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DFT study of the activation of dimethylzirconocenes by aluminium-containing activators

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The participation of two and three Al≡ Lewis acid sites in the formation of the catalytic particle $Cp^*_2ZrMe^+A^-$ for olefin polymerization reactions stabilizes it with respect to neutral precursor $Cp^*_2ZrMe_2$ and $AlMe_2X$, and decreases the energy of heterolysis, *i.e.*, complete spatial separation of the ions $Cp^*_2ZrMe^+$ and A^-, enhancing the catalytic activity of these particles in olefin polymerization.

Cationic moieties of the ion pairs $Cp^*_2MAlk^+A^-$ serve as catalytic centres for olefin polymerization by metallocenes. Here, Cp^* is substituted cyclopentadienyl ligand η^5-C_5H_5, M stands for a transition metal (for instance, Zr), and A^- is a counterion. Chemical nature and structure of the counterion A^- depends on the type of the activator, usually, an Al- or B-containing compound. Currently, the most practically valid is the Al-containing activator polymethylalumoxane (MAO). For MAO-containing systems, a substantial surplus of Al with respect to M (≥ 100) is required for effective polymerization.

The notion of 'double' activation[1,2] was supported[3,4] by the example of the activator $Al(C_6F_5)_3$. The double activation mechanism is based on the fact that Al forms strong bridge bonds Al–Me–Al. As a result, one metallocene molecule interacts with two Al-containing activator molecules (or two Lewis acid sites in MAO).

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

Here, we consider the possibility of double activation in MAO-containing systems. We optimized the geometries of a number of counterions with a Me bridge $[\equiv Al–Me–Al\equiv]^-$ and calculated the energies of their dissociation into ≡Al and $[Me–Al\equiv]^-$. We found that stable Al–Me–Al bridges are formed only from the compounds $AlMe_2X$ (X = C≡, O–). This conclusion led us to our models of A^- for the active centres of polymerization, which are the ion pairs $Cp^*_2ZrMe^+A^-$ (Cp^* = η^5-C_5H_5, η^5-C_5Me_5). Solvent effects were ignored.

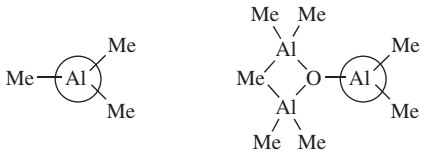
DFT calculations were performed with the use of the Priroda program[6] with PBE functional,[7] with three exponential Gauss type basis set TZ2p and corrections for relativistic effects by the electron core potentials.[8] The same approach was used earlier.[5] Geometry optimization was performed without any restriction on the system symmetry. Vibration spectra (in the harmonic oscillator approximation) of all of the structures do not reveal imaginary frequencies.

Since the compounds $AlMe_2X$ were considered as models for the fragments $AlMe_2O$– in MAO, we ignored the contribution of $AlMe_2X$ dimerization process in $Cp^*_2ZrMe^+A^-$ formation reaction. According to our calculations, dimerization energies were estimated at –16.0 kcal mol^{-1} for $AlMe_3$ and –14.4 kcal mol^{-1} for $AlMe_2F$. According to experimental data,[9] the enthalpy of $AlMe_3$ dimerization in the gas phase is –20.4 kcal mol^{-1} (in the temperature range 70–140 °C).

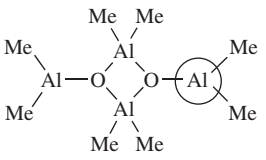
We have investigated the formation and dissociation of bridge counterions:

$$\equiv Al + \left[Me-Al\equiv\right]^- \rightleftharpoons \left[\equiv Al-Me-Al\equiv\right]^-$$

For modelling double counterions, we have considered three structures based on trimethylaluminium $AlMe_3$ (TMA) and tetramethylalumoxane $Me_2Al–O–AlMe_2$ (AO):



