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On the Structure of Titanium–Aluminum Catalytic Complexes

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A self-consistent all-valence electron molecular orbital study of the relative stabilities of different conformations of Ti–Al complexes has been made. A description of the reduction at the Ti site is given. The formation of the most stable (bipyramidal) structure and its relation to the catalytic activity of the complex are discussed.

INTRODUCTION AND METHODS

In a previous paper (*1*) a molecular orbital study of the reaction coordinates of the catalytic oligomerization of olefins by Ti–Al catalysts was given. The analysis was initiated as the olefin coordinates to a homogeneous catalyst consisting of a 2:1 aluminum–titanium complex. This coordination implied an activation energy because the ethyl group had to change from a bipyramidal to an octahedral site. The energy barrier for the whole catalytic reaction was, however, quite low because a Ti *d*-orbital played the role of transfer agent (*2*), thus favoring a *cis*-migration of the alkyl towards the olefin, so no radical breaking was present in the process.

In short, the whole oligomerization process was given a satifactory explanation and all the steps were calculated except for the formation of the catalyst, which was supposed to develop as in Fig. 1. The different structures in Fig. 1 were justified on the basis of various experimental studies (chemical, EPR, etc.) which were also reported in Ref. (*1*).

We proceed here to complete the theoretical study of the process by analyzing the sequence of steps given in Fig. 1 by the same method used for the rest of the reaction (*1*). This method uses the all-valence electron self-consistent field program of Armstrong *et al.* (*2*), which employs the CNDO approximation. Another approximation introduced was the replacement of all of the alkyls in Fig. 1 by methyls except for the ones directly involved in oligomerization, i.e., the Ti-coordinated ethyls and butyls. We shall also do so here. The details of the bond lengths and parameterization are reported elsewhere (*1*,*2*).

RESULTS AND DISCUSSION

As mentioned above we calculated the charge densities, energies, bond orders, etc. for the four structures depicted in Fig. 1. In Table 1 we report the Ti–ethyl bond order, the total charge and *d*-electron charge and also the valency of the Ti atom as they vary in the various configurations. The most notable changes are from structure A (in Fig. 1) to B, C, and D (Fig. 1). These are the changes brought about by reduction. In particular the Ti–alkyl bond order in A is rather small and increases substantially upon reduction (Table 1), especially so

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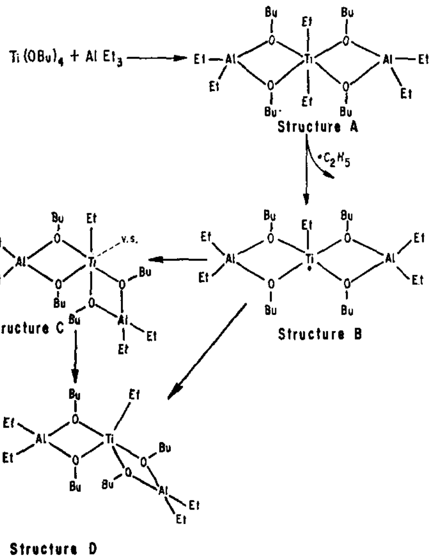

FIG. 1. Evolution of the Ti–Al complex formed from the reaction between triethyl aluminum and the tetrahedral $Ti(OBu)_4$ complexes. First, the octahedral structure A formed by oxygen bonding between a totally oxidized Ti and two Al atoms is obtained, after the interchange of Et and OBu ligands between the two metallic species. Then one of the ethyl radicals is liberated, thus reducing the titanium in structure B. Subsequently this *trans*-structure changes to a *cis*-complex (structure C or D). Structure C is the usually assumed octahedral structure with a vacant site (v.s.) while structure D has a bipyramidal geometry. This last structure has previously been suggested (*1,2*) as the most stable configuration for the catalyst complex. See the experimental evidence leading to this proposed sequence in Ref. (*1*).

when the final structure D is achieved. This low bond order in A is related to the breaking of one of the Ti–alkyl bonds, but we shall come back to this point later. A consequence of such a breaking is evident in the charge of the Ti atom (Table 1). The chemical image of the hexacoordinated structure A is with Ti completely oxidized (to Ti^{IV}). In a molecular orbital calculation, of course, the atoms never present a charge larger than between +1 and +2, so in fact the high value of the Ti charge in A is a good measure of its oxidation. The subsequent reduction manifests itself in B, C, and D by diminishing this excess positive charge drastically (this is described for structures B and D in Table 1). This denotes the appearance of an unpaired electron located at the Ti. Also notable is the fact that this flow of electronic charge to the Ti concentrates mainly on its *d*-orbitals. The low valency of the Ti in structures A (Table 1) is apparently surprising; it is the only hexacoordinated structure, yet it has the lowest "valency." This is only a manifestation, however, of the highly ionic character of the bonds in structure A, consistent with the large atomic charges mentioned above. For a more thorough discussion of this interpretation of the valency, see Armstrong *et al.* (*3*).

