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# Mechanism of Oligomerization of α-Olefins with Ziegler–Natta Catalysts

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A mechanism for the oligomerization of ethylene with homogeneous titanium–aluminum catalysts is proposed. The mechanism is established by a self-consistent all-valence electron molecular orbital calculation. It is shown that the original catalyst has a trigonal–bipyramidal structure that changes to an octahedral structure only after the monomer is coordinated. The reaction pathways are studied, showing that both the chain propagation and the β-transfer responsible for the α-alkene liberation are favored decisively by the Ti *d*-orbitals. This implies that chain growth can occur without any radical breaking and justifies the low activation energy of the process. Finally these results are related to experimental chemical data such as yields and rate constants and to physical measurements on the catalytic complex.

## INTRODUCTION

Several proposals of the mechanisms of Ziegler–Natta catalysis exist. Among these the now classical paper by Cossee (*1*) is perhaps the most favored. Most works, however, have given more consideration to polymer growth than to the process of the liberation of the products (*2*). Furthermore, these studies have given only "plausibility arguments" or at most crude ligand field theory estimations of the processes. It seems to us that the time for quantum-mechanical studies of the reaction coordinates has arrived. Very few calculations of this type exist, although their results (*3*) definitively seem encouraging.

The problem analyzed here is the homogeneous oligomerization of α-olefins with a titanium–aluminum catalyst complex. The mechanism of Cossee (*1*) can be used for the description of the oligomerization process, as has been discussed by Henrici-Olivé and Olivé (*4*).

In the present paper we approach the mechanism of Ziegler–Natta catalysis by solving self-consistently the quantum equations for the system. We show explicitly the characteristics of the addition of ethylene to the catalyst complex, the nature of the driving force of the chain propagation, and the way the end products are liberated. All these steps are given a clear description in terms of the molecular orbitals involved. The crucial role played by the titanium *d*-orbitals in these processes is confirmed (*1, 3*). On the other hand some meaningful discrepancies with previous assumptions are reported and discussed.

## METHOD

The calculations were carried out using the modified CNDO program of Armstrong *et al.* (*5*) with the original parametrization (*3*). At every step of the different reaction

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coordinates analyzed (i.e., chain growth, $\beta$-transfer, catalyst regeneration, etc.), the program solves (in the adiabatic approximation) the electrostatic system of all nuclei and valence electrons. Empirical parameters are used to account for inner-shell effects and to simplify interelectronic multicenter integrals (*6*). The calculation yields the total and molecular orbital energies, the charge distributions, bond orders, and valencies of the system as they change during the process. These results will be reported and used for the interpretation of the mechanism in the following sections.

Although we were particularly interested in the catalyst developed in our Institution (*7*), which is formed by the reaction between triethyl-aluminum and the complex

$$\mathrm{Ti\ (O\phi\text{-}}p\text{-}\mathrm{Me)_3O\text{-}}n\text{-}\mathrm{Bu} \qquad (1)$$

and which oligomerizes ethylene into butene-1 and hexene-1, the enormous expenditure of computer time forced us to substitute the larger alkyls except those involved in the polymerization itself. Thus OMe's were used instead of the real Ti substituents of (1). This is a mixed blessing, though, as our results are then equally valid for the system of Ref. (*7*) and other similar systems. Accordingly in the next section we present some experimental data for this and related Ziegler–Natta processes.

## EXPERIMENTAL DATA

The process of Ref. (*7*) is carried out in batch (discontinuous) conditions at a pressure of 12 Kg and a temperature of 40°C. Ethylene is converted almost completely (82.56%) with the following yields: butene, 73.01%; butane, 0.86%; and hexene, 26.13%. The alkenes are 100% $\alpha$-olefins. The solvent used is heptane.

The original complexes are mixed prior to ethylene addition. An excess of triethylaluminum [more than twice over complex (1)] is necessary for optimal catalytic complex formation. This may be partially due to the fact that the presence of water destroys the catalyst. $H_2O$ may be partially disposed of by the excess $AlEt_3$. During the formation of the catalyst complex, ethane is liberated.