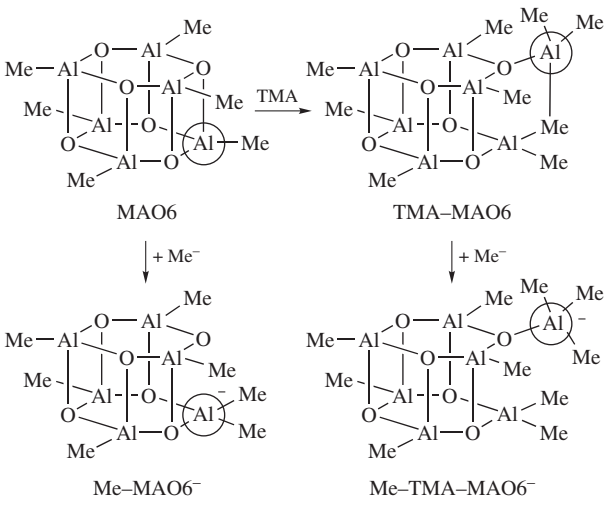
TMA TMA–AO



DAO

All these compounds have the terminal fragment $AlMe_2X$ (X = C≡, O–) (corresponding Al atoms are indicated by circles). The presence of TMA–AO fragments in MAO has been demonstrated experimentally.[10] For TMA, TMA–AO and DAO (tetramethylalumoxane dimer), the calculated energies of formation (or dissociation) of the corresponding bridge counterions $[XAl(Me)_2–Me–Al(Me)_2X]^-$ are close, –21.6, –23.5 and –22.6 kcal mol^{-1} (positive sign of energies for dissociation). These energies are notably lower (by absolute values) than that calculated earlier for $Al(C_6F_5)_3$ (–30.2 kcal mol^{-1}).[3,5]

More complex models of the MAO cage, $(AlOMe)_6$ and $AlMe_3(AlOMe)_6$ (we will use the abbreviations MAO6 and TMA–MAO6, respectively), containing both four-centred and six-centred cycles were studied previously.[11] Here, we used MAO6 and TMA–MAO6 models and corresponding anions $[Me–MAO6]^-$ and $[Me–TMA–MAO6]^-$ presented in Scheme 1 for the investigation of energy characteristics of double counterions $[\equiv Al–Me–Al\equiv]^-$.



Scheme 1

$$MAO6 + [Me–MAO6]^- \rightarrow [MAO6–Me–MAO6]^- \quad (1)$$

$$TMA–MAO6 + [Me–TMA–MAO6]^- \rightarrow [MAO6–TMA–Me–TMA–MAO6]^- \quad (2)$$

$$MAO6 + [Me–TMA–MAO6]^- \rightarrow [MAO6–Me–TMA–MAO6]^- \quad (3)$$

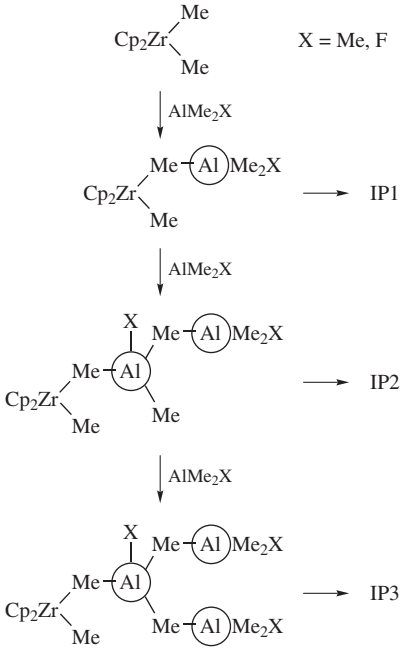
$$TMA–MAO6 + [Me–MAO6]^- \rightarrow [MAO6–Me–TMA–MAO6]^- \quad (4)$$

Terminal Al atoms involved into the formation of double counterions [≡Al–Me–Al≡]$^-$ are indicated by circles in Scheme 1.

Our calculations show that the energies of formation (dissociation) of the anions [MAO6–Me–MAO6]$^-$ [reaction (1)] and [MAO6–TMA–Me–TMA–MAO6]$^-$ [reaction (2)] are –7.5 and 24.0 kcal mol^{-1}, respectively. The energy of formation (dissociation) of the mixed anion [MAO6–Me–TMA–MAO6]$^-$ from (to) MAO6 and [Me–TMA–MAO6]$^-$ [reaction (3)] is –10.2 kcal mol^{-1}. The energy effect for the formation (dissociation) of [MAO6–Me–TMA–MAO6]$^-$ from (to) TMA–MAO6 and [Me–MAO6]$^-$ [reaction (4)] is –21.5 kcal mol^{-1} (dissociation energies are positive). For estimation of the double anion stability, it seems reasonable to take the lowest dissociation energy of 10.2 kcal mol^{-1}. The data obtained show that stable double anions [≡Al–Me–Al≡]$^-$ would be formed if both Al atoms are in the terminal positions, $AlMe_2X$ (X = C≡, O–), rather than the ring-centred atoms. In the latter case, the formation of bridge counterions is less profitable energetically, as compared to terminal Al atoms.

