Exploring the Activation of Olefin Polymerisation Catalysts with Density Functional Theory

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T2N1N4

SUMMARY : Density Functional Theory has been used to study the activation of different olefin polymerisation catalysts by different activators. The results show that biscyclopentadienyl catalyst systems would act as the best catalysts and the activators of the type $[CPh_3^+][A^-]$ would be the best at activating such systems. The competition between different species present in solution for the vacant active site in the catalyst was studied for the $[(1,2Me_2Cp)_2ZrMe^+][B(C_6F_5)_3CH_3^-]$ system and the pre-catalyst and $AlMe_3$ were found to be the compounds most likely to form dormant products in solution.

Introduction

Single-site homogeneous catalysts have become the focus of active research in recent years due to their superior performance in achieving high stereoselectivity, narrow molecular weight distribution, and high activity. These systems produce structurally well defined mononuclear active species. Among the more highly active homogenous catalysts are metallocenes and related organometallic compounds containing a group 4 transition metal. The metallocenes by themselves are not very effective as polymerization catalysts, but require activation by a co-catalyst. The general structure of these pre-catalysts contain a transition metal center (M) co-ordinated to two ligands (L) and two alkyl groups (R_1, R_2) : $\{L\}_2\ MR_1R_2$. The co-catalysts are generally Lewis acids whose function is to abstract one of the alkyl groups to produce the activated metal catalyst, which is generally accepted[1-11)] to be an electrophilic species with cationic character : $\{L\}_2MR^+$. The generally accepted polymerisation scheme for such systems is shown in Figure 1, for the polymerisation of ethylene.

CCC 1022-1360/00/$ 17.50+.50/0

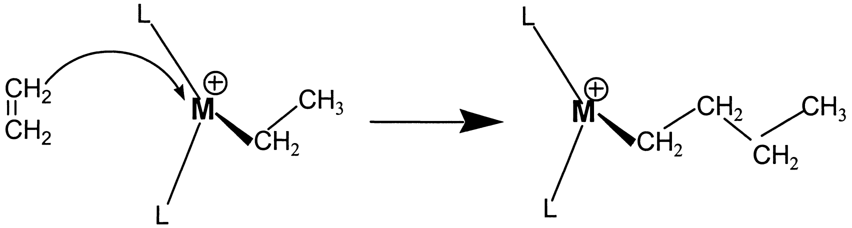


Fig. 1: Polymerisation scheme for the insertion of ethylene

The activation of the dialkyl precatalysts using a variety of co-catalysts such as boranes[7-11)] and aluminum based[12-14)] systems have been investigated experimentally. Methylalumoxane (MAO) has been the oldest and the most commonly used co-catalyst in industry. More recently[15-21)] salts of carbenium ions have been used successfully as activators.

In an ideal situation, the cationic catalyst would be readily formed and would then proceed to insert the alkene monomer, leading to the formation of the polymer chain. However the path to polymerisation may be impeded in several ways. The isolated products as well as in situ NMR[7,8)] studies indicate the formation of a variety of species associated with the catalyst, the co-catalyst, the solvent and the olefin. There is strong experimental evidence[21-24)] to suggest that the co-catalyst and solvent have strong effects on catalyst activity. A complex equilibrium is established between these species when the polymerization is carried out in solution. A possible scheme for this equilibration is depicted in Figure 2. The activation of the dimethyl pre-catalyst by a Lewis acid can lead to the formation of a contact ion-pair in which the co-catalyst is co-ordinated to the metal center as shown in pathway *A* of Figure 2. The enthalpy for this reaction is depicted as ΔHipf (enthalpy of ion-pair formation). Once produced in the reaction mixture, the contact ion-pair can dissociate completely into cation and anion such as in path *B*, with a reaction enthalpy ΔHips (enthalpy of ion-pair separation). Alternatively, a molecule of the solvent can interact with the cationic moiety, pushing away the anion to form the solvent separated ion-pair as shown in pathway *C* of Figure 2, with a reaction enthalpy ΔHss (enthalpy of forming the solvent separated ion-pair). Pathway *E* indicates that further solvation of such an ion-pair can lead to the formation of a solvent complexed cation with the counterion sufficiently far away that no electrostatic interaction is possible. In the presence of the olefin, a molecule of the olefin can insert itself between the contact ion-pair in a similar fashion to produce the olefin separated ion-pair (pathway *D*), with an enthalpy ΔHes (enthalpy of forming the olefin - ethylene - separated ion-pair). Further dissociation of this ion-pair results in the formation of the olefin complexed cation as shown in Pathway *F* of Figure 2.

