W$(O\text{-}2,6\text{-}C_6H_3X_2)_2Cl_4$/Bu$_4$Sn as metathesis catalyst of 1-alkenes

C. van Schalkwyk, H.C.M. Vosloo [*], J.A.K. du Plessis

SASOL Centre for Separation Technology, Potchefstroomse Universiteit vir Christelike Hoër Onderwys, Potchefstroom 2520, South Africa

Abstract

Tungsten compounds with aryloxo ligands, i.e., W(O-2,6-C$_6$H$_3$X$_2$)$_2$Cl$_4$ (X = Cl, Ph) and Bu$_4$Sn, were investigated as catalytic systems for the metathesis of 1-alkenes of varying carbon lenghts. The catalytic system was activated at 85°C for 20 min prior to use. Optimum metathesis activity with 1-alkenes was observed at 85°C and a Sn/W molar ratio = 3. The W(O-2,6-C$_6$H$_3$X$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system is very active for the metathesis of 1-alkenes with a carbon chain length of about six to eight and it favours a more polar solvent such as chlorobenzene. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Alkene metathesis; 1-Alkenes; Tungsten(VI) oxaryl derivatives; Solvent polarity

1. Introduction

Over the years, many homogeneous catalytic systems were developed for the metathesis of 1-alkenes. Tungsten(VI) aryloxide complexes of the type W(OAr)$_n$Cl$_{6-n}$ (OAr = phenoxide or substituted phenoxide) in particular are effective alkene metathesis catalysts that could easily be synthesized from WCl$_6$ and phenol derivatives [1–3].

Trans-W(OAr)$_4$Cl$_2$ in combination with EtAlCl$_2$ or Et$_3$Al$_2$Cl$_3$ are active catalytic systems for the metathesis of alkenes [2]. Quignard et al. [1,3] reported that W(OAr)$_2$Cl$_4$ with EtAlCl$_2$ or R$_4$M (R = methyl or butyl; M = Sn or Pb) are also active catalytic systems for the alkene metathesis reaction. Due to the versatil-

ity of the electronic and steric properties of the various aryloxide ligands, it is possible to control the activity and sometimes the stereoselectivity of the metathesis reaction [3,4]. If the electron-withdrawing properties of the aryloxo ligand are increased, an increase in the metathesis activity is observed [4]. Another factor influencing the metathesis reaction is the position of the substituent on the aryloxide ligands. Complexes with substituents on positions 2 and 6 of the aryloxide ligands were found to be the more active catalysts for the metathesis of 1-alkenes [1].

In this study, W(O-2,6-C$_6$H$_3$X$_2$)$_2$Cl$_4$ (X = Cl, Ph) with Bu$_4$Sn were investigated as catalytic system for the metathesis of 1-alkenes with different carbon chain lengths. Various parameters, i.e., Sn/W molar ratio, reaction temperature, solvent, type of aryloxide ligand

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[*] Corresponding author.

and the chain length of the terminal alkenes, were varied.

2. Experimental

2.1. Reagents

2.1.1. Tungsten compounds

The $W(O\text{-}2,6\text{-}C_6H_3X_2)_2Cl_4$ (X = Cl, Ph) catalyst was synthesized using WCl_6 and the appropriate phenol. The WCl_6 (Merck) was purified by sublimation and stored under nitrogen [4–6]. The phenolic compounds, 2,6-dichlorophenol and 2,6-diphenylphenol (Aldrich), were used as obtained from the supplier.

2.1.2. Cocatalyst

The Bu_4Sn (Aldrich) was used as obtained from the supplier.

2.1.3. Solvents

Chlorobenzene (Merck), benzene (Holpro), carbon tetrachloride (Saarchem), octane and hexane (Merck) were distilled from P_2O_5 and stored under a nitrogen atmosphere.

2.1.4. Substrates

The alkenes, 1-pentene, 1-hexene, 1-heptene, 1-octene and 1-decene (Aldrich), were degassed and stored under a nitrogen atmosphere.