This process is depicted in Fig. 1. The formation of a 2:1 Al/Ti complex with a reduced $Ti^{III}$ atom has been confirmed experimentally by the EPR spectrum of our catalyst (*8*). The classical 11-line spectrum (*9*) showing that a paramagnetic

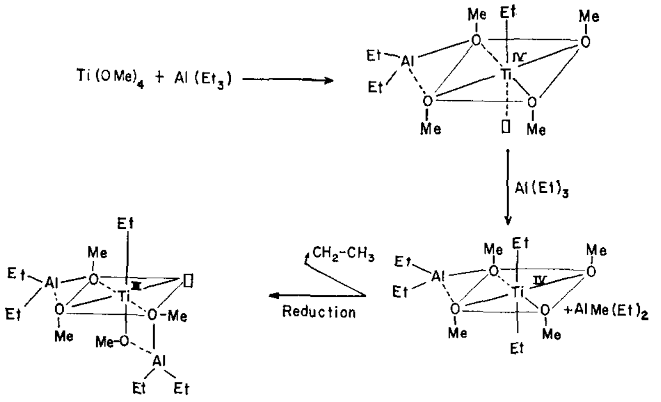


Fig. 1. Formation of initial catalyst complex. Notice that although this complex (the last structure above) is depicted as an octahedral structure, our calculations show that the most stable complex is a trigonal-bipyramidal one, with the Ti–Et bond at an intermediate position between two octahedral sites.

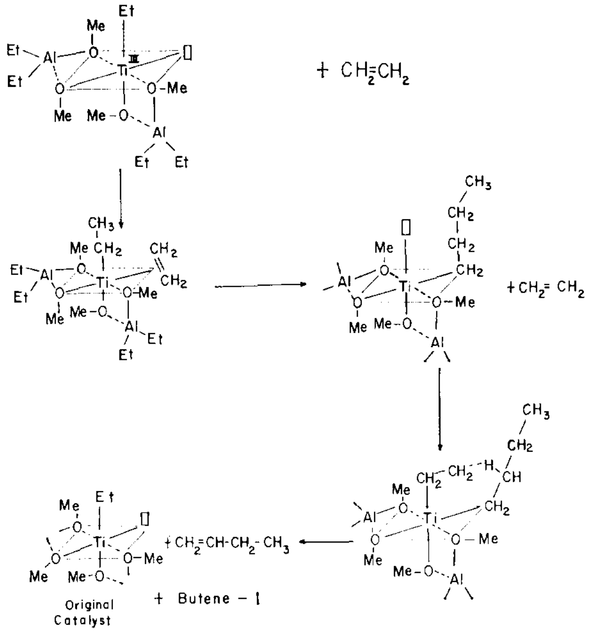


FIG. 2. Mechanism of oligomerization showing the crucial stages: coordination of ethylene to the initial catalyst complex, chain propagation and β-transfer to another coordinated ethylene. This last step implies α-butene liberation and the regeneration of the initial catalyst complex.

Ti atom is related to two equivalent Al atoms was obtained. Thus our study started with the calculation of the initial catalytic complex (final step in Fig. 1) and continued with the addition of ethylene and later the chain growth and chain termination; all these steps are depicted in Fig. 2. The dimerization and trimerization coordinates were studied by essentially reproducing the steps proposed by Armstrong, Perkins, and Stewart (*3*). We discuss this in more detail in the next section. The liberation of the α-olefins is depicted in Fig. 2 as a β-transfer process involving a new ethylene molecule coordinated to the Ti site and was thus calculated. Most studies (*4*) traditionally proposed direct β-transfer to the Ti atom. However, recent work (*10*) on the rate constants of β-abstraction clearly shows their dependence on ethylene concentration. We also give a justification of these results (*10*) from a molecular point of view.

