

Oligomerization of 1-hexene with bimetallic catalysts based on titanium or zirconium derivatives and organoaluminum compounds

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Abstract

The oligomerization of 1-hexene at 20° C in the presence of various bimetallic systems obtained by reaction of titanium (IV) and zirconium (IV) derivatives with organoaluminum compounds has been studied. The transition metal, the nature of its substituents, and that of those attached to aluminum, strongly affect the catalytic activity. Oligomerization only proceeds with systems which contain Ti or Zr reduced forms. Two series of low molecular weight oligomers are formed, C_{6n} and C_{6n+2}. Each is composed of both saturated and unsaturated hydrocarbon homologues. The large amount of saturated products after hydrolysis shows that aluminum metal alkyls are either involved in the propagation or are very efficient transfer agents.

Introduction

We have reported (1,2) that bimetallic initiators issued from the reaction of tetrabenzylzirconium and triethylaluminum are active for the oligomerization of styrene : dimers are almost selectively obtained. These were identified as the head to tail and tail to tail derivatives and their mechanism of formation was investigated (2).

We have recently examined in the same way the oligomerization of α -olefins in the presence of bimetallic initiators.

Olefin oligomers are of industrial interest and found applications in various fields of chemistry. They can be utilized as plasticizers and as reactive materials in detergent synthesis or, for the α -unsaturated ones, as comonomers in the LLDPE polymerization process. The branched-ones are potential candidates for improving gasoline octane number or as synthetic

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lubricants in replacement of fluids derived from petroleum. For most of these applications, however, well-defined oligomer structures are required or at least preferred. Conventional cationic catalysts (usually AlX_3 , BF_3 or protonic acids ...) are very active for olefin oligomerization but give extensive cracking and isomerization reactions which result in ill-defined oligomer structures (3 - 6).

An alternative route to the cationic process involves the use of Ziegler-like catalysts for which the chain transfer reaction is deliberately enhanced by suitable combinations of transition metal derivatives and organoaluminum compounds. This procedure was mainly applied to ethylene oligomerization (7 - 9), because for higher α -olefins activities were low (10 - 11) and oligomer structures more complex, depending on the two possible modes of monomer addition.

Different bimetallic combinations resulting from the reaction of a series of zirconium and titanium derivatives with various organoaluminum compounds have been examined as potential initiators for 1-hexene oligomerization. The influence of the transition metal, of the nature of its substituents and of the groups fixed on aluminum on both catalytic activity and structure of the reaction products has been investigated.

Results and discussion

Oligomerizations of 1-hexene were performed at 20° C, under vacuum, in glass flasks equipped with PTFE stopcocks. Conversion of monomer and distribution of reactive products with time were followed by sampling the reaction mixture and gas chromatographic analysis.

Among the different organic solvents examined as potential reaction media, methylene dichloride leads, for a given system, to the highest catalytic activity and therefore was used in the whole study.

The absence of catalytic activity of transition metal derivatives and of organoaluminum compounds, when they are used separately, was first controlled in experimental conditions of the oligomerization study. Only AlEtCl_2 reacts with 1-hexene, presumably by a cationic mechanism (6). For the other compounds association between a transition metal derivative and an organoaluminum was necessary to observe 1-hexene consumption.

The catalytic activity of various bimetallic combinations was then investigated further. The influence of the transition metal and of the nature of its substituents was studied in experiments in which oligomerizations were initiated by a series of bimetallic systems obtained by addition of AlEt_2Cl on different zirconium and titanium derivatives. The molar ratio between the two metals $[\text{Al}]/[\text{M}_{\text{et transition}}]$ was kept in the range 12 to 15 since highest catalytic efficiencies were observed for these proportions for the couple $\text{Zr}(\text{OnPr})_4 - \text{AlEt}_2\text{Cl}$ (12). All the combinations examined, except the one based on ZrCl_4 , gave transparent to brown soluble systems. These remained homogeneous in presence of 1-hexene, at least for the first hours of reaction. Initial rates of 1-hexene consumption (within the first hour of reaction) and final conversions are given in table 1. Alkoxide and benzylzirconium derivatives lead to almost complete α -olefin conversions but other transition metal compounds give only limited yields.

