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# Heavy-Atom Kinetic Isotope Effects, Cocatalysts, and the Propagation Transition State for Polymerization of 1-Hexene Using the *rac*-($C_2H_4$(1-indenyl)$_2$)$ZrMe_2$ Catalyst Precursor

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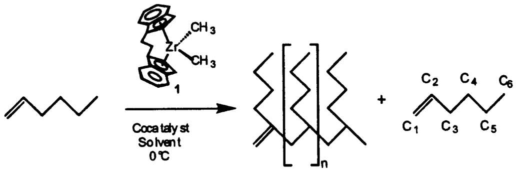
Cocatalysts influence the activities, stereoselectivities, and molecular weights of polyalkenes produced by metallocene catalysts.[1] Examples include (1) large increases in catalyst activities with lessened coordinating ability of the anions (e.g., $B(C_6F_5)_4^-$ more active than $MeB(C_6F_5)_3^-$) and (2) substantial affect of the cocatalyst on the stereoselectivities of both syndiotactic[2] and stereoblock polymerizations[3] of propene. It is generally agreed that the role of cocatalysts is the creation of catalytically active metallocenium cations with cocatalyst-derived counterions. The profound influences exerted by cocatalysts in polymerization reactions raise fundamental mechanistic questions: Do changes in the counterion change the transition state for incorporation of alkene into the metal−alkyl bonds? Is the nature of this transition state primarily binding of the alkene to the metal or migration of the polymer chain onto the coordinated alkene? To address these questions, we undertook the experimental determination of $^{12}C/^{13}C$ kinetic isotope effects (KIEs) and computational modeling of these effects for the polymerization of 1-hexene catalyzed by *rac*-($C_2H_4$(1-indenyl)$_2$)$ZrMe_2$ (**1**) with different cocatalysts.

Previous applications of KIEs to probe mechanisms of alkene polymerization have focused on D isotope effects and yielded widely varying results.[4] For example, Stille and co-workers[4c] reported that D KIEs for cyclization of titanocene 2-alkyl-6-heptenyl chlorides are very different for $MgCl_2$ and MAO activators. In their review of olefin insertion reactions in metallocene polymerization catalysis, Grubbs and Coates[4a] propose that the variability of observed KIEs arises from changes in (1) the rate-limiting step (alkene binding vs insertion) and (2) the extent of α-agostic interaction in the transition state.

Direct kinetic measurements of the effect of cocatalyst on metallocene-catalyzed alkene polymerizations are hampered by the difficulty of determining active site concentrations.[5] The advantage of the KIE as a kinetic probe is its insensitivity to active site concentration. Application of the $^{13}C$ NMR techniques recently popularized by Singleton and co-workers[6] to metallocene-catalyzed polymerization of 1-hexene yields precise KIEs[7] for positions $C_1$−$C_4$ of 1-hexene (Table 1).

Three observations warrant comment: (1) There is no KIE for positions $C_3$ and $C_4$. (2) The KIE at $C_2$ is consistently about twice that for $C_1$. (3) Although the observed productivities varied by more than 2 orders of magnitude, there is no significant difference in KIEs among the cocatalysts (solvent polarity, chlorobenzene vs toluene, slightly affects the KIEs). We conclude that, within the sensitivity of the KIE measurements, *the transition state in which alkene is irreversibly fixed into the growing polymer does not change significantly as a function of the cocatalyst*.

***Table 1.*** Experimental KIEs[a] for the Polymerization of 1-Hexene with Different Cocatalysts



| cocatalyst[b] | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ |
|---|---|---|---|---|---|
| $B(C_6F_5)_3$ | 1.009(4) | 1.019(6) | 0.999(1) | 1.001(1) | 1 |
| $Al(C_6F_5)_3$ | 1.010(2) | 1.017(3) | 1.000(0) | 1.000(2) | 1 |
| $PhNMe_2H^+B(C_6F_5)_4^-$ | 1.009(1) | 1.017(1) | 1.001(2) | 1.001(2) | 1 |
| MAO | 1.007(4) | 1.018(1) | 1.000(1) | 1.000(1) | 1 |
| $B(C_6F_5)_3$[c] | 1.003(1) | 1.013(2) | 0.999(1) | 0.999(1) | 1 |

[a] Standard deviations are shown in parentheses. [b] Toluene as solvent. [c] Chlorobenzene as solvent.