## RESULTS

To analyze all the steps represented in Fig. 2, 15 points of the reaction coordinate were obtained. Each implied the solution of a system of over 100 valence electrons and 50 nuclei. The results are presented below, divided into subsections concerning (1) ethylene addition, (2) polymer growth, and (3) β-transfer. In the first two, frequent reference to the masterful analysis of Armstrong, Perkins, and Stewart (*3*) (APS) is made, as we basically followed and generalized their study (which considered a much smaller system). This notwithstanding, we obtained significant differences from some of their results.

A different situation arises in (3), because no calculation of this sort exists for the crucial problem of chain transfer and catalyst regeneration. The outstanding result obtained here is the evidence of many common aspects with the chain-propagation mechanism proposed by APS showing that the continuing growth of the polymer chain and the oligomer liberation are alternative and competing processes that depend on subtle changes in the Ti-alkyl bond. We thus provide a unified standpoint for the mechanism of all processes depicted in Fig. 2.

### *1. Bonding of the Olefin with the Transition Metal Atom and the Driving Force*

First of all, we made a calculation on the initial catalytic complex in the absence of ethylene. The most stable configuration corresponds not to an octahedral complex with a vacant site but to a trigonal-bipyramidal (pentacoordinated) complex. This was remarked before by APS (*3*) although we obtain a rather smaller energy difference (1.43 eV) between the two structures. Thus it is relatively easier for the complex to shift from the bipyramidal to the octahedral (hexacoordinated) structure when ethylene coordinates to the Ti site. Before going into this, however, two comments on the initial complex: First of all, the fact that the bipyramidal structure is the most stable agrees nicely with the EPR information, as it corresponds to two aluminum atoms genuinely equivalent with respect to the $\mathrm{Ti^{III}}$ site. Also, the Ti unpaired electron is strongly localized in the highest stable orbital ($d_{xz}$) and contributes significantly to the Ti–alkyl bond as shown in Table 1. This is precisely the "$t_{2g}$" orbital proposed for the $\pi$ bonding between Ti and ethylene in the Cossee mechanism, which we discuss immediately.

TABLE 1

PRINCIPAL CONTRIBUTIONS TO THE HIGHEST-ENERGY (SEMI-) OCCUPIED MOLECULAR ORBITAL OF INITIAL CATALYST COMPLEX[a]

| | Atom | | | | |
|---|---|---|---|---|---|
| | Titanium | | α-Carbon (in butyl) | | |
| | $d_{xz}$ | $d_{x^2-y^2}$ | $s$ | $p_x$ | $p_z$[b] |
| Coefficient | 0.742 | 0.105 | 0.146 | 0.376 | −0.336 |

[a] Orbital energy: −0.09 eV.

[b] Other minor contributions of $p$-orbitals of oxygen atoms and rest of butyl chain.

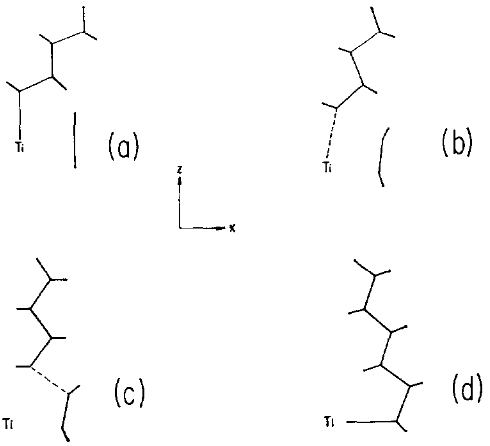


FIG. 3. A very schematic description of the propagation coordinate where only the involved Ti–alkyl and Ti–olefin bonds are depicted, ethylene lies in a perpendicular plane to the figure. The stages shown are: (a) the initial bonds as projected on the $xz$ plane, (b) the labilization of the Ti–butyl bond and its *cis*-migration toward ethylene, (c) the interaction of the alkyl α-Carbon with the ethylene moiety, and (d) trimerization.