Comparing the energy effect in the most complex system TMA–MAO6 (–24.0 kcal mol^{-1}) and other models (TMA, TMA–AO and DAO), we conclude that the energy of the double anion formation is practically independent of the nature of the X atom and the structure of a fragment containing this atom. Therefore, we have chosen the $AlMe_2F$ as the simplest model for the $AlMe_2X$ (X = O–) compound. The calculated energy of the anion [FMe_2Al–Me–$AlMe_2F$]$^-$ formation is 24.6 kcal mol^{-1}, which is the same as that for [MAO6–TMA–Me–TMA–MAO6]$^-$ (–24.0 kcal mol^{-1}). This circumstance prompted us to study the formation and properties of catalytic particles, the ion pairs $Cp^*_2ZrMe^+A^-$ (Cp^* = = η^5-C_5H_5, η^5-C_5Me_5) in the dimethylzirconocene/Al-containing activator systems with the use of the simplest activator models: TMA and $AlMe_2F$ (see below).

In contrast to the activator $Al(C_6F_5)_3$ considered earlier,[3–5] terminal Al-containing moieties $AlMe_2X$ can form not only the double but also the triple anions with two Al–Me–Al bridges: [XMe_2Al–Me–Al(Me)(X)–Me–$AlMe_2X$]$^-$. The energies of formation of the double and triple counterions from [$AlMe_3X$]$^-$ and one or two molecules of $AlMe_2X$ are –21.6 and –37.2 kcal mol^{-1} for $AlMe_3$, and –24.6 and –42.1 kcal mol^{-1} for $AlMe_2F$, respectively. Therefore, in this work, we consider the formation of $Cp^*_2ZrMe^+A^-$ ion pairs with the participation of one, two or three activator molecules.



Scheme 2

Scheme 2 presents the main transformations including the formation of three types of particles (IP1, IP2 and IP3), which could serve as more or less efficient catalytic centres for olefin polymerization. For the particles IP1, IP2 and IP3, we use the term 'ion pairs', although they can also be named as 'bridge compounds'. Earlier,[3–5] we investigated the formation of IP1 and IP2 type adducts by the example of the activator $Al(C_6F_5)_3$.

Table 1 lists the energies of ion pair formation (E^{form}) from $Cp^*_2ZrMe_2$ and one, two or three molecules of the activator $AlMe_2X$. Parameter E^{form} can be considered as a measure of the ability of a metallocene to form active particles in the presence of an activator. Its value is mainly determined by the nature of the activator and depends only weakly on substitutions in the Cp ligand. For TMA, the addition of the second and third molecules of the activator caused the increase of E^{form} by 5 kcal mol^{-1}. For $AlMe_2F$, an absolute value of E^{form} increases by ~10 kcal mol^{-1} at each step. A similar value of 7 kcal mol^{-1} has been obtained for the activator $Al(C_6F_5)_3$. The energies of formation of the ion pairs IP3 are close to that for IP2 for systems with the activator $Al(C_6F_5)_3$. For this activator, the ion pairs of the IP3 type cannot be formed owing to the lack of the Me groups at the Al atom.

The heterolysis energy (E^{het}) is an informative characteristic of an ion pair. Parameter E^{het} allows one to evaluate the relative reactivity of ion pair with regard to the substrate (olefin molecule); therefore, parameter E^{het} could characterize the poly-

Table 1 The energies of formation E^{form} and heterolysis E^{het} (kcal mol^{-1}) of the ion pairs $Cp^*_2ZrMe^+A^-$ (IP1, IP2, and IP3) with the participation of one, two or three Al-containing activator molecules.

Ligand	Activator	IP1		IP2		IP3	
		E^{form}	E^{het}	E^{form}	E^{het}	E^{form}	E^{het}
η^5-C_5H_5	TMA	–7.1	120.3	–13.2	104.8	–18.5	94.4
η^5-C_5Me_5	TMA	–7.9	101.8	–14.7	87.1	–20.1	76.8
η^5-C_5H_5	$AlMe_2F$	–10.2	117.5	–19.1	101.7	–28.9	94.0
η^5-C_5Me_5	$AlMe_2F$	–12.0	100.1	–22.1	85.6	–32.4	78.3
η^5-C_5H_5	$Al(C_6F_5)_3$	–21.3[a]	90.0	–27.8[a]	66.3	–	–
η^5-C_5Me_5	$Al(C_6F_5)_3$	–23.7	73.2	–30.7	49.9	–	–