Computational and empirical data support the proposition that propagation proceeds via two distinct steps: alkene coordination followed by irreversible insertion.[8] Most compellingly, empirical data from the Casey group[9] demonstrate that alkene coordination to neutral $Cp^*_2Y$-alkyls occurs as a distinct, reversible step prior to insertion. Empirical measurements of the free energies of alkene dissociation in tethered alkyl−alkene complexes of zirconocene cations reveal activation free energies for alkene dissociation (in $CD_2Cl_2$, 245−248 K) that are generally smaller (11.1−14.4 kcal/mol,[10a] 10.5−12.8 kcal/mol[10b]) than the activation free energies for initiation and propagation (17.5 and 14.6 kcal/mol, respectively, extrapolated to 248 K) measured[5] in toluene solution for 1-hexene polymerization catalyzed by **1**.

We have computed $^{12}C/^{13}C$ KIEs for the reaction of propene with $Cp_2Zr(i\text{-}Bu)(ClCH_3)^+$ (**2**) cation (Scheme 1).[11] This model was chosen for three reasons: (1) Very different rates of insertion into Zr−Me vs Zr−$CH_2$−polymer bonds[5] ordain a more realistic model, the *i*-Bu group, than Me for the growing poly-1-alkene. (2) Extensive computational times and complicated reaction pathways preclude modeling with a full anion. (3) Trial computations revealed that gas-phase displacement of $ClCH_3$ is approximately thermoneutral; thus, replacement of the anion with $ClCH_3$ minimizes computational times but avoids the bias of an unreasonably exo- or endothermic alkene association step. Reactants, products, and transition states were computed for four elementary steps: alkene association and insertion steps along both 1,2- and 2,1-pathways. For each elementary step, multiple transition states were found, corresponding to either different conformations of the *i*-Bu group or different orientations of attack at the metal center by propene. We were unable to locate a transition state for a concerted association/insertion pathway.

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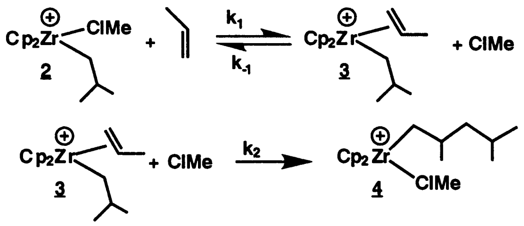
*Scheme 1*



Computed KIEs decisively discriminate between reversible and irreversible alkene association processes. Numerical results are listed in Table 2. Not unexpectedly, the computed $\text{KIE}_1$ ($={}^{12\text{C}}k_1/{}^{13\text{C}}k_1$) and $\text{EIE}_1$ ($={}^{12\text{C}}K_1/{}^{13\text{C}}K_1$; EIE represents the equilibrium isotope effect) values for the association step are close to unity, indicating that alkene association is isotope insensitive. In contrast, $\text{KIE}_2$ for the migratory insertion reaction is substantial, with average values ca. 1.02 and 1.04 at $C_1$ and $C_2$, respectively.[12] If alkene association were reversible, the expected KIE would be the product $\text{EIE}_1 \times \text{KIE}_2$. If alkene association were irreversible, the KIE would be fixed at the forward association step and be equal to $\text{KIE}_1$. As the results in Table 2 demonstrate, *only if alkene binding is reversible are the computed KIEs consistent with those observed*.