The addition of an ethylene molecule to the complex has the following characteristics. The equilibrium structure is now hexacoordinated octahedral complex, the α-carbon on the alkyl chain augments its already high negative charge (from −0.28 to −0.32), the ethylene charge distribution is unaltered, and only a weak bond is formed between ethylene and Titanium (bond order 0.10). Also important is the fact that a residual interaction between the α-carbon and the olefin is already present (of the order of $\frac{1}{5}$ of the Ti-ethylene coordination) coming from the first's high negative charge. This had been observed before by APS, who consider this as the driving force of the chain propagation, (*3*).

In contrast, in Cossee's scheme (*1*) the reaction is supposedly started by the stabilization of the $t_{2g}$ orbital of the octa-

TABLE 2

PRINCIPAL ATOMIC CONTRIBUTIONS TO THE SAME ORBITAL OF TABLE 1, AFTER ETHYLENE IS COORDINATED TO TI[a]

| | Atom | | | | |
|---|---|---|---|---|---|
| | Ti | α-C (in butyl) | | $C_1$ (ethylene) | $C_2$ (ethylene) |
| | $d_{xz}$ | $s$ | $p_z$ | $p_x(\pi^*)$ | $p_x(\pi^*)$[b] |
| Coefficient | 0.900 | 0.084 | −0.241 | −0.068 | +0.073 |

[a] Orbital energy: −0.51 eV.
[b] Other minor contributions as in Table 1.

hedral complex ($d_{xz}$ of Ti in our study) and the back-donation of the charge to the $\pi^*$ orbital in ethylene. Armstrong, Perkins, and Stewart discard this as a minor effect. We, however, conclude that in our complex the stabilization of $d_{xz}$ is quite important (its energy is −0.51 eV, $d_{xy}$ and $d_{yz}$ have +4.2 eV) although back-donation is not too high (see Table 2).

### *2. Mechanism of the Propagation Reaction*

From the preceding discussion we have that ethylene coordination implies a rearrangement at the Ti site. Furthermore a weak bonding exists between alkyl and olefin (in Table 2 in fact, the $t_{2g}$ orbital contributions from both show that they interact, however slightly, through the $d_{yx}$ Ti orbital). Thus the propagation reaction starts at the earliest stage of Fig. 2. Its evolution is a consequence of the high concentration of electronic charge on the alkyl α-carbon. All Ti ligands are of course highly negative, as these bonds are quite polar. The oxygens, for instance, carry a charge of about −0.6 electronic charges, and even the less electronegative α-carbon carries a charge of −0.32. This charge is prone to extend toward the ethylene and favor the alkyl's movement.

Such a movement is depicted in Fig. 3, where only the relevant ligands are shown. The reaction coordinate was chosen following APS (*3*), that is, the butyl and olefin move in a concerted fashion by equal steps until the trimer is formed. This process is energetically favorable, as shown in Fig. 4. This is a consequence of the role played by the Ti $d_{xz}$ orbital, which acts as a "transfer agent" (*3*); that is, it reinforces the Ti-butyl bond as it advances. This is clearly evidenced in Table 3, which shows how the second ethylene carbon $C_2$ interacts more and more intensely with the butyl's α-carbon through the $d_{xz}$ orbital. In the final step of Table 3 the $C_1$ carbon of ethylene is now the α-carbon of the new hexyl chain.

Thus the role of the catalyst becomes transparent: It favors the movement of the labile alkyl ligand through the Ti *d*-orbi-

TABLE 3

CHANGE IN THE ATOMIC CONTRIBUTIONS TO THE MOLECULAR ORBITAL THAT CORRESPONDS TO THE TI–ALKYL BOND ($u_2$ IN FIG. 4), AS THE PROPAGATION REACTION PROCEEDS[a]

| Step | Atom | | | | | | |
|---|---|---|---|---|---|---|---|
| | Titanium | | α-Carbon (alkyl) | | | $C_2$ (ethylene) | |
| | $d_{xz}$ | $d_{z^2}$ | $s$ | $p_z$ | $p_x$ | $p_x$ | $s$ |
| Initial ethylene complex | 0.277 | 0.259 | 0.154 | 0.585 | — | 0.134 | — |
| Second | 0.348 | 0.176 | 0.129 | 0.619 | — | 0.173 | — |
| Fourth | 0.412 | 0.159 | 0.133 | 0.444 | 0.244 | 0.532 | 0.130 |
| Final (trimer) | 0.586 | — | 0.160 | 0.299 | 0.411 | | |

[a] Notice that in the last step the alkyl chain has grown a rung.