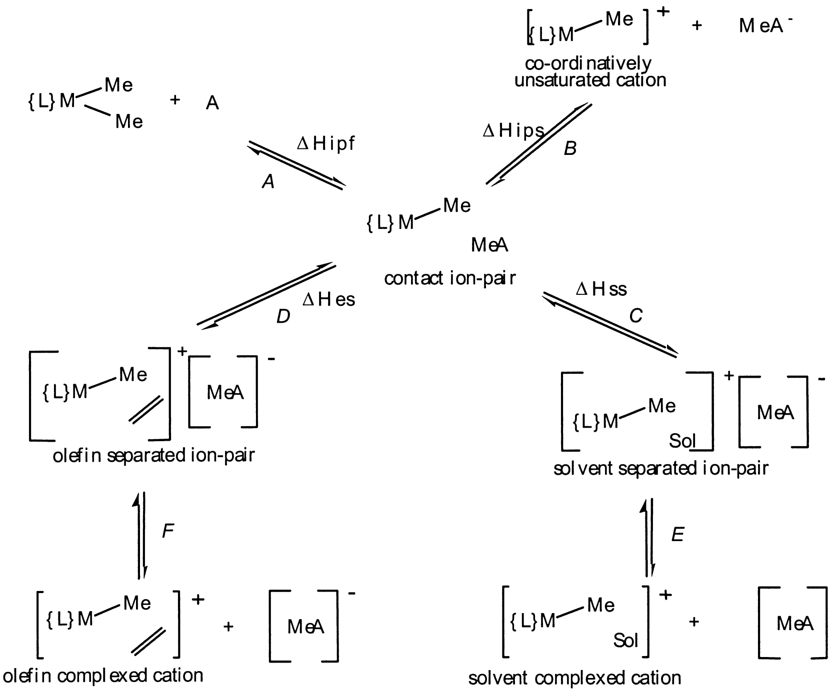


Fig. 2: Possible reactions of the ion-pair under typical polymerisation conditions

Experimental studies[10,25-27)] have also revealed the possibility of the pre-catalyst, co-catalyst and other species present in solution (like trimethyl aluminium) competing for the vacant cationic site of the catalyst to form dormant complexes. Such dormant complexes would have to be dissociated before catalysis can proceed.

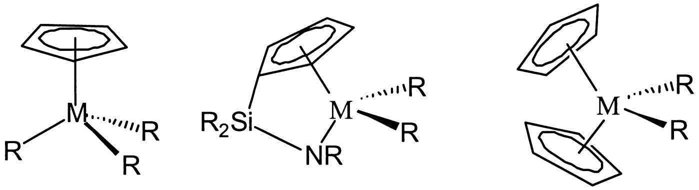
The well defined molecular structure of these metallocene catalysts and their analogues allows for more thorough mechanistic studies by theoretical methods. Many theoretical studies[28-35)] have been conducted on the olefin uptake, insertion, and termination steps of the polymerization process, but studies on the first step, the activation, and on the insertion process in the presence of the counterion have only recently started to emerge.[36-41)] Our objective was to do a theoretical study using density functional theory, of the different processes that occur in solution during the activation process.