Table 1 : Influence of the nature of the transition metal atom and of its substituents on the activity of transition metal derivative - AlEt₂Cl systems in 1-hexene oligomerization

M _t _{tr} X _n Y _{4-n}	[1-hexene] (M)	Reaction time (h)	R _M .10 (mol. h ⁻¹)	Final conversion (%)
Zr(O _n Pr) ₄	1.1	1	23	97
ZrBz ₄	1.0	4	8	98
ZrCl ₄	4.9	6	7	46
ZrCp ₂ Cl ₂	5.0	6	0.0	~1
Ti(O _n Bu) ₄	4.9	6	10	38
Ti(O _i Pr) ₄	4.9	6	3	29
TiCp ₂ Me ₂	5.0	6	0.5	14
TiCp ₂ Cl ₂	5.0	6	0.0	~1

[M_t_{tr}X_nY_{4-n}] = 7.10⁻² mol.l⁻¹ ; [AlEt₂Cl] = 1 mol.l⁻¹ ; Solvent : CH₂Cl₂ ; T = 20° C

In series based on the same transition metal, i.e zirconium or titanium, alkoxides show higher activities zirconium derivatives leading to complete conversions. On the contrary, cyclopentadienyl derivatives ZrCp₂Cl₂ on the one hand, TiCp₂Cl₂ on the other hand give very poorly active systems. ZrCl₄ which is only weakly soluble in CH₂Cl₂, even in presence of AlEt₂Cl in excess, leads also to low mol.wt. 1-hexene oligomers : in similar conditions, TiCl₄ converts 1-hexene to a high mol.wt. polymer. Therefore, if we don't take into account the particular situation of transition metal tetrachlorides, these results tend to show, independently of the nature of the transition metal, a rather similar and strong effect of the nature of the substituents on the activity.

The influence of the nature of the organoaluminum compound on the resulting activity of the catalysts, has been examined in a second set of experiments (see table 2). Different organoaluminum compounds have been added, in constant proportion ([Al]/[Zr]=15), to a solution of Zr(O_nPr)₄ in CH₂Cl₂. Activities of the different combinations with AlEt₂Cl towards 1-hexene oligomerization are collected . AlEt₃ and AlEt₂I lead also to active bimetallic systems, but monomer conversions are incomplete, indicating that the active species initially formed are unstable. Darkening and precipitation of organometallic species in the case of AlEt₃ systems strongly suggest that an important reduction of Zr(O_nPr)₄ takes place : this process might be responsible of the rapid activity loss of the system.

Table 2 : Influence of the nature of organoaluminium compounds on the activity of $Zr(O_nPr)_4 - AlEt_xX_{3-x}$ systems in 1-hexene oligomerization

$AlEt_xX_{3-x}$	[1-hexene] $mol.l^{-1}$	Reaction time (h)	$R_M \cdot 10$ ($mol. h^{-1}$)	Final conversion (%)
$AlEt_3$	2.7	5		16
$AlEt_2Cl$	3.5	2.5	66	98
$AlEt_2Cl^a$	4.9	7	21	55
Et_2AlO_nPr	4.9	29	0	0
$Et_2AlOCOCH_3$	3.2	6	0	0
$AlEtCl_2^b$	3.6	6	n.d	90

$[AlEt_xX_{3-x}] = 1 mol.l^{-1}$; $[Zr(O_nPr)_4] = 7 \cdot 10^{-2} mol.l^{-1}$; Solvent: CH_2Cl_2 ; $T = 20^\circ C$ a) in toluene b) cationic polymerization

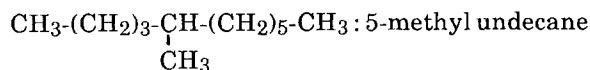
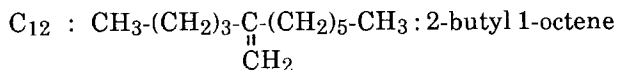
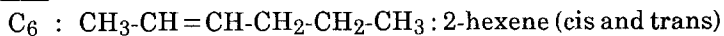
No apparent reduction was observed with Et_2AlO_nPr and $Et_2AlOCOCH_3$ which both lead to inactive bimetallic systems. Absence of reduction of $Zr(O_nPr)_4$ by these two organometallic compounds was confirmed by ESR. In contrast, all the systems leading to conversion of 1-hexene exhibit an ESR signal ($g = 1,975$ to $1,980$) indicating the presence of Zr (III) species in the medium. Attempts to correlate activity and concentration in Zr (III) species were however unsuccessful, making difficult to further confirm a direct contribution of the reduced species to the reaction process.

