Observation of an Inverse Kinetic Isotope Effect in a Co(III)-Catalyzed Polymerization of Ethylene

Martha J. Tanner, M. Brookhart,* and J. M. DeSimone

Department of Chemistry
University of North Carolina at Chapel Hill
Chapel Hill, North Carolina 27514

Received April 24, 1997

Development of homogeneous, well-defined metallocene-based catalysts for olefin polymerization has received close attention from both academic and industrial laboratories.[1] It is now agreed that the active species are d^0, 14-electron alkyl complexes, generally of the type Cp_2M-R^{n+} ($n = 0$ (Sc); $n = 1$ (Ti, Zr, Hf)). Kinetic isotope effects have been used to probe details of the insertion of the olefin into the metal alkyl bond.[2−4] Values of $k_{\alpha-H}/k_{\alpha-D}$ in the range of $1.2-1.3$[3] support a transition state in which there is an α-agostic interaction between the metal and the α-CH bond of the alkyl group (Figure 1).

We have shown that the late metal d^6-Co(III) alkyl complexes of general structure **1** are catalysts for the living polymerization of ethylene.[5] Spectroscopic studies have established that the β-agostic complex **1** is the catalyst resting state and that the alkyl olefin complex **2** is present in low equilibrium concentrations during polymerization[6] (Scheme 1). We report here a substantial *inverse* isotope effect for the Co(III)-catalyzed polymerization of C_2H_4 versus C_2D_4. This observation provides further insight into the mechanism of ethylene insertion in these systems and is in sharp contrast to the observations in the early metal d^0 systems.

Polymerization[7] rates were measured by injecting a chlorobenzene solution (25 mL, 6.6×10^{-4} M) of $[C_5Me_5$-$(P(OCH_3)_3)CoCH_2CH_2-\mu-H]^+$ BAr'_4^- ($Ar' = 3,5$-$(CF_3)_2C_6H_3$),[8] **1a**, into a 0.5-L bulb attached to a manometer and filled with either C_2H_4 or C_2D_4 (660 mm). The rates of gas uptake at room temperature as measured by the pressure drop were averaged
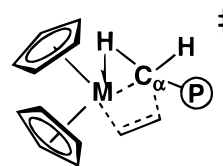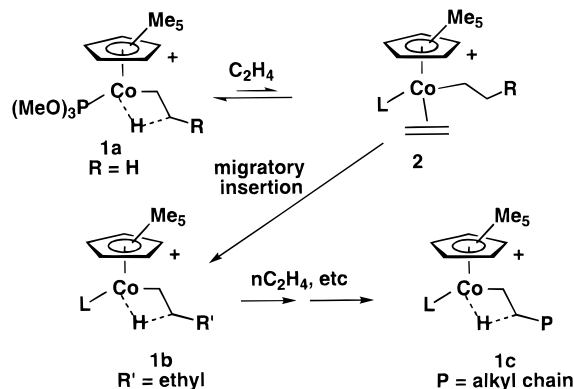

Figure 1.

Scheme 1

over the first hour for C_2D_4 (initial turnover rate = 3.7/min) and the first two hours for C_2H_4 (initial turnover rate = 1.7/min). At these times *ca.* 20% of the monomer had been consumed. These turnover frequencies reveal an inverse isotope effect of $k_H/k_D = 0.48$.

When a solution of **1** (8.26×10^{-4} M, 50 mL) is exposed to a constant 1 atm purge of C_2H_4 for 2 h, 0.37 g of polyethylene is produced ($\langle M_n \rangle = 9.5 \times 10^3$, MWD = 1.21). Polymerization of C_2D_4 under identical conditions yields 0.84 g of polyperdeuterioethylene ($\langle M_n \rangle = 19.9 \times 10^3$ MWD = 1.13).[9] The isotope effect calculated from these results is again inverse, $k_H/k_D = 0.48$.

We propose that the substantial inverse isotope effect observed for ethylene polymerization with **1** is due to the presence of a β-agostic Co- - -H- - -C (Co- - -D- - -C) interaction in the catalyst resting state. The release of the agostic interaction necessary for binding the incoming monomer results in the conversion of the β-agostic bond into a terminal C−H(D) bond in the transition state.[10] The lower C−H(D) vibrational frequencies of the agostic C−H(D) bonds in the ground state species relative to the terminal bonds in the transition state result in a smaller zero point energy difference in the ground state relative to the transition state[11] (Scheme 2) and thus an inverse isotope effect ($\Delta H_D^{\ddagger} < \Delta H_H^{\ddagger}$) is predicted.

