulb C of the apparatus prior to distillation of the ether.

2.5 ANALYTICAL TECHNIQUES:

2.5.1 GAS LIQUID CHROMATOGRAPHY :

Gas liquid chromatography technique was used to determine the purity of the liquid materials.

In gas chromatography, the various components in a mixture are partitioned between the gas phase and a stationary phase. The stationary phase is usually a non-volatile liquid supported on an inert matrix and the mobile phase is an inert gas. Since different components have different partition ratios they are eluted in sequence from the end of the chromatographic column, where they pass through a detector to give an electrical signal related to the composition of the gas passing through it.

The important characteristic of the peak for quantitative analysis is its area. A comparison suitable for most quantitative purposes may be made by triangulation, i.e. approximating the area of the peak by taking the product of its height and its width at half height.

The gas liquid chromatograph used was Pye Unican (GCD Chromatograph) with a flame ionisation detector fitted with a column being 25% silicon grease on phaseprep A, 60 - 80 mersh.

2.5.2 INFRARED SPECTROSCOPY :

Infrared spectroscopy technique was used in order to determine the relative proportion of cis and trans double bonds in the polypentenamer. The trans double bond absorbs at 10.35µ and the cis at 13.5µ.

Samples were prepared by dissolving the polymer in chloroform followed by casting into thin films by allowing the chloroform to evaporate. The instrument used to record the infrared spectrum was a Perkin Elmer 599 or 237 grating infrared spectrophotometer.

CHAPTER 3

POLYMERISATION STUDIES

3.1 INTRODUCTION :

The ring opening polymerisation of cyclic alkenes is a special case of olefin metathesis and normally catalysed by bimetallic system based upon tungsten or molybdenum compounds. Amass and co workers(23) reported that tungsten hexachloride alone could act as a metathesis catalyst suggesting that two-component catalyst systems are not essential for the metathesis polymerisation of cyclic alkenes. Assuming that such monometallic initiation could provide valuable information concerning the mechanism of olefin metathesis, attempts were made in this project to study the kinetic laws of ring opening polymerisation initiated by such catalyst systems.

3.2 POLYMERISATION OF CYCLOPENTENE INITIATED BY WCl_6 ALONE

Following the report by Amass and co workers(23) disclosing the monometallic initiation of cyclopentene polymerisation using tungsten hexachloride alone as a catalyst, a dilatometric technique was used to study the rates of polymerisation of toluene or chlorobenzene solutions of cyclopentene. These experiments were carried out as described in section 2.4.1.2(a).

3.2.1. KINETIC STUDIES IN TOLUENE : EFFECT OF THE CONCENTRATION OF WCl_6 ON THE RATE OF POLYMERISATION OF CYCLOPENTENE

A series of experiments were carried out using toluene as solvent to study the effect of tungsten hexachloride concentration on the rate of polymerisation of cyclopentene, the concentration of which was held constant during this series.

In a typical polymerisation a breakseal containing 1 ml of 0.051 M solution of WCl_6 in toluene was sealed to the apparatus shown in fig. 2-4. 17.9 ml of cyclopentene and 3.3 ml of toluene were successively distilled under vacuum into the apparatus to produce a solution for which $[WCl_6] = 2.3 \times 10^{-3}$ mol. dm^{-3} and $[CP] = 9.2$ mol. dm^{-3}.

The rate of polymerisation of cyclopentene was determined as described in section 2.4.1.2(a). In other experiments in this series the volumes of WCl_6 solution, cyclopentene and toluene were adjusted so that the concentration of cyclopentene was constant.

Fig. 3-1 shows the polymerisation curves for the various catalyst concentrations used in these experiments.

The dependence of initial rate of polymerisation on tungsten hexachloride concentration is shown in fig. 3-2. When the experiments were repeated under identical conditions the error in the measurement of the rate of polymerisation is shown. It would appear from fig. 3-2 that there is not a simple relationship between the initial rate of polymerisation and the concentration of tungsten hexachloride. Within experimental error, however, the reproducibility of the results obtained support the observation that the rate of polymerisation is a maximum under these conditions at a W : CP molar ratio of 1:2000.

Fig. 3-1 Polymerisation curves of toluene solutions of cyclopentene for various concentrations of tungsten hexachloride

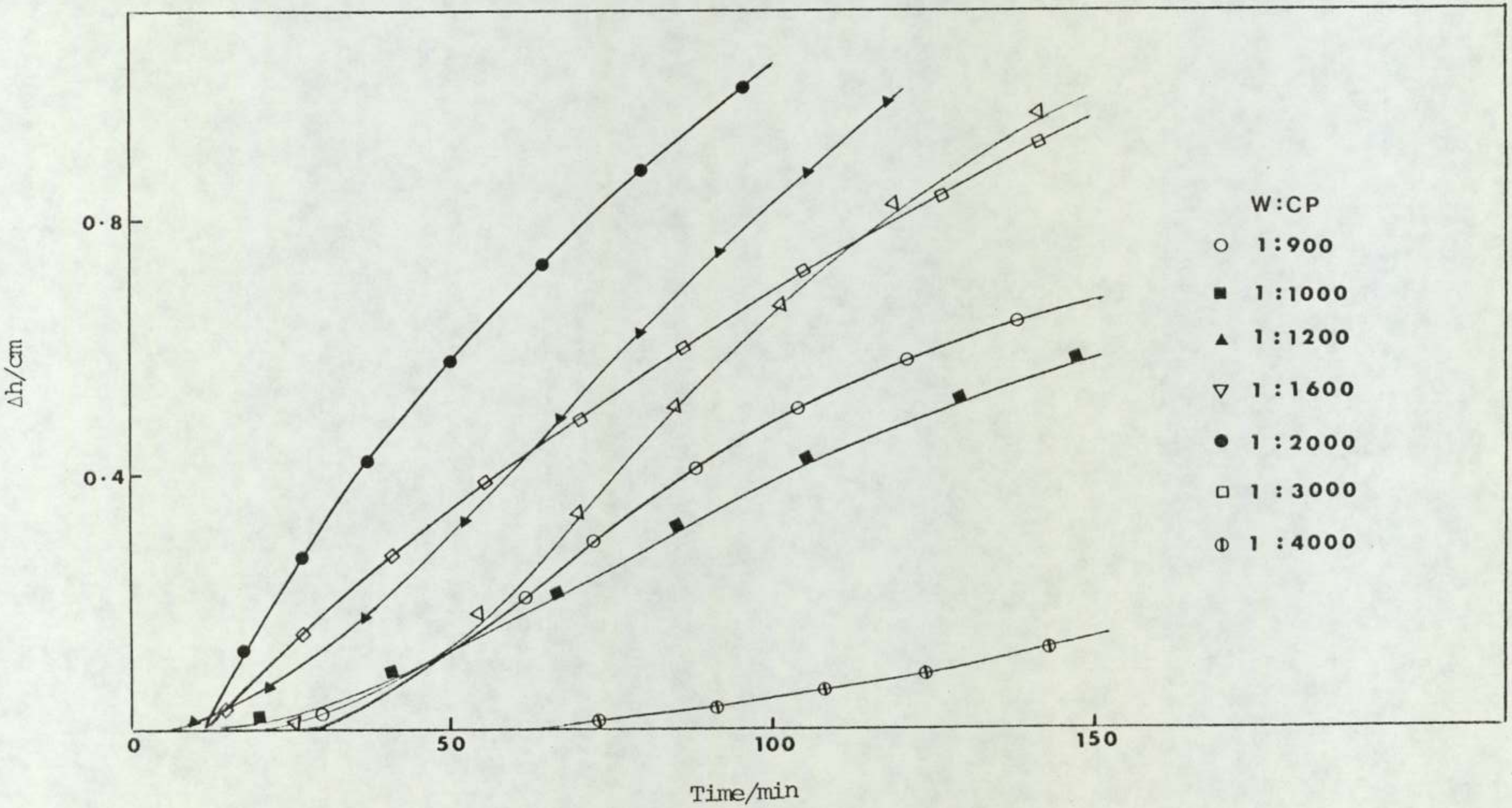
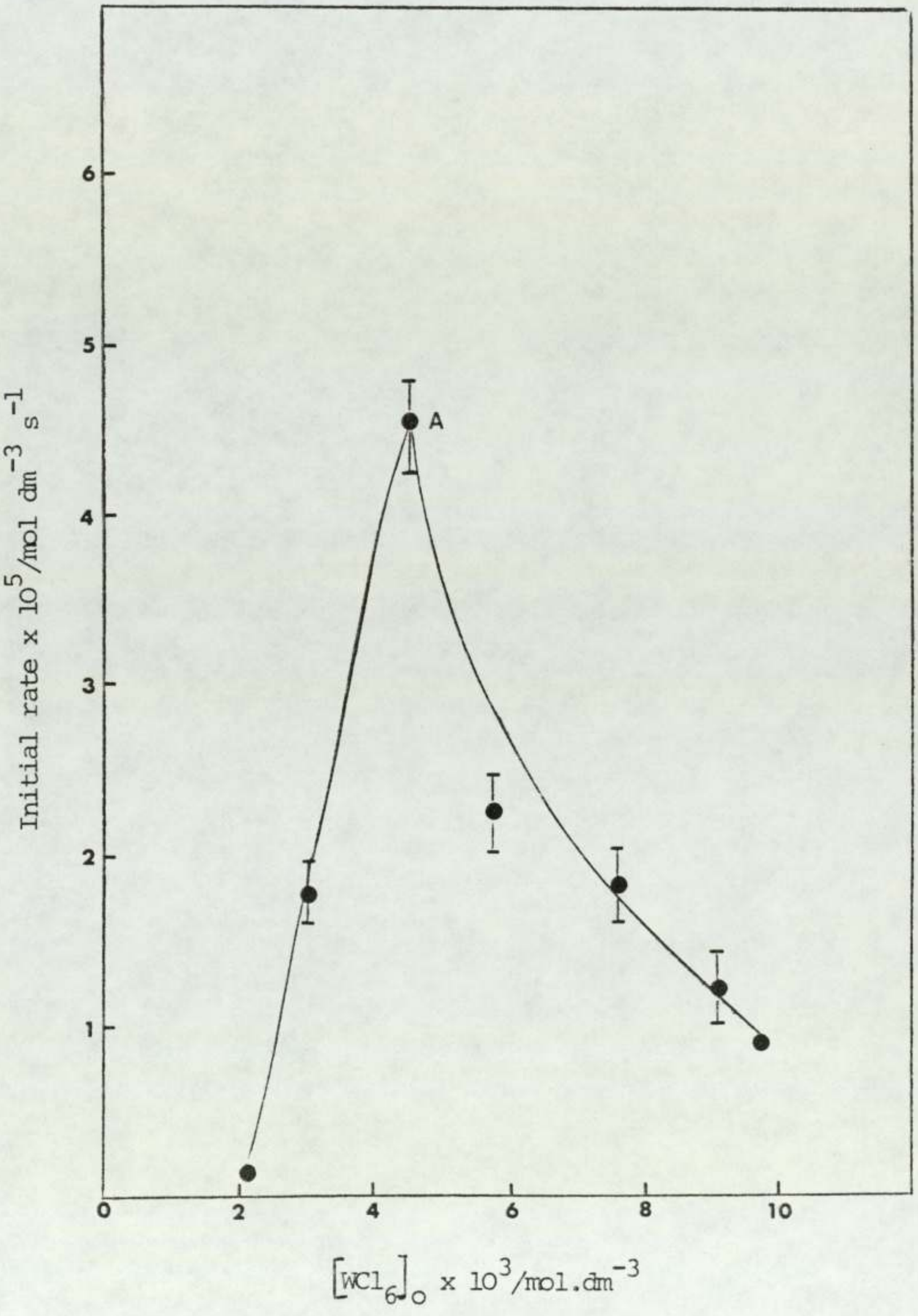


Fig. 3-2 Dependence of the initial rate of polymerisation of toluene solutions of cyclopentene on the concentration of tungsten hexachloride



This behaviour could be explained if there are two competitive effects in the system which may be summarised as:

(i) production of an active centre
(ii) destruction of the active centre.

At low concentrations of catalyst, the destruction effect is negligible and therefore the rate of polymerisation increases as the concentration of the tungsten hexachloride is increased to the point A. At concentrations of catalyst greater than this, the rate of destruction of the active centre once it is formed becomes predominant and this has a dramatic effect upon the rate of polymerisation as the catalyst is effectively removed from the system.

Whenever tungsten hexachloride was added to cyclopentene in the course of polymerisation, the blue solution immediately turned brown and furthermore, the reaction was accompanied by the slow appearance of an oily precipitate on the walls of the apparatus. This feature was most marked in those polymerisations using higher concentrations of tungsten hexachloride, whereas at lower concentrations very little precipitate was observed.

However changing the concentration of cyclopentene at concentrations of WCl_6 that produce large precipitates did not produce a homogeneous system. In such an experiment a breakseal containing 1 ml of 0.055 M solution of tungsten hexachloride in toluene was sealed to the apparatus shown in fig. 2-6. 8.4 ml of cyclopentene and 11.0 ml of toluene were successively distilled under vacuum into the apparatus to produce a solution for which $\left[CP\right] = 4.7$ mol. dm^{-3} and $\left[WCl_6\right] = 2.7 \times 10^{-3}$ mol. dm^{-3}. The polymerisation was then allowed to proceed for a period of 24 hours. Similar to other experiments in this series an oily precipitate was formed around the walls of the apparatus indicating that a decrease in the concentration of cyclopentene has no effect on the heterogeneity of the system.

The kinetics of the ring opening polymerisation of toluene solutions of cyclopentene initiated by tungsten hexachloride were found to be complex due to the heterogeneous nature of the system. The achievement of useful information regarding the metathesis polymerisation of cyclopentene therefore requires the amendment of the system. This could be done by either using very low concentrations of the catalyst where the amount of precipitate formed is negligible or changing the solvent to one in which the precipitate remains soluble. The former option has the following disadvantages:

(i) the rates of polymerisations of cyclopentene will be very low requiring long reaction times.

(ii) the ratio of impurities : W will be very high, hence the degree of accuracy will be low.

(iii) slight errors in the volume of catalyst solution added would result in marked errors in the concentration of catalyst.

On these grounds attempts were made to find a solvent which could provide a homogeneous system.

3.2.2 KINETIC STUDIES IN CHLOROBENZENE : PRELIMINARY STUDY

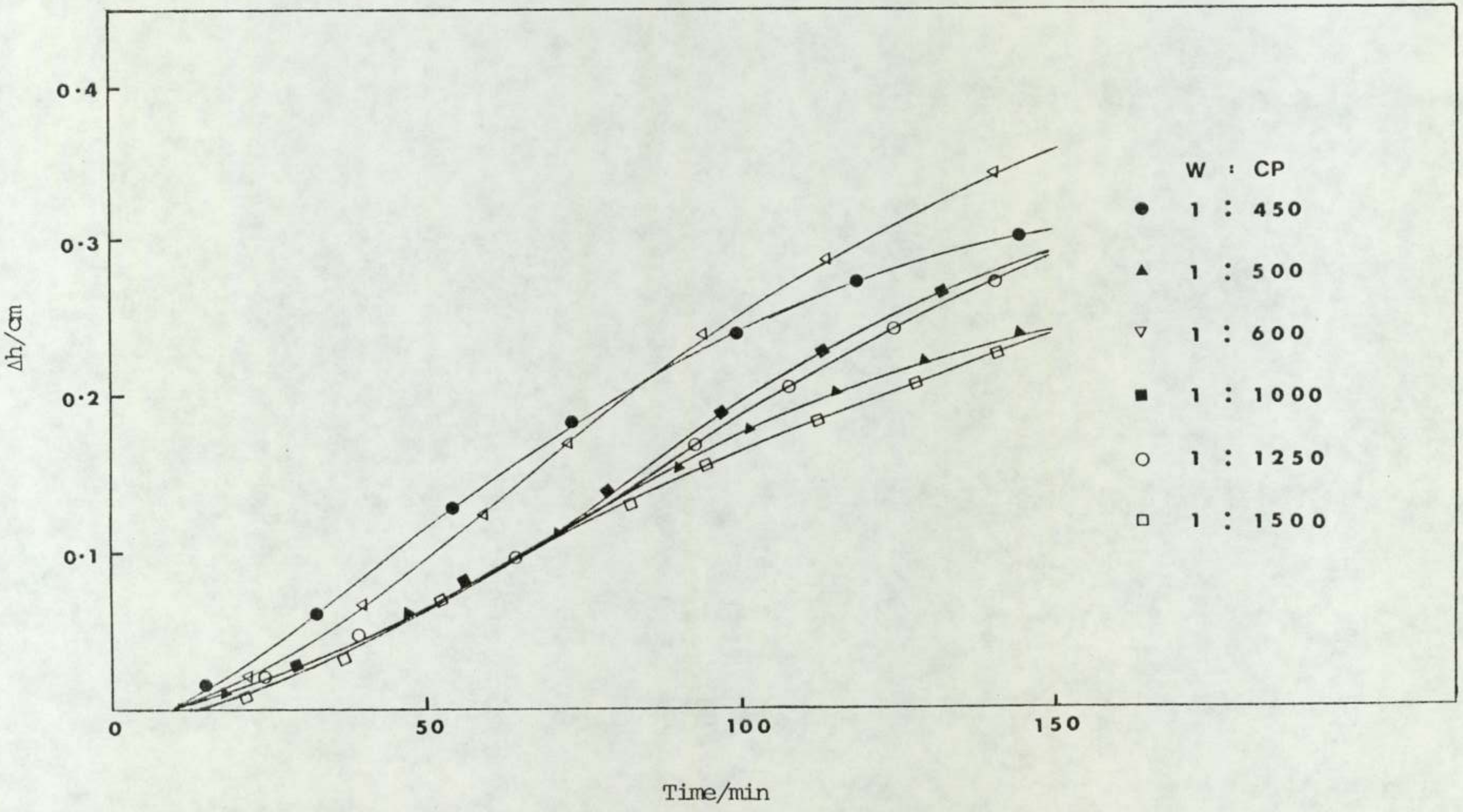
In order that the system might remain homogeneous during the polymerisation an attempt was made to polymerise cyclopentene using the slightly more polar solvent chlorobenzene (Dielectric Constant = 5.621) instead of toluene (DC = 2.379). In a typical polymerisation 7.9 ml of cyclopentene and 10 ml of chlorobenzene were successively distilled into the apparatus shown in fig. 2-6. When the system reached the thermal equilibrium 1 ml of tungsten hexachloride of 0.051 M was added to the solution by breaking the breakseal. The system was allowed to stand for a period of 24 hours. No precipitation around the walls of the vessel occurred whereas such a polymerisation carried out in toluene would have produced significant quantities of precipitate. The solution had become viscous after 24 hours and a small amount of polymer was obtained.

There was however a limiting cyclopentene : chlorobenzene volume ratio of 70 : 30, i.e. $\left[CP \right] = 7.9$ mol. dm^{-3}, for such a homogeneity beyond which the system became heterogeneous.

3.2.2.1. EFFECT OF WCl_6 CONCENTRATION ON THE RATE OF POLYMERISATION OF CYCLOPENTENE :

Based on such observations, the rate of polymerisation was determined at a constant monomer concentration using the dilatometric technique. Fig. 3-3 shows the dilatometric polymerisation curves for six

Fig. 3-3 Dilatometric polymerisation curves of chlorobenzene solutions of cyclopentene for various concentrations of tungsten hexachloride



different tungsten hexachloride concentrations at a constant monomer concentration of 4.7 mol. dm^{-3}.

A plot of the initial polymerisation rate against the initial concentration of the catalyst, $[WCl_6]_o$, shows a linear dependence, apparently indicating a first order reaction with respect to the concentration of the catalyst as shown in fig. 3-4. That the line does not go through the origin could be either due to experimental error or to the reaction of tungsten hexachloride with impurities. The rate constant for the reaction determined from the slope / $[CP]_o$ was 4.25×10^{-4} dm^3 mol^{-1} s^{-1}.

However, based on the experimental data the order of reaction with respect to the catalyst concentration was determined from a conventional plot of log (initial rate / $[CP]_o$) against log $[WCl_6]_o$. From this plot values of 1.5 and 4.16×10^{-3} dm^3 mol^{-1} s^{-1} were derived for the order, n, and the rate constant, kp, respectively. Fig. 3-5 shows a plot of initial rate of polymerisation against $[WCl_6]_o^{1.5}$. It can be seen that this plot is also a straight line but when compared with fig. 3-4 the extrapolation is closer to the origin and the rate constant obtained was 3.34×10^{-3} dm^3 mol^{-1} s^{-1}. The slopes of the lines in figs. 3-4 and 3-5 were determined by the method of least squares and gave correlation factors of 0.988 and 0.985 respectively. On these grounds, the initial rate of polymerisation, Rp_o, at a constant monomer concentration could be described by either of the following equations:

Fig. 3-4 Dependence of the initial rate of polymerisation of chlorobenzene solutions of cyclopentene on the initial concentration of tungsten hexachloride

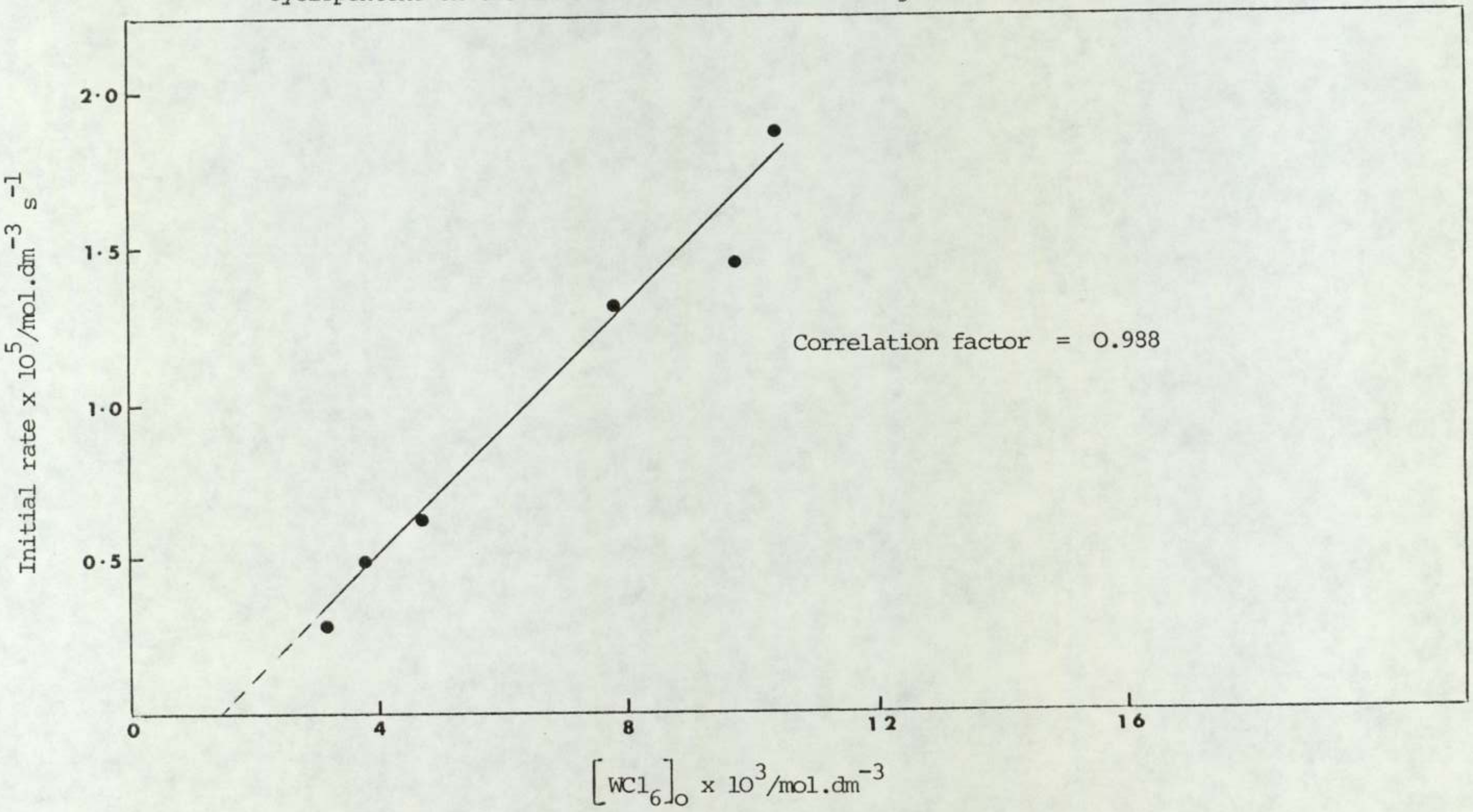
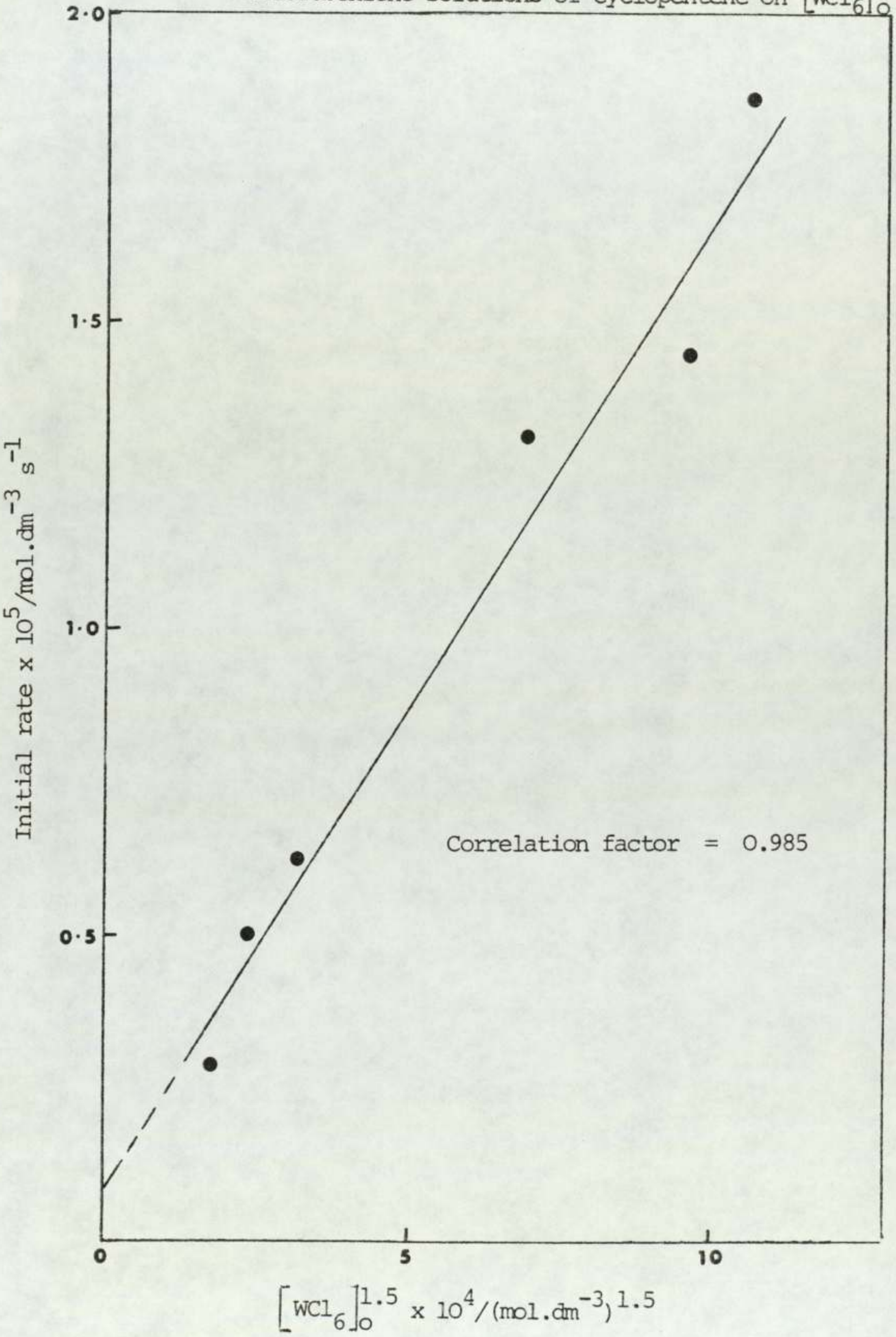


Fig. 3-5 Dependence of the initial rate of polymerisation of chlorobenzene solutions of cyclopentene on $[WCl_6]_o^{1.5}$



$$Rp_o = k\acute{p}_1 \left[WCl_6 \right]_o$$

$$\text{or} \quad Rp_o = k\acute{p}_{1.5} \left[WCl_6 \right]_o^{1.5}$$

$$\text{where} \quad k\acute{p} = kp \left[CP \right]_o^a$$

The polymerisation studies at constant concentration of WCl_6 might provide an answer to this problem and illustrate the order of the reaction with respect to the catalyst concentration.