[a]Calculated previously.[3]

merizing ability of an ion pair. As shown earlier,[12–14] with the use of B-containing activators, the olefin binding to an active particle (ion pair) results in a spatial separation of counterions accompanied by a significant rise in the system energy. This circumstance would diminish an exothermic effect and cause an increase in the energy barrier of key stage of the olefin interactions with an active particle. Previously,[5,15] we made similar conclusions for the activator $Al(C_6F_5)_3$ and demonstrated that the participation of a second molecule of the Al-containing activator led to a significant decrease in the heterolysis energy of the ion pair (~23 kcal mol^{-1}), as well as caused a decrease in the global energy barrier on the reaction path. Relevant data for the activator $Al(C_6F_5)_3$ are presented in Table 1.

Results of our study of activators $AlMe_2X$ are in excellent agreement with our previous data for $Al(C_6F_5)_3$ (Table 1). The participation of the second activator molecule leads to diminishing the heterolysis energy by 14–16 kcal mol^{-1}. The total drop of heterolysis energy with three activator molecules comprises 22–26 kcal mol^{-1}, depending on the system considered.

Heterolysis energy depends mainly on the substitution in Cp ligands. The introduction of electron donor substituents (Me groups) in Cp rings significantly diminishes the heterolysis energy of an ion pair. Otherwise, the energy of the ion pair formation, as shown above, depends predominantly on the activator nature.

Thus, we conclude that the participation of the second and third Lewis acid sites (Al≡) in MAO stabilizes the ion pair (catalytic particle) with regard to the initial neutral compounds $Cp^*_2ZrMe_2$ and nAl≡ (n = 1, 2 or 3) and causes an essential decrease in the heterolysis energy of the ion pair $Cp^*_2ZrMe^+A^-$ (complete separation of ions $Cp^*_2ZrMe^+$ and A^-). Both these effects enhance the catalytic activity of the particles in olefin polymerization reactions. The participation of the second and third Al≡ Lewis acid sites in the ion pair formation is a probable reason for a high Al/transition metal ratio, which is necessary for a considerable catalytic activity.

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References

1 E. Y.-X. Chen, W. J. Kruper, G. Roof and D. R. Wilson, *J. Am. Chem. Soc*., 2001, **123**, 745.
2 J. L. Eilertsen and J. A. Støvneng, *Inorg. Chem.*, 2005, **44**, 4843.
3 L. Yu. Ustynyuk and E. A. Fushman, *Zh. Fiz. Khim*., 2004, **78**, 1080 (*Russ. J. Phys. Chem*., 2004, **78**, 936).
4 L. Yu. Ustynyuk, E. A. Fushman and A. Razavi, *Kinet. Katal*., 2006, **47**, 215 [*Kinet. Catal*. (*Engl. Transl.*), 2006, **47**, 213].
5 L. Yu. Ustynyuk and E. A. Fushman, *Mendeleev Commun*., 2009, **19**, 182.
6 D. N. Laikov, *Chem. Phys. Lett*., 1997, **281**, 151.
7 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett*., 1996, **77**, 3865.
8 T. R. Cundari and W. J. Stevens, *J. Chem. Phys*., 1993, **98**, 5555.
9 C. H. Henrickson and D. P. Eyman, *Inorg. Chem*., 1967, **6**, 1461.
10 S. Lasserre and J. Derouault, *Nouv. J. Chim*., 1983, **7**, 659 and references cited therein.
11 E. Zurek and T. Ziegler, *Prog. Polym. Sci*., 2004, **29**, 107.
12 G. Lanza, I. L. Fragala and T. J. Marks, *J. Am. Chem. Soc*., 1998, **120**, 8257.
13 M. S. W. Chan and T. Ziegler, *Organometallics*, 2000, **24**, 5182.
14 I. E. Nifant'ev, L. Yu. Ustynyuk and D. N. Laikov, *Organometallics*, 2001, **20**, 5375.
15 L. Yu. Ustynyuk, D. V. Besedin, Yu. A. Ustynyuk, I. E. Nifant'ev, E. A. Fushman and V. V. Lunin, *Vestn. Mosk. Univ., Ser. 2: Khim*., 2009, **50**, 428 (*Moscow Univ. Chem. Bull*., 2009, **64**, 343).

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