



Metal–carbon bond strengths under polymerization conditions: 2,1-insertion as a catalyst stress test



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ABSTRACT

Quantitative agreement between experimentally determined M–C bond dissociation energies (BDE) and DFT predictions (M06-2X/TZ//TPSSTPSS/DZ) can be reached by choosing the correct anchor for experimentally derived BDE. For the example of the archetypical metallocene catalyst Cp₂TiCl₂, it is shown that titanium–carbon bonds are very weak under polymerization conditions and fluctuate; steric strain is introduced after 2,1 insertion and via olefin capture. Thus, homolysis can become competitive with chain propagation. Depending on the catalyst and temperature, 2,1 insertion can be only a temporary inconvenience (dormancy) or a definitive decay event. It is then shown for a set of nine common Ti and Zr polymerization catalysts how ligand variation affects the metal–carbon BDE. Predicted stabilities of the M(IV) oxidation state with respect to homolysis are in nice agreement with the experimentally observed temperature tolerance of the various catalysts: homolysis is easier for Ti than for Zr, and cyclopentadienyl groups in particular facilitate homolysis, especially in bis-cyclopentadienyl systems.

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1. Introduction

Catalytic olefin insertion polymerization represents one of the most important synthetic transformations, with a worldwide production exceeding 100 Mt/yr [1,2]. Most polymers are still produced via classical heterogeneous multisite Ti(*d*¹)-based Ziegler–Natta systems. The discovery that *ansa*-metallocenes can control tacticity sparked intense research efforts in single-center olefin polymerization catalysis [3], which went well beyond the initial scope. As a matter of fact, organometallic *d*⁰ catalysts have opened routes to a wide range of polymer structures that were previously inaccessible [4–6]. The ease of ligand modification to allow the synthesis of fine-tuned polymer structures (specialty polymers) is particularly compelling. Nowadays, a growing market share of specialty value-added polymers are produced using metallocenes or post-metallocenes [7]. Interestingly, while industrially used metallocenes are usually Zr- or Hf-based, hemimetallocenes are often Ti-based. Among the hemimetallocenes that have been commercialized are different varieties of CGC catalysts, phosphinimide-based catalysts, and ketimide and amidinate complexes, to name but a few [7]. Notably, Ti-metallocene systems

have not been commercialized because they deactivate rapidly at elevated temperatures [8,9].

Chain transfer in catalytic olefin polymerization usually occurs via β-hydrogen transfer to the monomer (BHT) or β-hydrogen elimination to the metal (BHE), although numerous other mechanisms have also been identified (β-methyl elimination, hydrogenolysis, etc.) [10]; these events limit polymer molecular weight (MW) but usually not catalyst productivity. The latter can be limited most notably by dormancy issues, e.g., tight cation–anion interactions [1], TMA binding [1], formation of η³-allylic species [11], and 2,1-insertion of 1-alkene monomers [12,13], and of course by deactivation reactions. Among the latter are, for example, reduction of the active complex by alkylaluminum species [8,14], catalyst decomposition via ligand loss, catalyst poisoning by trace amounts of donor species, anion activation [15], and, in particular for Ti(IV) catalysts, M–C homolysis. While tremendous progress has been made in understanding factors influencing intrinsic catalyst activity, those affecting catalyst stability (“catalyst mileage”) are much less understood; in particular, Brintzinger and co-authors noted, “it remains to be elucidated which circumstances are responsible for the stability of some titanium-containing constrained-geometry and titanocene-based olefin polymerization catalysts, which remain highly active for olefin polymerization at elevated temperatures” [8].

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We have recently shown that homolysis after 2,1 insertions in Ti(IV)–phosphinimide-catalyzed propene polymerization can lead to solvent incorporation via radical recombination [16]. In the present paper, we want to show how the metal–carbon bond strength fluctuates during polymerization and why 2,1 insertions can be responsible not just for dormancy but also for homolysis (leading to recombination or catalyst decay [17]).

2. Methods

The computational approach used in this study was benchmarked by us earlier in two studies focusing on the performance of DFT functionals in the modeling of alkylaluminum monomers and dimers, as well as insertion transition states; these showed nice agreement with CCSD(T)/QZ energies [18,19]. For the present study, we chose the naked cation approach to model resting states and transition states, as it was shown that weakly coordinating anions do not substantially influence propagation barriers, apart from initial anion displacement [20]. All geometries were fully optimized using the Gaussian 09 software package [21], employing the TPSSPTSS functional [22] in combination with correlation-consistent polarized valence double- ζ (Dunning) basis sets [23–30] from the EMSL basis set exchange library [31,32]. All calculations were performed at the standard Gaussian 09 quality settings [Scf = Tight and Int(Grid = Fine)]. Transition states were located using a suitable guess and the Berny algorithm [33] (Opt = TS).

All structures represent either true minima (as indicated by the absence of imaginary frequencies) or transition states (with exactly one imaginary frequency corresponding to the reaction coordinate). Final single-point energies were calculated at the M06-2X level of theory [34] employing triple- ζ Dunning basis sets [23–29]. Although M06-2X is usually recommended for main group thermochemistry, we found that it accurately reproduces different experimental problems concerning d^0 and d^1 early transition metal systems, such as absolute olefin polymerization propagation barriers [35], the copolymerization factor r_e [36], chain transfer to solvent in polymerization catalysis with titanium complexes [16], and titanium d^1 hydrodefluorination catalysis [37–39].

