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NOTE

MECHANISTIC STUDIES WITH HOMOGENEOUS ZIEGLER–NATTA CATALYSTS★

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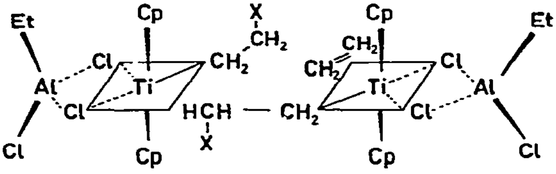
Cossee's theoretical interpretation of Ziegler–Natta polymerization[1] is based on the concept of coordination of the olefin to the transition metal, leading to a destabilization of the metal–carbon bond (metal-growing chain). This coordination was suggested by analogy with stable, isolated (non-catalytic) olefin–metal complexes such as Zeise's salt.

Shilov *et al.*[2,3] reported the alkylation of α-olefins with the system $Cp_2TiMeCl \cdot AlMeCl_2$, accompanied by the reduction $Ti^{IV} \rightarrow Ti^{III}$. Their results can be taken as evidence for the coordination of α-olefins to the transition metal center. Later on, however, the concept of coordination of the monomer to the transition metal has been questioned by Boor[4], who points to the inadequacy of the experimental evidence.

Homogeneous systems of the general formula $Cp_2TiRCl \cdot R'AlCl_2$ ($R,R' =$ alkyl) undergo the reduction[5] $Ti^{IV} \rightarrow Ti^{III}$, involving the opening of the Ti–C bond and elimination of R from the complex[6,7]. In the special case of $R = R' =$ ethyl we observed that the rate of reduction was considerably increased if ethylene is admitted to the system. Taking into account that the reduction is a second order reaction in the monomer-free system[6] as well as in the polymerizing system[8] the following bimolecular formulation was suggested for the reduction step[6,9]:



(I)

A β-hydrogen of an ethyl group ($X = H$: catalyst) or a growing chain ($X = C_nH_{2n+1}$: polymerizing system) occupies the empty coordination site of a second complex unit. The H is transferred to the alkyl group of this unit, which leaves the complex as a saturated molecule: the remaining radical on the right hand side complex is stabilized as an α-olefin which also leaves the complex. Both Ti^{IV} units are reduced to Ti^{III}.

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Two reasons may then be given for the higher reduction rate in the polymerizing system.

(1) *Coordination of the olefin*

In the presence of ethylene the vacancy in the right hand complex may be occupied by a monomer molecule (see formula I). According to Cossee's hypothesis this coordination would provoke a strong destabilization of the vicinal Ti–C bond, and thus favor the concerted reduction process.

To check this we added non-polymerizable olefins to the system $Cp_2TiEtCl/EtAlCl_2$, and determined the reduction rate by magnetic susceptibility measurements*. Fig. 1 shows that this rate is remarkably increased in the series *trans*-2-octene < *cis*-2-octene $\leqslant$ 1-octene which also represents the series of the coordination ability of the three octenes. Thus, the results not only agree with the observations of Shilov *et al.*[2,3] concerning the increased rate of reduction on addition of α-olefins to such systems, but show that other olefins are also active. We consider this as supporting evidence for the general concept of coordination of olefins to a transition metal center prior to reaction.

(2) *Difference in bond energy in* $>CH_2$ *and* $-CH_3$

In the polymerizing system the hydrogen atom to be transferred comes from the β-methylene group of a growing chain, whereas in the catalyst solution it comes from the methyl group of the ethyl ligand of the Ti. The bond dissociation energy for a C–H bond in a $>CH_2$ group is about 3 kcal/mol smaller than for a $-CH_3$, and this difference should favor the reduction step in the polymerizing system. This hypothesis can be tested separately by observing the reduction behavior of the system $Cp_2Ti(n\text{-}C_8H_{17})Cl/EtAlCl_2$, in the absence of ethylene. In this case the n-octyl group is taken as a model for the growing polyethylene chain. (The system is thus represented

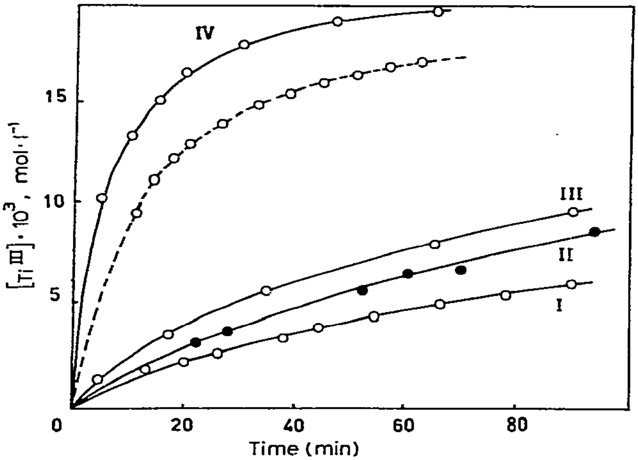

Fig. 1. Reduction $Ti^{IV} \rightarrow Ti^{III}$ in the system $Cp_2TiRCl/EtAlCl_2$. [Ti] $20 \cdot 10^{-3}$ mol/l; Al/Ti 2; *T* 20°; Solvent toluene. —— R = Et; without additives (I); with *trans*-2-octene (II); with *cis*-2-octene (III); with 1-octene (IV); [octene] = $20 \cdot 10^{-3}$ mol/l. --- R = octyl, without additives.

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* For experimental details, see ref. 6.

by formula I with $R = C_6H_{13}$, and eliminating the coordinated ethylene molecule.) The considerably increased reduction rate compared with that in the system $Cp_2TiEtCl/EtAlCl_2$ is shown in Fig. 1.

The reported experiments clearly provide additional evidence for the proposed model of the active species[6,7,10].

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