Computational Details

The density functional theory calculations were carried out using the Amsterdam Density Functional (ADF) program version 2.3.3 developed by Baerends *et al.*[42-45)] and vectorized by Ravenek[46)]. The numerical integration scheme applied was developed by te Velde *et al.*[47,48)] and the geometry optimization procedure was based on the method of Verslius and Ziegler.[49)] Geometry optimizations were carried out using the local exchange-correlation potential of Vosko *et al.*[50)] without any symmetry constraints. The electronic configurations of the molecular systems were described by a triple-ζ basis set on zirconium for 4s, 4p, 4d and 5s, augmented with a single 5p polarisation function. A triple-ζ basis set was also used for titanium for 3s, 3p, 3d and 4s, augmented with a 4p polarisation function. Double-ζ STO basis were used for carbon (2s,2p), hydrogen (1s) and nitrogen (2s,2p), augmented with a single 3d polarisation function except for hydrogen where a 2p polarisation function was used. A set of auxiliary s,p,d,f and g STO functions centred on all nuclei was used to fit the molecular density and represent Coulomb and exchange potentials accurately in each SCF cycle.[51)] The gas phase energy difference was calculated by augmenting the local density approximation energy with Perdew and Wang's non-local correlation and exchange corrections (PW91).[52)] The energy difference in solution were corrected from the gas phase energy by accounting for the solvation energy calculated by the Conductor-like Screening Model (COSMO) that has recently been implemented into the ADF program.[53,54)] The solvation calculations were performed with the dielectric constant 2.38 for toluene, 5.71 for chlorobenzene and 9.93 for dichlorobenzene. The radii used for the atoms in Å were as follows : for hydrogen - 1.16, boron 1.15, carbon 2.0, oxygen 1.5, fluorine 1.2, silicon 2.2, titanium 2.3 and zirconium 2.4. These values were obtained by optimization using least-squares fitting to experimental solvation energies. The enthalpies (ΔH) reported in the following sections are potential energy differences without zero point corrections or vibrational finite temperature corrections. Such corrections are still too expensive to calculate for the size of molecules considered here. We expect these corrections to be of the order of ± 2-3 kcal/mol.

Study of Different Catalysts Activated by $B(C_6F_5)_3$

In this section we investigate the activation of different metallocene based precatalysts of the type $\{L\}_2MR_2$ by the the activator, or cocatalyst $B(C_6F_5)_3$. The general structures of precatalysts are shown in Figure 3 : the mono-cyclopentadienyl system, the constrained geometry system and the bis-cyclopentadienyl system.



M = Ti or Zr
R = alkyl group

Fig. 3: General structures for the mono-cyclopentadienyl, constrained geometry and bis-cyclopentadienyl catalyst precursors

The activation of the dimethyl precursors $\{L\}MMe_2$ by $B(C_6F_5)_3$ for the three classes of catalysts of interest in this study has been examined experimentally.[8,9,55-57)] These studies suggested the formation of a contact ion-pair $[\{L\}MMe]^+[MeB(C_6F_5)_3]^-$ as opposed to completely separated ions $[\{L\}MMe]^+$ and $[MeB(C_6F_5)_3]^-$. It was observed that the metal M was bound to the anion via an unsymmetrical M-Me-B bridge, the M-Me (bridging) bond being on average 0.3Å longer than the terminal M-Me bond while the B-Me (bridging) bond is just slightly longer than in the free anion $MeB(C_6F_5)_3^-$. The geometries of the experimentally obtained crystal structures were used as models for the starting structure in the optimization procedure for the ion-pairs in this study. The calculated structures obtained are similar to those of the crystal structures.

The calculated enthalpy for the methide abstraction reaction is reported in Table 1. Out of the systems examined in Table 1, the only experimental value reported is for the Cp_2ZrMe_2 pre-catalyst where a Hipf of -23.1 kcal/mol was measured by titration calorimetry.[11)] The calculated value of -19.1 kcal/mol is in reasonable agreement with this number. It was observed that the zirconium based catalysts systems formed more stable ion-pairs in comparison to the titanium analogs.

Table 1. Enthalpy change (ΔHipf) for methide abstraction from the pre-catalysts by $B(C_6F_5)_3$.