3.2.2.2 EFFECT OF CONCENTRATION OF CYCLOPENTENE :

Keeping the concentration of the catalyst constant, the rate of polymerisation was determined dilatometrically for five cyclopentene concentrations. Fig. 3-6 shows the typical dilatometric curves for these polymerisations at a constant concentration of tungsten hexachloride of 4.7×10^{-3} mol. dm^{-3}.

A first order reaction with respect to the monomer concentration was observed from the plot of initial polymerisation rate against the initial concentration of cyclopentene, $\left[CP\right]_o$, as shown in fig. 3-7. Based on the results the initial rate of polymerisation, RP_o, could then be described by either:

$$Rp_o = kp_1 \left[CP\right]_o \left[WCl_6\right]_o$$

$$\text{or} \quad Rp_o = kp_{1.5} \left[CP\right]_o \left[WCl_6\right]_o^{1.5}$$

depending on the order of reaction with respect to the catalyst concentration. A plot of log (initial rate/$\left[WCl_6\right]_o$ against log $\left[CP\right]_o$, shown in fig. 3-8 gives a value of 4.0×10^{-4} dm^{-3} mol^{-1} s^{-1}

Fig. 3-6 Dilatometric polymerisation curves of chlorobenzene solutions of cyclopentene for various concentrations of cyclopentene

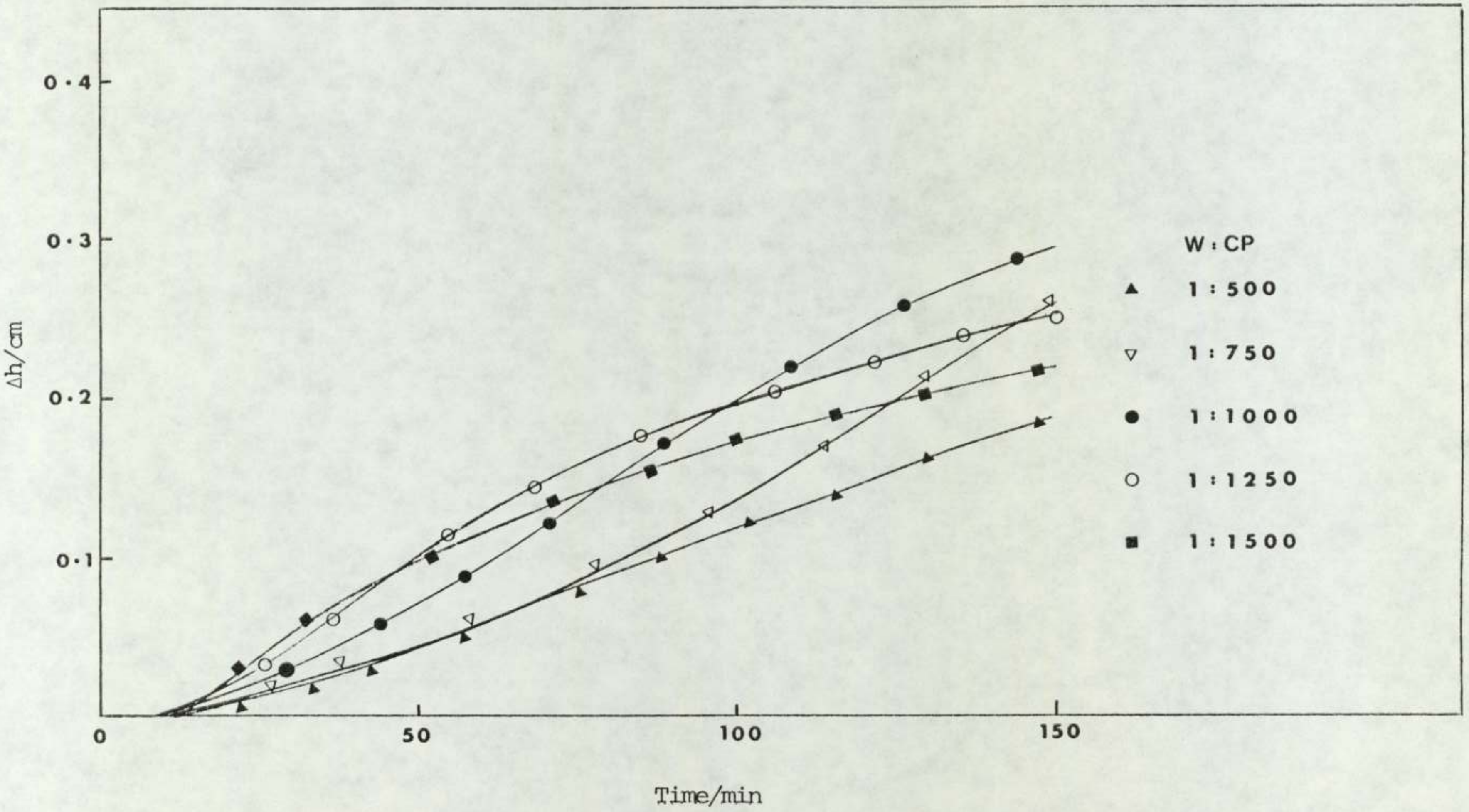
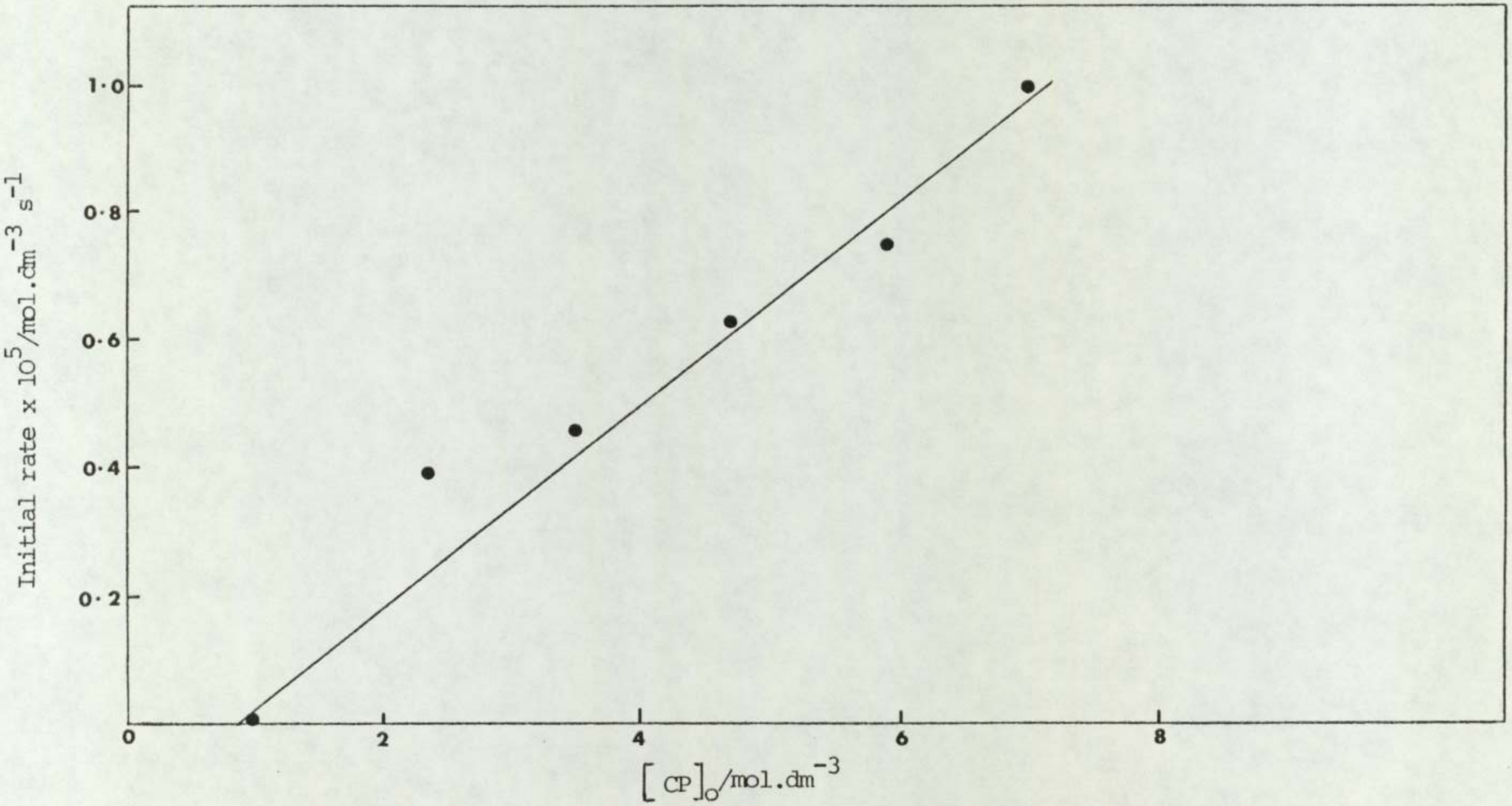


Fig. 3-7 Dependence of the initial rate of polymerisation of chlorobenzene solutions of cyclopentene on the initial concentration of cyclopentene



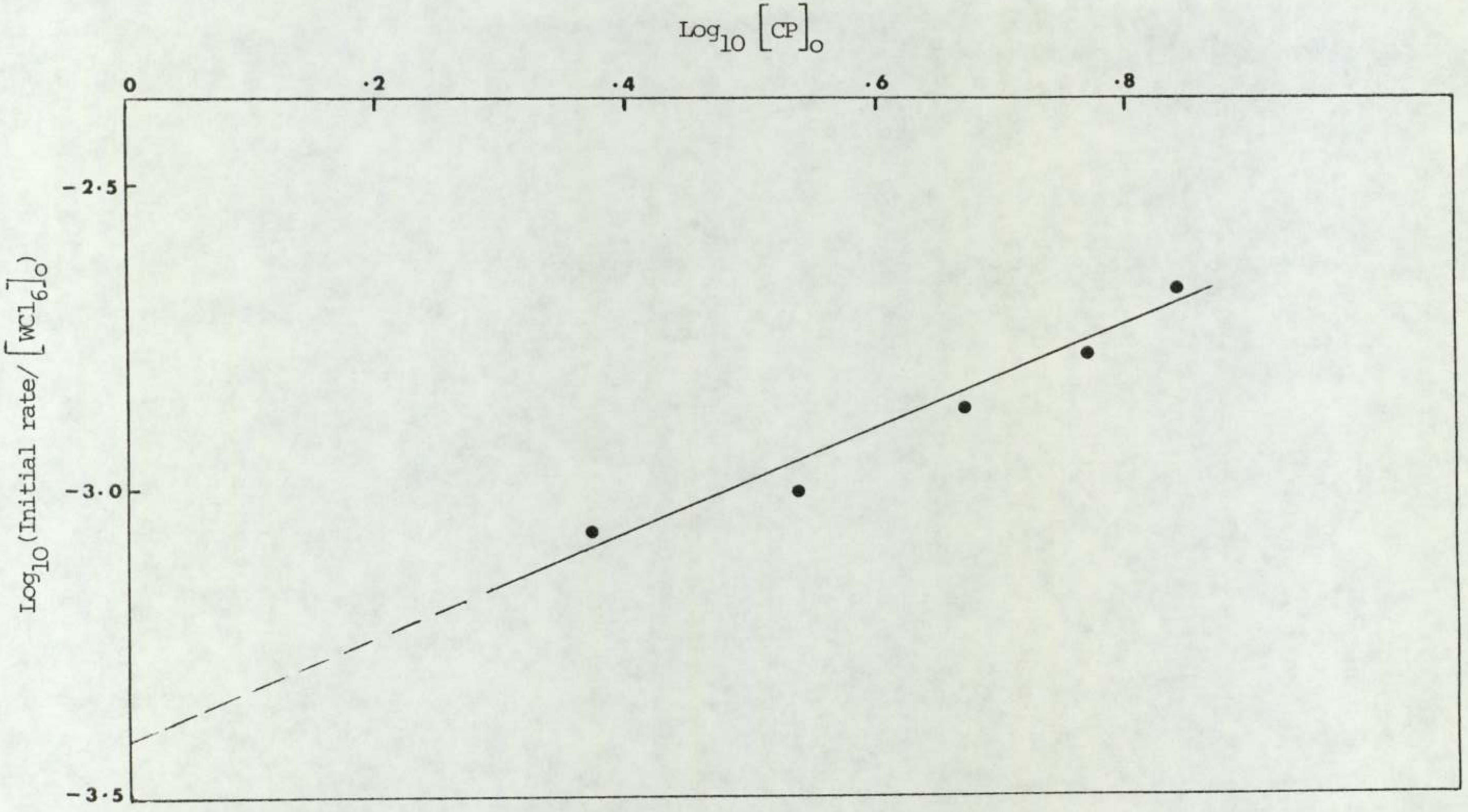


Fig. 3-8 Dependence of $\log_{10}(\text{initial rate}/\left[\mathrm{WCl}_6\right]_o)$ on $\log_{10}\left[\mathrm{CP}\right]_o$

for kp_1 which corresponds well with the value derived from the fig. 3-4, i.e. 4.25×10^{-4} dm^3 mol^{-1} s^{-1}. On the other hand, a plot of log (initial rate / $\left[WCl_6\right]_o^{1.5}$) against log $\left[CP\right]_o$, as shown in fig. 3-9, gives a value of 4.46×10^{-3} dm^3 mol^{-1} s^{-1} which does not correspond with the value of $kp_{1.5}$ obtained from fig. 3-5, i.e. 3.34×10^{-3} dm^3 mol^{-1} s^{-1}. On these grounds it is reasonable to suggest that the reaction is first order in the monomer concentration and probably first order with respect to the catalyst concentration hence :

$$\text{Rate} = kp\left[CP\right]\left[WCl_6\right]$$

3.2.2.3 ANALYSIS OF POLYMERISATION CURVE :

A typical dilatometric polymerisation curve is shown in fig. 3-10. According to the polymerisation conversion-time curve the following features are significant:

(i) The overall conversion of monomer to polymer is usually less than 3% therefore, for most polymerisations, the concentration of monomer could be considered constant during the course of the experiment.

(ii) The rate of polymerisation is very low; this indicates that the species produced is either of low activity or present in very low concentrations.

(iii) The rate of polymerisation is not constant during the course of the experiment and this must be due to the fact that the concentration of active species is not constant. Moreover the shape of the curve suggest that there is a maximum concentration of active species after a given reaction time

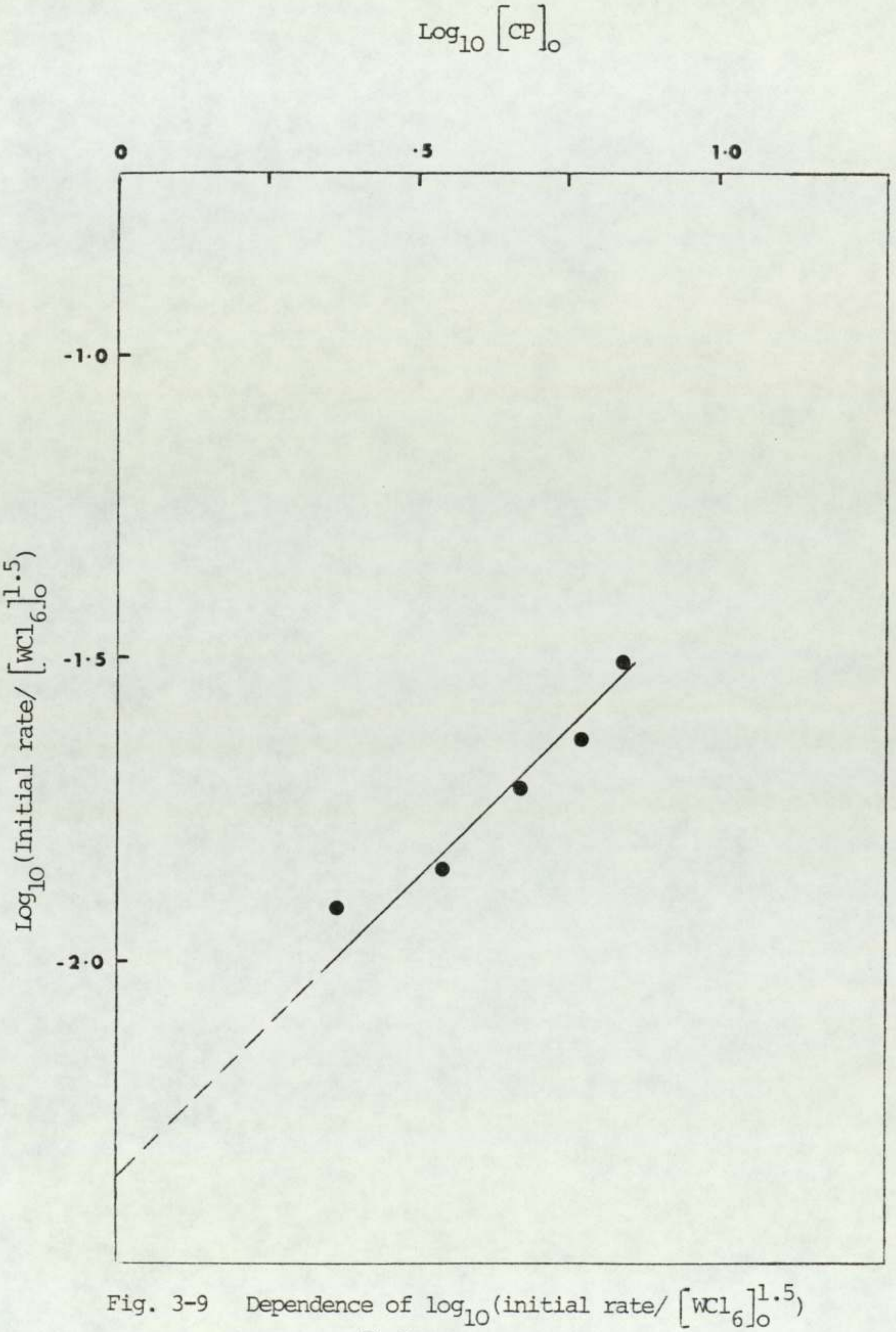
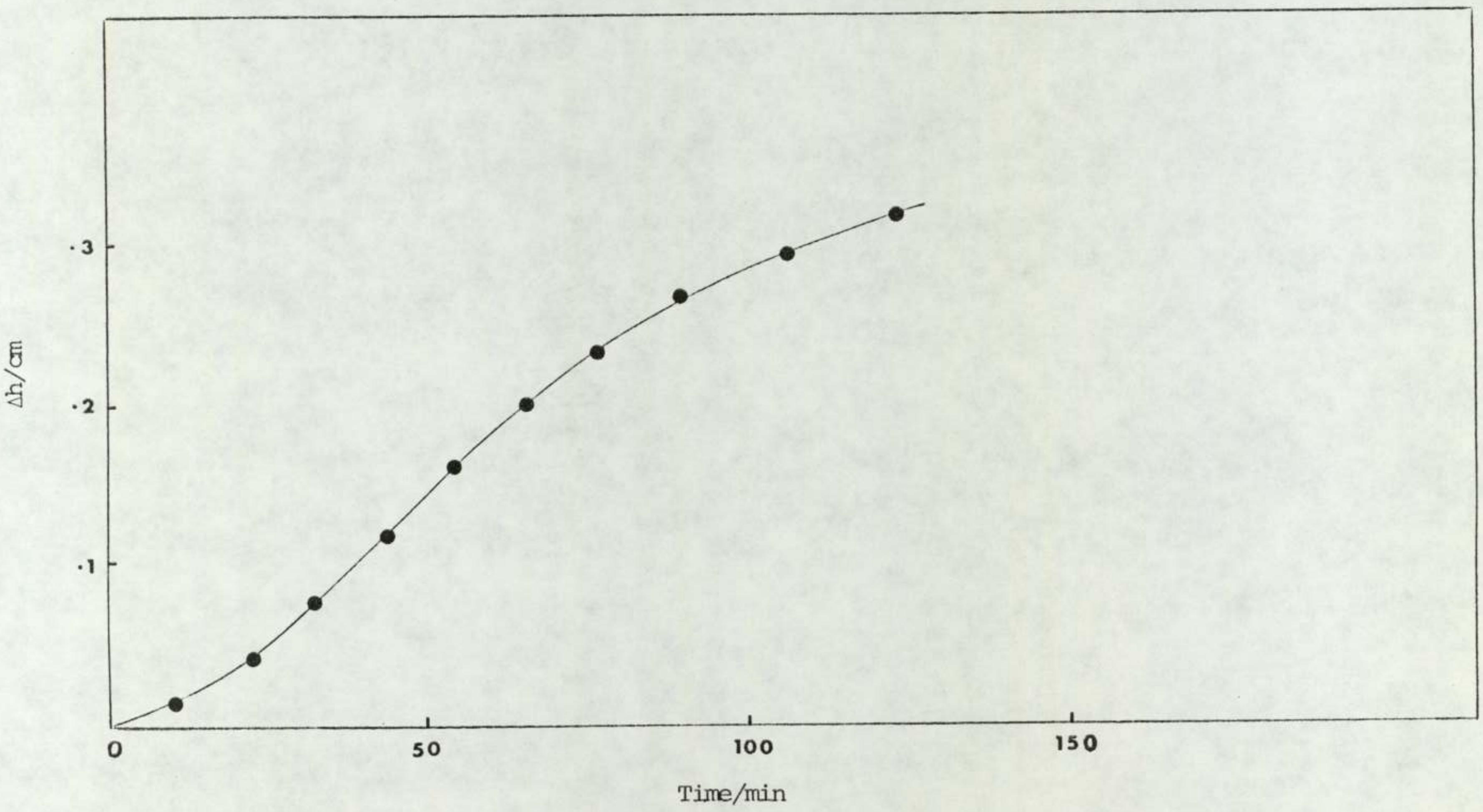


Fig. 3-9 Dependence of $\log_{10}(\text{initial rate}/\left[\mathrm{WCl}_6\right]_o^{1.5})$ on $\log_{10}\left[\mathrm{CP}\right]_o$

Fig. 3-10 A typical polymerisation curve



and this can only be explained by the presence of a series of reactions involving tungsten compounds. This series would involve the production and the consumption of the active species so that it can either propagate or take part in what are best described as termination reactions.

Whenever tungsten hexachloride was added to the cyclopentene solution there was an immediate colour change in the system indicating an instantaneous reaction between cyclopentene and tungsten hexachloride. Using gas chromatographic and spectroscopic techniques, Zurimendi$^{(121)}$ studied the disappearance of the cyclopentene with time during its reaction with tungsten hexachloride and found that at least one mole of cyclopentene per mole of WCl_6 was consumed immediately after mixing. Based on these results, the following scheme seems reasonable.

$$WCl_6 + CP \xrightarrow{\text{very fast}} W_1$$

so that WCl_6 is immediately completely transferred in some way to a species of unknown structure (W_1), and

$$[W_1]_o = [WCl_6]_o$$

where $[W_1]_o$ = initial concentration of the species W_1

$[WCl_6]_o$ = initial concentration of tungsten hexachloride

Assuming that this reaction occurs in the monometallic polymerisation of cyclopentene, the shape of the conversion-time curve can be partly explained if W_1 undergoes some further reactions to produce an active species for polymerisation. Furthermore the work of

Zurimendi(121) can be interpreted to suggest that the reaction of W_1 to produce the active species W_2 also involves cyclopentene for the concentration of cyclopentene continues to decrease slowly after the initial W : CP 1:1 complex formation. The disappearance of cyclopentene molecules under these conditions is not due to the polymerisation reaction because the concentration of cyclopentene is well below the equilibrium concentration of monomer at 25°C, i.e. $[CP] \ll [CP]_e$. Therefore it seems reasonable to suggest that:

$$W_1 + CP \xrightarrow{k_1} W_2$$

$$W_2 + nCP \xrightarrow{kp} \text{polymer}$$

$$W_2 \xrightarrow{k_t} \text{inactive W compound}$$

If this is the case, the concentration of intermediate W_2 should rise to a maximum and then decrease with time. Ultraviolet-visible studies discussed in the next chapter indicate that the concentration of an intermediate indeed goes through a maximum.

3.2.2.4 EFFECT OF CONCENTRATION OF WCl_6 ON CONVERSION :

Although tungsten hexachloride alone is capable of the metathesis polymerisation of cyclopentene, the conversion of monomer to polypentenamer was found to be very low even after long reaction times. The percentage of conversion however depended on the concentration of tungsten hexachloride. Table 3-1 shows the dependence of the conversion of monomer on the catalyst concentration at a constant monomer concentration of 4.7 mol. dm^{-3}.

TABLE 3-1. DEPENDENCE OF % CONVERSION OF

MONOMER ON THE CONCENTRATION OF WCl_6

$\frac{[WCl_6]_o \times 10^3}{\text{mol dm}^{-3}}$	Molar Ratio W : CP	% Conversion
10.4	1:450	3.7
9.7	1:500	4.9
7.8	1:600	3.5
4.7	1:1000	1.9
3.8	1:1250	1.7
3.1	1:1500	1.1

$[CP] = 4.7$ mol. dm^{-3}
Reaction Time = 3 hours
Temperature 25°C

As can be seen from the data in table 3-1, an increase in the concentration of tungsten hexachloride causes an increase in the conversion of monomer. This could be due to an increase in the concentration of the intermediate W_2 since:

$$W_1 + CP \xrightarrow{k_1} W_2$$

$$W_2 + nCP \xrightarrow{kp} \text{polymer}$$

therefore the concentration of polymer obtained could be given as:

$$\left[\text{Polymer}\right] = \int_o^t Rpdt = \int_o^t kp\,[CP]\,[W_2]\,dt$$

Keeping the concentration of cyclopentene constant, the equation could be written as:

$$\left[\text{Polymer}\right] = k\acute{p} \int_0^t \left[W_2\right] dt$$

$$\text{where } k\acute{p} = kp \left[CP\right]_0$$

$$\left[CP\right]_0 = \text{initial concentration of cyclopentene}$$

3.2.2.5 EFFECT OF MONOMER CONCENTRATION ON CONVERSION :

It was found that an increase in the concentration of monomer causes a decrease in the conversion of monomer to polypentenamer after a constant reaction time (3 hours). Table 3-2 shows the dependence of the conversion on the concentration of cyclopentene at a constant catalyst concentration of 4.7 x 10^{-3} mol dm^{-3}.

TABLE 3-2. DEPENDENCE OF % CONVERSION OF MONOMER ON THE CONCENTRATION OF CYCLOPENTENE

$[CP]_0$ / mol. dm^{-3}	Molar Ratio W : CP	% Conversion
2.35	1:500	3.1
3.50	1:750	2.7
4.70	1:1000	1.9
5.90	1:1250	1.3
7.00	1:1500	1.0

$\left[WCl_6\right]$ = 4.7 x 10^{-3} mol dm^{-3}

Reaction time = 3 hours

Temperature 25°C

This behaviour indicates that an increase in the cyclopentene concentration will have a considerable effect upon the dependence of the concentration of W_2 on time. The results appear to indicate that the average concentration of W_2 over this period is significantly reduced by an increase in cyclopentene concentration. An increase in the monomer concentration therefore, may cause a faster formation but also decay of the intermediate W_2; although this may result in an increase in the initial rate of polymerisation, decrease in the conversion of monomer to polymer at a given time may occur as a result of the faster rate of decay of the rate of polymerisation.

