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DFT study of dimethylzirconocene activation by one or two $Al(C_6F_5)_3$ molecules, formation of ion pairs and their reactions with ethylene

Leila Yu. Ustynyuk*[a] and Elga A. Fushman[b]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 2677; e-mail: leila_ust@mail.ru*
[b] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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The interaction of ethylene with the catalytic particles, ion pairs $Cp_2ZrMe^+A^-$ [Cp = η^5-C_5H_5, A^- = $MeAl(C_6F_5)_3^-$ or $(C_6F_5)_3Al$–Me–$Al(C_6F_5)_3^-$], has been investigated. The participation of two molecules of Al-containing activator in the formation of a catalytic particle facilitates more efficiently the polymerization reaction as compared to one molecule of Al-containing activator.

According to the generally accepted point of view, the cationic moieties of ion pairs $Cp^*_2MAlkyl^+A^-$ serve as catalytic centres for the polymerization of olefins by metallocenes. Here, M stands for a metal (*e.g.*, Zr or Ti), and A^- is a counterion. In most theoretical works, $A^- = MeB(C_6F_5)_3^-$ was considered as a model for a counterion. This anion forms in the result of abstraction of Me^- from Cp_2MMe_2 by $B(C_6F_5)_3$. It is well known that such systems reveal high catalytic activity in reactions of olefin polymerization at M:B = 1:1. On the other hand, Al-containing activators, first of all, polymethylalumoxane (MAO), are the compounds of utmost practical value. In these systems, a noticeable catalytic activity is observed only if activator particles significantly surpass in a number of metallocene molecules.

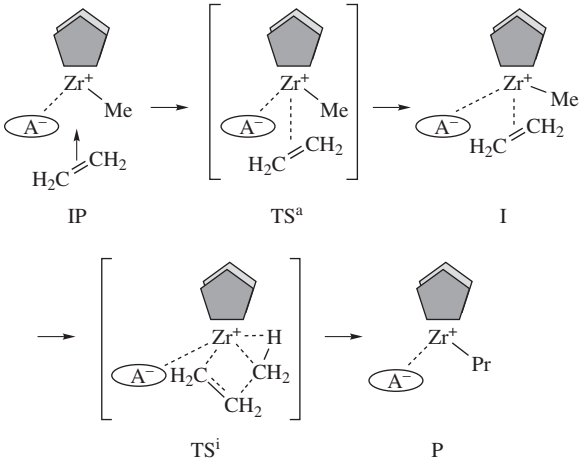
The idea of double activation[1,2] was validated previously[3,4] for the activator $Al(C_6F_5)_3$. The double activation mechanism is based on the fact that Al forms (in contrast to B) strong bridge bonds Al–Me–Al. As a result, one metallocene molecule interacts with two molecules of Al-containing activator (or two Lewis acid centres in MAO). This mechanism provides additional stabilization of the catalytic particle $Cp_2MMe^+[(C_6F_5)_3Al–Me–Al(C_6F_5)_3]^-$ (IP2), as compared to the compound $Cp_2MMe^+[Me–Al(C_6F_5)_3]^-$ (IP1) containing one Al. For M = Zr, the energy effect of the reaction

$$Cp_2MMe^+[Me–Al(C_6F_5)_3]^- + Al(C_6F_5)_3 \longrightarrow Cp_2MMe^+[(C_6F_5)_3Al–Me–Al(C_6F_5)_3]^-$$

comprises –6.5 kcal mol^{-1}; the energy of heterolysis (complete separation of counterions) decreases from 90.0 (IP1) to 66.3 kcal mol^{-1} (IP2). The latter parameter is important for olefin polymerization, since olefin attachment is accompanied by a significant increase in the distance between the ion pair components.

In this work, we compare reactions of the ion pairs $Cp_2ZrMe^+A^-$ with ehylene for the counterions $MeAl(C_6F_5)_3^-$ (IP1) and $(C_6F_5)_3Al–Me–Al(C_6F_5)_3^-$ (IP2). DFT calculations were performed with the use of the original program 'Priroda'[5] at the PBE/sbk level of theory,[6,7] with three exponential Gauss type basis set and corrections for relativistic effects by the electron core potentials. This approach was used recently[8] in a study of the gas phase reaction $Cp^*_2ZrMe^+ + C_2H_4$.

We optimized geometries and calculated energies of ion pairs IP1 and IP2. It has been found that IP2 can exist in two isomer forms (IP2-1 and IP2-2) with different positions of anion A^- with regard to cation Cp_2ZrMe^+. The energy difference between IP2-1 and IP2-2 is insignificant, 0.5 kcal mol^{-1}. Therefore, our calculations were performed for both isomers of IP2.



Scheme 1

The interaction of the catalytic particle $Cp_2ZrMe^+A^-$ with ethylene includes, in general, two stages (Scheme 1). On the first stage, the ethylene molecule binds to the ion pair with the formation of intermediate complex I. On the second stage, a coordinated ethylene molecule inserts into the Zr–C(Me) bond, resulting in the formation of a new C–C bond.