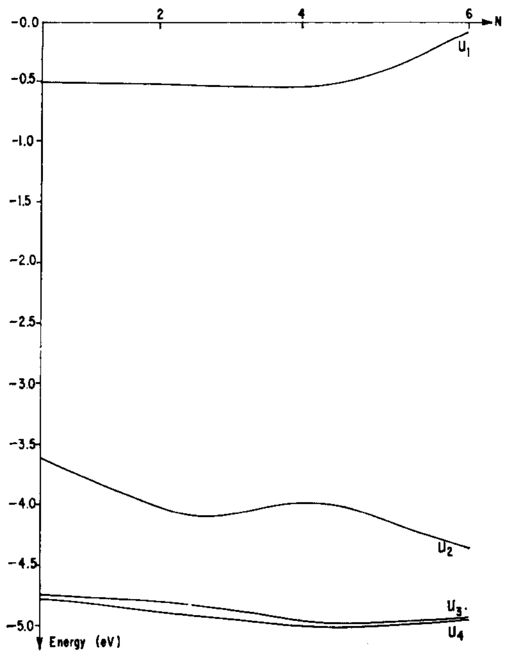


FIG. 4. Change in the orbital energies over the propagation reaction coordinate. The abscissa is simply the number $N$ of the calculation. The molecular orbitals depicted are: $u_1$, which is essentially the $d_{xz}$ orbital (see text); $u_2$, which is the one associated with the Ti–alkyl bond; $u_3$ and $u_4$ which are basically oxygen–metal bonds formed mostly from oxygen $p$ orbitals. These last molecular orbitals and also all the lower-energy ones not depicted here do not change appreciably during the reaction and neither does $u_1$, except of course after trimerization occurs and there is no Ti–olefin bond left. The energetics of the reaction then depend mostly on the changes in the energy of $u_2$. These are shown to be quite favorable; the alkyl movement does not have to surmount any significant barrier.

tals, while the ethylene gradually evolves, also because of its interaction with Titanium, and reaches the most favorable situation for trimerization to occur. This permits the propagation reaction without any appreciable activation barrier. The energy changes mainly concern the molecular orbital more directly related to the Ti-alkyl bond; all other molecular orbitals hardly suffer any changes during the process (see Fig. 4). Thus the role of the rest of the catalyst complex is mostly that of a substrate that allows for the ethylene's coordination to Titanium.

All these results were obtained for the trimerization process, although they can be easily extended to dimerization (changing butyl for ethyl). In fact the qualitative features of the above mechanism agree completely with the previous study (*3*) of the interaction between methyl and ethylene. The quantitative aspects may differ considerably, however; contrast our Fig. 4 with (*3*, Fig. 3).

The most important aspects are, in any case, that no radical breaking is necessary to produce polymerization and that the Ti *d*-orbitals permit and in fact promote the process while the olefin and alkyl are firmly attached to the catalytic site.

### *3. Mechanism for the β-Transfer Process*

The oligomer liberation has been described as a β-hydrogen abstraction from the alkyl chain, thus forming a double bond between the first two carbons of the chain while breaking the Ti–α-C bond (*4*). This mechanism was supposed to be completely independent of the chain propagation, with which it apparently had no common features. We propose, in contradistinction, a sequence of steps that stem from the same initial situation as the propagation reaction.