However on the ground of the results reported by Amass and Zurimendi[(108)] indicating a second order termination reaction during the polymerisation of cyclopentene initiated by $WCl_6/AliBu_3$, it is reasonable to suggest a bimolecular termination reaction for the intermediate W_2 probably to a species of a very low activity.

$$W_2 + W_2 \xrightarrow{k_t} W_x$$

Therefore the higher the concentration of cyclopentene, the faster will be the formation of W_x, and hence the lower the conversion of monomer to polymer.

3.2.2.6 STUDIES ON THE MAXIMUM RATE OF POLYMERISATION :

The conversion-time curve, shown earlier in fig. 3-10, reveals that the rate of polymerisation of cyclopentene reaches a maximum value and subsequently decays. The time for the rate of polymerisation to reach this maximum value, t_{max}, could depend upon the monomer and/or the catalyst concentration. Table 3-3 shows the dependence of t_{max}

on the cyclopentene concentration at a constant catalyst concentration of 4.7×10^{-3} mol. dm^{-3}.

TABLE 3-3. DEPENDENCE OF t_{max} ON THE CONCENTRATION OF CYCLOPENTENE

$\frac{[WCl_6]_o \times 10^3}{\text{mol dm}^{-3}}$	$\frac{[CP]_o}{\text{mol dm}^{-3}}$	t_{max}
4.7	2.35	140 ± 15
4.7	3.50	120 ± 15
4.7	4.7	100 ± 15
4.7	5.9	50 ± 15
4.7	7.0	30 ± 15

Reaction time = 3 hours

Temperature 25°C

As can be seen from the data in table 3-3, an increase in the concentration of cyclopentene results in a decrease in t_{max}, the time required for the rate of polymerisation to reach its maximum value. There is not however a simple linear relationship between the concentration of monomer and t_{max}.

The dependence of the t_{max} on the concentration of tungsten hexachloride is shown in table 3-4.

TABLE 3-4. DEPENDENCE OF t_{max} ON THE CONCENTRATION OF TUNGSTEN HEXACHLORIDE

$\frac{[WCl_6]_o \times 10^3}{mol\ dm^{-3}}$	$\frac{[CP]_o}{mol\ dm^{-3}}$	t_{max}
10.4	4.7	30 ± 15
9.7	4.7	80 ± 10
7.8	4.7	70 ± 15
4.7	4.7	100 ± 15
3.8	4.7	100 ± 10
3.1	4.7	50 ± 15

Reaction time = 3 hours

Temperature 25°C

The results, shown in table 3-4, indicate that there is no simple relationship between the concentration of WCl_6 and the t_{max}. Within experimental error however, the t_{max} could be considered constant and therefore independent of the catalyst concentration.

3.3 POLYMERISATION OF CYCLOPENTENE INITIATED BY WCl_6/O_2 :

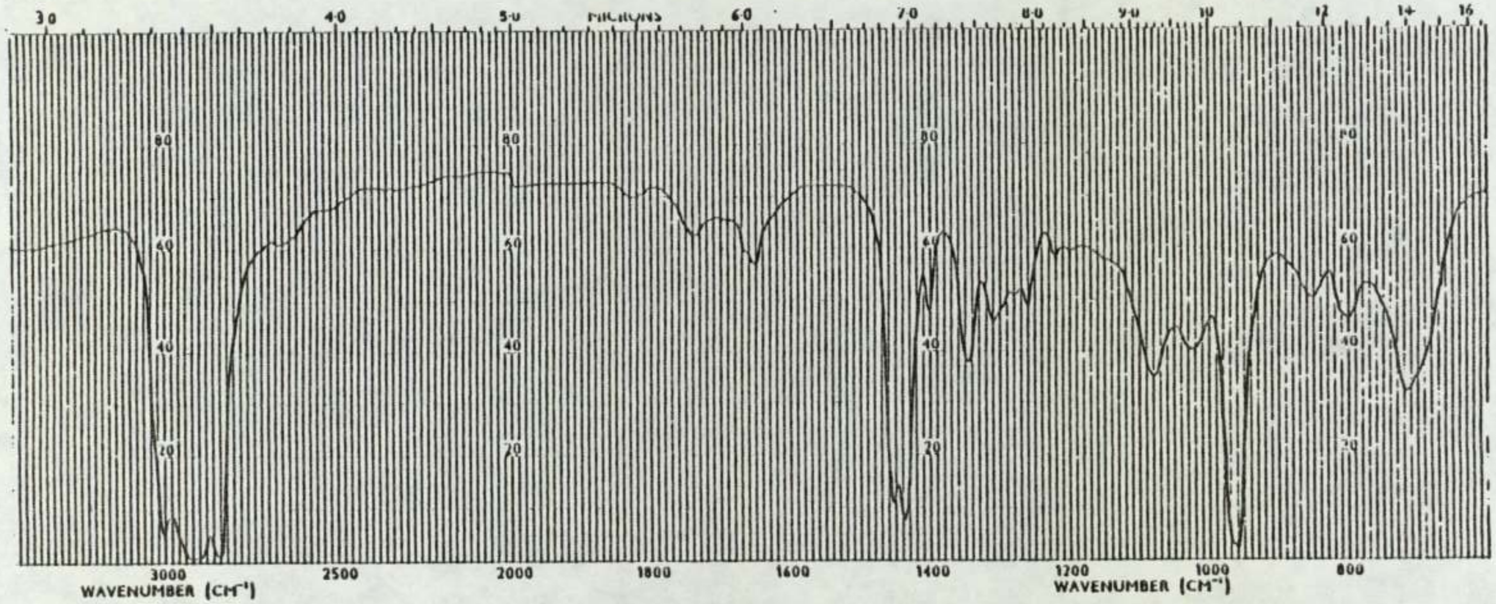
During the monometallic initiation studies of ring opening polymerisation of cyclopentene using tungsten hexachloride, McGourty(122) observed that oxygen could activate the system to a polymerisation similar to that of bimetallic initiation. In these studies the conversion of monomer to polymer one hour after the addition of oxygen was taken as a measure of the activity of the catalyst species. The results showed a strong dependence of the catalyst activity on the tungsten hexachloride/cyclopentene reaction time before oxygen addition, suggesting that the catalytically active species is produced from the oily precipitate resulting from the reaction of tungsten hexachloride with cyclopentene. In further investigation using a titrimetric method, McGourty$^{(122)}$ showed that addition of oxygen to the product of the reaction of tungsten hexachloride with 2-pentene in toluene did not cause any further change in the oxidation state of the tungsten atom suggesting a role other than oxidation for the activating role of oxygen.

In this project attempts were made to determine the rate of polymerisation of cyclopentene initiated by WCl_6/O_2. The experiments were carried out in toluene or chlorobenzene using dilatometric and/or calorimetric techniques as described in sections 2.4.1.2(b) and 2.4.2.2. respectively.

3.3.1. PRELIMINARY POLYMERISATION STUDIES IN TOLUENE :

The rate of polymerisation of cyclopentene initiated by tungsten hexachloride alone was found to be very low. However on addition of oxygen to such a system a very rapid polymerisation to very high conversion takes place. Since the polymerisation of cyclopentene initiated by tungsten hexachloride was always accompanied by the appearance of an oily precipitate around the walls of the apparatus, it was not clear at that stage whether the source of active species on addition of oxygen to the system was the tungsten remaining in the solution or the oily precipitate. Indirect studies by McGourty(122) indicated that the catalytically active species was produced from the oily precipitate since lengthening of the time of reaction of cyclopentene with tungsten hexachloride increased the rate of conversion of monomer to polymer. In order to confirm this an attempt was made to separate the oily precipitate from the solution using the apparatus shown in fig. 2-14. In a typical polymerisation experiment cyclopentene and toluene were vacuum-distilled into the vessel followed by addition of a solution of tungsten hexachloride in toluene. After a period of 24 hours, the oily precipitate was separated from the solution by the technique described in section 2.4.4.2. Fresh cyclopentene was then distilled into the bulb containing the solid phase and allowed to react for a period of one hour after which dry oxygen was introduced into the system. There was a rapid increase in the viscosity of the system and this was taken to indicate the presence of catalyst activity. Quantitative studies were not carried out in these preliminary experiments because it was felt that gravimetric determinations were liable to large errors. The quantitative assessment of this system is a subject for discussion in a later section. The polymer was however collected by precipitating the polymerisate in methanol and analysed by infrared spectroscopy. A typical spectrum is shown in fig. 3-11. According to the peak at 962 cm^{-1} the polymer contained a substantial proportion of trans carbon-carbon double bonds. However it is apparent that the polymer was produced by a ring opening metathesis mechanism similar to that of a bimetallic system.

Fig. 3-11 A typical infrared spectrum of polypentenamer obtained from toluene heterogeneous catalyst system



In a similar experiment, addition of oxygen to the supernatent clear solution obtained in the filtration process did not cause a change in the viscosity indicating that the oily precipitate should be considered as the principal source of active sites. This is in parallel with the results reported by Amass and McGourty(11).

Cyclohexene is inert towards the ring opening polymerisation due to the absence of ring strain in the molecule but reacts with tungsten hexachloride to produce an oily precipitate similar to that formed by cyclopentene. If cyclopentene is distilled on to this precipitate the viscosity changes indicate that such a precipitate initiates the polymerisation of cyclopentene when oxygen is introduced into the system.

That this solid could in fact be the active site in the polymerisation of cyclopentene initiated by tungsten hexachloride remains to be answered. However Muetterties and Busch(19) demonstrated that the colourless filtrate from an active WCl_6-BuLi system was inactive towards metathesis of 2-pentene, whereas the solids produced showed a catalytic activity nearly as high as the standard unfiltered reaction system. This could well be the case in the monometallic polymerisation of toluene solutions of cyclopentene.

3.3.1.1. DILATOMETRIC DETERMINATION OF RATE OF POLYMERISATION :

In order to determine the rate of polymerisation of cyclopentene initiated by WCl_6/O_2, it was necessary to allow a predetermined period of time for WCl_6 to react with cyclopentene and produce an oily precipitate before addition of oxygen. Fig. 2-7 shows a modified dilatometer designed for this purpose where the solution could be kept in the bulb K for a long period of time in the absence of oxygen, allowing the oily precipitate to be formed around the walls of the bulb. In a typical polymerisation 6.4 ml of cyclopentene and 8.2 ml of toluene were vacuum-distilled into the apparatus shown in fig. 2-6 followed by the addition of 1 ml of tungsten hexachloride of 0.055 M to the system from the breakseal ampoule. The solution was then transferred to the apparatus shown in fig. 2-7 by the method described in section 2.4.1.2(b). After a period of 24 hours dry oxygen was introduced into the system and the dilatometer was filled immediately with the solution and placed in a constant temperature water bath. The height of the meniscus of the capillary tube did not show any change after reaching thermal equilibrium. This can be accounted for by the fact that the oily precipitate even after reaction with oxygen remained on the walls of the reaction vessel and was not transferred to the dilatometer. Attempts were then made to follow the polymerisation rate using a calorimetric technique.

3.3.1.2. CALORIMETRIC DETERMINATION OF THE RATE OF POLYMERISATION :

The slight increase in temperature of a polymerisation caused by the release of ring strain during the polymerisation of cyclopentene can provide a suitable method, under adiabatic conditions, of determining the rate of polymerisation.

In order to maintain both the solution and the oily precipitate, formed from the reaction of tungsten hexachloride with cyclopentene, in contact with each other when measuring the rate of polymerisation on addition of oxygen, a calorimeter similar to that designed by Zurimendi(121) was used. The calorimeter is shown in fig. 2-8. In a typical polymerisation 8.2 ml of cyclopentene and 11.0 ml of toluene were distilled into the apparatus shown in fig. 2-6 followed by the addition of 1.5 ml of tungsten hexachloride of 0.055 M. The solution was then transferred to the calorimeter by the method described in section 2.4.2.2(a). In order to allow the oily precipitate to form, the solution was kept for a period of 24 hours under a stream of dry nitrogen. The calorimeter was then connected to the balancing bridge and oxygen was introduced into the system. Although the viscosity of the solution increased rapidly, the thermistor failed to signal any significant change in the temperature of the system. The determination of the rate of polymerisation of cyclopentene initiated by tungsten hexachloride/oxygen using this technique was considered unsuccessful at this stage suggesting that further studies on the subject are necessary to find out the causes for such a failure. It is possible that the rapid increase in viscosity prevented efficient heat transfer to the thermistor.

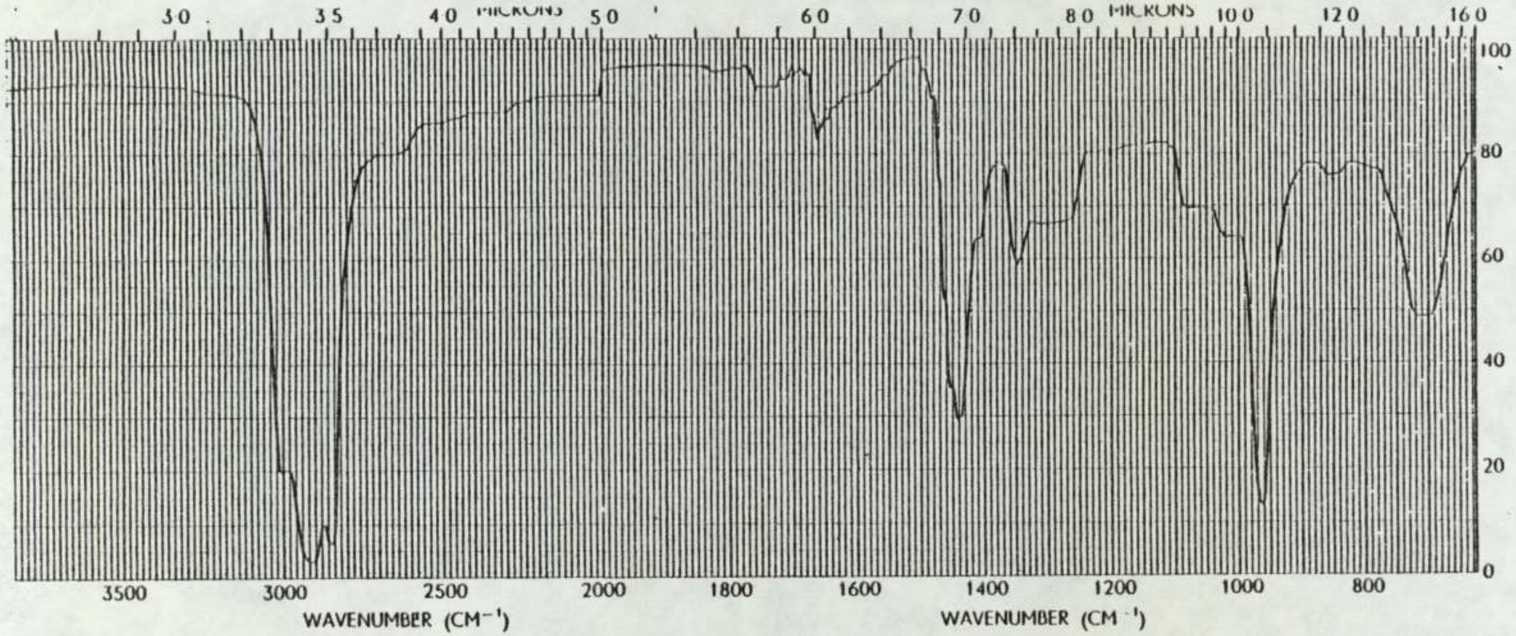
3.3.2. POLYMERISATION STUDIES IN CHLOROBENZENE :

As discussed in section 3.2.2, the polymerisation of cyclopentene with tungsten hexachloride in chlorobenzene does not produce any precipitate around the walls of the vessel and the system in fact remains homogeneous during the polymerisation. Since the rate of polymerisation of cyclopentene initiated by tungsten hexachloride alone like that of toluene was found to be very low attempts were made to study the effect of oxygen when chlorobenzene was used as solvent. In a typical polymerisation experiment, cyclopentene and chlorobenzene were distilled into the apparatus shown in fig. 2-6. The polymerisation was allowed to proceed by addition of a solution of tungsten hexachloride to the system. After a period of 24 hours dry oxygen was introduced into the system and allowed to react for one hour. In this case the rate of increase in the viscosity of the system was not as fast as that in toluene. The polymer however was collected by precipitating the polymerisate in methanol and was analysed by infrared spectroscopy. A typical spectrum is shown in fig. 3-12. According to the peak at 962 cm^{-1} the polymer contained a substantial proportion of trans carbon-carbon double bonds. It is apparent from the spectrum that the polymer has been produced through a ring-opening mechanism similar to that of a bimetallic system.

3.3.2.1. CALORIMETRIC DETERMINATION OF THE RATE OF POLYMERISATION :

Attempts were made to determine the rate of polymerisation of cyclopentene initiated by WCl_6/O_2 using the calorimeter shown in fig. 2-10. In a typical experiment 11.2 ml of cyclopentene and 9.2 ml of chlorobenzene were vacuum-distilled into the apparatus shown in fig. 2-6 followed by the addition of 1.5 ml of tungsten hexachloride of 0.082 M. The reaction was allowed to proceed for a period of 48 hours after which the solution was transferred to the calorimeter, shown in fig. 2-10, by the method described in section 2.4.2.2(b). The calorimeter was then connected to the balancing bridge and oxygen was allowed into the system. The thermistor did not signal any significant change in the temperature

Fig. 3-12 A typical infrared spectrum of polypentenamer obtained from chlorobenzene homogeneous catalyst system



of the system. Similar results were obtained when the reaction was allowed to proceed for 24 hours before the addition of oxygen. Further investigations on the subject are necessary since the failure of the thermistor to signal might have been:

(i) due to insufficient amount of oxygen present in the system

(ii) due to the presence of impurities in the system

(iii) because of the destruction of the species responsible for the formation of the active site, on its reaction with oxygen, due to the long reaction times before the addition of oxygen.

The dependence of conversion of monomer to polymer on the tungsten hexachloride/cyclopentene reaction time before oxygen addition was studied gravimetrically as described in section 2.4.3.

3.3.2.2. GRAVIMETRIC STUDIES

Keeping the concentrations of both cyclopentene and tungsten hexachloride constant at 5.5 and 5.5 x 10^{-3} mol. dm^{-3} respectively, a series of experiments were carried out varying the reaction time between cyclopentene and the catalyst before the addition of oxygen. In a typical polymerisation 4.1 ml of cyclopentene and 3.3 ml of chlorobenzene were vacuum-distilled into the apparatus shown in fig. 2-11 followed by the addition of 1 ml of tungsten hexachloride of 0.046 M. The solution was then transferred to the vessel shown in fig. 2-12 by the method described in section 2.4.3. After a predetermined reaction time the initial effect of oxygen was studied by introduction of known amounts of oxygen into the system and allowing this to react for a period of 10 minutes. At the end of each polymerisation the polymer was collected by precipitating the polymerisate in methanol and purified by successive precipitations in methanol from chloroform solutions. The polymer was then dried under vacuum for 3 hours and weighed. The dependence of the conversion of monomer to polymer on the WCl_6/cyclopentene reaction time is shown in table 3-5.

TABLE 3-5. DEPENDENCE OF CONVERSION OF MONOMER TO POLYMER ON THE WCl_6/CP REACTION TIME BEFORE ADDITION OF OXYGEN

Time of reaction of CP with WCl_6 before the addition of O_2 (hours)	% Conversion 10 minutes after the addition of O_2
1.0	1.0
3.5	1.35
7.0	1.90
8.5	2.18
15.0	2.50

$[CP] = 5.5\ mol.dm^{-3}$

$[WCl_6] = 5.5 \times 10^{-3}\ mol.dm^{-3}$

Temperature 25°C

As can be seen from the data in table 3-5, the initial activity of the species formed by addition of oxygen to the system is low although this increases slowly as the mixing time is increased. However if the species W^* is produced on the addition of oxygen to the system, its formation could be due to either of the following reactions:

$$W_2 + O_2 \longrightarrow W^*$$

$$W_x + O_2 \longrightarrow W^*$$

If the reaction of oxygen with the species W_2 is the prime source of the formation of the species W^*, one could expect the concentration of W^* to be very low for long reaction times between cyclopentene and WCl_6 due to the termination reaction of W_2.

$$W_2 + W_2 \xrightarrow{k_t} W_x$$

Although further investigations on the subject are required, one can conclude that the polymerisation of cyclopentene initiated by tungsten hexachloride/oxygen has similarities with that of bimetallic initiation and that a series of reactions occur between either tungsten hexachloride and cyclopentene or between their products and oxygen.

3.4 POLYMERISATION OF CYCLOPENTENE INITIATED BY WCl_6/EtOH :

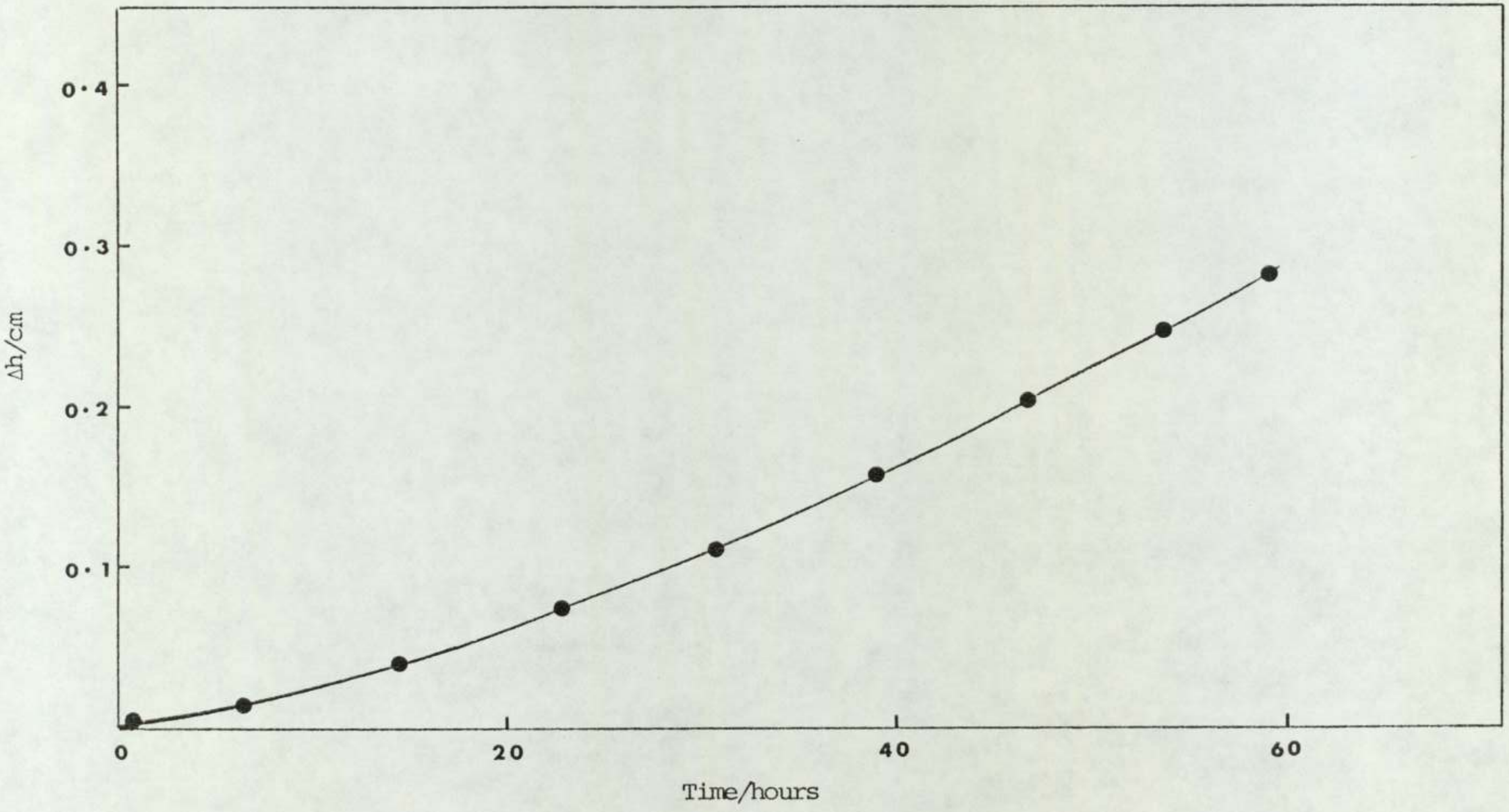
Various oxygen containing compounds have been used as activator for the metathesis reaction of olefins. The systems containing such activators have been reported to be more efficient and reach a conversion close to that at equilibrium. On these grounds attempts were made to study the rate of polymerisation of cyclopentene initiated by WCl_6/EtOH. In a typical polymerisation 6.5 ml of cyclopentene and 3.3 ml of toluene were distilled into the apparatus shown in fig. 2-5 followed by injection of 3.7 ml of WCl_6/EtOH solution of 0.02 M so that the molar ratio of tungsten hexachloride : ethanol : cyclopentene was 1 : 1 : 1000. The dilatometric studies showed a rate much lower than that of tungsten hexachloride alone indicating that the species formed from the reaction of WCl_6 with ethanol has a very low metathetic activity towards the ring opening polymerisation of cyclopentene when it is used in the absence of any cocatalyst (fig.3-13).

Further studies similar to those described in section 3.3.1. indicated that oxygen does not have any significant effect when it is introduced to such a system.

3.5 NATURE OF METATHETICAL ACTIVE CENTRE :

According to the report by Ast et al (120), the minimum number of methylene groups required between an oxygen atom and a double bond, in order that any unsaturated ether may undergo metathesis reaction, is 2. Based on these results the nature of metathetical active species, produced from the reaction of cyclopentene with WCl_6, was investigated using n-butyl vinyl ether as the reactant. If the active species showed any cationic character it would be expected to lead to the polymerisation of the ether whereas metathesis of the ether would not be expected.