2.2. Synthesis of $W(O\text{-}2,6\text{-}C_6H_3X_2)_2Cl_4$

$W(O\text{-}2,6\text{-}C_6H_3X_2)_2Cl_4$ (X = Cl, Ph) was synthesized using the method of Quignard et al. [5,6]:

$$WCl_6 + HO\text{-}2,6\text{-}C_6H_3X_2 \xrightarrow[\text{reflux}]{CCl_4}$$

$$W(O\text{-}2,6\text{-}C_6H_3X_2)_2Cl_4 + 2HCl$$
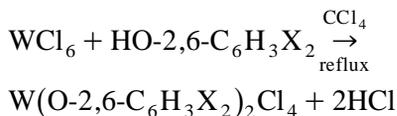
A solution of $HO\text{-}2,6\text{-}C_6H_3X_2$ (5×10^{-3} mol) in CCl_4 (20 cm^3) was added to a solution of WCl_6 (2.5×10^{-3} mol) in CCl_4 (20 cm^3). The mixture was stirred under reflux for 4 h. The complex was filtered and dried under nitro-

gen. The $W(O\text{-}2,6\text{-}C_6H_3Cl_2)_2Cl_4$ complex was recrystallized with ethanol and the $W(O\text{-}2,6\text{-}C_6H_3Ph_2)_2Cl_4$ complex was washed with hexane. Yields of 79% black microcrystals and 80% dark-green microcrystals were obtained for the Cl and Ph derivatives, respectively. Both complexes are air-stable, but because they are known to slowly decompose and deactivate with continued exposure to air (detected by a colour change to grey), the complexes were stored under nitrogen [5].

2.3. Catalytic reactions

All catalytic reactions were carried out under nitrogen using standard techniques, and all additions of liquids were made using gas-tight syringes.

The tungsten precatalyst (5×10^{-5} mol) was placed in a minireactor filled with nitrogen. This was followed by the addition of the solvent, chlorobenzene (2.5 cm^3), and Bu_4Sn (1.5×10^{-4} mol). The catalyst mixture was then heated to 85°C. After 20 min, the alkene (2.5×10^{-3} mol) was added to the mixture and the reaction mixture was stirred until equilibrium was reached. An excess amount (ca. 0.5 cm^3) of water was added to terminate the catalytic reaction followed by 1,2-dichlorobenzene (internal standard for GC (gas chromatography) analyses).

These reaction conditions were used throughout, unless otherwise indicated.

2.4. Analysis

Reaction mixtures were analysed with a Carlo Erba HRGC 5300 gas chromatograph equipped with an Alltech SE-30 capillary column (30 m × 0.32 mm × 0.25 μm) and flame ionization detector (FID). The following instrumental conditions were used: inlet temperature of 300 °C, injection volume of 0.2 μl, oven programmed from 70–250°C at 10°C min^{-1}, N_2 carrier gas with a flow rate of 2 cm^3 min^{-1} at 20°C and FID temperature of 350°C.

The internal standard method was used to calculate the % mol 1-alkene and metathesis products formed.

3. Results and discussion

3.1. Reaction products

The W(O-2,6-$C_6H_3X_2$)$_2$Cl$_4$/Bu$_4$Sn (X = Ph, Cl) catalytic systems show a high activity and selectivity towards the metathesis of terminal and internal alkenes. Gas chromatographic analyses of the reaction mixtures indicated the formation of primary and secondary metathesis products. All the secondary metathesis products have a carbon chain length longer than the substrate and shorter than the high molecular mass primary metathesis product [4]

$$2CH_3(CH_2)_nCH{=}CH_2 \rightleftharpoons CH_2{=}CH_2$$
$$+ CH_3(CH_2)_nCH{=}CH(CH_2)_nCH_3$$
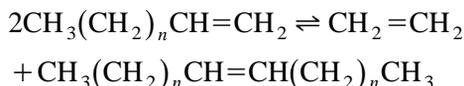
with n = 2, 3, 4, 5 or 7.

An unknown product, not related to any metathesis product, was also observed in small yields ($< 5\%$). Although no isomerisation was observed during the metathesis reaction, the appearance of the secondary metathesis products is proof that isomerisation also took place [4].