The test of the sequence of Fig. 1 is of course to determine whether it is energetically feasible. The change of the structure of the reduced species from B to C to D was shown to be quite favorable energetically in our calculations. From B to C the total energy is lowered by 8 eV, and the change from the octahedral structure C to the bipyramidal configuration D further lowers the energy by about 1.5 eV. This last step is basically favored by the stabilization of the molecular orbital that corre-

TABLE 1

Ti–Ethyl Bond Orders and Ti Charges and Valencies for the Different Structures of Fig. 1

	Diethyl-Ti complex, structure A	Reduced Ti–ethyl complex, structure B	Catalytic complex, structure D
Ti-ethyl bond order	0.488	0.768	0.813
Total charge of Ti atom	+1.351	+0.810	+0.823
d-Orbital population on Ti atom	1.85	2.45	2.42
Titanium valency	3.99	4.83	4.50

TABLE 2

Energy and Principal Contributions to the Highest-Occupied Molecular Orbital Essentially Related to the Ti–Ethyl Bond

Coefficients of the atomic orbitals that contribute most to the highest-occupied molecular orbital	Structure A -3.50 eV[a]	Structure B -4.30 eV[a]	Structure C -3.69 eV[a]	Structure D -4.34 eV[a]
Titanium				
d_{z^2}	-0.003	$+0.217$	$+0.299$	$+0.069$
d_{xz}	-0.002	-0.004	-0.012	-0.586
Ethyl P_z	-0.590	-0.459	-0.677	-0.299
(α-Carbon) P_z'	-0.590[b]			

[a] Molecular orbital energy.

[b] Notice that there are two P_z orbitals on structure A corresponding to the α-carbons of the two *trans*-coordinated ethyls.

sponds to the Ti–ethyl bond as will be evident from the following.

In Table 2 the molecular orbital energy of the last-occupied eigenstate in the different Ti–Al structures is given. Although in such large complexes no molecular orbital can be solely associated with a particular bond, we have found in different calculations (*1,2,4*) on quite a few diverse oxo- and chloro-Ti–Al complexes that the highest-occupied orbital has always been largely formed from Ti *d*-orbitals and ethyl *p*-orbitals, i.e., it has been shown (*1,2,4*) to be essentially associated with the Ti-alkyl bond. The results of Table 2 also confirm such assignment of this molecular orbital to the bond. The largest atomic orbital coefficients for the highest doubly occupied state are given and they correspond to bonding between the α-carbon *p*-orbitals and Ti *d*-state (d_z in octahedral configurations, d_{xz} in the bipyramidal situation). The only notable exception is in structure A where no *d*-orbital contribution is evident. The signs of the *p*-orbital coefficients of the two ethyls furthermore show that the orbital is antibonding and has a node in the *xy*-plane. This is in marked contrast with the aforementioned calculations of this molecular orbital (*1,2,4*). Thus we deem this as the cause of the liberation of one of the ethyl radicals and the subsequent reduction of Ti. This is also evidenced by the low bond orders of the two Ti–ethyl bonds and by the rather small molecular orbital energy in A as compared to those of the singly alkylated structures (see Table 2). As discussed elsewhere (*1*), this bond breaking is fully confirmed from experimental data.

In Table 3 the location of the unpaired electron in different molecular orbitals in the reduced structures B, C, and D is given. As was discussed from Table 1 the unpaired electron always concentrates in the Ti *d*-orbitals, but in structures B and C it is concentrated in orbitals that from symmetry (see Fig. 1) cannot contribute to any ligand bonding, especially with the

TABLE 3

Energy and Dominant Character of the Molecular Orbitals Where the Unpaired Electron is Located after Reduction

	Structure B $+2.23$ eV[a]	Structure C $+2.23$ eV[a]	Structure D -0.09 eV[a]
Dominant atomic orbitals in the semi-occupied molecular orbital	d_{xz} d_{yz}	d_{xz} d_{xy} d_{yz}	s, $P_z(\alpha - \mathrm{C})$ d_{xz}

[a] Molecular orbital energy.

ethyl. Therefore this orbital's energies are quite high, only slightly lower than the energy of the lowest unoccupied orbital of structure A for example (+2.23 vs +2.90 eV). In contrast, in structure D the electron is exclusively in d_{xz}, i.e., precisely the one directed towards the ethyl. The orbital's energy is substantially lowered to a negative value (−0.09 eV) This, no doubt, contributes to making structure D the one with the lowest total energy.

This brings us to the starting point of the catalytic reaction discussed in Ref. (*1*) Let us add a few comments concerning the latter in light of the present results. First, the initial catalyst structure has been confirmed here to be the bipyramidal complex assumed previously. Second, the coordination of ethylene has been found in Ref. (*1*) to imply the rearrangement of the ethyl to produce an octahedral (hexacoordinated) configuration. Now it is seen also to be related to the unpaired electron which is originally contributing to the Ti–alkyl bond and goes on to play a crucial role (*1*) in the formation of the Ti–olefin ligand and in the subsequent alkyl–ethylene reaction. It is notable that this role is always associated with the d_{xz} orbital (*1*).

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