Enthalpies and Gibbs free energies, necessary to compare homolysis with propagation pathways in olefin polymerization, were then obtained from these single-point energies and the thermal corrections from the TPSSPTSS/cc-pVDZ vibrational analyses; entropy values were scaled by a factor of 0.67 to account for decreased entropy in the condensed phase [40–42], but no explicit solvent corrections were included.

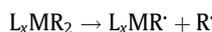
3. Results and discussion

Metal–carbon bond dissociation energies (BDEs) are the key to understanding the ease of homolysis. The only experimental data available for cationic group (IV) systems is for ligandless M-alkyl⁺ (Me, Et) species [43,44]. Concerning neutral complexes related to olefin polymerization, experimental data are limited to Cp₂MR₂ and Cp₂MR₂ [45]. We therefore chose these metallocene systems to test the reliability of DFT calculations of BDE [46], employing a protocol that was previously validated for olefin polymerization catalysis [16,18,19,35,36]. We then proceeded to study the variation of the M–C BDEs along the steps of the polymerization catalysis path.

3.1. Comparing experimental and calculated bond dissociation energies for neutral group 4 M(IV) systems

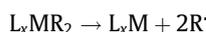
M–X BDEs have been experimentally determined for MCl₄ and for several homoleptic MR₄ complexes (M = Ti or Zr; see Table 1). For these, agreement between calculated and experimental results

is quite good, providing some confidence in the reliability of predictions for heteroleptic systems. Trends in the homoleptic TiR₄ and ZrR₄ compounds are similar, i.e. CH₂tBu < Bz (+ 1–3 kcal/mol) < CH₂TMS (+ 13–15 kcal/mol) < Cl (+ 56–59 kcal/mol) [43]. Evaluation of M–C BDEs for heteroleptic Cp₂MR₂ complexes is more complicated, however. In principle, the BDE of an M–C bond in an L_xMR₂ complex can be evaluated from the relevant enthalpies of formation using the equation [45]



$$D(M-C) = \Delta_f H^0(L_xMR, g) + \Delta_f H^0(R, g) - \Delta_f H^0(L_xMR_2, g). \quad (1)$$

Since typically data for L_xMR are not available, one usually attempts to evaluate the average \bar{D} of the first and second BDEs:



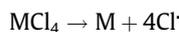
$$\bar{D}(M-C) = 1/2[\Delta_f H^0(L_xM, g) + 2\Delta_f H^0(R, g) - \Delta_f H^0(L_xMR_2, g)]. \quad (2)$$

In practice, the enthalpies of formation of L_xM fragments are also not directly available, but they can be derived from experimentally known systems by combination with the equation [45]



$$\bar{D}(M-Cl) = 1/2[\Delta_f H^0(L_xM, g) + 2\Delta_f H^0(Cl, g) - \Delta_f H^0(L_xMCl_2, g)]. \quad (3)$$

This can be solved for $\Delta_f H^0(L_xM, g)$ assuming equality of the average M–Cl bond strengths in Cp₂MCl₂ and MCl₄, using the equation



$$\bar{D}(M-Cl) = 1/4[\Delta_f H^0(M, g) + 4\Delta_f H^0(Cl, g) - \Delta_f H^0(MCl_4, g)] \quad (4)$$

This demonstrates that the evaluation of “experimental” BDEs for M–C bonds in, e.g., Cp₂MR₂ is by no means straightforward and depends on several assumptions. In the case of group 4 Cp₂MR₂ complexes, the main assumption is that $\bar{D}(M-Cl)$ in MCl₄ (averaged over all four M–Cl bonds) is equal to $\bar{D}(M-Cl)$ in Cp₂MCl₂ (averaged over two M–Cl bonds); all derived values are anchored to this assumption. As shown below, this assumption is problematic, and indeed the accuracy of experimental Ti–C BDE in Cp₂TiR₂ systems has already been called into question by Simoes and Beauchamp [43,47].

The well-known ease of formation of Ti(III) from Ti(IV) is reflected in the TiCl₄ first to fourth BDE (D_1 to D_4), which have been individually measured: 82.5, 101.6, 122.6, 105.3 kcal/mol [43]. The variation in M–Cl BDE is such that the averages over D_1 and D_2 (91.3 kcal/mol) differ substantially from the average over D_1 – D_4 (102.9 kcal/mol), and our calculated values reproduce this difference (87.2 vs. 98.8 kcal/mol). This alone invalidates the transferability assumption mentioned above, and correction for it would reduce all derived Ti–C BDEs by ~12 kcal/mol. However, our DFT results indicate that in addition $\bar{D}_{12}(Ti-Cl, Cp_2TiCl_2)$ is nearly 7 kcal/mol smaller than $\bar{D}_{12}(Ti-Cl, TiCl_4)$: 80.1 vs. 87.2 kcal/mol. Thus, the abovementioned equality assumption is not justified. If we use the computationally predicted $\bar{D}_{12}(Ti-Cl, Cp_2TiCl_2)$ as an anchor, all Ti–C BDEs for Cp₂TiR₂ become lower by 22.8 kcal/mol (relative values are not affected). Table 1 includes our proposed reanchored values for experimental determinations of Cp₂MR₂ compounds. The new values agree much better with the intuitive expectation that $\bar{D}(Ti-C) < \bar{D}(Zr-C)$. The corresponding correction calculated for Zr is much smaller (approx. 6 kcal/mol) and to

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