Catalyst Precursor	ΔHipf gas phase$^{a,b)}$	ΔHipf solution$^{a,b)}$
$CpTiMe_3$	-12.9	-12.2
$CpZrMe_3$	-15.7	-14.9
$H_2SiCp(NH)TiMe_2$	-13.9	-14.4
$H_2SiCp(NH)ZrMe_2$	-16.6	-17.5
Cp_2TiMe_2	-15.5	-16.3
Cp_2ZrMe_2	-19.1	-19.1

[a)] Corresponding to the process $\{L\}_2MR_2 + B(C_6F_5)_3 \rightarrow L_2M(R)\text{-}(\mu\text{-}R)\text{-}B(C_6F_5)_3 + \Delta Hipf$

[b)] kcal/mol

The corresponding values of ΔHips, ΔHss and ΔHes for these systems were also calculated. They are shown below in Table 2. Based on the results obtained and discussed in Tables 1 and 2, the most succesful catalysts are likely to be the biscyclopentadienyl based systems - they form the most stable ion-pairs, (as evidenced by their ΔHipf values in comparison to the other systems), and they show a preference for forming olefin separated ion-pair complexes - which would lead to polymerization - as opposed to solvent separated ion-pair complexes, as seen by their ΔHes and ΔHss values from table 2. This is in contrast to the other catalysts systems. Therefore the biscyclopentadienyl based systems are predicted to have the highest activity amongst the three systems studied.

Table 2. Enthalpy change for the formation of solvent separated, monomer separated and totally separated ion-pairs in solution.

Catalyst Precursor	ΔHips [a,b]	ΔHss [b,c]	ΔHes [b,d]
$CpTiMe_3$	51.5	-0.5	13.5
$CpZrMe_3$	57.4	-8.0	12.6
$H_2SiCp(NH)TiMe_2$	51.6	4.6	14.3
$H_2SiCp(NH)ZrMe_2$	57.9	-5.2	10.0
Cp_2TiMe_2	40.3	17.3	6.1
Cp_2ZrMe_2	48.5	14.1	8.2

[a] Corresponding to the process $\{L\}_2MR_2 + B(C_6F_5)_3 \rightarrow L_2M(R)\text{-}(\mu\text{-}R)\text{-}B(C_6F_5)_3 + \Delta Hipf$

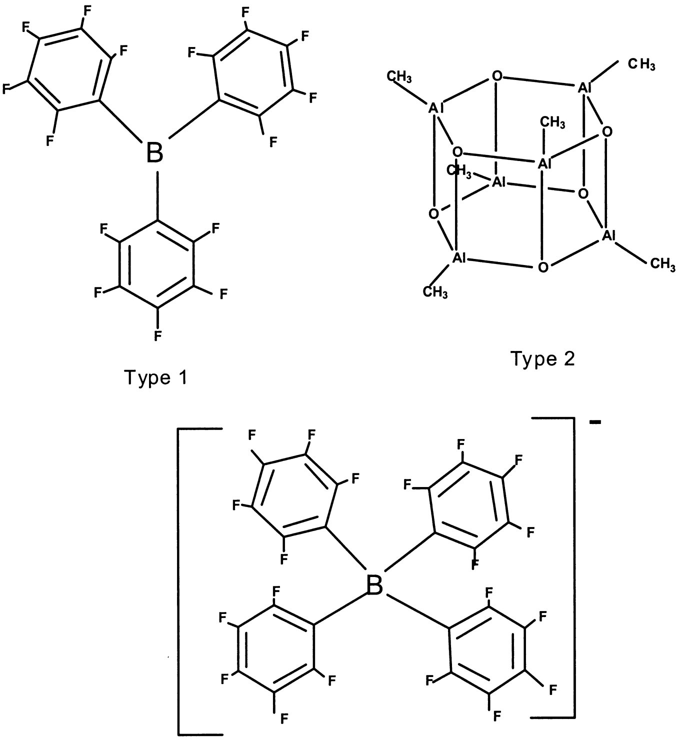
[b] kcal/mol

[c] Corresponding to the process $L_2M(R)\text{-}(\mu\text{-}R)\text{-}B(C_6F_5)_3 + S \rightarrow [L_2MR^+]\text{-}S\text{-}[RB(C_6F_5)_3^-]$