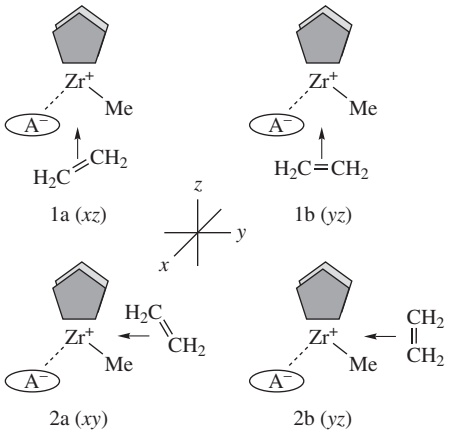
We have studied the energy profiles of ethylene attachment to IP1 and IP2. Initial distances between Zr and carbon atoms C(1) and C(2) of ethylene were 5.0 Å. Then, these distances were shortened step by step (0.1 Å) to 2.5 Å. Other geometry parameters varied freely in the course of geometry optimization. We have considered two possible directions of the ethylene attachment to IP1 and IP2: (1) between the Me ligand and the anion A^-, and (2) from the side of the Me ligand. Besides, we have scrutinized two modes of ethylene orientation relatively to the ion pair: (a) the C(1)–C(2) bond of the ethylene molecule was oriented approximately perpendicular to the plane equidistant from Cp ligands, and (b) atoms C(1) and C(2) of C(1)–C(2) bond of the ethylene molecule was positioned approximately in this plane (Scheme 2).

We found that, in both cases, IP1 and IP2, reaction channel 1a is characterized by the lowest energy barrier for the stage of

Table 1 Energies of two key transition states (TS^a, TS^i) and intermediates (I) in Scheme 1 calculated for the cation Cp_2ZrMe^+ and ion pairs IP1 and IP2 (isomers IP2-1 and IP2-2) relatively to the sum of energies of ethylene and Cp_2ZrMe^+, IP1, IP2-1 and IP2-2.

Anion A^-	$E(TS^a)$/ kcal mol^{-1}	$\nu_i(TS^a)$/ cm^{-1}	Zr–C(1), Zr–C(2)/Å	E(I)/ kcal mol^{-1}	$E(TS^i)$/ kcal mol^{-1}	$\nu_i(TS^i)$/ cm^{-1}	C(1)–C(3)/Å
$MeAl(C_6F_5)_3^-$, IP1	—	—	—	—	19.3	271i	2.14
$(C_6F_5)_3AlMeAl(C_6F_5)_3^-$, IP2-1	10.2	35i	4.6	–6.3	–0.9	247i	2.16
IP2-2[a]	3.8	54i	3.7	–7.1	–0.6	265i	2.15
Free cation Cp_2ZrMe^+	—	—	—	–20.2	–16.8	206i	2.23

[a]The energy of isomer IP2-2 is by 0.5 kcal mol^{-1} higher than that of IP2-1.



Scheme 2

ethylene attachment. Earlier,[9] using this approach to investigate the ion pairs $Cp_2ZrEt^+[MeB(C_6F_5)_3]^-$, it was demonstrated that such a direction of the ethylene attachment is characterized by minimal energy expenses over all the possible reaction channels. All the data presented below are related to reaction channel 1a (Scheme 2); other directions are not considered.

The attachment of ethylene to IP1 is associated with a monotonic increase in the system energy. The stationary points corresponding to TS^a and I were not found. Conversely, the ethylene binding to IP2 leads to a decrease in the system energy (Table 1). Each of isomers of IP2 (IP2-1 or IP2-2) has its own channel for the frontal incorporation of the ethylene molecule between the Me ligand and anion A^- (Table 1, Figure 1). Transition states TS^a for these channels were found by the scanning of energy *versus* Zr–C distance; that is, without complete optimization of geometry. The lenghts of two Zr–C bonds were taken equal, and changed with steps of 0.1 Å. Each energy maximum has only one imaginary mode of vibrations. However, it was impossible to get complete optimization of TS^a geometries, because in the vicinity of energy maximum the energy depended only weakly on Zr–C(1) and Zr–C(2) distances.

The relaxation† of transition states TS^a for IP2-1 and IP2-2 towards intermediate I leads to similar structures. The only difference between these structures is an insignificant shift of the counterion relatively the cation Cp_2ZrMe^+, the energy difference is 0.3 kcal mol^{-1}. Therefore, the search for transition state TS^i was performed for both structures. As one could expect, both transition states are characterized by very close geometries and energies (Table 1).

The geometries of transition states TS^i for IP1, IP2-1 and IP2-2 and intermediates I for IP2-1 and IP2-2 were optimized completely. The types of the stationary points were identified by the analysis of vibrational frequencies in harmonic approximation. For IP1, IP2-1 and IP2-2 in TS^i, the lengths of newly formed bonds C(1)–C(3) equal to 2.14, 2.16 and 2.15 Å, respectively (Figure 1, Table 1).