3.2. Influence of cocatalyst / W molar ratio

Various cocatalysts are known to activate the W(O-2,6-$C_6H_3X_2$)$_2$Cl$_4$ precatalyst [1,3]. Bu$_4$Sn was the cocatalyst of choice because it was economical, safe to handle and gave better reproducibility of results in previous studies [4]. The results of the reactions of different alkenes with the W(O-2,6-$C_6H_3Cl_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system at different Sn/W molar ratios are given in Fig. 1.

In all cases, an increase in primary metathesis product yield was observed with an increase in the Sn/W molar ratio. A maximum yield of primary metathesis products is obtained at Sn/W molar ratios of 2 to 5 and the yields generally decrease at higher Sn/W molar ratios. A similar trend was observed for the W(O-2,6-$C_6H_3Ph_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system, although the decrease in yields at higher molar ratios is more gradual (Fig. 2).

3.3. Influence of reaction temperature

Quignard et al. [1] and Vosloo et al. [4] indicated that a reaction temperature of 85°C is essential for optimum activity of the tungsten aryloxide precatalysts. The effect of the reaction

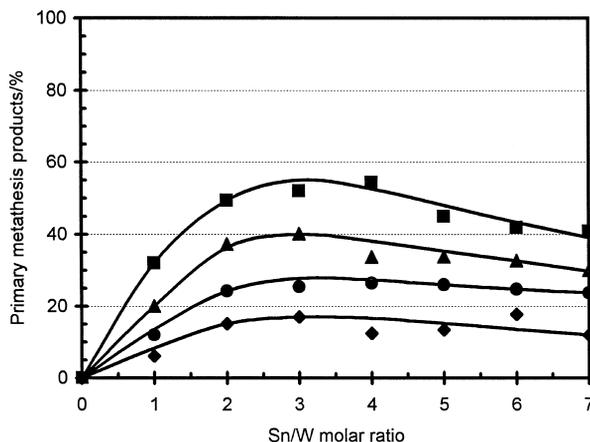Fig. 1. Influence of the Sn/W molar ratio on the metathesis activity of the W(O-2,6-$C_6H_3Cl_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system (temperature = 85°C; time = 2 h). (●) 1-Decene; (♦) 1-Octene; (■) 1-Hexene; (▲) 1-Pentene.
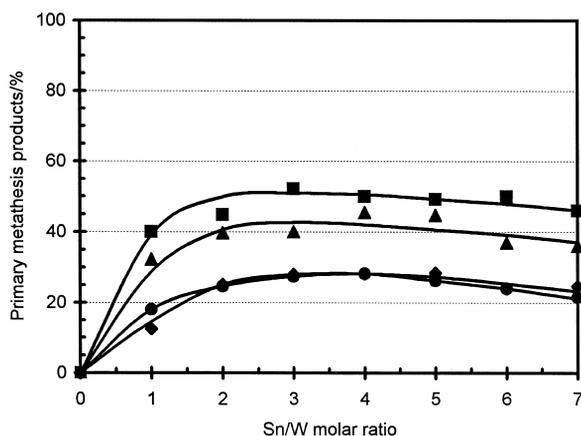
Fig. 2. Influence of the Sn/W molar ratio on the metathesis activity of the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Bu_4Sn$ catalytic system (temperature = 85°C; time = 2 h). (●) 1-Decene; (♦) 1-Octene; (■) 1-Hexene; (▲) 1-Pentene.

temperature on the catalytic activity of the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Bu_4Sn$ catalytic system towards the different alkenes was also investigated. The results are shown in Fig. 3.

A very low yield of primary metathesis products was observed in the presence of the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Bu_4Sn$ catalytic system from 0 to 40°C for all the alkenes. A drastic increase in primary metathesis products is observed from 60 to 80°C. A maximum yield of primary metathesis products is obtained at 85°C and the yields decrease at higher temperatures. 1-Hexene gives the highest yield of primary metathesis products at 85°C and 1-octene the lowest.