Fig. 3-13 A typical polymerisation curve for cyclopentene initiated by WCl_6/EtOH system

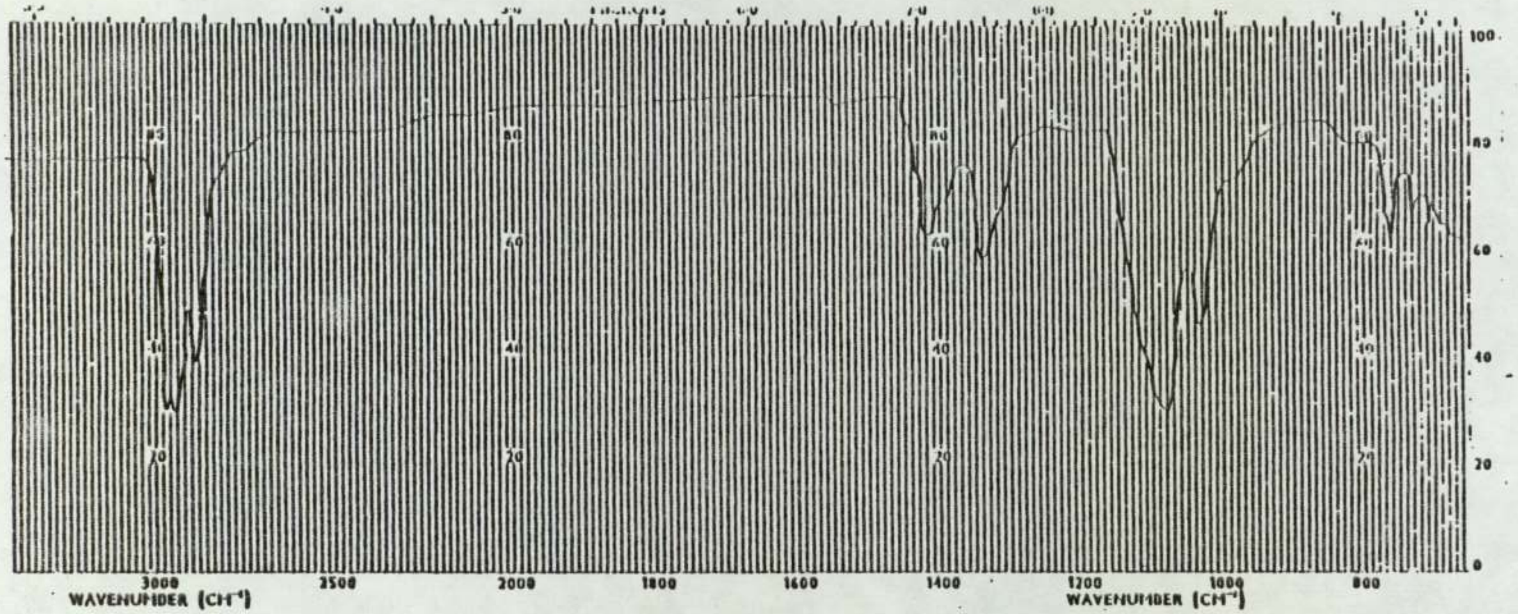


3.5.1 POLYMERISATION OF n-BUTYL VINYL ETHER :

In order to produce a metathetically active species, WCl_6 was allowed to react with cyclopentene before the addition of n-butyl vinyl ether, bearing in mind that the concentration of cyclopentene should be below the equilibrium concentration to prevent the production of polypentenamer. In a typical experiment 0.4 ml of cyclopentene and 16.6 ml of chlorobenzene were successively distilled under vacuum into the bulb E of the apparatus shown in fig. 2-17 followed by distillation of 3.3 ml of n-butyl vinyl ether into the bulb C as described in section 2.4.6. 1 ml of a 0.088 M solution of WCl_6 was mixed with the cyclopentene solution and allowed to react for a period of ten minutes after which it was added to the ether. After a period of 30 minutes the reaction was terminated by the addition of wet chlorobenzene to the system and polymer was collected by precipitating the polymerisate in methanol. The analysis of the infrared spectrum of the polymer sample, shown in fig. 3-14, indicates that the species formed from the reaction of cyclopentene with WCl_6 can initiate the polymerisation of n-butyl vinyl ether. This could be due to the cationic nature of the active species presumably of the structure $\overset{\delta-}{W} - \overset{\delta+}{CHR}$ or to the formation of hydrogen chloride during the reaction of WCl_6 with cyclopentene; the production of HCl was suspected during the ring opening polymerisation of cyclopentene.

To distinguish between these two possibilities, attempts were made to mop up any proton present in the system using 1,8 bis (dimethyl amino) naphthalene (proton sponge). However by repeating the

Fig. 3-14 A typical infrared spectrum of poly (n butyl vinyl ether)



experiment in the presence of the proton sponge (PS) of W : PS molar ratio of 1:6 it was found that on addition of the naphthalene compound to the mixture of tungsten hexachloride and cyclopentene an immediate formation of a brown precipitate occurred which was inactive towards the polymerisation of n-butyl vinyl ether. The formation of the brown precipitate was found to be due to the reaction of the proton sponge with tungsten hexachloride. Consequently the use of 1,8 bis (dimethyl amino) naphthalene for the illustration of polymerisation of n-butyl vinyl ether could be considered as a failure.

Attempts were however made to find out whether such a precipitate initiates the polymerisation of cyclopentene. In a typical experiment 8.4 ml of cyclopentene was distilled under vacuum into the bulb E of the apparatus shown in fig. 2-17. Following the procedure described in section 2.4.6, 0.07 grams of the proton sponge was transferred into the bulb C of the apparatus. 1 ml of tungsten hexachloride of 0.053 M was then added to the cyclopentene by breaking the breakseal and after a period of two minutes the mixture was added to the naphthalene compound in the bulb C. A brown precipitate was immediately formed which inhibited the polymerisation of cyclopentene.

3.5.2 FORMATION OF HYDROGEN CHLORIDE :

The evolution of hydrogen chloride was suspected while studying the ring opening polymerisation of cyclopentene; therefore attempts were made to investigate the possible evolution of HCl during the reaction of tungsten hexachloride with cyclopentene using polyvinylpyridine cross-linked with 2% divinyl benzene as a hydrogen chloride absorber. In a typical experiment 2.4 grams of polyvinylpyridine was placed in the bulb G of the apparatus shown in fig. 2-13 and evacuated until a constant weight was obtained. 0.8 grams of tungsten hexachloride was then transferred into the bulb D of the apparatus, under a stream of dry nitrogen. Finally 1.4 ml of toluene and 1.1 ml of cyclopentene were successively distilled under vacuum into the bulb D giving W : CP molar ratio of 1:6. Following the procedure described in section 2.4.4.1, the amount of hydrogen chloride was found to be 1.35 moles per mole of WCl_6 after 48 hours.

Therefore the polymerisation of n-butyl vinyl ether could be due to the formation of hydrogen chloride resulting from the reaction of cyclopentene with WCl_6. However this is not a satisfactory technique to rule out the possible ionic nature of the metathesis active centre. The occurrence or otherwise of block copolymerisation of cyclopentene with n-butyl vinyl ether is thought to provide a satisfactory solution to whether the metathesis active centre is involved in the polymerisation of n-butyl vinyl ether.

CHAPTER 4

SPECTROSCOPIC STUDIES

4.1 INTRODUCTION:

The reaction between tungsten hexachloride and cyclopentene has associated with it many colour changes. The nature of these colour changes in the toluene heterogeneous system was studied by Zurimendi(121) using an ultraviolet/visible spectroscopic technique and found that when cyclopentene is added to tungsten hexachloride in W : CP molar ratios ranging from 1:1 to 1:4 an instantaneous absorption at 520 mμ was observed, the height of which was dependent on the W : CP molar ratio. Furthermore the species formed was found to be unstable; the peak at 520 mμ disappeared slowly whenever a solution of a given W : CP molar ratio was allowed to stand. McGourty(122) suggests that such a decrease in the absorption band is accompanied by the slow appearance of a precipitate in the system, while Zurimendi(121) argues that the species giving rise to this peak could undergo further reaction with cyclopentene when the solution is allowed to stand.

As discussed in the previous chapter, the monometallic polymerisation of cyclopentene in chlorobenzene could provide a homogeneous system and the kinetic studies of such polymerisations indicate that a series of reactions takes place between cyclopentene and tungsten hexachloride. Attempts were therefore made in this project to characterise the kinetic nature of these reactions using ultraviolet/visible spectroscopic technique as described in section 2.4.5.3.

4.2 PRELIMINARY STUDIES:

In order to follow the ultraviolet/visible spectral changes of the reaction of tungsten hexachloride with cyclopentene in chlorobenzene, the apparatus shown in fig. 2-15 was designed. In a typical experiment 2 ml of a 4.4 x 10^{-3} M solution of tungsten hexachloride, 0.25 ml of chlorobenzene and 0.75 ml of cyclopentene solution of 3.52 M were injected into the apparatus; the W : CP molar ratio was 1:300. Following the procedure described in section 2.4.5.3 the spectral changes of the reaction were recorded as a function of time. The absorption at 458 mμ of the ultraviolet/visible spectra, shown in fig. 4-1, indicates that on addition of cyclopentene to the tungsten hexachloride solution a new species is formed, the concentration of which increases to a maximum and then decays with time. The isobestic point at 480 mμ is an indication of the elimination of one resonating system and the formation of another, having a common value of extinction coefficient at this wavelength.

As shown in fig. 4-2, the decrease in the concentration of the new species, resulting from the reaction of WCl_6 with cyclopentene, is accompanied by the appearance of a new peak at λ_{max} = 390 mμ, the height of which increases to a maximum as that of the former is decreased.

On addition of cyclopentene to the tungsten hexachloride there is an immediate colour change in the system indicating that tungsten

Fig. 4-1 Typical ultraviolet/visible spectral changes during the reaction of tungsten hexachloride with cyclopentene in chlorobenzene

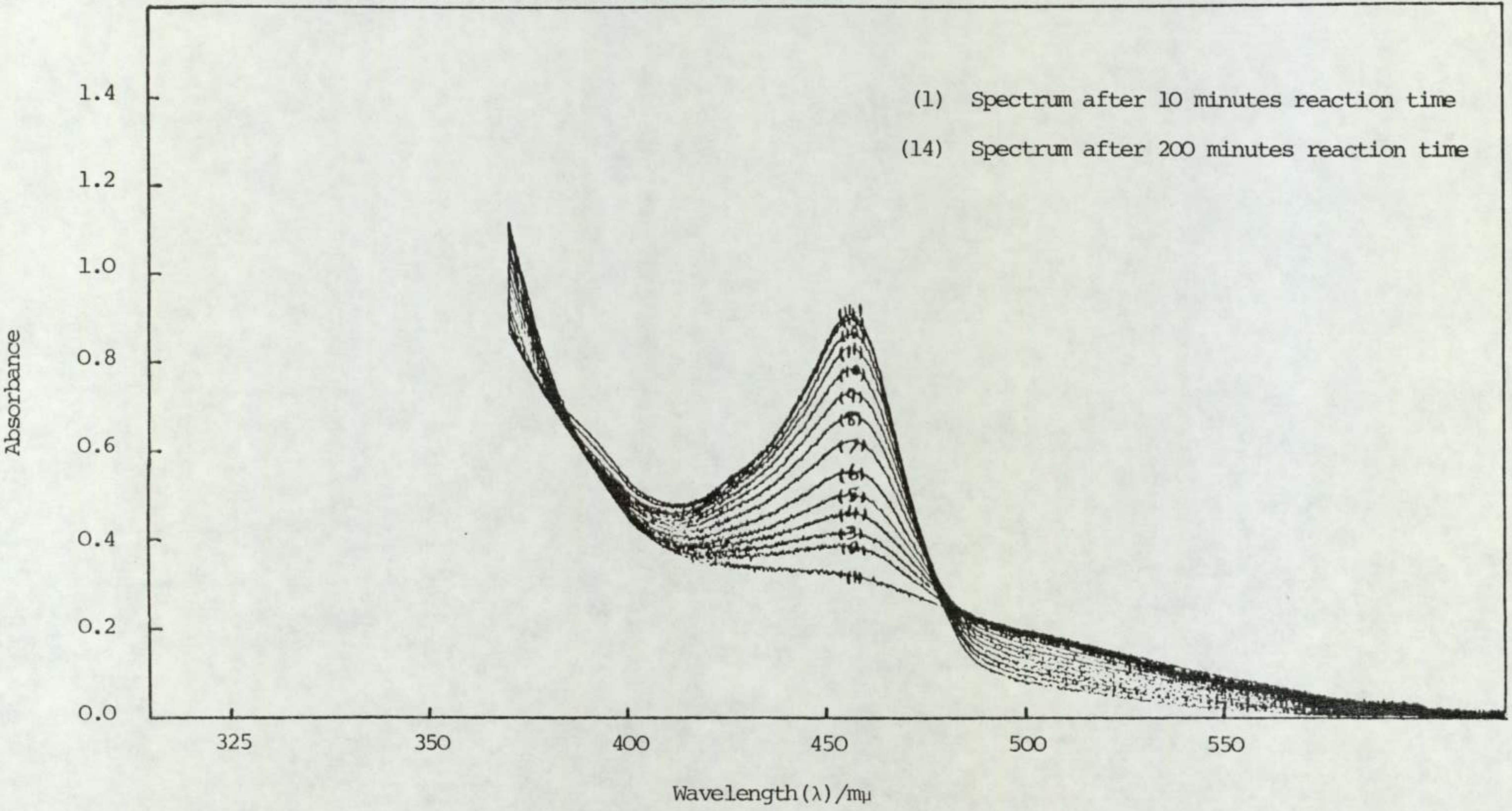
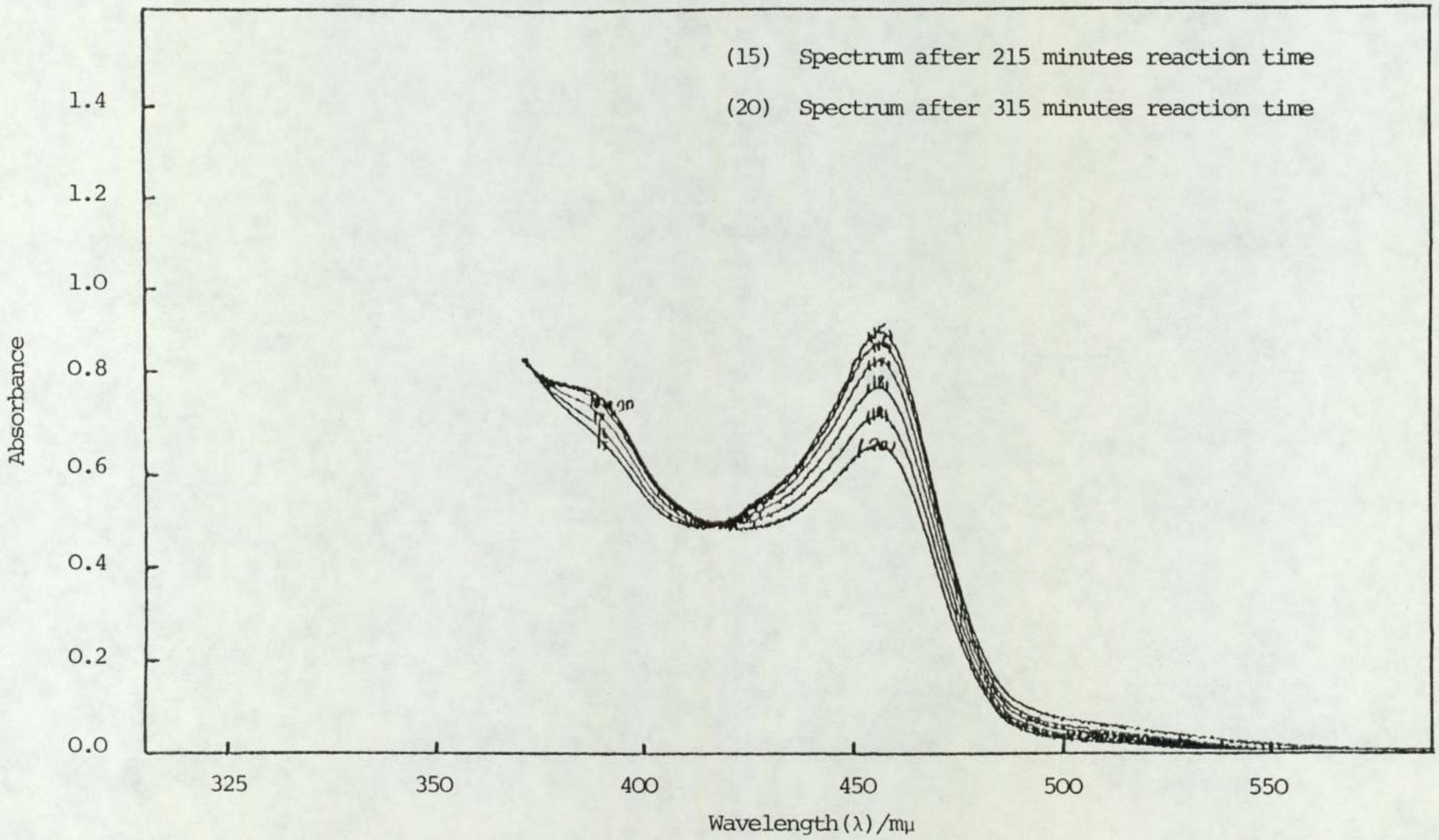


Fig. 4-2 As Fig. 4.1 with longer reaction time



hexachloride is immediately completely transformed in some way to a species of unknown structure W_1, therefore:

$$WCl_6 + CP \xrightarrow{\text{very fast}} W_1$$

so that $\left[W_1\right]_o = \left[WCl_6\right]_o$

where: $\left[W_1\right]_o$ = the initial concentration of W_1

$\left[WCl_6\right]_o$ = the initial concentration of WCl_6

The spectral changes shown in fig. 4-1, indicate that W_1 undergoes some further raction presumably with cyclopentene as discussed in section 3.2.2.3, to produce the intermediate species W_2.

$$W_1 + CP \xrightarrow{k_1} W_2$$

Therefore the absorption at 390 mμ could well be due to the termination reaction of species W_2 leading to the formation of a new species, W_x.

$$W_2 \xrightarrow{k_t} W_x$$

The kinetic studies of these reactions might provide valuable information concerning the initiation and termination steps in the ring opening polymerisation of cyclopentene.

4.3 KINETIC STUDIES:

The preliminary spectrophotometric studies on the reaction of tungsten hexachloride with cyclopentene in chlorobenzene indicated an increase in the concentration of the intermediate W_2 to a maximum value with time, hence providing a technique to study the dependence of the rate of formation of the species W_2 on the concentrations of the reactants, cyclopentene and tungsten hexachloride. Using the apparatus shown in fig. 2-15, the procedure described in section 2.4.5.3 was followed.

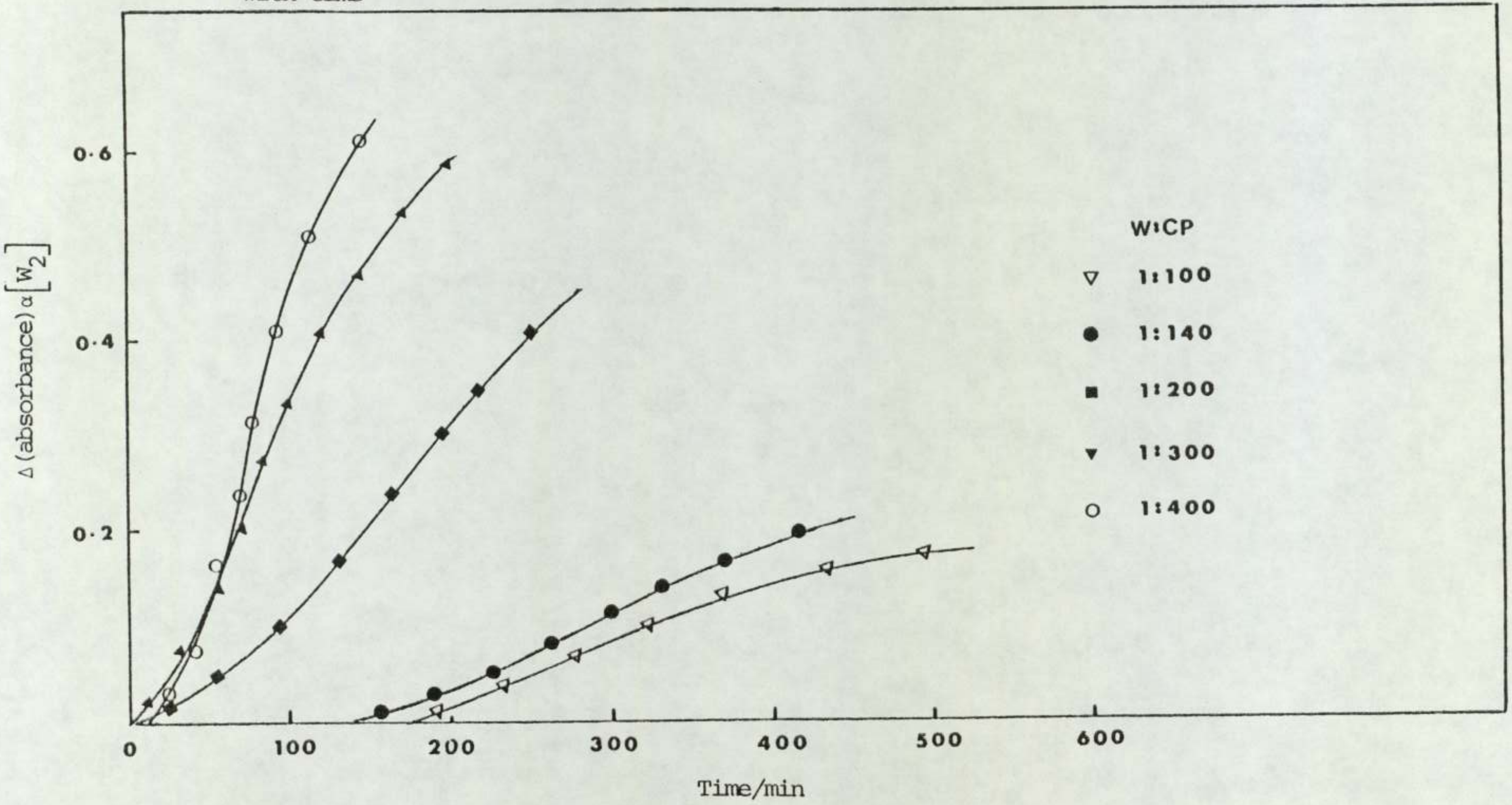
4.3.1 EFFECT OF CONCENTRATION OF CYCLOPENTENE :

4.3.1.1 RATE OF FORMATION OF W_2 :

Keeping the concentration of tungsten hexachloride constant at 2.93×10^{-3} mol. dm^{-3} and using chlorobenzene as solvent a series of experiments was carried out in order to study the effect of concentration of cyclopentene on the rate of formation of species W_2. In a typical experiment 2 ml of a 4.4×10^{-3} M solution of WCl_6, 0.75 ml of chlorobenzene and 0.25 ml of a 3.52 M solution of cyclopentene were injected into the apparatus shown in fig. 2-15, to produce a solution for which $\left[WCl_6\right] = 2.93 \times 10^{-3}$ mol. dm^{-3} and $\left[CP\right] = 0.29$ mol. dm^{-3}. The overall rate of formation of the intermediate species was then determined by following the change in the height of the peak at 458 mμ with time. In other experiments in this series the volume of tungsten hexachloride, chlorobenzene and cyclopentene were adjusted so that the concentration of the catalyst remained constant.

The reaction curves obtained for various concentrations of cyclopentene are shown in fig. 4-3, where Δ (absorbance) at any

Fig. 4-3 Effect of cyclopentene concentration on the changes in the absorbance (458mμ) with time



time t is proportional to the concentration of W_2 at that time (hence having the units of mol. dm^{-3}). The dependence of the initial rate of formation of species W_2 on the concentration of cyclopentene is shown in table 4-1.

TABLE 4-1. DEPENDENCE OF THE INITIAL RATE OF FORMATION OF INTERMEDIATE W_2 ON THE CONCENTRATION OF CYCLOPENTENE

$\frac{[CP]_o}{mol.dm^{-3}}$	Molar Ratio W : CP	$\frac{\text{Initial rate} \times 10^5}{mol.dm^{-3}\ s^{-1}}$
0.29	1:100	0.62
0.41	1:140	0.83
0.59	1:200	1.36
0.88	1.300	3.00
1.17	1:400	2.67

$[WCl_6] = 2.93 \times 10^{-3}$ mol.dm^{-3}

Temperature 25°C

As can be seen from the table 4-1, there is a simple relationship between the initial rate of formation of W_2 and the initial concentration of cyclopentene. That the initial rate decreases for the concentrations beyond the equilibrium concentration, i.e. $[CP]_o > [CP]_e$, could well be due to the involvement of the intermediate W_2 in reactions with a different mechanistic pathway.

The shapes of the reaction curves, shown in fig. 4-3, indicate that the concentration of W_2 has an auto-accelerating effect on the rate of formation of the intermediate W_2. This could be explained if the species W_1, instead of reacting with cyclopentene, alternatively reacts with the intermediate species W_2 to produce more W_2 presumably according to the following reactions:

$$W_1 + CP \xrightarrow{k_1} W_2$$

$$W_1 + W_2 \xrightarrow{k_2} 2W_2$$

However based on the experimental data the initial order of reaction with respect to the cyclopentene concentration was determined from a conventional plot of log (initial rate) against log $\left[CP\right]_o$ as shown in fig. 4-4. From this plot values of 1.1 and 2.5×10^{-5} $dm^3 \ mol^{-1} \ s^{-1}$ were derived for the order, n, and the rate constant, k_i, respectively. Therefore at constant concentration of tungsten hexachloride the initial rate of formation of W_2, $(R_i)_o$, could be described as:

$$(R_i)_o = k_i \left[CP\right]_o$$

$$\text{where} \quad k_i = 2.5 \times 10^{-5} \left[WCl_6\right]_o^a$$

4.3.1.2 MAXIMUM CONCENTRATION OF W_2 :

The difference between the maximum absorption and that of the isobestic point, i.e. $Abs_{max} - Abs_{iso}$, could be considered as an

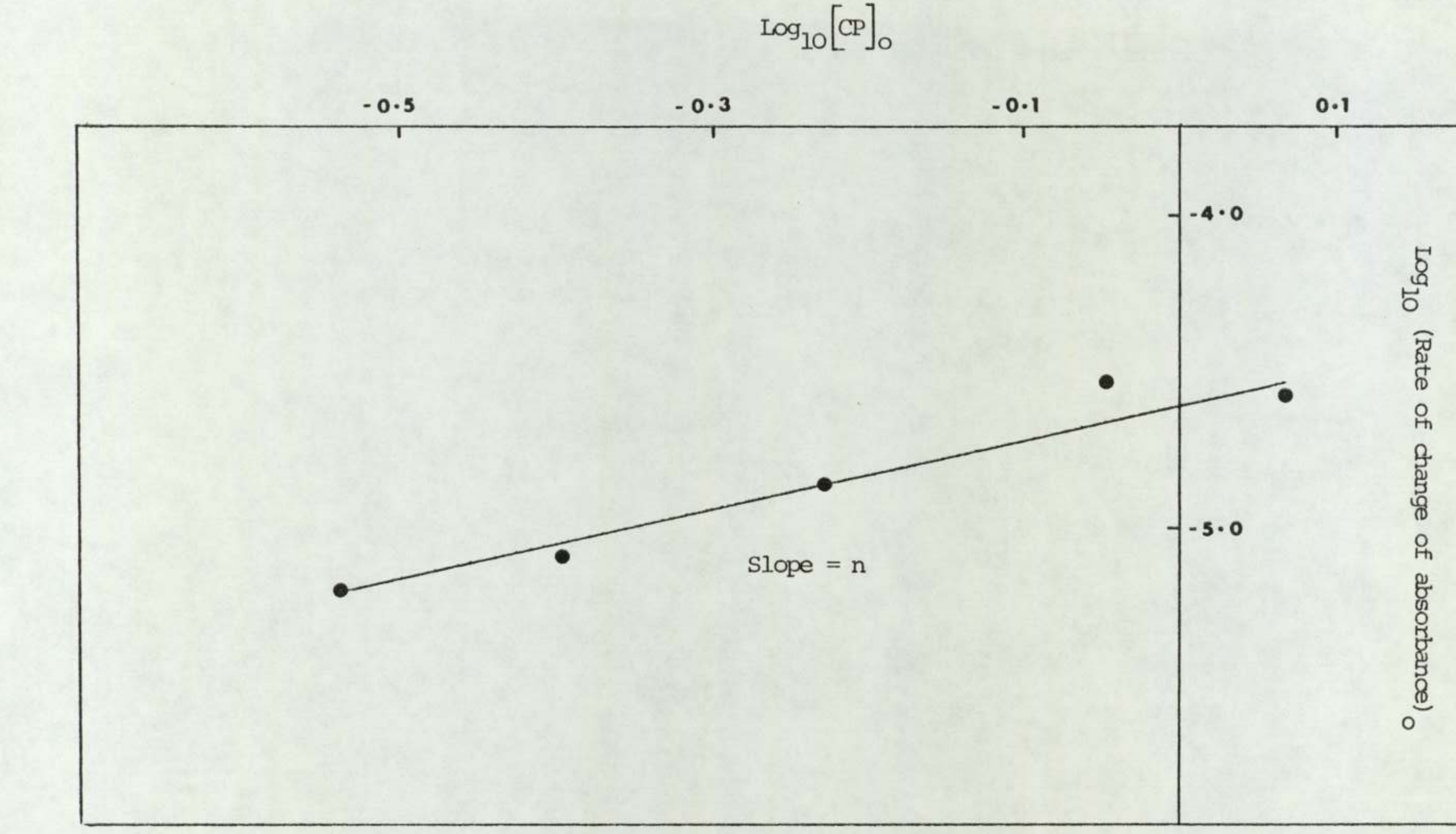


Fig. 4-4 Dependence of log_{10} (rate of change of absorbance)$_o$ on $log_{10}[CP]_o$

approximate measure of the concentration of the species W_2 present at the maximum point. The absorbance at the isobestic point should be amended to take account of the concentration of W_1 remaining but the change in the error involved is expected to be small over the range of concentrations studied. The maximum concentration of W_2 was observed to depend on the initial concentration of cyclopentene. As shown in fig. 4-5, the higher the concentration of cyclopentene, the higher the maximum concentration of W_2 and it appears that there is a limiting value of cyclopentene concentration beyond which the maximum concentration of W_2 remains constant. It was also found that an increase in the concentration of cyclopentene shortens the t_{max}, the time required for the concentration of W_2 to reach its maximum value. The dependence of t_{max} on the reciprocal of cyclopentene concentration is shown graphically in fig. 4-6. That an increase in the concentration of cyclopentene causes a faster formation and therefore decay of W_2 could be accounted for the decrease in the percent of conversion discussed in section 3.2.2.5.