The β-transfer reaction coordinate is partially depicted in Fig. 5. As no previous study of this process existed we had to use a "fine tooth comb" analysis of the coordinate and ten points were calculated, not all of them appearing in Fig. 5. In this study we analyzed the evolution of the butyl ligand toward ethylene without presupposing that it would reach it at an ideal position for trimerization. We instead followed the minimal energy pathway. This implied that at each step the Ti–α-C bond was strengthened (i.e., its bond order increased and its energy was lowered; see Table 4). This brought about the consequence, though, that the Ti-butyl distance did not increase enough so that the α-C would have reached the ethylene moiety at an ideal distance for trimerization.

In fact as the alkyl progresses toward the olefin one of the butyl's β-hydrogens comes too close to the ethylene's second carbon $C_2$. Up to this point the situation is as follows. During its movement the ethylene carbons become more and more negative, because they are progressively increasing their (polar) interaction with Titanium. At the same time the β-hydrogens in butyl become more and more positive as they approach the ethylene moiety. All this is shown in Table 5. Consequently when one of the β-hydrogens is close enough to $C_2$ an important ionic interaction is established (see Fig. 5). In a sense a pseudohydrogen bond between the β-carbon in butyl and $C_2$ in ethylene appears, and the total energy of the system is considerably lowered. This is an unstable situation, however, and finally the $C_2$ carbon abstracts the β-hydrogen from the chain as shown in Fig. 5.

The whole process is clearly seen by analyzing the change in the bond orders at each point of the reaction path, as given in Fig. 6. In it, the gradual growth of the $C_2$–β-hydrogen interaction and the breaking of the β-H with the butyl chain is clearly depicted. Notice that at $N = 7$ the transition state, marked by the crossing of all the bond order curves, appears. Thenceforth β-abstraction is consumated, $C_1$–$C_2$ becomes a single bond (in contrast with its double bond nature at the initial stages), the original Ti–alkyl bond is manifestly weakened while the changing Ti–ethylene interaction grows as it becomes a Ti–ethyl ligand. Thus Fig. 6 shows β-abstraction, chain liberation, and

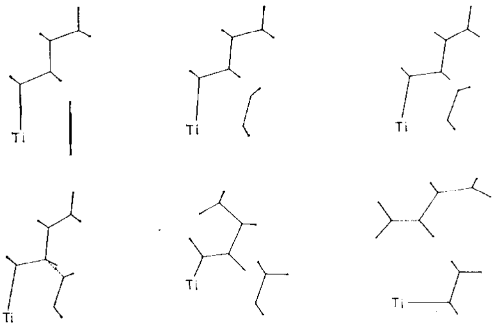


FIG. 5. Schematic description of the β-transfer coordinate. Different steps, starting as in Fig. 3 and continuing with the approach of the alkyl β-hydrogens to ethylene, are depicted. An ionic interaction (pseudo H-bond) between alkyl and olefin is apparent in the fourth drawing, this corresponds to the transition state ($N = 7$ in our calculations), where the highly positive β-hydrogen is abstracted by the negative ethylene carbon. Finally, α-butene is liberated.

TABLE 4

CHANGE IN THE BOND ORDER OF THE Ti–ALKYL BOND AND IN THE ORBITAL ENERGY OF THE MOLECULAR ORBITAL THAT CORRESPONDS TO THIS BOND[a]

| Step | Ti–butyl bond order | Orbital energy (eV) for Ti–alkyl bond |
|---|---|---|
| Initial stage | 0.495 | −3.62 |
| Second | 0.500 | −3.62 |
| Fourth | 0.525 | −3.87 |
| Sixth | 0.615 | −4.01 |
| Eighth | 0.16[b] | −3.75 |

[a] Notice that in the eighth step the bond order given is the one corresponding to Ti-butene, as the β-hydrogen abstraction takes place in the previous transition state (step 7 in our coordinate).

[b] This is now the Ti–butene bond.