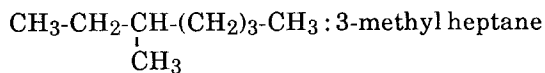
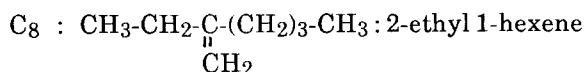
Structure of the reaction products

Identification of the products formed, of their structures and the determination of their proportion have been performed by gas chromatography and 1H and ^{13}C NMR.

Except the $TiCl_4-AlEt_2Cl$ (1 : 15) system which lead to polyhexene (mol.wt. $\sim 10\ 000$ in polystyrene eq.) other bimetallic catalysts lead to compounds of DP_n corresponding to a maximum of two successive hexene insertions : typically two series of compounds C_{6n} and C_{6n+2} , with $n = 1, 2$ are formed. Each series is composed both of alkenes and of the corresponding alkanes. Structures of hydrocarbons formed were characterized by ^{13}C NMR after fractionation. The main products formed are listed below :

C_{6n} series



C_{6n+2} series

C₁₄ : traces

Formation of the C_{6n+2} series involves insertion of monomer into a metal-ethyl bond. This can be explained either by direct hexene insertion into an Al-ethyl bond or by a transfer of ethyl groups to zirconium prior to monomer insertion.

The relative proportions of the various compounds obtained for different bimetallic catalytic systems, at final conversions, are given in tables 3 and 4.

Table 3 : Influence of the nature of transition metal derivative in M_{tr}X_nY_{4-n} - AlEt₂Cl system (1 : 15) on products distribution.

M _{tr} X _n Y _{4-n}	Products distribution* (Σ = 100) (w%) ^f						
	C ₆ (isomers)		C ₈ (addition product)		C ₁₂ (dimers)		C ₁₄
	olef. a	hexane	olef. b	sat. c	olef. d	sat. e	olef. sat
Zr(O _n Pr) ₄	16	25	28	38	2	1	trace
ZrBz ₄	14	25	17	31	7	4	trace
ZrCl ₄	11	35	19	16	10	7	trace
Ti(O _n Bu) ₄	1	5	2	58	trace	5	6 18
Ti(O _i Pr) ₄	trace	trace	2	81	trace	trace	5 19
TiCp ₂ Me ₂	3	2	6	8	80	trace	trace

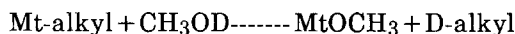
* Determined at final conversions : see table 1 for experimental conditions
a) 2-hexene, b) 2-ethyl 1-hexene, c) 3-methyl heptane, d) 2-butyl 1-octene, e) 5-methyl undecane, f) residual monomer is not considered.

Table 4 : Influence of the nature of the organoaluminum compounds in $Zr(OnPr)_4-AlEt_xX_{3-x}$ systems on products distribution a)

$AlEt_xX_{3-x}$	Products distribution ($\Sigma = 100$) (w%) ^b						
	C_6 (isomers)		C_8 (addition product)		C_{12} (dimers)		C_{14}
	olef.	hexane	olef.	sat.	olef.	sat.	olef. + sat
$AlEt_3$	58	13	6	19	2	1	trace
$AlEt_2Cl$	22	19	20	15	11	9	trace
$AlEt_2I_a$	3	10	12	38	7	19	9
$AlEtCl_2$	Oligomers with ill defined structure						

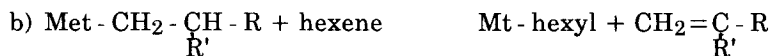
a) Determined at final conversions : see table 2 for experimental conditions and table 3 for product description, b) residual monomer is not considered.

Alkanes result from the methanolysis, at the end of reaction, of Met-alkyl compounds. This was demonstrated by adding CH_3OD at the end of an oligomerization experiment and identification by ^{13}C NMR of the corresponding monodeuterated alkanes.



