

The dissociation free energy of  $[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3][\text{H}_2\text{SiCp}_2\text{ZrMe}(\text{C}_2\text{H}_4)]$  ion pair catalyst in Molecular Dynamics Simulation

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### Introduction

In any polymerization reaction, ion-pair formation is a crucial step for the activation of catalyst in the initiation process.<sup>1</sup> Many experimental investigations have therefore been conducted for characterising the features of ion pair complexes.<sup>2</sup> Orientation of counter anion (CA) with respect to catalyst and the rate and stereo chemical aspects of polymerization reactions are the main characteristic features. Owing to the wide acceptance of “counter anion effect” on the reactivity and stereo regularity of polymer, quantum mechanical studies have contributed enormously for explaining the influence of CA on the stable agostic species as well as the energetics of reaction mechanism. Problems to solved using theoretical methods, however, still remain, because an ion-pair shows fluxional behavior in position and orientation of CA relative to the cation and monomer conformation. For instance, an ion pair can have inner- (**1a**) or outer-sphere (**1b**) structures; in **1a**, CA occupies the vacant site of the activated catalyst and in **1b** CA resides in the second coordination sphere of the catalyst (Scheme 1). Experimental evaluation of dissociation energy between monomer inserted catalyst and CA is not reported until now, because such species is highly unstable to crystallise. Though molecular dynamics (MD) studies of these points are desired, owing to the lack of the force field parameters MD studies on the organometallic complexes are limited. Hence, we set to investigate the fluxional behaviour of CA ( $\text{Cl}^-$ ,  $\text{Al}(\text{CH}_3)_4^-$  and  $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ ) and its influence on the structure of  $[\text{H}_2\text{SiCp}_2\text{ZrMe}(\text{C}_2\text{H}_4)]^+$  (**1c**?) using MD simulation.

### Computational method

The optimizations of structures were performed by DFT method at M06 level using Gaussian 09 D software. LANL2DZ basis set was applied to Zr with f polarization function and for other atoms we used 6-31++G(d,p) basis set. SMD method was used for describing the solvation effect. Concerned with the MD simulations, the total energy of the system was calculated as implemented in AMBER12 software. Potential mean forces (PMFs) were calculated using Weighted Histogram Analysis method (WHAM) in conjunction with AMBER 12.<sup>34</sup> In the final stage, WHAM program was used for finding the free energy.

### Results and discussion

We have calculated the free energy profiles for (1) dihedral rotation of ethylene ligand in the presence of  $\text{Cl}^-$ ,  $\text{Al}(\text{CH}_3)_4^-$  and  $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$  and for (2) the dissociation of ion-pair using pmf-MD method. The free energy for (1) in the presence of  $\text{Al}(\text{CH}_3)_4^-$  has slightly decreased (3.1 kcal/mol) as compared to MM rotation (4.3 kcal/mol). A shallow PMF curve minima for (2) are at the Zr-B and Zr-Al distances of about 6.64 and 6.10 Å for  $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$  and  $\text{Al}(\text{CH}_3)_4^-$ , respectively. The free energy profile of dissociation on ethylene bound catalyst shows that CA is slightly displaced with negligible energy. Hence it renders a space for the parallel orientation of ethylene to Zr-CH<sub>3</sub> axis. This tends to be a reactant species for the ethylene uptake for the polymerisation reaction to proceed.

### References:

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