[d] Corresponding to the process $L_2M(R)\text{-}(\mu\text{-}R)\text{-}B(C_6F_5)_3 + C_2H_4 \rightarrow [L_2MR^+]\text{-}C_2H_4\text{-}[RB(C_6F_5)_3^-]$

Study of Different Activators Activating $[(1,2Me_2Cp)_2ZrMe_2$

The theoretical studies discussed in the previous section suggest that the biscyclopentadienyl based systems would make the best catalysts. However, all the catalyst systems discussed above were activated by the activator $B(C_6F_5)_3$. It would be interesting to compare the activating abilities of different activators, as that would give us further insight into finding the most effective catalyst system. We thus decided to look at the activation of the biscyclopentadienyl based catalyst $(1,2Me_2Cp)_2ZrMe_2$ using different kinds activators studied in experiment, examples of each type of which are shown in Figure 4 below.


Type 1

Type 2

Type 3

Fig. 4 : The different types of activators studied

The cocatalyst activators of Type 1 and 2 form methide bridged contact ion-pairs with the catalyst precursor, similar to the ion-pairs discussed in the previous section. These contact ion-pairs then undergo reactions as shown in Figure 2. The activators of Type 3 are however, counterions that are initially associated with cations such as $[CPh_3]^+$. The activation of the pre-catalyst by such systems leading to formation of contact ion-pairs , is shown below in equation 1 :

$$L_2M(R)_2 + [CPh_3]^+A^- \rightarrow [L_2MR]^+[A]^- + RCPh_3 \qquad (1)$$

$[A]^-$ = Activator of Type 3

The contact ion-pairs formed in these cases are not methide bridged as in Types 1 and 2. The other processes in solution for these ion-pair systems are the same as for the systems of Types 1 and 2. The formation energies for methide bridged ion-pairs (ΔHipf) for the systems of Types 1 and 2 are collected below in Table 3.

Table 3. Formation energies (ΔH_{ipf}) for methide bridged ion-pairs

Co-catalyst	ΔHipf[b,c] calc.	ΔH_{ipf} expt.[a,c]
$B(C_6F_5)_3$	-23.8	-24.2
$B(C_{10}F_7)_3$	-25.8	--
MAO	-15.9	-10.9
MBO	-22.3	--
$AlMe_3$	-8.1	--
$Al(C_6F_5)_3$	-30.8	--

[a] Obtained from reference 11.

[b] Corresponding to the process : $(1,2Me_2Cp)_2ZrMe_2 + A \rightarrow (1,2Me_2Cp)_2ZrMe\text{-}(\mu\text{-}Me)\text{-}A + \Delta H_{ipf}$.

[c] kcal/mol

From the values of ΔH_{ipf} above, one can immediately observe that compounds like $AlMe_3$ would not be very good activators, as the ion-pairs formed in this case are not very stable, whereas compounds like $Al(C_6F_5)_3$, $B(C_6F_5)_3$ and $B(C_{10}F_7)_3$ could possibly be good activators. The results compare well to the experimental values, where available. However one has also to consider the corresponding values of ΔHips and ΔHss for these systems to gauge completely their efficacy as good activators. These values are shown below in Table 4, along with the corresponding values of ΔHips and ΔHss for systems formed with activators of Type 3.

Table 4. Enthalpy of ion-pair dissociation (ΔH_{ips})[a] for ion-pairs with a methide bridge.