To be sure that TS^i poses the only energy barrier on the path of the reaction of IP1 with ethylene molecule, we searched for

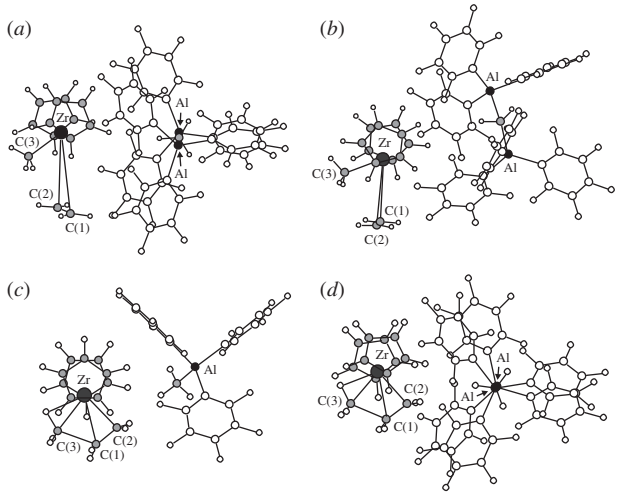


Figure 1 Structures of transition states TS^a for ion pairs (*a*) IP2-1 and (*b*) IP2-2, and TS^i for ion pairs (*c*) IP1 and (*d*) IP2-1.

energy minimum nearest to TS^i in the direction of reagents. The relaxation† of TS^i towards reagents starts with the rotation of the ethylene molecule in the coordination sphere of Zr, and follows by a spatial separation of reagents. The distances between Zr and both C atoms of ethylene increase, whereas the distance between Zr and C atom of the methyl group of the counterion $MeAl(C_6F_5)_3^-$ becomes shorter. The energy barrier TS^i of 19.3 kcal mol^{-1} is high for bimolecular reaction. A similar barrier was obtained earlier for the transition state in the reactions $Cp_2ZrMe^+A^- + C_2H_4$ for the model of counterion $A^- = [AlMe_3Me(AlOMe)_6]^-$ in systems with MAO.[10]

The energy profile changes dramatically if we consider the interaction of ethylene with IP2. The first stage of the reaction, the attachment of ethylene to IP2 with the formation of stable intermediate complex I, is accompanied by a noticeable energy decrease of –6.3 or –7.1 kcal mol^{-1} (Table 1), the energy barrier TS^a is 10.2 or 3.8 kcal mol^{-1}, depending on the reaction channel. The energy barrier of the second stage TS^i, as related to the sum of energies of IP2 and C_2H_4, is negligible (Table 1). The relaxation† of transition states TS^i for IP2-1 and IP2-2 towards reagents is accompanied by turning ethylene molecule inside the coordination sphere of Zr, leading to the formation of intermediates I. This proves that there are no other intermediates on the reaction pathway between I and TS^i (*i.e.*, an intermediate with another orientation of ethylene in the coordination sphere of Zr, type b).

Thus, for the ethylene interaction with IP1, the global energy maximum corresponds to TS^i, whereas, in the case of IP2, the

† Here, the term 'relaxation' determines the optimization of geometry from the starting configuration of a system in the transition state towards the state of the nearest local minimum. In order to provide the optimization towards the reagent (product) direction, the distances related to the reaction coordinate [Zr–C(1)/Zr–C(2) for TS^a, and C(1)–C(3) for TS^i] were previously increased (decreased) by 0.1 Å for TS^a and 0.01 Å for TS^i.

energy maximum corresponds to TS[a]. Note that the reaction with the participation of IP1 needs to overcome a much higher energy barrier as compared to IP2.

Let us compare the above results with data obtained for the cation Cp_2ZrMe^+ by the same method[8] (Table 1). The attachment of ethylene to Cp_2ZrMe^+ is essentially a down-hill process without the energy barrier. The energy barrier TS[i] of the second stage of the reaction is close to analogous barriers for IP2. As can be seen in Table 1, the energy profile of the reaction $Cp_2ZrMe^+ + C_2H_4$ differs essentially from the profiles for the reactions of IP1 and IP2 with ethylene. Therefore, we conclude that the counterion plays an important role in the reaction of olefin polymerization on such ion pairs. Similar conclusion has been made[9] for the ion pairs $Cp_2ZrEt^+[MeB(C_6F_5)_3]^-$.

In summary, we conclude that the participation of two Al-containing activator molecules in the formation of the catalytic particle $Cp_2ZrMe^+A^-$ leads to a significant decrease in the global energy barrier of the reaction of this ion pair with the ethylene molecule as compared to activation by one molecule of Al-containing activator. To our opinion, this result proves the double activation mechanism for metallocene and Al-containing compound interaction in olefin polymerization catalytic systems.[1–4]

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