4.3.1.3 RATE OF DECAY OF W_2 :

As mentioned earlier, fig. 4-2, the concentration of the intermediate W_2 decreases with time after reaching a maximum value. Such a decrease in the height of the peak at 458 mμ with time is shown in fig. 4-7 for various concentrations of cyclopentene and it is expected that the concentration of the species W_1 is very small at this stage. Therefore if the rate of formation of W_2 is ignored, the linearity of the graphs, shown in fig. 4-7, indicates that the rate of decay in the concentration of the species

Fig. 4-5 Dependence of maximum concentration of W_2 on the initial concentration of cyclopentene

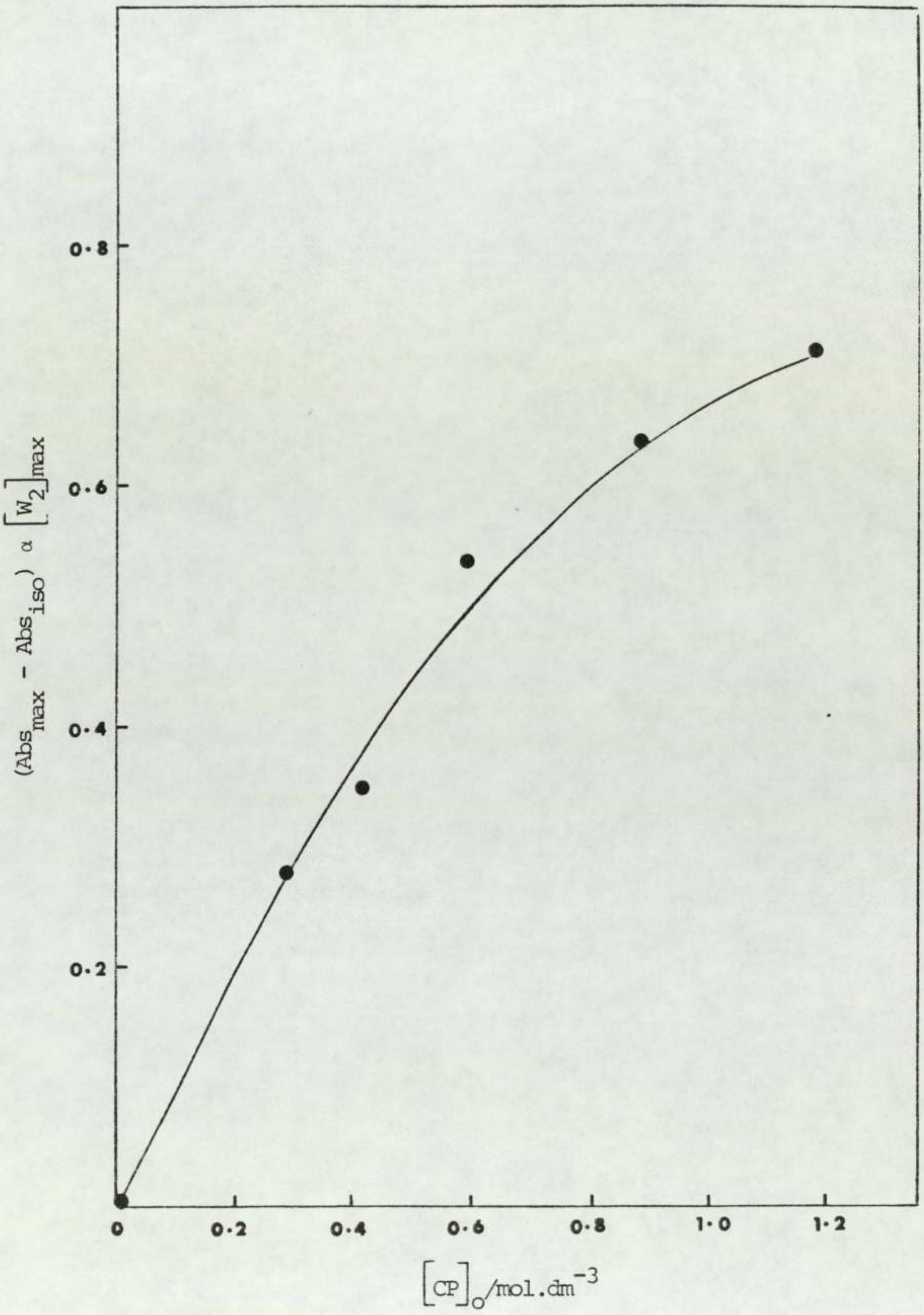


Fig. 4-6 Dependence of t_{max} on the reciprocal of cyclopentene concentration

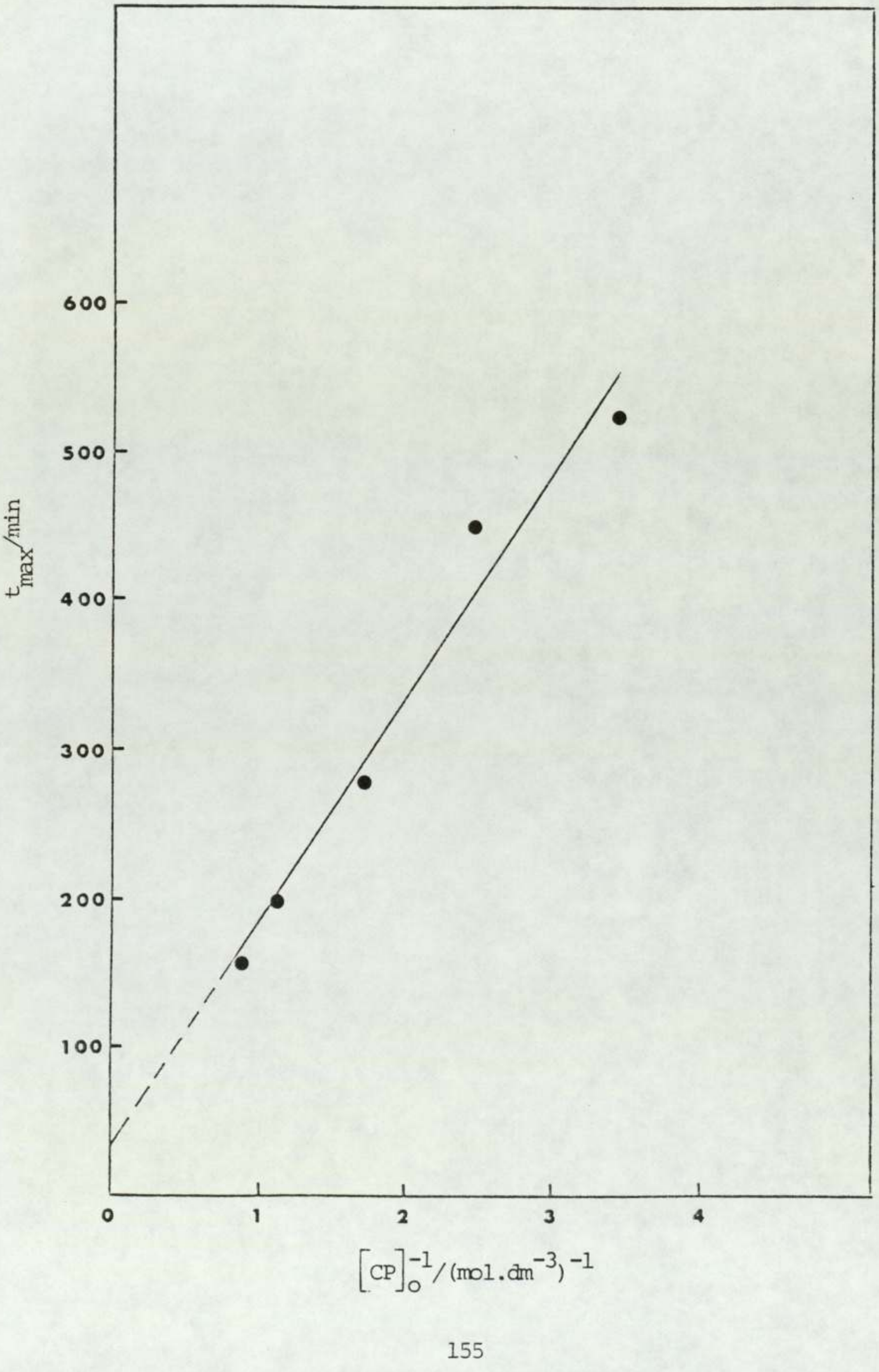
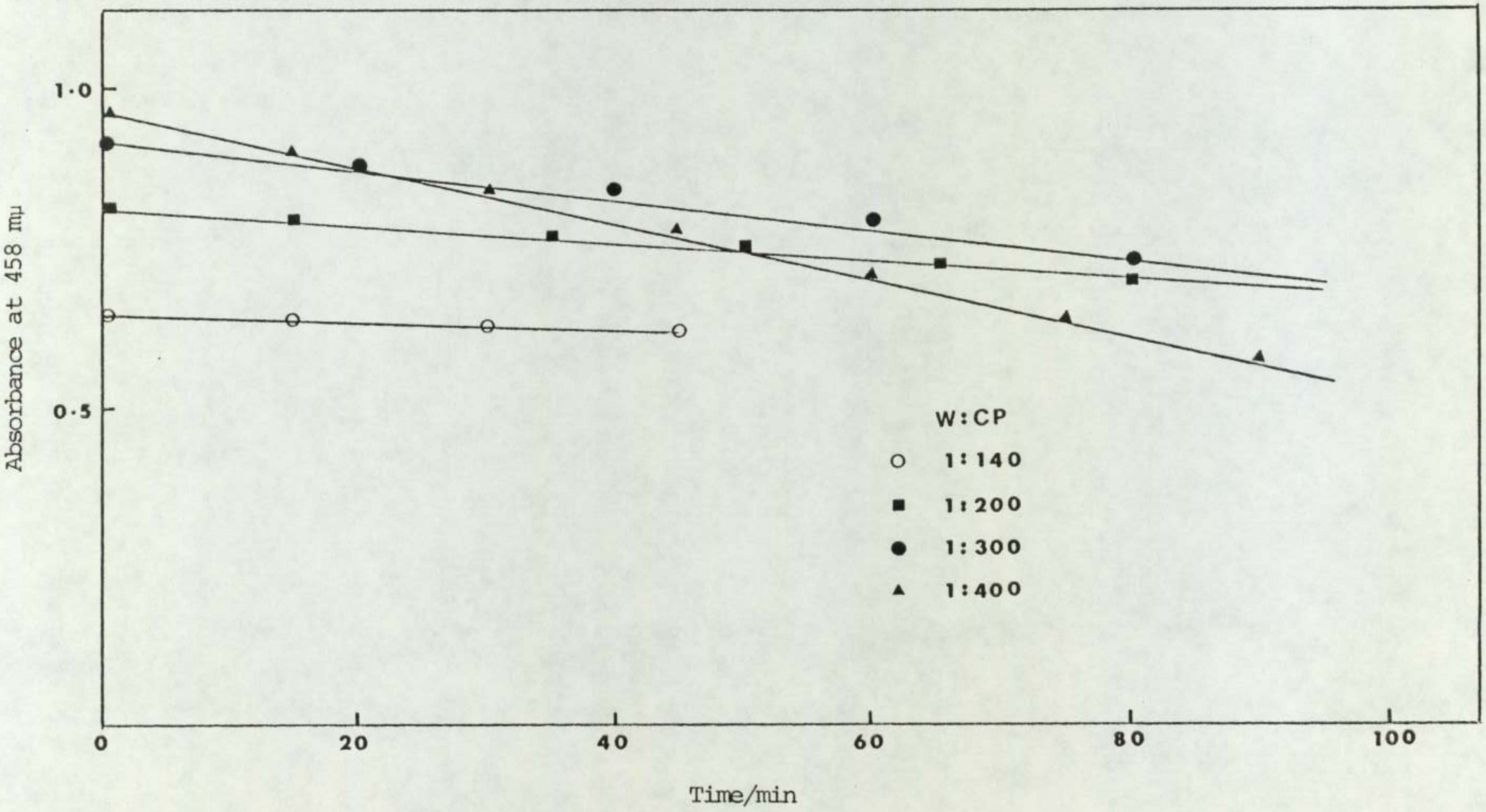


Fig. 4-7 Dependence of the rate of decrease in the absorbance (458 mμ) with time for various concentrations of cyclopentene



W_2, $- d[W_2]/dt$, is constant and the reaction is apparently zero order with respect to the cyclopentene concentration. That different rates of decay are obtained for different concentrations of cyclopentene could be therefore due to the $[W_2]_{max}$, the concentration of W_2 at the maximum point. The plot of rate of decay against the maximum concentration of W_2, shown in fig. 4-8, indicates that the higher the $[W_2]_{max}$ the faster the rate of decay of W_2.

Based on the experimental data, the order of the reaction with respect to the maximum concentration of the intermediate W_2 was determined from a conventional plot of log (rate of decay) against log ($Abs_{max} - Abs_{iso}$) as shown in fig. 4-9. From this plot values of 2.2 and 1.15×10^{-4} dm^3 mol^{-1} s^{-1} were derived for the order, n, and the rate constant, k_t, respectively. On these grounds, the decrease in the concentration of the intermediate W_2 could therefore be due to the following reaction

$$W_2 + W_2 \xrightarrow{k_t} W_x$$

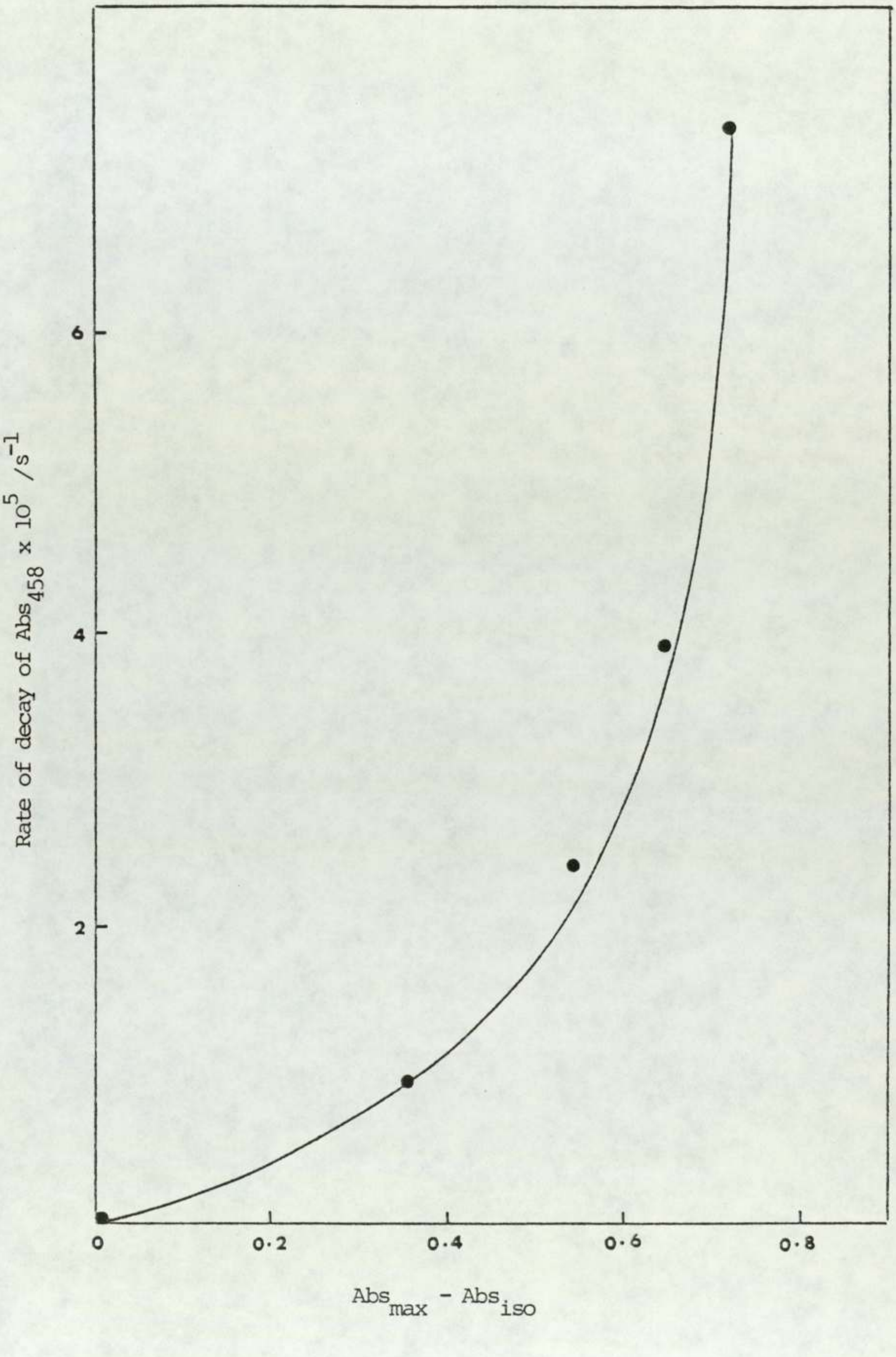
Inspection of the fig. 4-7 shows that the rate of decay of W_2 could depend on either:

(i) the maximum concentration of W_2

or (ii) the initial concentration of cyclopentene.

The order of reaction with respect to the initial concentration of cyclopentene may be obtained from a plot of log (rate of disappearance of W_2) against log $[CP]_o$. This plot is shown in fig. 4-10. From the slope of this plot the order of the reaction was found to be 1.8 and the rate constant for the reaction was

Fig. 4-8 Dependence of rate of decay of absorbance at 458 mμ on (Abs_{max}-Abs_{iso})



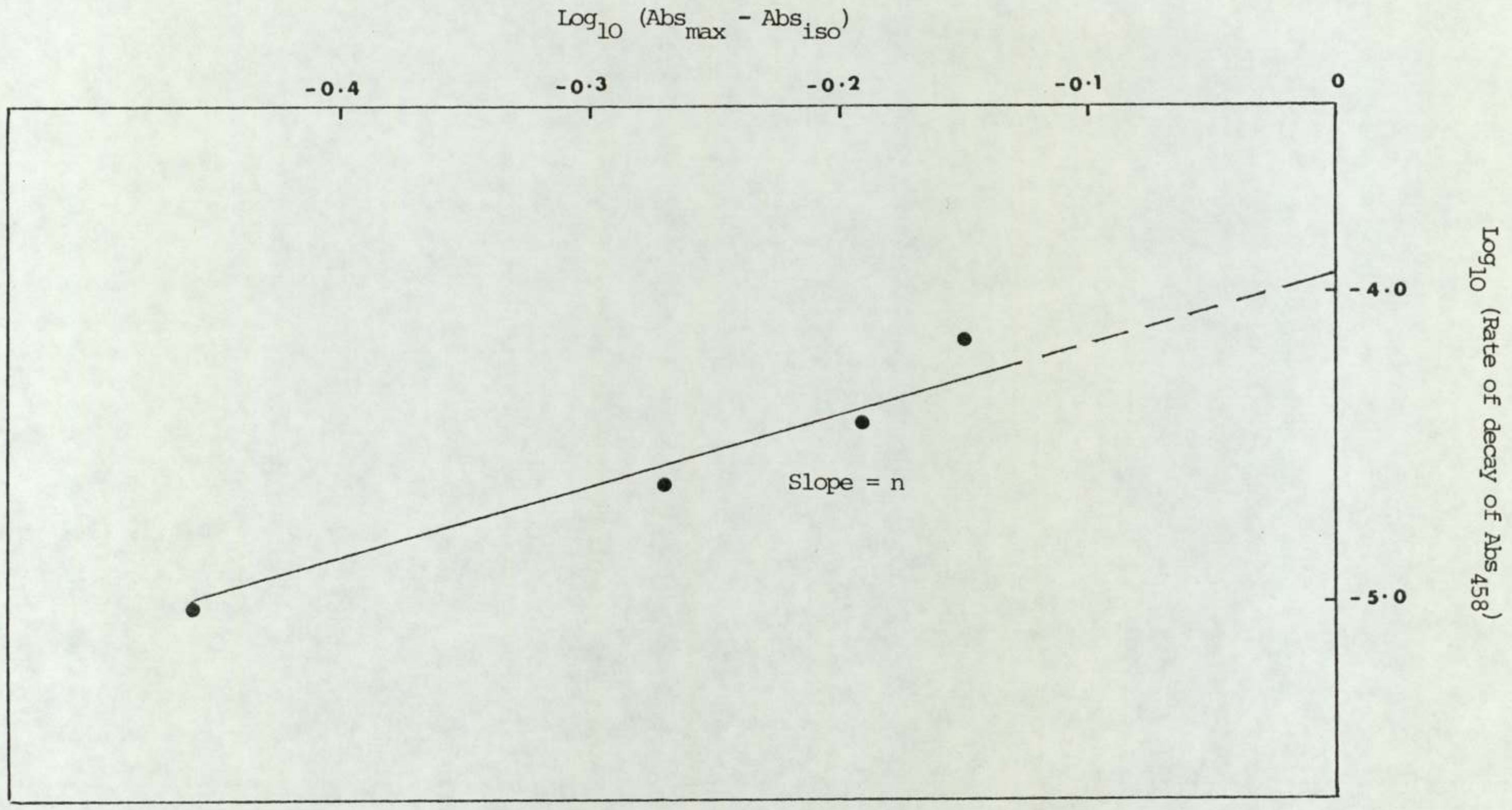


Fig. 4-9 Dependence of $\log_{10}$ (rate of decay of absorbance at 458) on $\log_{10}$ $(Abs_{max} - Abs_{iso})$

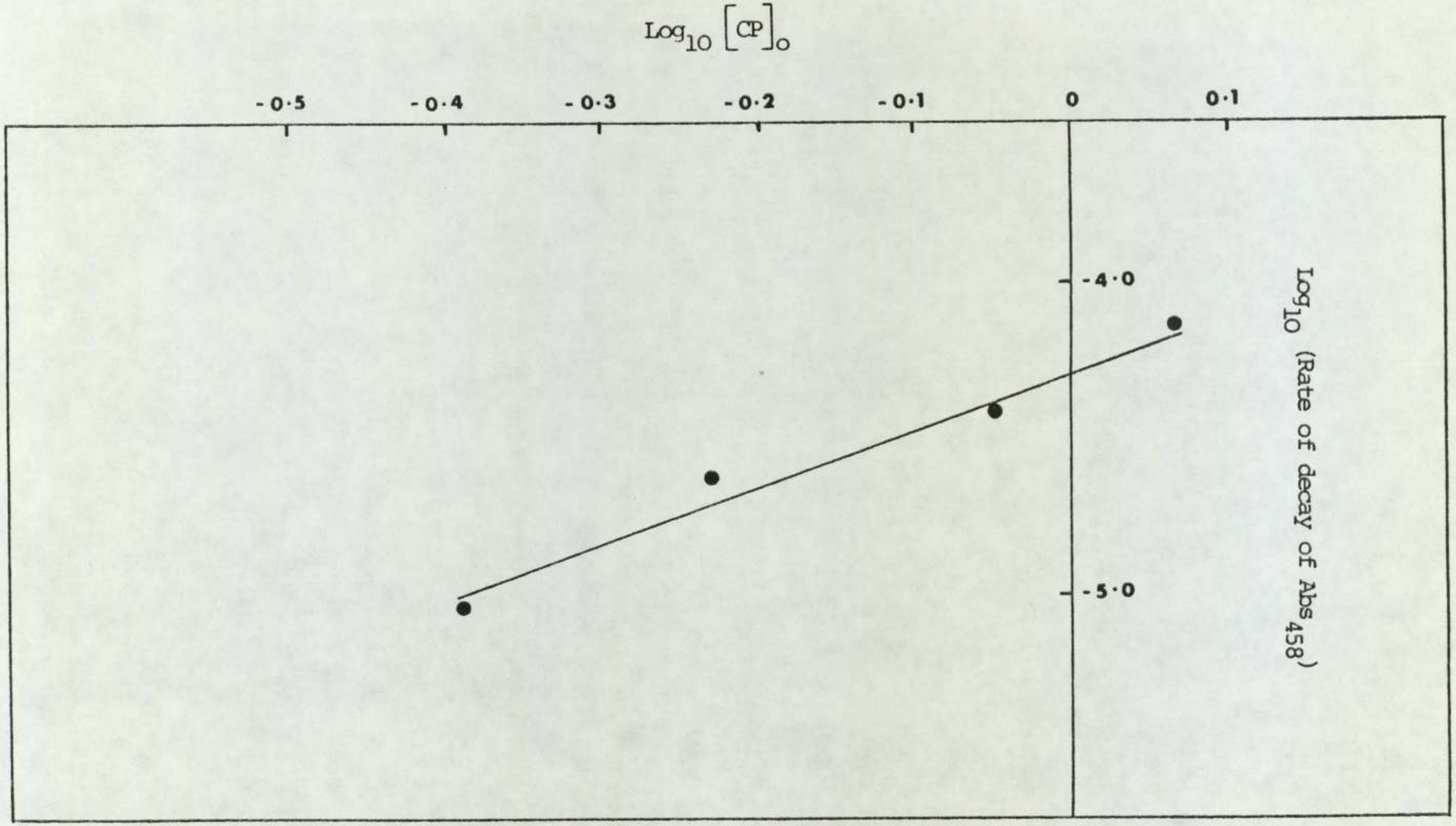


Fig. 4-10 Dependence of $\log_{10}$ (rate of decay of absorbance at 458 mμ) on $\log_{10}\left[\mathrm{CP}\right]_o$

5×10^{-5} dm^3 mol^{-1} s^{-1}. The interpretation of this information has to be approached cautiously for the maximum concentration of W_2 was shown previously to be related to the initial concentration of cyclopentene and it is possible that the two orders of the reaction obtained, i.e. with respect to the concentration of W_2 and the cyclopentene concentration, are expected to be identical. A detailed discussion of the kinetics of the reaction of W_2 will be undertaken in chapter 5 but it appears that the disappearance of W_2 may be described by:

$$\text{(i)} \quad -d[W_2]/dt = k_t[W_2]^2 ,$$

$$\text{(ii)} \quad -d[W_2]/dt = k_t[W_2]\,[CP]$$

or by a linear combination of these equations.