Co-catalyst/Counterion	Type	ΔHips(calc)[a,b]	ΔH_{SS} [b,d]	ΔHss(expt.)[b,c]
$B(C_6F_5)_3$	1	38.0	18.7	24.2
$B(C_{10}F_7)_3$	1	43.6	18.9	--
MAO	2	57.0	32.4	--
MBO	2	46.9	25.3	--
$AlMe_3$	2	69.2	35.3	--
$Al(C_6F_5)_3$	2	48.3	18.7	--
$B(C_6F_5)_4^-$	3	22.06	-4.2	--
$Al(C_6F_5)_4^-$	3	26.20	0.76	--
$[(C_2B_9H_{11})_2Co]^-$	3	34.86	7.5	--
$\{^tBuCH_2CH[B(C_6F_5)_2]_2H\}^-$	3	26.70	-0.58	--

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[a] Corresponding to the process ($Cp_2M(Me)\text{-}(\mu\text{-}Me)\text{-}A\ )_{solv} \rightarrow ([Cp_2MMe]^+)_{solv} + ([MeA]^-)_{solv} + \Delta H_{ips}$.

[b] kcal/mol.

[c] Obtained from reference 11.

It becomes clear from a perusal of the numbers that the counterions - activators of Type 3 would do a better job than activators of Type 1 and 2 in dissociating from the ion-pair, thereby freeing the cation and facilitating the approach of the monomer before insertion and the subsequent polymerisation. Hence systems activated by the activators of Type 3 should provide the best performance in catalyst polymerisation. This has been verified by experiment.[16-17]

Study of Competing Processes in Solution

The values above clearly indicate the possibility of forming these solvent separated ion-pair complexes in solution. The sole experimental value available, calculated by Marks et. al.[11)] which was assumed to have been for ion-pair dissociation, was seen to quite comparable to the value of ΔH_{SS} for that system. The possible influence of the solvent on the polymerisation process brings forth another question - how could other species present in solution affect the polymerisation process? The other prominent species present in solution, apart from the solvent (toluene, in our case) are the cocatalyst, the precatalyst and $AlMe_3$ which would be present in MAO based systems and as a scavenger in other systems. These competing species can complex to the cation and form dormant products that would have to be dissociated before insertion can proceed. The reaction leading to the formation of such dormant compounds is shown below in Eq. 2, with D representing the species coordinating to the cation in solution.

$$(1,2Me_2Cp)_2ZrMe^+ + [D] \rightarrow [((1,2Me_2Cp)_2ZrMe^+] [D] + \Delta H_{dp} \qquad (2)$$

ΔHdp = Enthalpy of dormant product formation

The values of ΔHdp was calculated for the $[(1,2Me_2Cp)_2ZrMe^+)][B(C_6F_5)_3CH_3^-]$ system for the different species present in solution. The values of ΔHdp for these systems is shown in Table 5 below.

Table 5. Enthalpy of formation of dormant products (ΔHdp)[a,b] from the coordinated complex for different species in solution.

Species	ΔHdp Calc.[a,b)]
$(1,2Me_2Cp)_2ZrMe_2$	-25.8
$B(C_6F_5)_3$	-9.9
$C_6H_5CH_3$	-10.1
$AlMe_3$	-25.5

[a)] Corresponding to the process $(1,2MeCp)_2ZrMe^+ + [D] \rightarrow [(1,2Me_2Cp)_2MMe^+] [D] + \Delta H_{dp}$

[b)] kcal/mol.

It is clear that the real "threats" to the polymerisation process would be $(1,2Me_2Cp)_2ZrMe_2$ and $AlMe_3$ as they form the most stable dormant complexes. A further study of ΔHdp was done for dormant complexes formed by $(1,2Me_2Cp)_2ZrMe_2$ and $AlMe_3$ with the catalyst with an extended chain, i.e., after insertion of one ethylene monomer unit into the Zr-Me bond. This was done to examine if such dormant complex formation would persist once the catalysis was underway. The values of ΔHdp for such complexes are shown below in Table 6.

Table 6. Enthalpy of formation of dormant products (ΔHdp)[a,b] after the insertion of the ethylene monomer.