3.4. Influence of solvents

Different solvents (1-octene, hexane, octane, benzene and chlorobenzene) were investigated to optimise the reaction conditions for the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Bu_4Sn$ catalytic system. The influence of solvents on the metathesis of 1-octene was investigated and the results are shown in Fig. 4.

In both hexane and octane, low yields of primary (ca. 8% in each case) and secondary (20 and 13%, respectively) metathesis products are observed. Similar low yields are obtained if 1-octene is used as solvent and substrate. In benzene, very little primary metathesis products
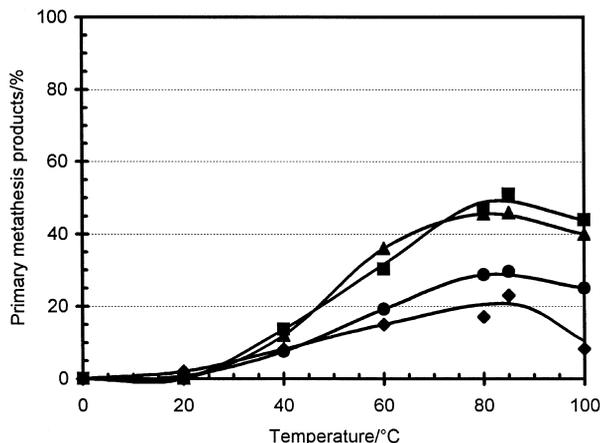

Fig. 3. Influence of the reaction temperature on the primary metathesis products of the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Bu_4Sn$ catalytic system (Sn/W molar ratio = 3; time = 2 h). (●) 1-Decene; (♦) 1-Octene; (■) 1-Hexene; (▲) 1-Pentene.
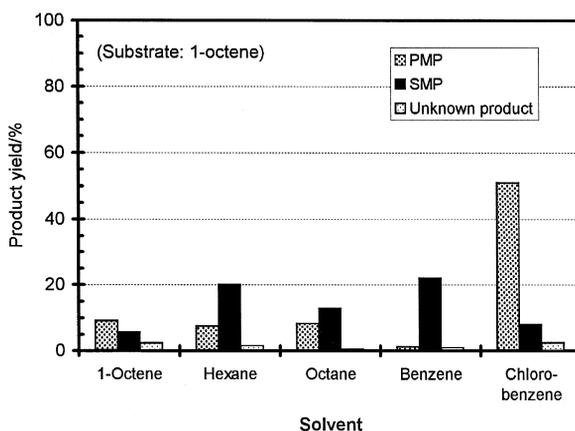
Fig. 4. Influence of various solvents on the products formed in the presence of the $W(O-2,6-C_6H_3Ph_2)_2Cl_4/Bu_4Sn$ catalytic system (Sn/W molar ratio = 3; time = 2 h).

is observed, while 22% secondary metathesis products are formed. Only in chlorobenzene equilibrium is reached with 50% primary metathesis products being formed.

From these results it seems as if polarity plays a major role in determining the activity and selectivity of the catalytic system. To determine if solvent polarity do indeed play a role, mixtures of varying composition of chlorobenzene and hexane were used as solvent (Fig. 5).

With an increase in hexane content of the solvent mixture a gradual increase in secondary metathesis products is observed from 8 to 20%. Initially, the primary metathesis products show a

steady decrease until the solvent mixture contains 50% of hexane. This is followed by a dramatic decrease if the amount of hexane content is increased further. The primary metathesis reaction is almost terminated at hexane contents greater than 70%. This strengthens the observation that the catalytic system is more active in a polar medium.