4.3.2 EFFECT OF CONCENTRATION OF TUNGSTEN HEXACHLORIDE :

In experiments similar to those described in section 4.3.1, the ultraviolet/visible spectral changes for various concentrations of tungsten hexachloride were studied at a constant concentration of cyclopentene of 0.67 mol. dm^{-3}. In a typical experiment 1.5 ml of tungsten hexachloride of 4.8×10^{-3} M, 0.5 ml of chlorobenzene and 0.5 ml of a 3.34 M solution of cyclopentene were successively injected into the apparatus shown in fig. 2-15 to produce a solution for which $[CP] = 0.67$ mol. dm^{-3} and $[WCl_6] = 2.9 \times 10^{-3}$ mol. dm^{-3}. The spectral changes of the reaction were similar to those shown in figs. 4-1 and 4-2 and the results tend to indicate that an increase in the concentration of tungsten hexachloride shortens the t_{max}, the time required for the concentration of W_2

to reach its maximum value. Fig. 4-11 shows the dependence of the t_{max} on the reciprocal of the initial concentration of tungsten hexachloride. However other meaningful kinetic data could not be obtained for the system under study; therefore further studies on the subject are required.

4.4 EFFECT OF OXYGEN:

As mentioned earlier, the spectroscopic studies of the reaction of cyclopentene with tungsten hexachloride indicate that the concentration of the intermediate W_2 increases to a maximum and then decays when the system is allowed to stand. The effect of oxygen on such a system was investigated by allowing the concentration of the W_2 to reach its maximum value after which oxygen was introduced into the system and the spectral changes recorded. The increase in the absorbance at 458 mμ to a maximum for a reaction containing 0.15 ml of a 0.046 M solution of WCl_6, 2.05 ml of chlorobenzene and 0.3 ml of a 5.53 M solution of cyclopentene is shown in fig. 4-12. When the absorbance reached a maximum oxygen was admitted, as described in section 2.4.5.3, and according to the subsequent spectral changes, shown in fig. 4-13, a rapid decrease in the concentration of $W_2(\lambda_{max} = 458$ mμ) ensued whereas the concentration of $W_x(\lambda_{max} = 390$ mμ) remained unchanged. The plot of absorbance at 458 against time for the system under study indicates that most of the species W_2 disappears almost immediately after oxygen is allowed into the system (fig. 4-14). A much longer time is required for such a disappearance (longer than 24 hours) to occur when oxygen is not present. Oxygen

Fig. 4-11 Dependence of t_{max} on the reciprocal of concentration of tungsten hexachloride

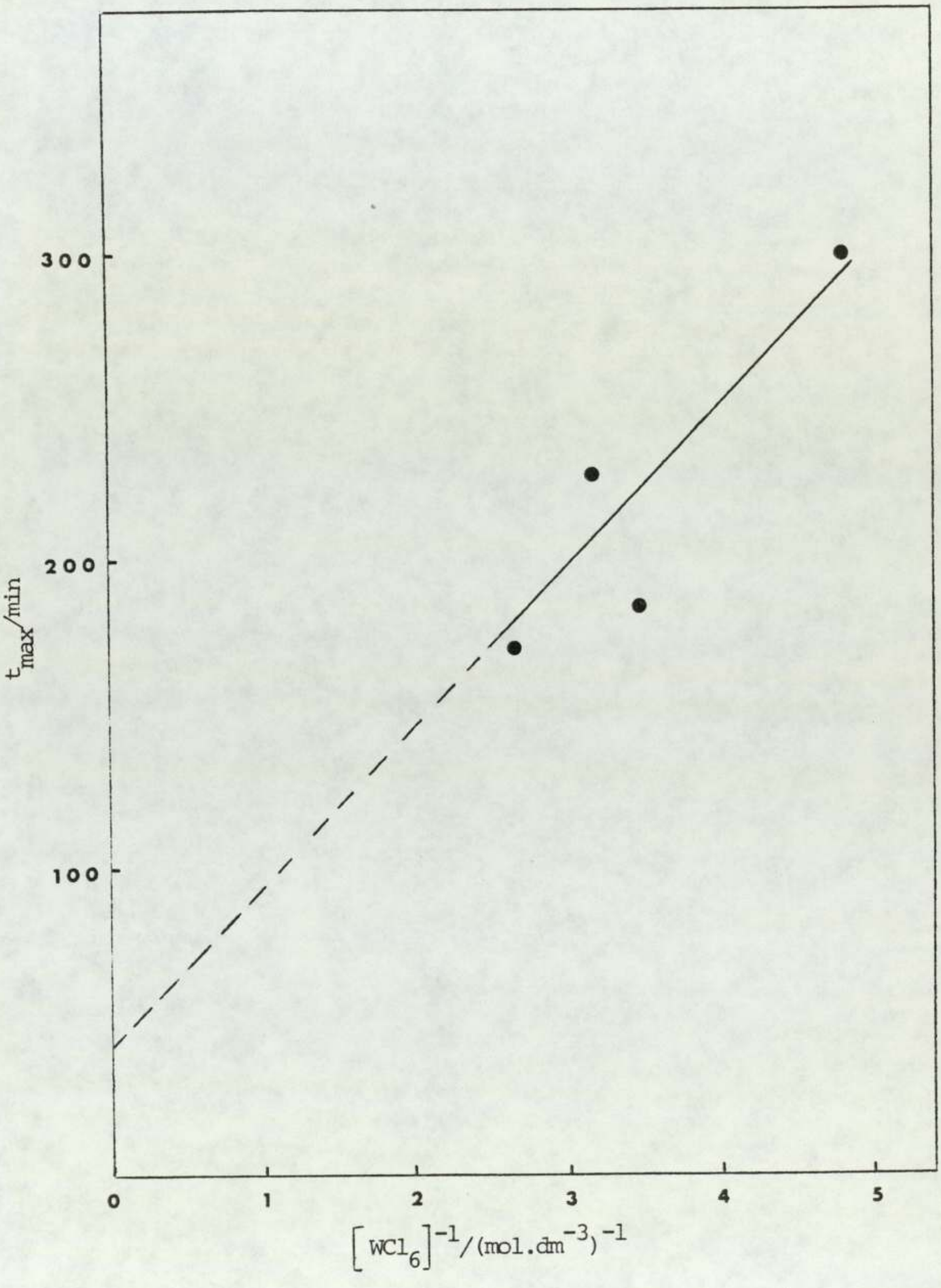


Fig. 4-12 Changes in the absorbance at 458 mμ with time before the addition of oxygen

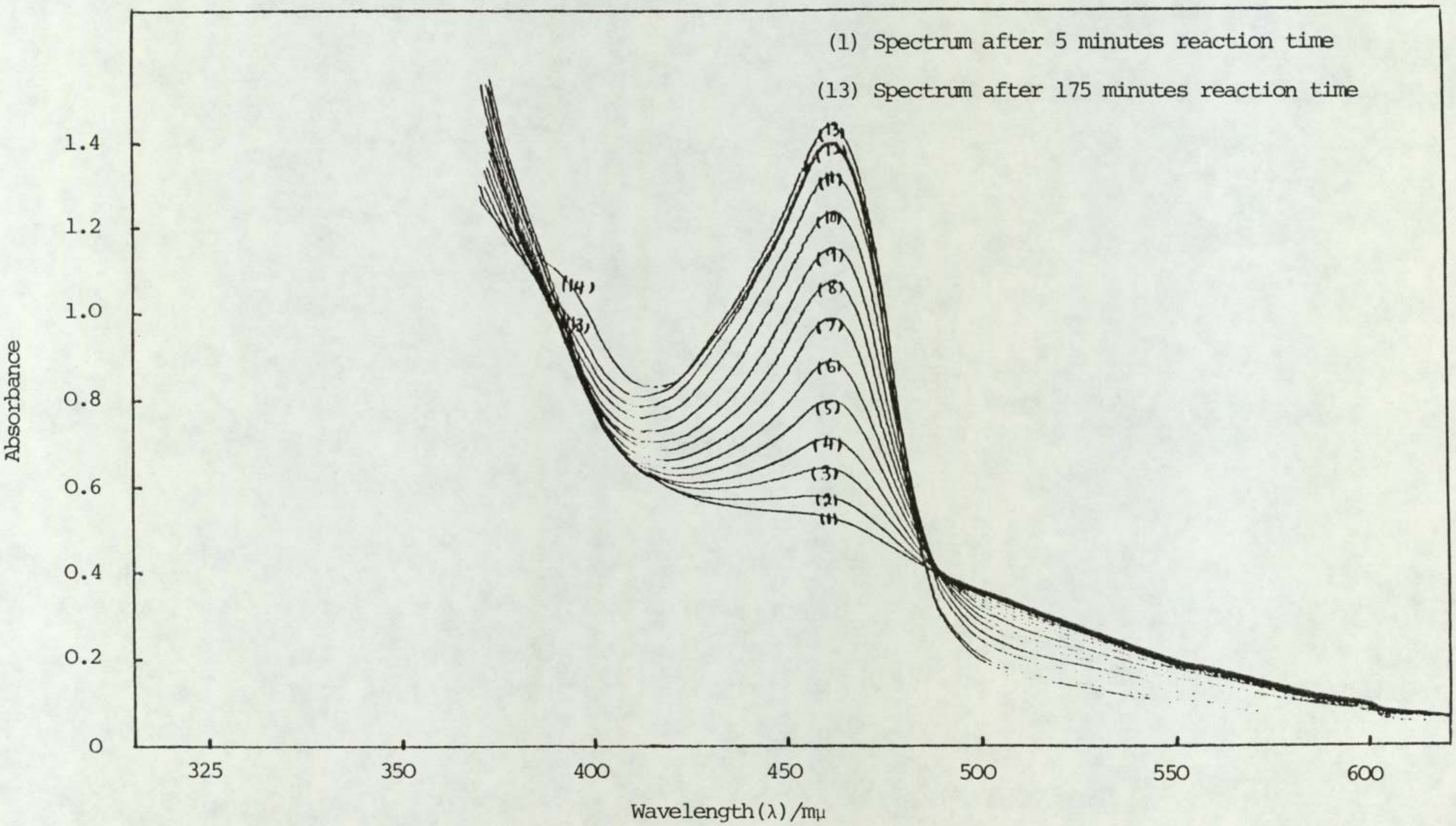


Fig. 4-13 Changes in the absorbance at 458 mμ with time after the addition of oxygen

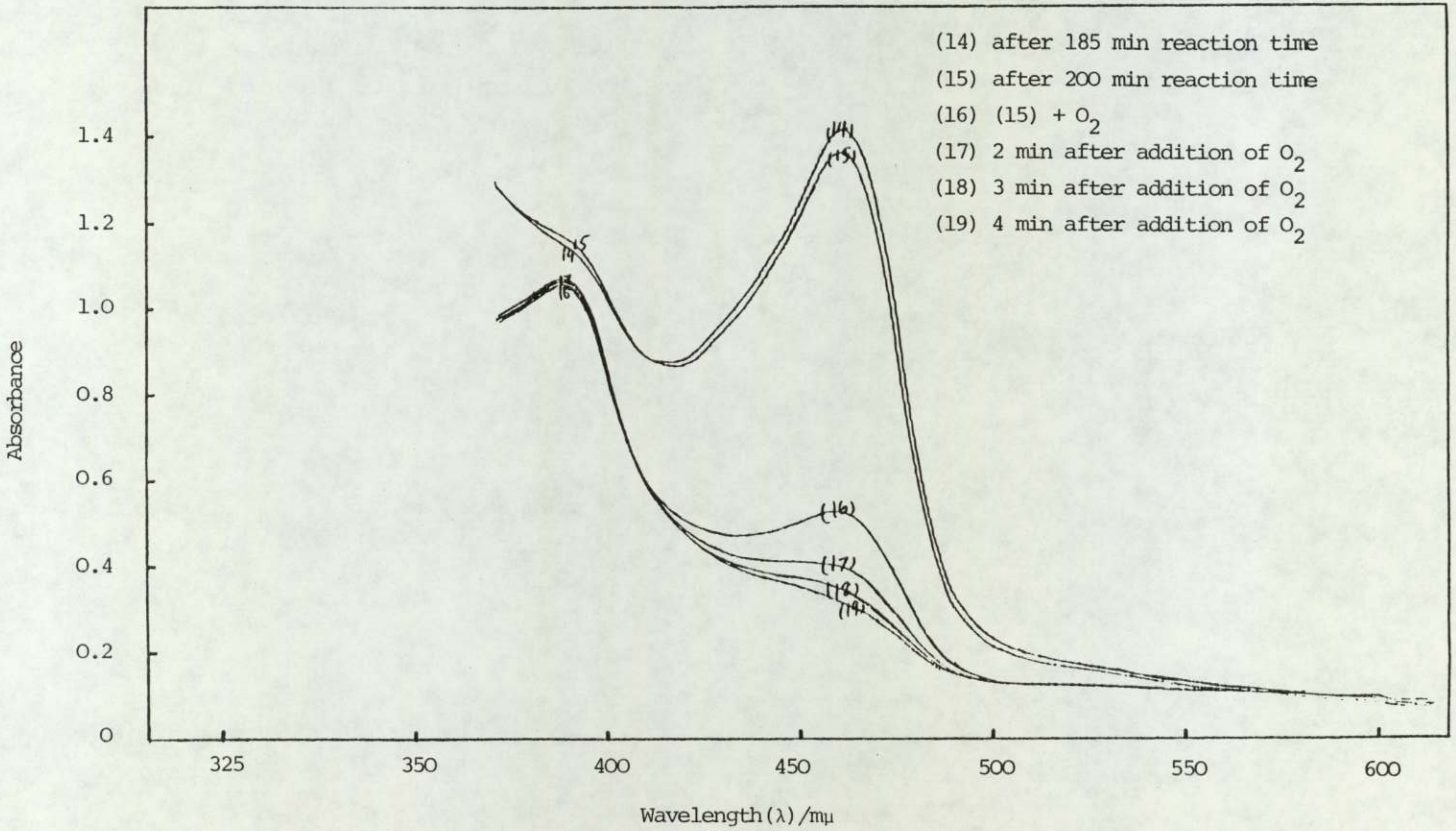
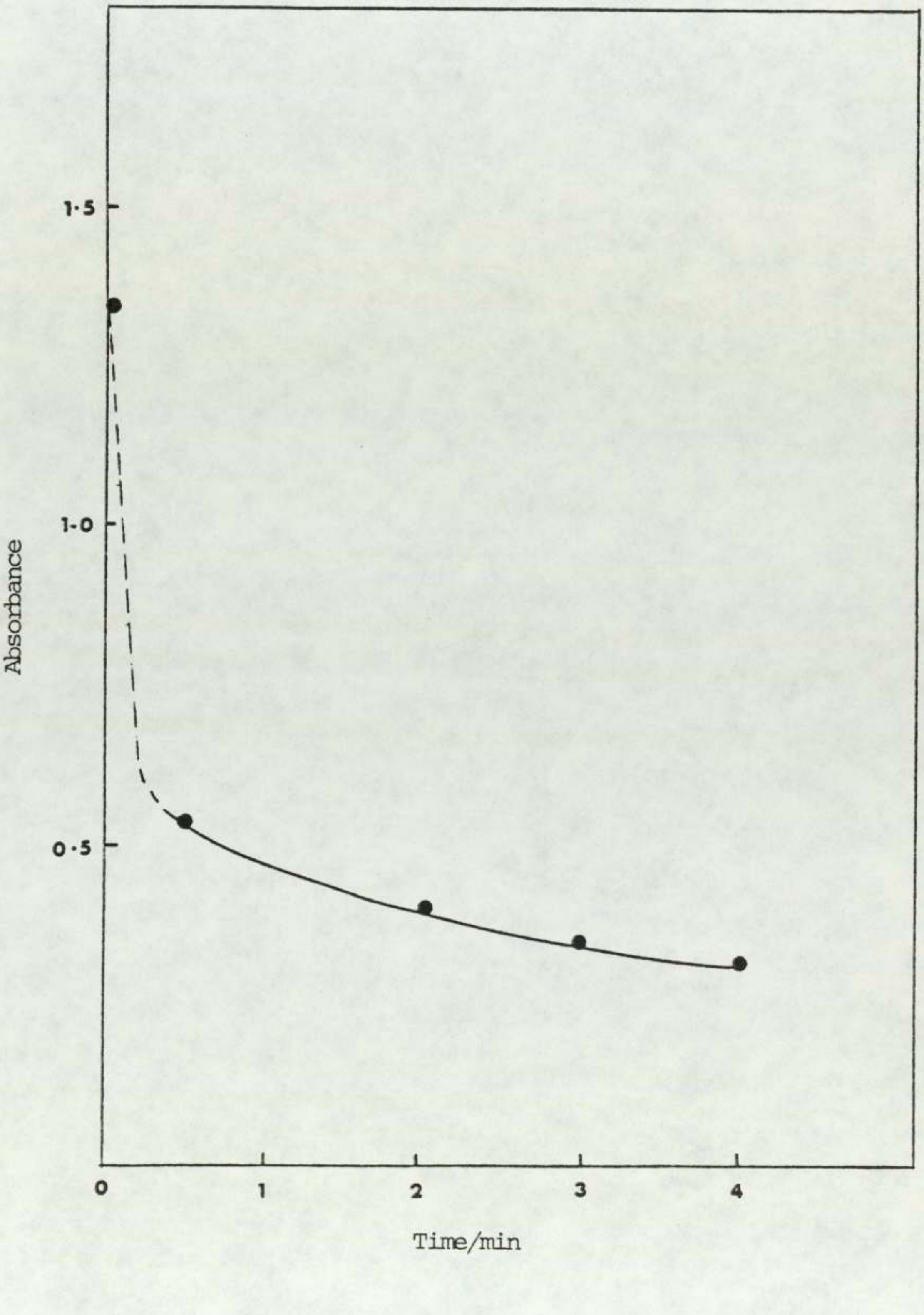


Fig. 4-14 Changes in the concentration of W_2 with time after the addition of oxygen



therefore, once introduced, reacts with the intermediate W_2 to produce W^* presumably according to the following reaction:

$$W_2 + O_2 \longrightarrow W^*$$

That the species W_2 is the principal source of formation of W^* could account for the failure in the determination of the rate of polymerisation of cyclopentene discussed in section 3.3.2.1.

4.5 POLYMERISATION OF CYCLOPENTENE INITIATED BY W_2/O_2 :

The spectroscopic studies indicate that cyclopentene, even at concentrations below the equilibrium concentration, reacts with WCl_6 to produce an intermediate species W_2. In order to study the metathetical activity of the species formed attempts were made to polymerise cyclopentene using W_2/O_2 as the catalyst system. In a typical experiment 0.2 ml of tungsten hexachloride of 0.046 M, 1.6 ml of chlorobenzene and 0.25 ml of a 5.53 M solution of cyclopentene were successively injected into the bulb D of the apparatus shown in fig. 2-16 to produce a solution for which $\left[CP\right] = 0.67$ mol. dm^{-3} and $\left[WCl_6\right] = 4.5 \times 10^{-3}$ mol. dm^{-3}. The solution was allowed to stand for a period of 2.5 hours as described in section 2.4.5.3. In the meanwhile 10 ml of cyclopentene was vacuum-distilled into the bulb H through J. Oxygen was then introduced into the bulb F and allowed to react for 2 minutes after which the mixture was added to the cyclopentene and the procedure described in section 2.4.5.3. was followed. The conversion after 45 minutes reaction time was 1.0% slightly higher than would have been expected for a polymerisation in the absence of oxygen. On this basis one can suggest that the species W_2 formed from the reaction of cyclopentene, at concentrations both above and below the equilibrium monomer concentration at 25°C, with tungsten hexachloride is a metathesis active species for the polymerisation of cyclopentene.

CHAPTER 5

DISCUSSION

5.1 SPECTROSCOPIC STUDIES:

The ultraviolet/visible spectroscopic studies of the reaction of cyclopentene with tungsten hexachloride in chlorobenzene indicate that an immediate reaction takes place between these compounds leading to the formation of the species W_1. This species then reacts with more cyclopentene to produce an intermediate species W_2 which shows an absorbance maximum at 458 mμ. The concentration of this intermediate, however, goes through a maximum with time indicating the presence of at least two consecutive reactions; one leading to the formation of W_2 and the other its destruction. The maximum height of the spectral peak at 458 mμ, Abs_{max}, and the time required for the concentration of W_2 to reach its maximum value, t_{max}, are dependent on the initial concentration of the reactants, cyclopentene and tungsten hexachloride. Figs. 4-6 and 4-11 show the dependences of t_{max} on the concentrations of cyclopentene and WCl_6 respectively which may be summarised as :

$$t_{max} \propto \frac{1}{[CP]_o}$$

$$t_{max} \propto \frac{1}{[WCl_6]_o} \qquad \ldots\ldots \quad (5.1)$$

The spectroscopic kinetic studies discussed in chapter 4 indicate that the following reactions could be involved in the formation of the species W_2, to explain the non-linear absorbance-time curves.

$$W_1 + CP \xrightarrow{k_1} W_2 \qquad \ldots\ldots \quad (5.2)$$

$$W_1 + W_2 \xrightarrow{k_2} 2\,W_2 \qquad \ldots\ldots \quad (5.3)$$

The reaction (5.2) is believed to predominate in the initial stages of the reaction whereas in the later stages, as the concentration of W_2 increases, the formation of W_2 by reaction (5.3) may become more important. The initial rate of formation of W_2, when the rate of reaction (5.3) ≈ o , shows a first order dependence with respect to the cyclopentene concentration indicating the involvement of the cyclopentene molecule in the initial step of the reaction.

The rate of decay of W_2 from its maximum concentration has been described as :

$$-d\left[W_2\right] / dt = k_{t_1} \left[W_2\right]^2 \quad ,$$

$$-d\left[W_2\right] / dt = k_{t_2} \left[W_2\right] \left[CP\right]$$

or a linear combination of these equations, therefore :

$$W_2 + W_2 \xrightarrow{k_{t_1}} W_x \qquad .....(5.4)$$

$$W_2 + CP \xrightarrow{k_{t_2}} W_y \qquad .....(5.5)$$

The termination reaction of W_2 shows a second order dependence with respect to the concentration of W_2 at the maximum point (W_{max}). The reaction also shows a second order dependence with respect to the initial concentration of cyclopentene, $\left[CP\right]_o$, and since W_{max} depends on $\left[CP\right]_o$ it is possible that this second order dependence can be explained by reaction (5.5).

The rate of disappearance of W_1 and formation of W_2 may be given by equations (5.6) and (5.7) respectively:

$$-\frac{d[W_1]}{dt} = k_1 [CP][W_1] + k_2 [W_1][W_2] \qquad .....(5.6)$$

$$\frac{d[W_2]}{dt} = k_1 [CP][W_1] + k_2 [W_1][W_2] - k_{t_1} [W_2]^2 - k_{t_2} [W_2][CP] \qquad .....(5.7)$$

5.1.1 - COMPUTER SIMULATION OF THE KINETIC SCHEME :

The integration of the equation (5.7) to obtain the dependence of the concentration of W_2 on time was assumed to require a numerical procedure. To assist with the manipulation of this equation to show the effects of the cyclopentene concentration on the values of t_{max} and the maximum absorbance, a computer program was written for the Apple II microcomputer in the APPLESOFT BASIC language. The program was designed so that the curves shown in fig. 4-3 could be simulated for various concentrations of cyclopentene, once values of the various rate constants and the tungsten hexachloride concentration had been fed in.

In order to apply the program an experiment was selected ($[CP] = 1.17$ mol. dm^{-3} and $[WCl_6] = 2.9 \times 10^{-3}$ mol. dm^{-3}) and the appropriate rate constants were adjusted so that the shape of the absorbance-time curve and the value obtained for t_{max} were similar to those obtained experimentally. The same values of the rate constants were used for simulating other experimental conditions but large deviations from experimental data were observed as shown in table 5-1.

TABLE 5 - 1 COMPARISON OF COMPUTED t_{max} AND W_{max} WITH EXPERIMENTALLY OBSERVED VALUES USING EQUATION (5.7)

$[CP]_o$ mol.dm^{-3}	t_{max} minutes (experiment)	t_{max} minutes (computed)	W_{max}x10^3 mol.dm^{-3} (experiment)	W_{max}x10^3 mol.dm^{-3} (computed)
1.17	155(155)*	150	1.63	1.63
0.88	200(200)	160	1.47	1.70
0.59	280(290)	170	1.24	1.78
0.41	450(400)	180	0.80	1.83
0.29	525(560)	190	0.64	1.87

* Values shown in brackets are maximum times obtained from fig. 4-6.

W_{max} = Maximum concentration of W_2

$k_1 = 6 \times 10^{-6}$, $k_2 = 0.26$, $k_{t_1} = 0.05$ and $k_{t_2} = 5 \times 10^{-5}$ dm^{3}mol^{-1}s^{-1}

$[WCl_6] = 2.9 \times 10^{-3}$ mol.dm^{-3}

The large discrepancies shown in table 5-1 required an adjustment of the kinetic model if correlation was to be obtained between the experimentally observed and computed values of t_{max} and W_{max}. It was considered that the basic features of the kinetic system would remain essentially unchanged but could be amended to take account of the fact that any active species in the system, particularly W_1, may be able to complex with cyclopentene, which would then assume a more important kinetic role. The kinetic scheme was then adjusted to :

$$W_1 + CP \xrightarrow{k_1} W_2$$

$$W_1 + CP \xrightleftharpoons{K} W_1^*$$

$$W_1^* + W_2 \xrightarrow{k_2} 2\,W_2$$

According to this scheme the formation of W_2 can be described as :

$$\frac{d[W_2]}{dt} = k_1 [CP][W_1] + k_2 [W_1][W_2][CP] - k_{t_1} [W_2]^2 - k_{t_2} [W_2][CP] \qquad \text{.....(5.8)}$$

which indicates that W_1 could alternatively complex with cyclopentene to produce a more active species W_1^* which would then react with W_2 to produce W_2. k_2 in equation (5.8) incorporates the equilibrium constant K.

Using equation (5.8) as the basis of the program improved correlation was obtained as shown in table 5-2. As can be seen from table 5-2, the relative maximum concentrations of W_2 (W_{max}) are computed to be

TABLE 5 - 2 COMPARISON OF COMPUTED t_{max} AND W_{max} WITH EXPERIMENTALLY OBSERVED VALUES USING EQUATION (5.8)

$[CP]_o$ mol.dm^{-3}	t_{max} minutes (experiment)	t_{max} minutes (computed)	W_{max}x10^3 mol.dm^{-3} (experiment)	W_{max}x10^3 mol.dm.$^{-3}$ (computed)
1.17	155(155)*	140	1.72	1.72
0.88	200(200)	180	1.53	1.62
0.59	280(290)	260	1.31	1.47
0.41	450(400)	360	0.85	1.31
0.29	525(560)	480	0.68	1.15

*Values shown in brackets are maximum times obtained from fig. 4-6.

W_{max} = Maximum concentration of W_2

$k_1 = 6 \times 10^{-6}$, $k_2 = 0.26$, $k_{t_1} = 0.05$ and $k_{t_2} = 5 \times 10^{-5}$ dm^{3}mol^{-1}s^{-1}

$[WCl_6] = 2.9 \times 10^{-3}$ mol.dm^{-3}

somewhat higher than expected. It is possible that the species W_1, which is the principal source of formation of W_2, is also removed from the system by a reaction that does not involve the formation of W_2. This may be summarised as :

$$W_1 \xrightarrow{k_3} W_z$$

The overall change in the concentration of W_1 could then be given by :

$$-\frac{d[W_1]}{dt} = k_1 [W_1][CP] + k_2 [W_1][W_2][CP] + k_3 [W_1] \qquad \ldots.(5.9)$$

which would affect the instantaneous concentration of W_1 used in equation (5.8). This modification produced remarkable similarities between the computed and experimental data (see table 5-3) suggesting that on the reaction of cyclopentene with WCl_6 only a fraction of W_1 can produce W_2 .