Species	ΔHdpCalc.[a,b)]
$(1,2Me_2Cp)_2ZrMe_2$	-14.5
$AlMe_3$	-15.0

[a)] Corresponding to the process $(1,2Me_2Cp)_2ZrPr^+ + [D] \rightarrow [(1,2Me_2Cp)_2ZrPr^+] [D] + \Delta Hdp$

[b)] kcal/mol.

The reduced value (by about 10 kcal/mol) of ΔHdp for the same species but with an extended alkyl chain on the catalyst suggests that the formation of dormant products would reduce after insertion of one or more units of monomer into the metal alkyl chain. However the possibility of such products forming at a later stage in the polymerisation cannot be entirely ruled out.

The competition of the monomer (ethylene) for the vacant coordinate site in the cationic catalyst with the solvent (toluene) was considered for a set of four different ion-pair systems of the type $[(1,2Me2Cp)2ZrMe+][AMe^-]$. This was done to observe if the monomer could compete successsfully with the solvent for the vacant cationic site in such ion-pair systems - crucial for the success of polymerisation in these systems. The values of ΔHes and ΔHss are collected together in Table 7.

Table 7. Enthalpy of formation of ethylene separated ion-pair (ΔHes)[a,b] and the solvent separated ion-pair (ΔHss)[b,c]

Counterion	ΔH_{es} Calc.a,b)	ΔH_{ss} Calc.[b,c]
$B(C_6F_5)_3CH_3^-$	14.2	18.7
$B(C_{10}F_7)_3CH_3^-$	11.9	18.9
$B(C_6F_5)_4^-$	-10.9	-4.2
$[(C_2B_9H_{11})_2Co]^-$	2.3	7.5

[a] Corresponding to the process $[(1,2Me_2Cp)_2ZrMe^+][AMe^-] + C_2H_4 \rightarrow [(1,2Me_2Cp)_2ZrMe^+]\text{-}Et\text{-}[MeA^-] + \Delta Hes$

[b] kcal/mol.

[c] Corresponding to the process $[(1,2Me_2Cp)_2ZrMe^+][AMe^-] + S \rightarrow [(1,2Me_2Cp)_2ZrMe^+]\text{-}S\text{-}[MeA^-] + \Delta Hss$ (S = solvent,toluene)

The values clearly indicate that the ethylene would indeed "win" in the competition with the solvent for the vacant coordinate site for all the cases considered. It might however lose to $AlMe_3$ or to $(1,2Me_2Cp)_2ZrMe2$ but since these species are not present in as

high amounts in solution as the solvent, and since their respective concentrations will decrease in solution with the passage of time, it is to be expected that the ethylene monomer would eventually be able to compete successfully with all the species in solution for the vacant cationic site.

Conclusion

The activation of olefin polymerisation catalysts was conducted using density functional theory. Three different catalysts were studied - the monocyclopentadienyl, constrained geometry and the bis-cyclopentadienyl systems, activated by the cocatalyst $B(C_6F_5)_3$. Based on the results obtained, it was concluded that the bis-cyclopentadienyl based catalysts systems would be best activated.

Activation of the bis-cyclopentadienyl pre-catalyst $(1,2Me_2Cp)_2ZrMe_2$ was done by boron (Type1) and aluminium (Type2) based activators, and activators of the type $[CPh_3^+][A^-]$ (Type 3). Based on the results obtained, the activators of Type 3 were found to be the most effective activators with lowest value of ion-pair dissociation energy.

The competition for the vacant catalytic site in the cation was considered for different species present in solution for the $[(1,2Me_2Cp)_2ZrMe^+][B(C_6F_5)_3CH_3^-]$ system. The results showed that the pre-catalyst $(1,2Me_2Cp)_2ZrMe_2$ and $AlMe_3$ would be the strongest competitors for the active site. However the stability of the dormant complexes formed was found to decrease with the increase in the chain length.

Acknowledgement. This investigation was supported by the Natural Science and Engineering Research council of Canada (NSERC) and by Novacor Research and Technology (NRTC) of Calgary.

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