3.5. Influence of 1-alkenes with different carbon chain lengths

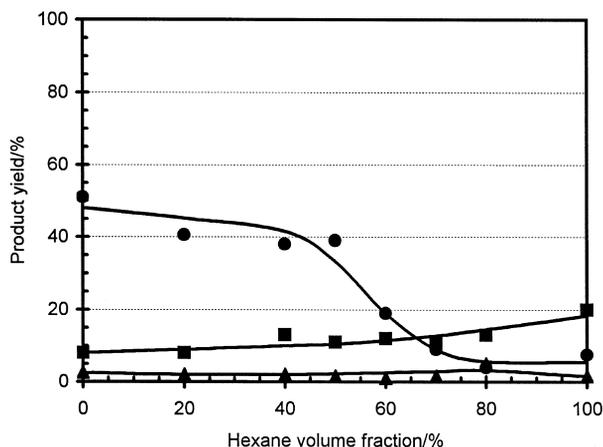If the influence of the carbon chain length of the alkene on the metathesis activity of the

Fig. 5. Influence of hexane/chlorobenzene solvent mixtures on the metathesis activity of the $W(O-2,6-C_6H_3Ph_2)_2Cl_4$ catalytic system with 1-hexene (temperature = 85°C; Sn/W molar ratio = 3; time = 2 h). (■) PMP; (♦) SMP; (●) unknown products.
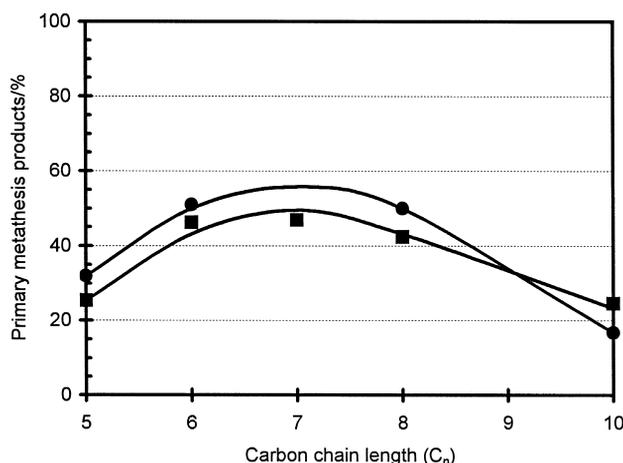
Fig. 6. Influence of different carbon chain length alkenes on the metathesis activity of the W(O-2,6-$C_6H_3X_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system (Sn/W molar ratio = 3; time = 2 h). ($\blacksquare$) X = Cl; ($\blacklozenge$) X = Ph.

W(O-2,6-$C_6H_3X_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system (X = Ph, Cl) is investigated, the results shown in Fig. 6 are obtained.

It is evident from these results that both the catalytic systems are the most active for alkenes with carbon chain lengths ranging from C_6 to C_8. In this region, the W(O-2,6-C_6H_3Cl$_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system gives a higher yield of primary metathesis products than the phenyl-substituted derivative.

4. Conclusions

It is clear that the W(O-2,6-$C_6H_3X_2$)$_2$Cl$_4$ complexes (X = Ph, Cl), in the presence of Bu$_4$Sn, have a high activity for the metathesis of the C_6 to C_8 1-alkenes and a higher selectivity for primary metathesis products. The optimum conditions for the W(O-2,6-$C_6H_3X_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system (X = Ph, Cl) can be summarised as follows:

(a) Sn/W molar ratios between 2 and 5;
(b) Reaction temperatures between 60 and 90°C; and
(c) A polar solvent such as chlorobenzene.

The mechanism for metathesis requires a metal carbene as active species [7–11]. The metal carbene for the W(O-2,6-$C_6H_3X_2$)$_2$Cl$_4$/Bu$_4$Sn catalytic system (X = Ph, Cl) can be obtained by the double alkylation of the tungsten atom [3].

Double bond isomerisation was not observed directly but the presence of secondary metathesis products is an indication of double-bond migration taking place [4]. The extent of the secondary metathesis reactions is rather limited and because no isomerisation products are observed, it can be concluded that the formation of the metal carbene is favoured.

It seems as if it is necessary for the catalyst to have an electrophilic metal centre in order to be an active metathesis catalyst.

In addition to its role in forming the metal carbene, the cocatalyst, Bu$_4$Sn, may also play a role to enhance the electrophilic character of the metal centre [12,13]. The increased electrophilic character can be further stabilised by a polar solvent, which may explain the higher metathesis activity observed when a polar solvent is used.

Acknowledgements

tion for Research Development (THRIP Programme) is gratefully acknowledged.

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