The computer program (see appendix 2) based on the equations (5.8) and (5.9) could also be used to elucidate the mechanism of removal of W_2 from the system since the relative importance of the two reactions (5.4) and (5.5) could be assessed. It was found that the elimination of the $k_{t_1} [W_2]^2$ term from the program, i.e. $k_{t_1} = o$, produced large deviations from experimental results as shown in table 5-4; whereas elimination of the $k_{t_2}[W_2][CP]$ term from the program, i.e. $k_{t_2} = o$, produced similar results to those obtained experimentally, as shown in table 5-5. The significance of reaction (5.5) was assessed to be less than reaction (5.4) since increasing the value of k_{t_2} when $k_{t_1} = 0.05\ dm^3\ mol^{-1}s^{-1}$ led to progressively larger deviations from the shape of the experimental curves. One can

TABLE 5 - 3 COMPARISON OF COMPUTED t_{max} AND W_{max} WITH EXPERIMENTALLY OBSERVED VALUES USING EQUATIONS (5.8) AND (5.9)

$[CP]_o$ mol.dm^{-3}	t_{max} minutes (experiment)	t_{max} minutes (computed)	$W_{max} x10^3$ mol.dm^{-3} (experiment)	$W_{max} x10^3$ mol.dm^{-3} (computed)
1.17	155(155)*	140	1.52	1.52
0.88	200(200)	190	1.35	1.37
0.59	280(290)	270	1.15	1.14
0.41	450(400)	390	0.75	0.91
0.29	525(560)	540	0.60	0.69

*Values shown in brackets are maximum times obtained from fig. 4-6

W_{max} = Maximum concentration of W_2

$k_1 = 6 \times 10^{-6}$, $k_2 = 0.26$, $k_3 = 2 \times 10^{-5}$. $k_{t_1} = 0.05$ and $k_{t_2} = 5 \times 10^{-5}$ dm^{3}mol^{-1}s^{-1}

$[WCl_6] = 2.9 \times 10^{-3}$ mol.dm^{-3}

TABLE 5 - 4 COMPARISON OF THE COMPUTED DATA WITH EXPERIMENTAL RESULTS WHEN W_2 IS REMOVED BY REACTION (5.5)

$[CP]_o$ mol.dm^{-3}	t_{max} minutes (experiment)	t_{max} minutes (computed)	W_{max} x10^3 mol.dm^{-3} (experiment)	W_{max} x10^3 mol.dm^{-3} (computed)
1.17	155(155)*	160	1.91	1.91
0.88	200(200)	210	1.72	1.82
0.59	280(290)	320	1.45	1.65
0.41	450(400)	480	0.94	1.44
0.29	525(560)	700	0.75	1.17

*Values shown in brackets are maximum times obtained from fig. 4-6

W_{max} = Maximum concentration of W_2

$k_1 = 6 \times 10^{-6}$, $k_2 = 0.26$, $k_3 = 2 \times 10^{-5}$, $k_{t_1} = o$ and $k_{t_2} = 5 \times 10^{-5}$ dm^{3}mol^{-1}s^{-1}

$[WCl_6] = 2.9 \times 10^{-3}$ mol.dm^{-3}

TABLE 5 -5 CORRELATION BETWEEN THE COMPUTED AND EXPERIMENTAL RESULTS WHEN W_2 IS REMOVED BY REACTION (5.4).

$[CP]_o$ mol.dm^{-3}	t_{max} minutes (experiment)	t_{max} minutes (computed)	$W_{max} x 10^3$ mol.dm^{-3} (experiment)	$W_{max} x 10^3$ mol.dm^{-3} (computed)
1.17	155 (155)*	140	1.83	1.83
0.88	200 (200)	190	1.65	1.65
0.59	280 (290)	270	1.39	1.37
0.41	450 (400)	390	0.90	1.09
0.29	525 (560)	540	0.72	0.84

*Values shown in brackets are maximum times obtained from fig. 4-6.

W_{max} = Maximum concentration of W_2

$k_1 = 6 \times 10^{-6}$, $k_2 = 0.26$, $k_3 = 2 \times 10^{-5}$, $k_{t_1} = 0.05$ and $k_{t_2} = 0$ dm^{3}mol^{-1}s^{-1}

$[WCl_6] = 2.9 \times 10^{-3}$ mol.dm^{-3}

therefore conclude that the principal reaction for the removal of W_2 is

$$W_2 + W_2 \xrightarrow{k_{t_1}} W_x$$

on this basis, the rate of decay of W_2 shows a zero order dependence with respect to the initial concentration of cyclopentene, $\left[CP\right]_o$, but a second order dependence with respect to the maximum concentration of W_2 which itself depends on $\left[CP\right]_o$.

The computer program, shown in appendix 2, was also used to simulate other experiments for various concentrations of tungsten hexachloride using the same values of the rate constants. The correlation between the computed and experimental data, shown in table 5-6, supports the kinetic model proposed for the system.

5.1.2 - EFFECT OF CYCLOPENTENE CONCENTRATION ON λ_{max} :

The spectral studies were carried out over a range of cyclopentene concentrations, both above and below the ring opening polymerisation equilibrium concentration of monomer at 25°C.$^{(42)}$ It was shown that the values of λ_{max}, for all the species produced during the reaction between WCl_6 and cyclopentene were independent of the concentration of monomer, as also were the shapes of the spectra produced at various stages of the reaction. Furthermore cyclopentene, when reacting with tungsten hexachloride, was able to produce a metathesis active species at concentrations below the equilibrium monomer concentration for polymerisation at 25°C, i.e. $\left[CP\right]_o < \left[CP\right]_e$, indicating that the species W_2 might be formed by

TABLE 5 - 6 CORRELATION BETWEEN COMPUTED AND EXPERIMENTAL RESULTS USING EQUATIONS (5.8) AND (5.9).

$[WCl_6] \times 10^3$ mol.dm^{-3}	t_{max} minutes (experiment)	t_{max} minutes (computed)	$W_{max} \times 10^3$ mol.dm^{-3} (experiment)	$W_{max} \times 10^3$ mol.dm^{-3} (computed)
3.8	175(170)*	190	1.73	1.73
3.2	230(200)	220	1.30	1.39
2.8	185(225)	250	1.10	1.16
2.1	300(300)	320	0.52	0.77

*Values shown in brackets are maximum times obtained from fig. 4-11.

W_{max} = Maximum concentration of W_2

$k_1 = 6 \times 10^{-6}$, $k_2 = 0.26$, $k_3 = 2 \times 10^{-5}$, $k_{t_1} = 0.05$ and $k_{t_2} = 5 \times 10^{-5} dm^3 mol^{-1} s^{-1}$

$[CP] = 0.67$ mol.dm^{-3}

a reaction that does not involve cleavage of the ring.

5.2 POLYMERISATION STUDIES :

The monometallic initiation of cyclopentene polymerisation shows kinetic behaviour as complex as the bimetallic catalyst especially in the case of polymerisations carried out in toluene where the system becomes heterogeneous on the slow appearance of an oily precipitate and hence more complex kinetically.

5.2.1 POLYMERISATION OF CHLOROBENZENE SOLUTIONS OF CYCLOPENTENE INITIATED BY TUNGSTEN HEXACHLORIDE :

The kinetic studies of the monometallic initiation of the ring-opening polymerisation of cyclopentene in chlorobenzene indicated that the initial rate of polymerisation shows first order dependences on the monomer and the catalyst concentrations. Therefore :

$$\text{Initial rate} = k_p \left[CP\right]_o \left[WCl_6\right]_o$$

The kinetic analysis of the maximum rate of polymerisation, Rp_{max}, on the other hand was not as simple. The maximum rate was obviously dependent on the initial concentration of the reactants, cyclopentene and WCl_6, but the kinetics were so complex that predictions were impossible, principally because the concentration of the active centres when the polymerisation rate was a maximum, W_{max}, was unknown. However, obvious plots could be made for :

(i) the maximum polymerisation rate against the initial monomer concentration (fig. 5-1)

and

(ii) the maximum polymerisation rate against the initial concentration of the catalyst (fig. 5-2)

Fig. 5-1. Dependence of the maximum rate of polymerisation of chlorobenzene solutions of cyclopentene on ($[CP]_o - [CP]_e$)

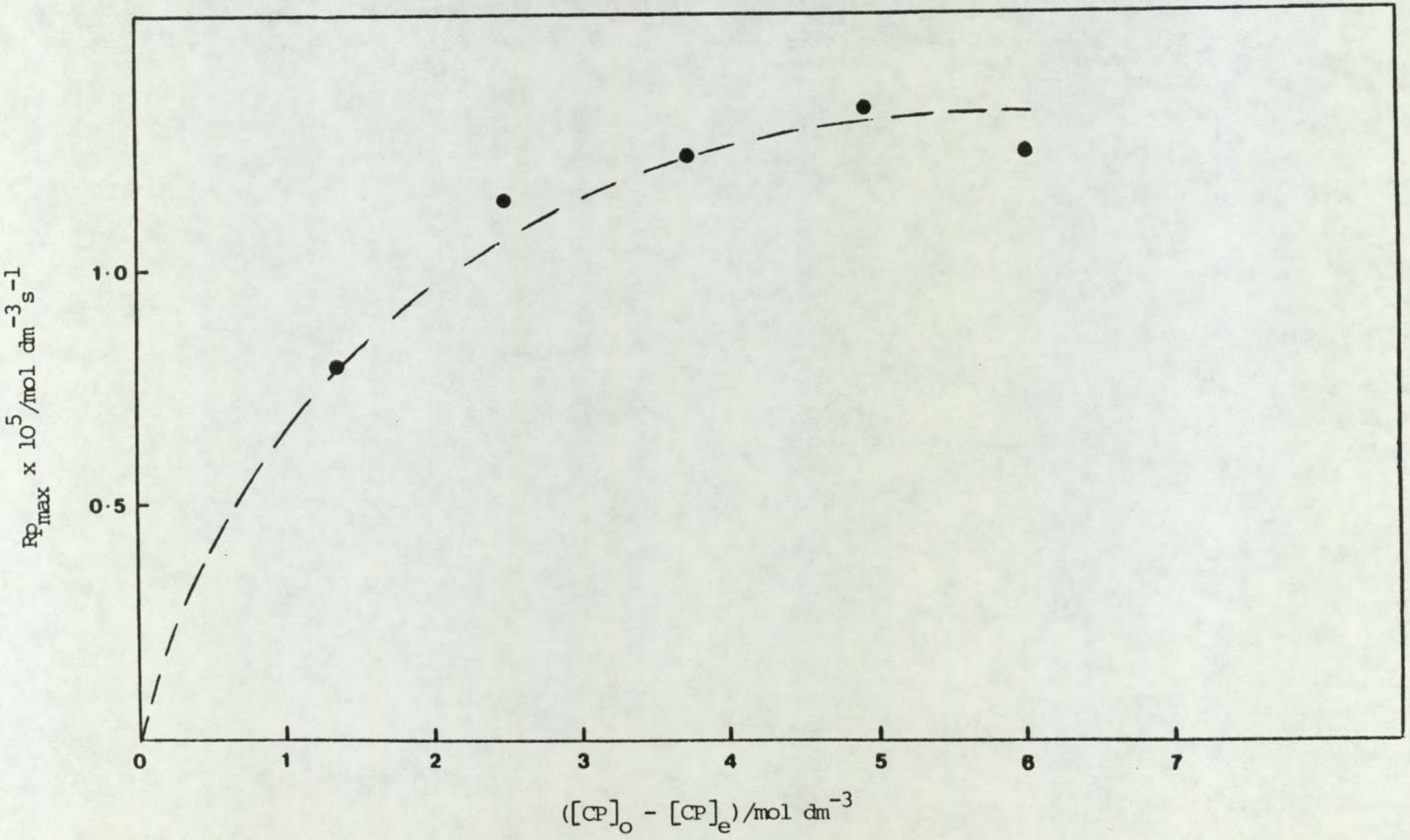
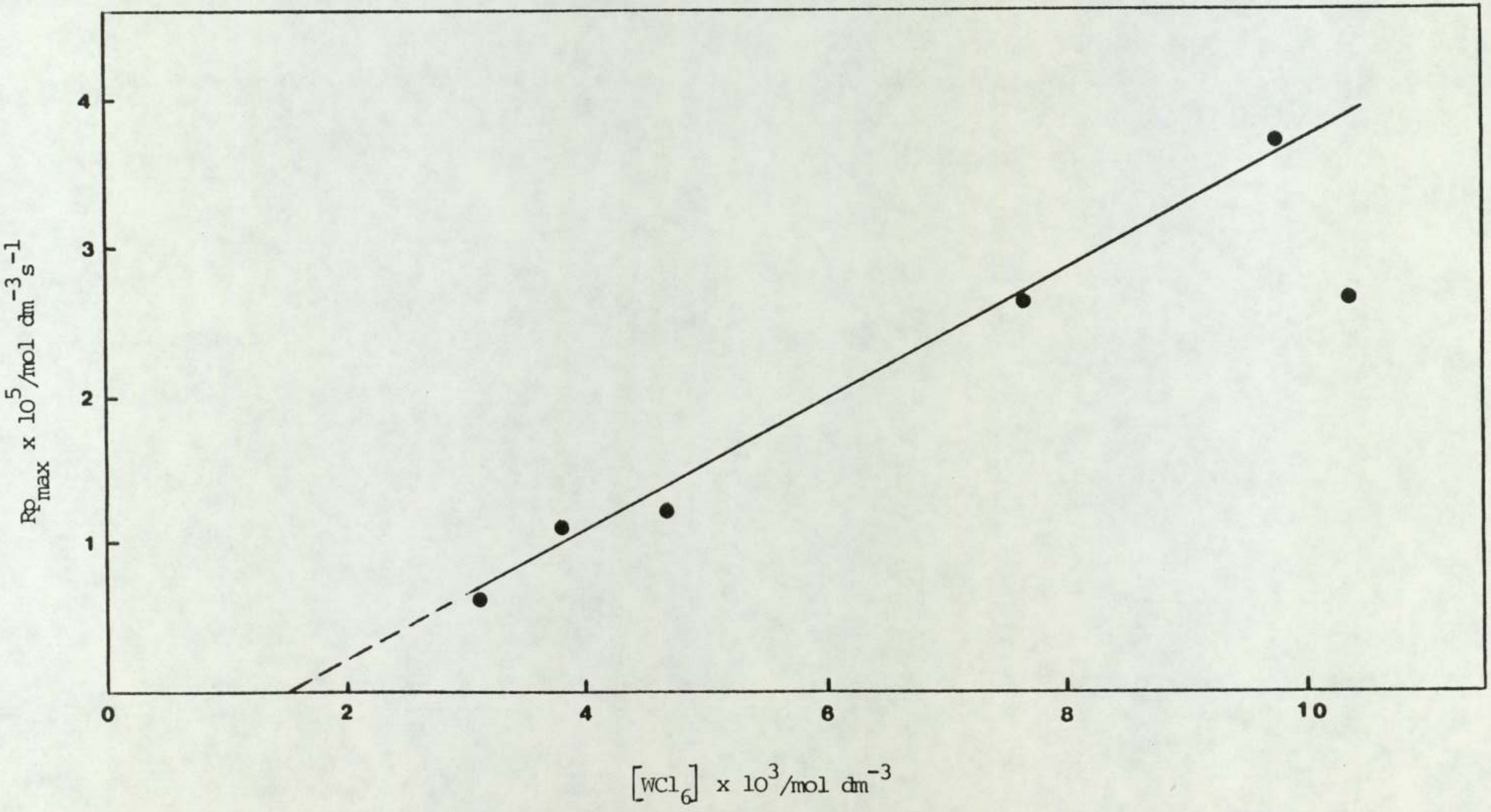


Fig. 5-2. Dependence of the maximum rate of polymerisation of chlorobenzene solutions of cyclopentene on the initial concentration of WCl_6.



By comparing fig. 5-1 with fig. 4-5, which shows the dependence of the maximum concentration of W_2 on the initial concentration of cyclopentene, it could be suggested that fig. 5-1 is of the same form as fig. 4-5 but extending over a larger range of concentrations of monomer. The concentration of the active centre at the maximum polymerisation rate, W_{max}, is dependent on the initial concentration of cyclopentene; however it is apparent that there is a limit for such dependence, beyond which the concentration of the active species is independent of the monomer concentration.

Fig. 5-2 shows a linear dependence of the maximum rate of polymerisation on the initial concentration of tungsten hexachloride. Extrapolation of the line, however intersects the concentration axis at 1.5×10^{-3} mol dm^{-3}. This could be due to the presence of impurities which could not be removed from the solvent or the monomer.

5.2.1.1 COMPUTER AIDED STUDIES :

The cyclopentene polymerisation curves discussed in chapter 3 suggest that the concentration of the active species goes through a maximum after a given reaction time. This can be explained if a series of reactions involving the tungsten compound takes place in the system. If relevant, the ultraviolet/visible spectroscopic studies could be considered as experimental evidence in support of such a proposal and a similar kinetic scheme could be adopted. However, using the same values of the rate constants in this kinetic scheme the computed results for the dependence of t_{max} on the concentrations of the monomer and the catalyst did not show similarities with those obtained experimentally, as shown in table 5-7.

TABLE 5 - 7 COMPARISON OF THE COMPUTED DATA WITH EXPERIMENTAL RESULTS FOR POLYMERISATION STUDIES USING EQUATIONS (5.8) AND (5.9).

$\frac{[CP]_o}{mol.dm^{-3}}$	$\frac{[WCl_6]_o \times 10^3}{mol.dm^{-3}}$	$\frac{t_{max}}{minutes}$ (experiment)	$\frac{t_{max}}{minutes}$ (computed)
2.35	4.7	140	50
3.50	4.7	120	35
4.70	4.7	100	25
5.90	4.7	50	20
7.00	4.7	30	15
4.7	10.4	30	15
4.7	9.7	80	15
4.7	7.8	70	15
4.7	3.8	100	30
4.7	3.1	50	35

$k_1 = 6 \times 10^{-6}$, $k_2 = 0.26$, $k_3 = 2 \times 10^{-5}$, $k_{t_1} = 0.05$ and $k_{t_1} = 5 \times 10^{-5} dm^3 mol^{-1} s^{-1}$

Although there was not any correlation between the experimentally observed and computed values of t_{max}, the shapes of the computed curves indicated that the kinetic model derived from the spectroscopic studies could be used to simulate the polymerisation system if different values of the rate constants were used. Therefore an experiment was selected ($[CP]_o$ = 4.7 mol.dm^{-3} and $[WCl_6]_o$ = 4.7 x 10^{-3} mol.dm^{-3}) and the appropriate rate constants were adjusted so that the shape of the curve and the value obtained for t_{max} were similar to those obtained experimentally. It was found that the only rate constant that had to be changed was k_2. This rate constant is for the reaction $W_2 + W_1^* \xrightarrow{k_2} 2\,W_2$. This could be due to a decrease in the number of effective collisions caused by the presence of a polymeric chain in the active species W_2.

When the adjusted value of k_2 (0.05 dm^{3}mol.$^{-1}$ s^{-1}) was applied to other experimental conditions reasonable correlation was obtained between the experimental and computed values of t_{max}, as shown in table 5-8.

The corresponding values of W_{max}, obtained from the computer program may now be used as an alternative method to examine the applicability of the kinetic model derived from the spectroscopic studies to the polymerisation system. If the kinetic scheme is applicable to the ring opening polymerisation of cyclopentene then the plot of maximum rate, Rp_{max}, against $[W_{max}]$ ($[CP]_o$ - $[CP]_e$) should be a straight line for a simple propagation reaction

$$(W_2)_n + CP \longrightarrow (W_2)_{n+1}$$

As can be seen from fig. 5-3, the maximum rate of polymerisation

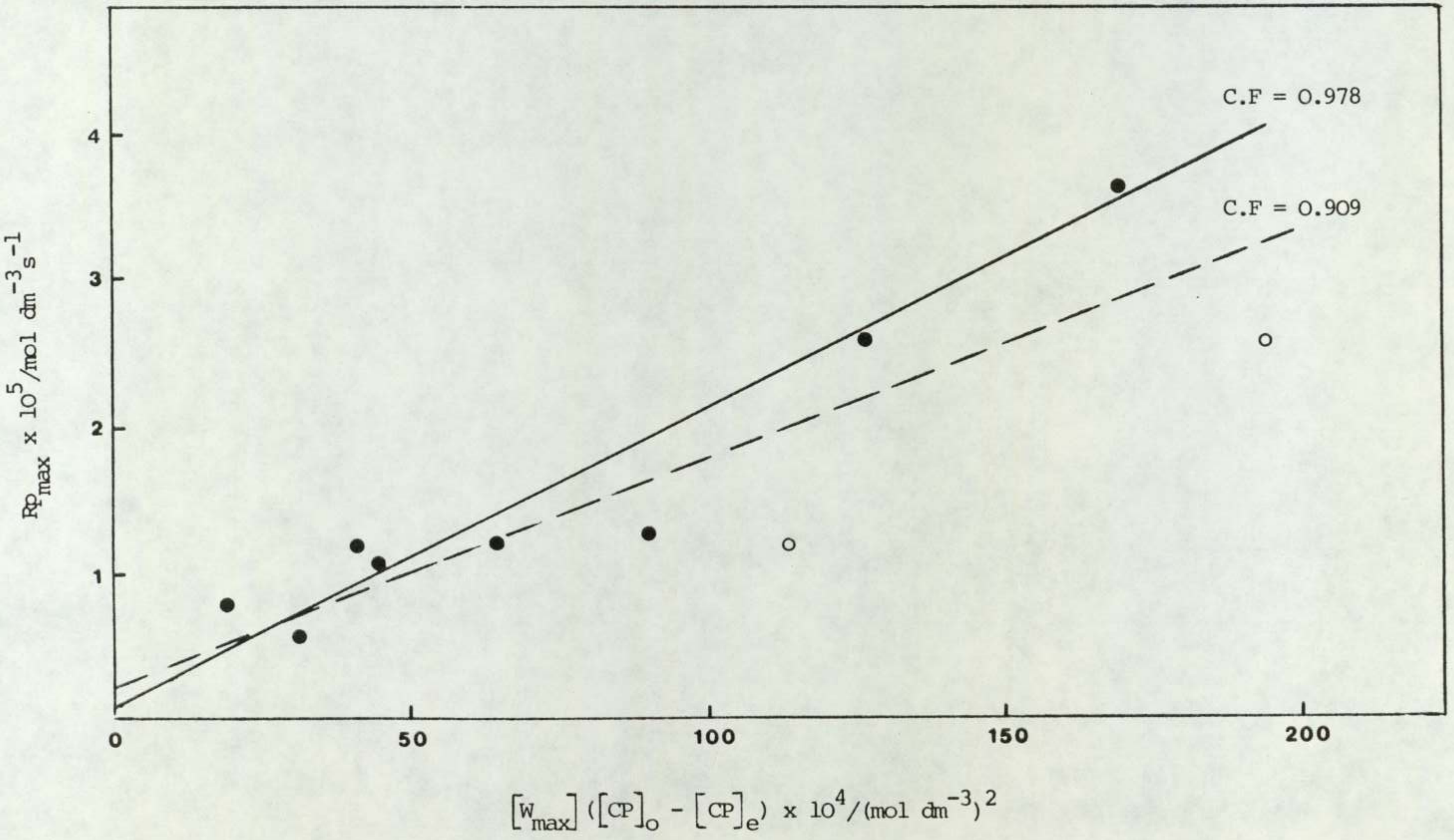
TABLE 5 - 8 CORRELATION BETWEEN THE COMPUTED AND EXPERIMENTAL RESULTS FOR POLYMERISATION STUDIES WHEN $k_2 = 0.05$ $dm^3 mol^{-1} s^{-1}$

$[CP]_o$ mol.dm^{-3}	$[WCl_6]_o \times 10^3$ mol.dm^{-3}	t_{max} minutes (experiment)	t_{max} minutes (computed)
2.35	4.7	140	160
3.50	4.7	120	110
4.70	4.7	100	85
5.90	4.7	50	70
7.00	4.7	30	60
4.7	10.4	30	45
4.7	9.7	80	50
4.7	7.8	70	60
4.7	3.8	100	100
4.7	3.1	50	110

$k_1 = 6 \times 10^{-6}$, $k_2 = 0.05$, $k_3 = 2 \times 10^{-5}$

$k_{t_1} = 0.05$ and $k_{t_2} = 5 \times 10^{-5}$ $dm^3 mol^{-1} s^{-1}$

Fig. 5-3. Dependence of the maximum rate of polymerisation of chlorobenzene solutions of cyclopentene on the product of $\left[W_{max}\right]\left(\left[CP\right]_o - \left[CP\right]_e\right)$.



shows a reasonably linear dependence on the product of $[W_{max}]([CP]_o - [CP]_e)$. The dotted line takes into account all the experimental points giving a correlation factor of 0.909, whereas the continuous line ignores the points which have been marked differently,(O), and gives a correlation factor of 0.978. The extrapolation of the continuous line is also close to the origin, as would be expected.

The correlation between the experimental and computed results indicates that the same kinetic scheme which was derived for the uv/visible spectroscopic studies can be applied to the polymerisation system. Significantly the computed plot of W_{max} against $[CP]_o$, shown in fig. 5-4, shows remarkable similarity with fig. 5-1 indicating that the monomer concentration has indeed a limiting effect on the maximum concentration of active species.

Fig. 5-5 shows the computed plot of W_{max} against the initial concentration of tungsten hexachloride. As can be seen from the plot, a linear dependence is shown between W_{max} and the range of the catalyst concentrations employed experimentally; the extrapolation of this linear dependence cut the concentration axis at 1.6×10^{-3} mol.dm^{-3} which corresponds well with that obtained experimentally from fig. 5-2 (1.5×10^{-3} mol.dm^{-3}). That the line in fig. 5-2 does not extrapolate to the origin may not therefore be due to the presence of impurities as suggested earlier but may be a feature of kinetics of the system.