***Table 2.*** Computed KIEs, EIE, and Free Energies for Propene Association and 1,2-Insertion Steps at **2**

| reaction step | isotope effect $C_1$ | isotope effect $C_2$ | isotope effect $C_3$ | $\Delta G$ or $\Delta G^\ddagger$ (kcal/mol) |
|---|---|---|---|---|
| $\text{KIE}_1$[a] | 1.023 | 1.001 | 0.985 | 11 |
| average[b] | 1.006(9) | 1.001(4) | 0.999(14) | 11 to 17 |
| $\text{EIE}_1$[a] | 1.007 | 0.991 | 0.980 | −3 |
| average[b] | 1.000(7) | 0.995(5) | 0.990(13) | −3 to 1.4 |
| $\text{KIE}_2$[a] | 1.010 | 1.035 | 1.012 | 10 |
| average[b] | 1.019(8) | 1.043(7) | 1.007(5) | 10 to 17 |
| $\text{EIE}_1 \times \text{KIE}_2$[a] | 1.017 | 1.035 | 0.992 | |
| average[b] | 1.019(8) | 1.039(7) | 0.997(12) | |
| obsd KIE[c] | 1.009(1) | 1.017(2) | 1.000(2) | |

[a] Value computed for lowest energy pathway. [b] Average value for all computed pathways, with uncertainties given in parentheses. [c] Average experimental KIE for all cocatalysts.

Computed KIE values, whether averaged over all trajectories or taken from the lowest energy path, consistently reproduce the signature experimental observation: $\text{KIE}(C_2) \approx 2 \times \text{KIE}(C_1)$. We emphasize that our computational and experimental results do not preclude a concerted (one-step) process with significant "insertion" character.

In summary, we report the first determination of empirical and computed ${}^{12}\text{C}/{}^{13}\text{C}$ kinetic isotope effects for metallocene-catalyzed polymerization of a simple alkene. Experimental KIE values demonstrate that the transition state in which the alkene is committed to irreversible insertion into the growing polymer does not vary significantly with the cocatalyst. Computations support reversible alkene association at the catalysts followed by irreversible migratory insertion, although a concerted process cannot be eliminated. Assuming a two-step process, the dramatic effect of cocatalyst on reaction rate arises from the effect of the counterion on the alkene association equilibrium constant.

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**Supporting Information Available:** Full experimental and computational procedures, NMR measurements, KIE calculations, NMR spectra, ab initio structures, energies, and vibrational frequencies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) For each run, the cocatalyst (12.5 μmol) was injected into a 50 mL solution of **1** ($2.5 \times 10^{-4}$ M) and 1-hexene (3 M) at 0 °C, with in situ monitoring by IR spectroscopy. After quenching with butanol at approximately 95% conversion of 1-hexene, conversion of 1-hexene was determined by gas chromatography, and unreacted 1-hexene was recovered by distillation. ${}^{13}\text{C}$ NMR spectra were obtained at 125 MHz with inverse gated decoupling, using 125 s delays between calibrated 45° pulses. KIEs were determined from the enrichment ratios obtained by integration and 1-hexene conversions using standard relationships.[6] Each polymerization run was performed at least in triplicate, and the NMR analysis for each run was repeated thrice.
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(11) All geometry optimization and frequency calculations used the Gaussian98 program with the B3LYP[a,b] density functional, the LANL2DZ basis set[c] for zirconium, and 6-31G(d)[d−h] basis sets for H, C, and Cl. The kinetic and equilibrium isotope computations used partition functions obtained from the quantum mechanical computations (273 K, scaling factor of 1) according to standard techniques:[i,j] (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310. (d) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−728. (e) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261. (f) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209. (g) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213−222. (h) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163. (i) Abu-Hasanayn, F.; Goldman, S. A.; Krogh-Jesperson, K. *J. Phys. Chem.* **1993**, *97*, 5890. (j) Abu-Hasanayn, F.; Krogh-Jesperson, K.; Goldman, S. A. *J. Am. Chem. Soc.* **1993**, *115*, 8020.
(12) To the best of our knowledge, the only related computed ${}^{12}\text{C}/{}^{13}\text{C}$ KIEs that have been previously reported are for addition of Cu-alkyls to ethylene (ref 6b). Values of 1.033 and 1.040 were found for neutral and anionic aggregates, respectively.

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