Molar amounts of alkanes (C_{6n} and C_{6n+2}) liberated during the methanolysis were calculated from GC chromatograms .

Unsaturated hydrocarbon homologues might result from a β -Hydride abstraction through either a spontaneous transfer, generating the corresponding metal hydride a), or from a transfer reaction involving monomer b).



The molar amount of formed alkanes is much higher (up to more than 4 times) than that of Zr or Ti compounds in the catalyst, which shows that Al is the main metal present in the metal alkyl compounds. It cannot be decided yet whether these higher aluminum alkyls are directly involved in the polymer growth or if they result from a very fast transfer (nearly as fast as propagation) to the aluminum derivative.

The rules which prevail for transfer, insertion and elimination and which lead to the observed structures, as well as mechanisms of these reactions, have been examined in more detail in the case of the

oligomerization of 1-hexene in the presence of the catalytic system $Zr(OnPr)_4-AlEt_2Cl$. These results will be reported in a forthcoming paper.

Experimental section

Materials :

1-hexene (JANSSEN, 99%) was distilled and introduced into a glass flask equipped with PTFE stopcocks. It was passed over CaH_2 and sodium mirror and stored in graduated tubes.

Methylene dichloride (SDS, 99%) was distilled, transferred into glass flasks and dried under vacuum over phosphorous anhydride and sodium mirrors.

Triethylaluminum, diethylchloroaluminum, ethyldichloroaluminum (Aldrich) were introduced under N_2 into glass flasks and flash distilled into graduated tubes.

Monopropoxy- and monoacetoxy-diethylaluminum were prepared by controlled addition, at $-50^\circ C$, of dry propanol and dry acetic acid, respectively, into a CH_2Cl_2 solution of $AlEt_3$.

Zirconium and titanium derivatives (Aldrich) were introduced into graduated tubes equipped with a PTFE stopcock, degassed for 24 hours under high vacuum and solubilised in a known volume of CH_2Cl_2 . $ZrCl_4$ was directly introduced in the polymerization vessel and degassed.

Oligomerization :

All experiments have been carried out in glass flasks under vacuum.

Monomer conversions were followed by sampling the reacting media at various reaction times. After deactivation of the catalyst with methanol, the reaction mixtures were analyzed by gas chromatography.

Structural analysis :

Products have been characterized by 1H and ^{13}C NMR on a Bruker AC 250 after fractionation of the reaction mixtures by distillation. ESR measurements have been performed at $-180^\circ C$, on a Varian CSE 109.

References

- 1 - P. Barthelemy, A. Deffieux and P. Sigwalt, *Nouveau J. de Chimie*, **9**, 3, 173 (1985)
- 2 - P. Barthelemy, A. Deffieux and P. Sigwalt, *Nouveau J. de Chimie*, **10**, 1, 33 (1986)
- 3 - C.M. Fontana, *the Chemistry of Cationic Polymerization*, Chapter 5, 205, P.M. Plesch ed. Pergamon Press Oxford (1963)
- 4 - J.P. Kennedy "Cationic Polymerization of Olefins - A critical inventory", 57, 64 Wiley - Interscience (1975)
- 5 - C. Corno, G. Ferraris, A. Priola and S. Cesca, *Macromolecules*, **12**, 3, 404 (1979)
- 6 - T. Higashimura, Y. Miyoshi and H. Hasegawa, *J. Appl. Pol. Sc.*, **27**, 2593 (1982)
- 7 - A.W. Langer, *J. Macromol. Sc. Chem. A4*, 775 (1970)
- 8 - G. Henrici-Olivé and S. Olivé in *Coordination Polymerization*, J.C.W. Chien ed. Academic Press. NY (1955)

- 9 - C.J. Attridge, R. Jackson, S.J. Maddock and D. Thompson, *J. Chem. Soc., Chem. Comm.* 132, (1973)
10 - H. Bestian and K. Klaus, *Angev. Chem.*, **75**, 1058 (1963)
11 - O.S. Vostrikova, A.G. Ibragimov, G.A. Tolstikov, L.M. Zelenova and U.M. Dzhemilev, *Bull. Acad. Sc. USSR*, **29**, 10 part 2, 1638 (1980)
12 - H.Q. Liu, *These de Doctorat, Université P. et M. Curie Paris* (1986)

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