Fig. 5-4. Dependence of computed W_{max} on the initial concentration of cyclopentene

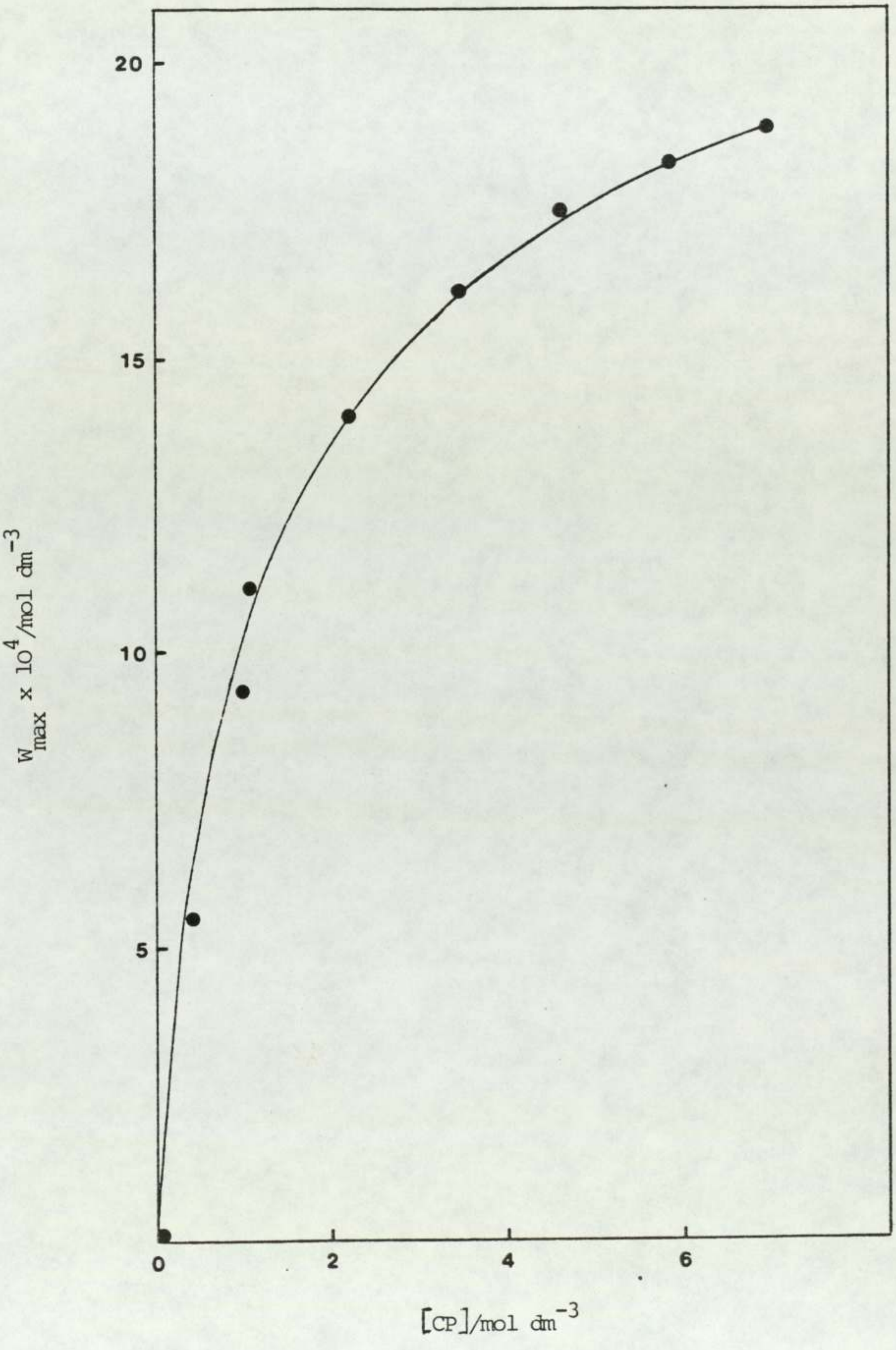
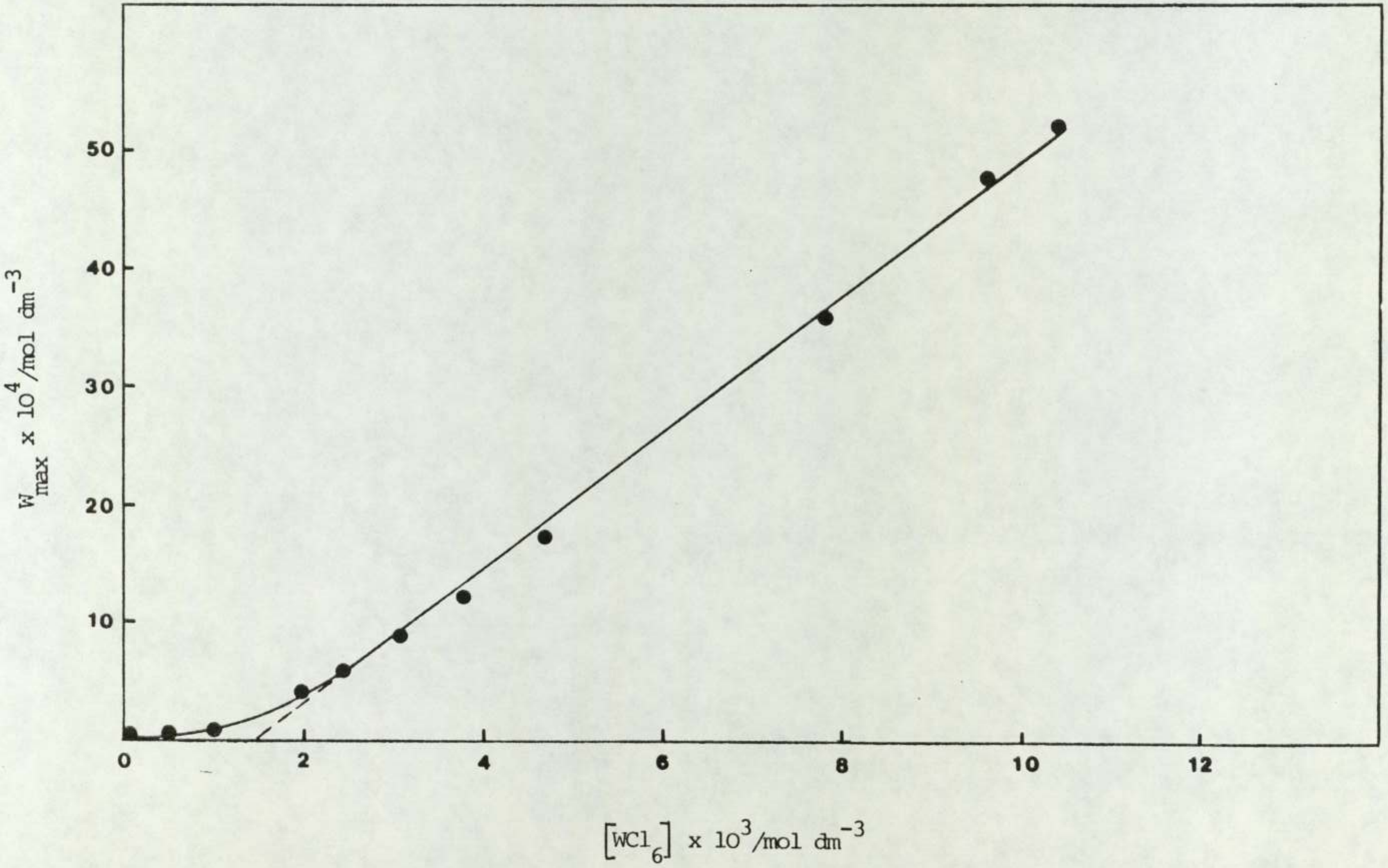


Fig. 5-5. Dependence of computed W_{max} on the initial concentration of tungsten hexachloride



The metathesis polymerisation studies of monometallic initiation of chlorobenzene solutions of cyclopentene indicated that an increase in the catalyst concentration increases the conversion of monomer to polymer for a given reaction time, as shown in table 3-1. This might be due to an increase in the concentration of active species. In contrast, an increase in the monomer concentration decreases the conversion of monomer (table 3-2). It appears that the average concentration of active species over the reaction time is significantly reduced by an increase in cyclopentene concentration. In other words, an increase in the monomer concentration may result in faster formation but also decay of the active intermediate leading to an increase in the initial polymerisation rate but a decrease in the % conversion of monomer at a given reaction time, due to a faster rate of disappearance of the active species.

Based on the equations (5.8) and (5.9) a computer program was written (see appendix 3) to show the effects of cyclopentene and tungsten hexachloride concentrations on the % conversion of cyclopentene to polypentenamer in order to examine whether the computed results would correspond with the experimentally observed % conversions. Using the same rate constants as in the preceeding polymerisation studies, a set of experimental conditions was selected ($\left[CP\right] = 4.7$ mol. dm^{-3} and $\left[WCl_6\right] = 4.7 \times 10^{-3}$ mol.dm^{-3}) and the new rate constant (k_p) was adjusted so that the computed value for % conversion after a given time could show similarity with that obtained experimentally. The value of k_p (8.2×10^{-3} dm^{3}mol^{-1}s^{-1}) was then used for simulating other experimental conditions. It can be seen from the data summarised in table 5-9 that there is a

TABLE 5 - 9 COMPARISON OF COMPUTED % CONVERSIONS WITH THOSE OBTAINED EXPERIMENTALLY FOR VARIOUS CONCENTRATIONS OF MONOMER AND CATALYST.

$[CP]_o$ mol.dm^{-3}	$[WCl_6]_o \times 10^3$ mol.dm^{-3}	% Conversion (experiment)	% Conversion (computed)
2.35	4.7	3.1	3.00
3.50	4.7	2.7	2.62
4.70	4.7	1.9	2.00
5.90	4.7	1.3	1.50
7.00	4.7	1.0	1.16
4.7	10.4	3.7	4.09
4.7	9.7	4.9	3.90
4.7	7.8	3.5	3.30
4.7	3.8	1.7	1.52
4.7	3.1	1.1	1.13

Reaction time = 180 minutes

$k_1 = 6 \times 10^{-6}$, $k_2 = 0.05$, $k_3 = 2 \times 10^{-5}$, $k_{t_1} = 0.05$, $k_{t_2} = 5 \times 10^{-5}$ and $k_p = 8.2 \times 10^{-3}$ dm^{3}mol.$^{-1}$s^{-1}

reasonable similarity between the computed and experimental results. More importantly, the % conversion of monomer after a given reaction time (180 minutes) is predicted to decrease with increasing monomer concentration. The observation, however, indicates that in the initial stages of the reaction the % conversion increases as the monomer concentration is increased but decreases at later stages of the reaction.

5.2.2 POLYMERISATION OF TOLUENE SOLUTIONS OF CYCLOPENTENE INITIATED BY TUNGSTEN HEXACHLORIDE :

The polymerisation studies of cyclopentene indicate that solvent has a crucial effect on the nature of the system. In contrast to chlorobenzene solutions of cyclopentene, the reaction of tungsten hexachloride with cyclopentene in toluene is accompanied by the slow appearance of an oily precipitate which turns the system to a heterogeneous state. This precipitate is adsorbed on the walls of the reaction vessel, but whether a chemical bond exists between the precipitate and any hydroxy groups on the glass remains unanswered.

However, the colour changes indicate that there is again a series of reactions between tungsten hexachloride and cyclopentene before the appearance of the precipitate. These could be summarised as :

$$WCl_6 + CP \xrightarrow{\text{very fast}} W_1$$

$$W_1 + CP \overset{K}{\rightleftharpoons} W_1^*$$

$$W_1 + CP \longrightarrow \text{precipitate}$$

If the oily precipitate, even in the absence of oxygen, is the principal source of catalytic activity in the metathesis polymerisation of cyclopentene one would expect the rate of polymerisation to increase as the surface area of the precipitate on the glass walls is increased. Furthermore, if the precipitate is the source of activity, the polymerisation should remain a living system if termination is bimolecular because this would presumably be prevented in this case.

The kinetic results of the polymerisation of toluene solutions of cyclopentene show that the initial rate of polymerisation, when the system is still homogeneous, reaches a maximum as the concentration of tungsten hexachloride is increased. This could be due to the occurrence of two competitive reactions; one producing the active centre and the other removing the species from the system having equal rates at the maximum point. The destructive effect is negligible for low catalyst concentrations but predominates at high concentrations and leads to a decrease in the rate of polymerisation.

The dependence of the change in the oxidation state of the tungsten atom upon the W:CP molar ratio, studied by McGourty(122), could be considered as an alternative explanation for such a kinetic behaviour. Studies on the changes in the oxidation state of the tungsten atom in a system consisting of cyclopentene, tungsten hexachloride and toluene showed that there was a limiting value to the mean oxidation state of tungsten depending on the W:CP molar ratio. At constant concentration of WCl_6 a mean oxidation state of 4.5 was observed when the W:CP molar ratio was 1:1000, whereas at 1:2000 a limiting value of 4.0 was obtained. Based on these results, the increase in the rate of polymerisation to a maximum value could be due to the change in the oxidation state of tungsten to its most effective value, perhaps IV, at W:CP molar ratios of 1:2000, beyond which the dilution effect causes a decrease in the polymerisation rate.

5.2.3 POLYMERISATION OF CYCLOPENTENE INITIATED BY WCl_6/O_2 :

The rate of polymerisation of cyclopentene initiated by tungsten hexachloride alone is very low indicating that the species responsible for polymerisation is either of low activity or present in very low concentrations. Molecular oxygen can however increase the rate of the ring opening polymerisation of cyclopentene to that of a very active bimetallic catalyst. On addition of oxygen to the chlorobenzene homogeneous system only a slight increase in the activity of the catalyst was observed, whereas introduction of oxygen to the toluene heterogeneous system, when an oily precipitate is formed, led to a very rapid polymerisation to very high conversions.

Further investigations showed that the oily precipitate was the source of activity in the toluene heterogeneous system. Therefore :

$$\text{Precipitate} + O_2 \longrightarrow W^*$$

$$W^* + n\text{CP} \longrightarrow \text{polymer}$$

The ultraviolet/visible spectroscopic data of chlorobenzene solutions of cyclopentene showed that oxygen, when introduced into the system, reacts rapidly with the intermediate species W_2 so that approximately 90% of W_2 is removed within 30 seconds of the addition of oxygen (see figs. 4-13 and 4-14). Therefore :

$$W_2 + O_2 \longrightarrow W^*$$

$$W^* + nCP \longrightarrow \text{polymer}$$

On these bases, the difference in the catalyst activity on the addition of oxygen to the chlorobenzene and toluene solutions could be due to :

(i) the low concentrations of W_2 in chlorobenzene solutions of cyclopentene due to the removal of W_2 by a bimolecular reaction before the addition of oxygen. Such a reaction cannot take place in the toluene heterogeneous system so the catalyst remains dormant.

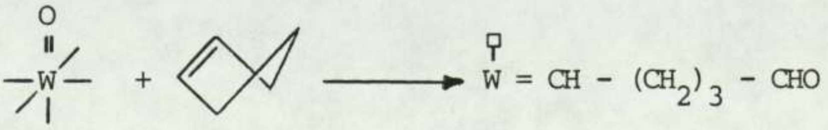
(ii) the presence of a bimolecular termination reaction of species W^* in the chlorobenzene solutions of cyclopentene. The overall effect of oxygen on the chlorobenzene homogeneous system will be negligible and this could account for the failure of attempts to determine calorimetrically the rate of polymerisation of chlorobenzene solutions of cyclopentene. On the other hand, in the toluene heterogeneous system, the oily precipitate remains insoluble on the addition of oxygen hence the activity of the catalyst is maintained leading to production of high molecular weight polymers.

Therefore molecular oxygen can only have a very effective cocatalyst activity if the system is heterogeneous where the source of activity before addition of oxygen remains dormant and the active species W^* insoluble.

An important feature of the polymerisation studies in toluene is the formation of a metathesis active oily precipitate on addition of cyclohexene to the tungsten hexachloride solution indicating that the oily precipitate is formed by a mechanistic route other than cleavage of the ring. On this basis one can suggest that the oily precipitate formed in the toluene system has a chemical structure similar to W_2 species formed in chlorobenzene homogeneous system. Furthermore both the oily precipitate in toluene and the species W_2 in chlorobenzene were found to be the principal source of activity on the addition of oxygen to the system.

5.2.4 POLYMERISATION OF CYCLOPENTENE INITIATED BY WCl_6/EtOH :

The species formed from the reaction of tungsten hexachloride and ethanol, i.e. WCl_5OEt, shows very low metathesis activity in the absence of a cocatalyst. Comparing the results with those obtained for WCl_6/O_2 catalyst system one can conclude that the bonds formed by the reaction of the oily precipitate or species W_2 with oxygen might not be similar in nature to the bond formed from the reaction between the tungsten hexachloride solution and ethanol. If this is the case the following mechanism might be operating for WCl_6/O_2 catalyst system :



$$\overset{O}{W} = CH - (CH_2)_3 - CHO$$

where the nature of the ligands is unknown.

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 CONCLUSIONS:

The studies on monometallic initiation of ring opening polymerisation of toluene or chlorobenzene solutions of cyclopentene indicated the occurrence of a series of reactions between tungsten hexachloride and cyclopentene.

The ultraviolet/visible spectroscopic studies of chlorobenzene solutions of cyclopentene, which supported the existence of more than one species in the system, provided an insight into the formation and destruction of active species. Based on this technique and by use of computer simulation the following equations were suggested to represent the kinetic behaviour of the reactions:

$$-\frac{d\left[W_1\right]}{dt} = k_1\left[CP\right]\left[W_1\right] + k_2\left[W_1\right]\left[W_2\right]\left[CP\right] + k_3\left[W_1\right]$$

$$\frac{d\left[W_2\right]}{dt} = k_1\left[CP\right]\left[W_1\right] + k_2\left[W_1\right]\left[W_2\right]\left[CP\right] - k_{t_1}\left[W_2\right]^2 - k_{t_2}\left[W_2\right]\left[CP\right]$$

According to these equations the species W_1 can assume a more important kinetic role when complexed with cyclopentene. The kinetic scheme also predicts that only a fraction of W_1 species could produce the metathesis active species W_2.

An important feature of ultraviolet/visible spectroscopic studies is the existence of a step in the system equivalent to termination. The species W_2 is believed to be removed from the system by the following reactions:

$$W_2 + W_2 \xrightarrow{k_{t_1}} W_x$$

$$W_2 + CP \xrightarrow{k_{t_2}} W_y$$

The bimolecular termination, however, is the predominant reaction for the removal of the species W_2 producing W_x which is not an air-sensitive species.

Significantly these equations could simulate the kinetic behaviour of the polymerisation of chlorobenzene solutions of cyclopentene. The correlation between the computed and experimental results suggested that the kinetic scheme derived from ultraviolet/visible spectroscopic studies could also be applied to the polymerisation system.

The polymerisation of toluene solutions of cyclopentene displayed a more complex kinetic behaviour than chlorobenzene solutions due to the slow appearance of an oily precipitate on addition of cyclopentene to a tungsten hexachloride solution. This oily precipitate could react with oxygen to produce a very active species for metathesis polymerisation of cyclopentene.

The source of activity on addition of oxygen to the polymerisation system of chlorobenzene solutions of cyclopentene was the species W_2 which due to the bimolecular termination was present in low concentrations. Therefore the WCl_6/O_2 system in chlorobenzene showed a catalytic activity as low as WCl_6 itself.

The polymerisation of n-butyl vinyl ether initiated by the metathesis active species W_2/O_2 indicate that this species might be cationic in nature.

6.2 SUGGESTIONS FOR FURTHER WORK:

Although the kinetic scheme suggested in this project enjoys the support of all experimental evidence, the following experiments could lead to a better understanding of the subject:

(i) The ultraviolet/visible spectroscopic studies of chlorobenzene solutions of cyclopentene indicate that on addition of tungsten hexachloride to cyclopentene a metathesis active species W_2 is formed. That the concentration of this species goes through a maximum with time can provide an insight into the role of cocatalyst. Addition of $AliBu_3$ and/or oxygen to the system at various stages of the reaction might provide valuable information on the function of the cocatalyst and its effect on t_{max}.

(ii) The uv/visible studies indicate that W_x which is the product of the termination reaction of W_2 is not an air-sensitive species. This could therefore provide an opportunity to study the structure of W_x species by conventional techniques. This could in turn give a better understanding of the structure of W_2 and hence W_1.

(iii) The species W_x is not active towards the ring opening polymerisation of cyclopentene. Incorporation of a cocatalyst such as $AlBr_3$ or $EtAlCl_2$ might however produce an active species for metathesis reaction. This in turn can illustrate the role of cocatalyst and hence provide improvements for polymerisation systems.

(iv) Toluene solutions of cyclopentene when incorporated with tungsten hexachloride produce an oily precipitate which could then react with oxygen to produce a very active metathesis catalyst. Analysis of this oily precipitate in the absence and also in the presence of oxygen might provide valuable information about the structure of the precipitate and also the function of oxygen.

(v) Preliminary studies on the polymerisation of n-butyl vinyl ether indicate that the metathesis active species, formed by reaction of cyclopentene with tungsten hexachloride, is cationic in nature. Occurrence of block copolymerisation of cyclopentene and n-butyl vinyl ether could provide further experimental evidence about the ionic nature of the species. This could also offer an attractive route for copolymerisation of cyclic alkenes with cyclic esters or cyclic ethers.

APPENDIX I

ABBREVIATIONS

a	Axial
Abs_{iso}	Absorbance at isobestic point
Abs_{max}	Maximum absorbance
C.F	Correlation factor
CP	Cyclopentene
D.C	Dielectric constant
e	Equatorial
L_n	Ligands
M	Transition metal
$[M]$	Monomer concentration
$[M]_e$	Equilibrium monomer concentration
P_n	Polymer chain
P.S	Proton sponge
X	Halogen

APPENDIX II

COMPUTER PROGRAM FOR DEPENDENCE OF W_2 ON TIME AND DETERMINATION OF t_{max}

```
5  REM  COMPUTED DEPENDENCE OF W2 ON TIME,DETERMINATION OF T(MAX)
10  HGR
20  HPLOT 10,10 TO 210,10 TO 210,130 TO 10,130 TO 10,10
30  HPLOT 110,10 TO 110,130
40  DIM W1(100),W2(100),W3(100),C1(100),C2(100),C3(100)
50  HOME
60  PRINT "PROGRAM TO PLOT FUNCTION"
70  VTAB (24)
80  INPUT "NO OF GRAPHS TO BE PLOTTED =";N
90  INPUT "K1=";K1
100  PR# 2
110  PRINT "K1=";K1
120  PR# 0
130 K1 = 60 * K1
140  INPUT "K2=";K2
150  PR# 2
160  PRINT "K2=";K2
170  PR# 0
180 K2 = K2 * 60
190  INPUT "K3=";K3
200  PR# 2
210  PRINT "K3 =";K3
220  PR# 0
230 K3 = K3 * 60
240  INPUT "KT(1)=";KT(1)
250  PR# 2
260  PRINT "KT(1)=";KT(1)
270 KT(1) = KT(1) * 60
280  PR# 0
290  INPUT "KT(2)=";KT(2)
300  PR# 2
310  PRINT "KT(2)=";KT(2)
320  PR# 0
330 KT(2) = KT(2) * 60
```

```
340  INPUT "(WCL6)=";W
350  PR# 2
360  PRINT "(WCL6)=";W
370  PR# 0
380  INPUT "TIME INTERVAL(MIN)=";P
390 S = P / 50
400  INPUT "REACTION TIME(MIN)=";TM
410  INPUT "A=";A
420  FOR I = 1 TO N
430  INPUT "(CP)=";M(I)
440  PR# 2
450  PRINT "(CP)=";M(I)
460  PR# 0
470  NEXT I
480 B = TM / P
490  FOR I = 1 TO N
500 W1(0) = W
510 W2(0) = 0
520 W3(0) = 0
530  FOR J = 0 TO B - 1
540  GOSUB 860
550 T = (J + 1) * P
560  GOSUB 680
570  NEXT J
580  GOSUB 730
590 J = 0
600  NEXT I
610  PRINT "DO YOU WANT TO REPEAT WITH THE SAME RATE CONSTANTS? Y/N"
620  INPUT A$
630  IF A$ = "Y" GOTO 340
640  PRINT "DO YOU WANT TO REPEAT WITH DIFFERENT RATE CONSTANTS? Y/N"
650  INPUT A$
660  IF A$ = "Y" GOTO 90
```

```
670  END
680  REM  "PLOT POINT"
690 D = (T * 200 / TM) + 10
700 E = 130 - (W2(J + 1) * 120 / A)
710  HPLOT D,E
720  RETURN
730 J = 0
740 WM = W2(J)
750  IF W2(J + 1) < WM GOTO 800
760 WM = W2(J + 1)
770 J = J + 1
780  IF J = B GOTO 800
790  GOTO 750
800 TI = J * F
810  PR# 2
820  PRINT "T(MAX)=";TI
830  PRINT "W(MAX)="; INT (WM * 1E6 + .5) / 1E6
840  PR# 0
850  RETURN
860 C1(0) = W1(J)
870 C2(0) = W2(J)
880 C3(0) = W3(J)
890  FOR L = 1 TO 50
900 C1(L) = C1(L - 1) - (K1 * M(I) * C1(L - 1) * S) - (K2 * C1(L - 1) * M(
     I) * C2(L - 1) * S) - (K3 * S * C1(L - 1))
910 C2(L) = C2(L - 1) + (K1 * M(I) * C1(L - 1) * S) + (K2 * C2(L - 1) * C1
     (L - 1) * M(I) * S) - (KT(1) * C2(L - 1) ↑ 2 * S) - (KT(2) * C2(L - 1
     ) * S * M(I))
920 W2(J + 1) = C2(L)
930 W1(J + 1) = C1(L)
940  NEXT L
950  RETURN
```

APPENDIX III

COMPUTER PROGRAM FOR DETERMINATION OF % CONVERSION

```
10  REM " COMPUTED % CONVERSION VS TIME PLOT"
20  HGR
30  HPLOT 10,10 TO 210,10 TO 210,130 TO 10,130 TO 10,10
40  HPLOT 110,10 TO 110,130
50  DIM W1( 100 ),W2( 100 ),W3( 100 ),C1( 100 ),C2( 100 ),C3( 100 ),CM( 100 )
60  HOME
70  PRINT "PROGRAM TO PLOT FUNCTION"
80  VTAB ( 24 )
90  INPUT "NO OF GRAPHS TO BE PLOTTED =";N
100  INPUT "K1=";K1
110  PR# 2
120  PRINT "K1=";K1
130  PR# 0
140 K1 = 60 * K1
150  INPUT "K2=";K2
160  PR# 2
170  PRINT "K2=";K2
180  PR# 0
190 K2 = K2 * 60
200  INPUT "K3=";K3
210  PR# 2
220  PRINT "K3 =";K3
230  PR# 0
240 K3 = K3 * 60
250  INPUT "KT( 1 )=";KT( 1 )
260  PR# 2
270  PRINT "KT( 1 )=";KT( 1 )
280 KT( 1 ) = KT( 1 ) * 60
290  PR# 0
```

```
300  INPUT "KT(2)=";KT(2)
310  PR# 2
320  PRINT "KT(2)=";KT(2)
330  PR# 0
340 KT(2) = KT(2) * 60
350  INPUT "KP=";KP
360  PR# 2
370  PRINT "KP=";KP
380  PR# 0
390 KP = KP * 60
400  INPUT "(WCL6)=";W
410  PR# 2
420  PRINT "(WCL6)=";W
430  PR# 0
440  INPUT "TIME INTERVAL(MIN)=";P
450 S = P / 50
460  INPUT "REACTION TIME(MIN)=";TM
470  INPUT "RANGE OF %CONVERSION =0 TO ";A
480  FOR I = 1 TO N
490  INPUT "(CP)=";M(I)
500  PR# 2
510  PRINT "(CP)=";M(I)
520  PR# 0
530  NEXT I
540 B = TM / P
550  FOR I = 1 TO N
560 W1(0) = W
570 W2(0) = 0
580 CM(0) = M(I)
590  FOR J = 0 TO B - 1
600  GOSUB 940
610 T = (J + 1) * P
```

```
620  GOSUB 740
630  NEXT J
640  GOSUB 790
650 J = 0
660  NEXT I
670  PRINT "DO YOU WANT TO REPEAT WITH THE SAME RATE CONSTANTS? Y/N"
680  INPUT A$
690  IF A$ = "Y" GOTO 400
700  PRINT "DO YOU WANT TO REPEAT WITH DIFFERENT RATE CONSTANTS? Y/N"
710  INPUT A$
720  IF A$ = "Y" GOTO 100
730  END
740  REM  "PLOT POINT"
750 D = (T * 200 / TM) + 10
760 E = 130 - (120 * (1 - (CM(J + 1) / M(I))) * 100 / A)
770  HPLOT D,E
780  RETURN
790 J = 0
800 WM = W2(J)
810  IF W2(J + 1) < WM GOTO 860
820 WM = W2(J + 1)
830 J = J + 1
840  IF J = B GOTO 860
850  GOTO 810
860 TI = J * P
870  PR# 2
880  PRINT "T(MAX)=";TI
890  PRINT "W(MAX)="; INT (WM * 1E6 + .5) / 1E6
900 F = (M(I) - CM(B)) * 100 / M(I)
910  PRINT "% CONVERSION="; INT (F * 100 + .5) / 100
920  PR# 0
930  RETURN
```

```
940 C1(0) = W1(J)
950 C2(0) = W2(J)
960 C3(0) = CM(J)
970  FOR L = 1 TO 50
980 C1(L) = C1(L - 1) - (K1 * M(T) * C1(L - 1) * S) - (K2 * C1(L - 1) * M(
    I) * C2(L - 1) * S) - (K3 * S * C1(L - 1))
990 C2(L) = C2(L - 1) + (K1 * M(I) * C1(L - 1) * S) + (K2 * C2(L - 1) * C1
    (L - 1) * M(T) * S) - (KT(1) * C2(L - 1) ↑ 2 * S) - (KT(2) * C2(L - 1
    ) * S * M(I))
1000 C3(L) = C3(L - 1) - (KP * C2(L) * S)
1010 W2(J + 1) = C2(L)
1020 W1(J + 1) = C1(L)
1030 CM(J + 1) = C3(L)
1040  NEXT L
1050  RETURN
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