TABLE 5

CHANGE IN THE ATOMIC CHARGE DISTRIBUTION IN THE β-HYDROGEN AND THE ETHYLENE CARBON ($C_2$) DIRECTLY INVOLVED IN THE TRANSFER PROCESS

| Step | Atomic charge | | | |
|---|---|---|---|---|
| | Initial complex | Third | Sixth | Final |
| $C_2$ | −0.135 | −0.29 | −0.34 | −0.14 |
| β–H | +0.04 | +0.17 | +0.37 | +0.08 |

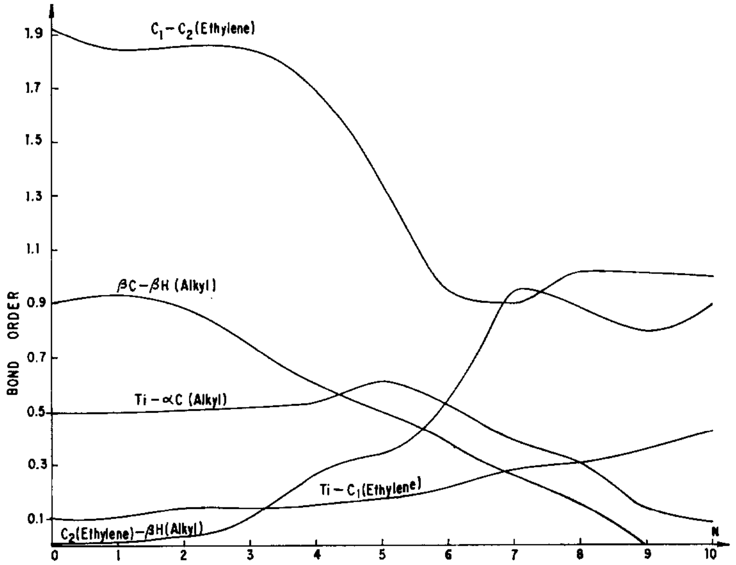


FIG. 6. Bond order changes along the β-transfer coordinate as a function of the number $N$ of the calculation. Notice that the Ti–ethylene ligand is gradually increased, as the second's double bond reduces to a single bond. The Ti–alkyl bond is not weakened by the latter's movement and only destabilizes when the alkyl becomes, through the β-transfer, an α-olefin. Also notable is the β-hydrogen bond, originally concentrated to the alkyl's β-carbon although with a residual interaction with the $C_2$ ethylene carbon. This residual interaction grows and reaches a maximum at the transition state while the βH–βC bond definitively disappears.

catalyst regeneration. All these comprise a chain transfer process as discussed by Henrici-Olivé and Olivé (*10*). We come back to this point in the next section.

## CONCLUSIONS

In synthesis the mechanism for the process of oligomerization has the following stages. The catalyst complex, which is formed through "oxygen bonding" (triatomic bonds) between the Ti and Al atoms, has a trigonal bipyramidal structure. The role of the Aluminum atoms is confirmed to be twofold: they exchange ligands with Ti (thus forming the labile Ti–alkyl bond) and through the oxygen bonding favor the geometrical structure and the reduction at the $Ti^{III}$ site. On the other hand the Al and their ligands remain practically inert during the reactions.

The addition of ethylene implies the movement of the labile Ti–alkyl bond to an octahedral site thus liberating a new vacant site. This involves an expenditure of energy that may be at least partially compensated by the ethylene coordination. Hence the interaction between the coordinated alkyl and ethylene begins at the earliest stage not only because of the rearrangement at the Ti site but also because a slight charge density between ethylene and the α-carbon in the alkyl chain appears from the onset.

The driving force of the reaction thus appears a consequence of the large concentration of electronic charge in the α-carbon, which in turn comes from the highly ionic character of all Ti ligands, as proposed by APS (*3*). Yet we have shown that Cossee's assumption (*1*) that the activation of the Ti–α-C bond comes from the stabilization of a $t_{2g}$ orbital of the octahedral complex by the ethylene coordination is clearly confirmed in our calculations. Armstrong, Perkins, and Stewart (*3*) discarded this as a negligible effect but this may be due to the fact that they did not make any assumptions about the oxidation state of the Titanium. We explicitly introduced a reduced $\mathrm{Ti^{III}}$ atom, as implied by the EPR spectrum, and we believe that for all such complexes at least, both factors, the high charge of the α-C and the $t_{2g}$ orbital stabilization, play a role in activating the reaction.

This description of the activation of the process is equally valid for the chain propagation and chain liberation processes. Our calculations show in fact that the interaction of the alkyl and the olefin can lead either to chain growth or to β-hydrogen abstraction from the chain by the second carbon of the ethylene moiety, with only subtle changes in the first steps of the reaction coordinate deciding the outcome. Consequently the mechanism of oligomerization is depicted as containing the alternative, at every step, of liberating the α-olefin or lengthening the chain. Changing the substituents, the solvents, etc, one could hope to change the yields. This is related to the idea of "catalyst tayloring" proposed by Henrici-Olivé and Olivé (*4*) and has been tried in our laboratory where the substitution of the complex (1) by

$$\mathrm{Ti(O\phi\text{-}\mathit{p}\text{-}OMe)_3O\text{-}\mathit{n}\text{-}Bu} \qquad (2)$$

in a polar (toluene) solvent has reversed the ratio of the α-butene to α-hexene yields (*7*). We are planning future calculations in the hope of guiding such attempts.

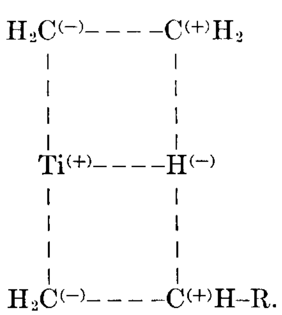
Finally let us remark that our results have something to say about some controversial alternatives proposed in the literature. The dispute whether chain growth proceeds via the ethylene insertion in the chain or by *cis*-migration of the alkyl still continues (*4*), this in spite of some conclusive evidence in favor of *cis*-migration (*11*). Our calculations imply a *cis*-migration without the liberation of an alkyl radical at any moment, as the alkyl remains attached to the Ti site, a fact that actually *favors* the alkyl attack energetically.

Another open question exists, referring to the α-olefin liberation. Traditionally the direct β-abstraction by the Ti atom itself has been proposed (*4*). Recently however the rate constants for the chain propagation and the chain transfer processes in homogeneous Ziegler–Natta catalysis have been obtained (*10*). Interestingly enough, both rate constants depend on the concentrations of active sites and of monomer; thus (*10*):

$$r_p = k_p[\mathrm{Ti}^*][\mathrm{C_2H_4}],$$
$$r_{t_r} = k_{t_r}[\mathrm{Ti}^*][\mathrm{C_2H_4}], \qquad (3)$$

where [Ti*] means the concentration of activated Titanium.

These results have many interesting features. The fact that both rate constants have the same dependence on catalytic site and ethylene concentration may be interpreted as the kinetic confirmation of the profound relation between the mechanisms of growth and liberation of the oligomer here proposed. Furthermore, the dependence of the chain-transfer on ethylene concentration lead Henrici-Olivé and Olivé to postulate a transition state for β-abstraction that goes halfway between the old ideas of direct hydrogen-abstraction by the Titanium atoms and the transition state obtained by us. Their proposition (*10*) is depicted below.



$$\begin{array}{ccc} \mathrm{H_2C^{(-)}} & \text{----} & \mathrm{C^{(+)}H_2} \\ \vdots & & \vdots \\ \mathrm{Ti^{(+)}} & \text{----} & \mathrm{H^{(-)}} \\ \vdots & & \vdots \\ \mathrm{H_2C^{(-)}} & \text{----} & \mathrm{C^{(+)}H\text{-}R.} \end{array} \qquad (4)$$

We have calculated such Ti–H interactions and have arrived at the conclusion that they can be discarded. This will be discussed elsewhere (*12*). Let us just remark that the mechanism proposed here seems particularly suited for the understanding of the rate constants obtained in Ref. (*10*).

## ACKNOWLEDGMENTS

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