Results of NMR spectroscopic experiments in which an equilibrium isotope effect was measured (eq 1) support the contention that the observed inverse kinetic isotope effect is associated with the release of the agostic bond. Treatment of **1a** or d_5-**1a** (*ca.* 8.6×10^{-2} M) with 2-fluoropyridine (1.4 equiv.) at -27 °C results in partial conversion to the adduct **3**

(1) For extensively referenced recent reviews, see: (a) Bochman, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (b) Brintzinger, H. H.; Fischer, D.; Muelhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (c) Fink, G.; Muelhaupt, R.; Brintzinger, H. H., Eds. *Ziegler Catalysts: Recent Scientific Innovations and Technological Improvement*; Springer-Verlag: Berlin, 1995.

(2) A recent review summarizes findings in this area: Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85.

(3) Studies which support an α-agostic-assisted transition state include the following: (a) Krauledat, H.; Brintzinger, H.-H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1412. (b) Leclerc, M. K.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **1995**, *117*, 1651. (c) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406. (d) Gilchrist, J. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 12021.

(4) In some studies, no isotope effect is observed: (a) Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377. (b) Analysis of the H/D ratios in the oligomers obtained from the reaction of mixtures of C_2H_4/C_2D_4 with $Cp_2Ti(C_2H_5)Cl + AlEtCl_2$ has been used to estimate $k_h/k_d = 1.0$ (no kinetic isotope effect): Soto, J.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4479. (c) The role of both α- and β-agostic interactions in intramolecular olefin insertions of Cp_2TiRCl has been reported, and the isotope effects vary with the cocatalyst: Barta, N.; Kirk, B. A.; Stille, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 8912.
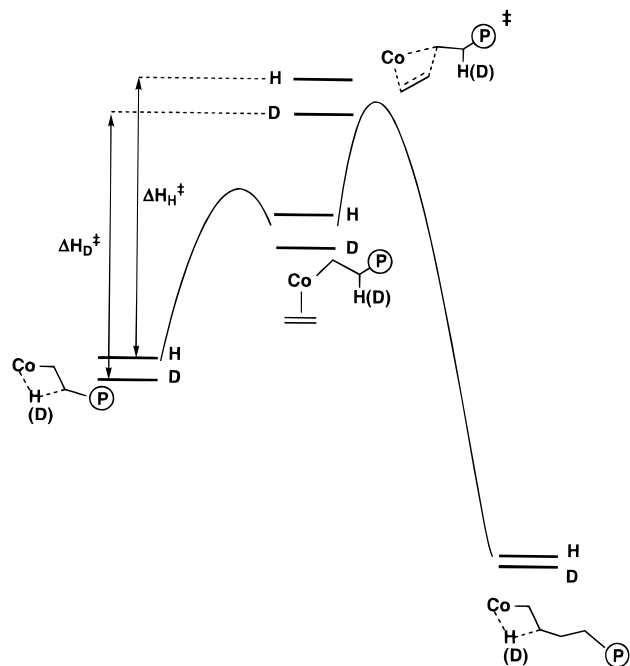
(5) (a) Brookhart, M.; Volpe, A. F., Jr.; DeSimone, J. M.; Lamanna, W. M. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1991**, *32*, 461. (b) Brookhart, M.; DeSimone, J. M.; Grant, B. E.; Tanner, M. J. *Macromolecules* **1995**, *28*, 5378. (c) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443.

(6) Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M.; Horvath, I. T.; Millar, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634.

(7) All of the polymerization reactions described were carried out in water and oxygen free conditions at room temperature (23 °C) in chlorobenzene. At the end of the reaction the system was evacuated to remove ethylene, and the polymerizations were terminated by hydrogenation. The polyethylene product was completely precipitated by the addition of acetone and collected and dried by vacuum filtration.

(8) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

(9) $\langle M_n \rangle$ for polyperdeuterioethylene was calculated with the assumption that GPC measures hydrodynamic volume, which is in turn largely dependent on chain length. The degree of polymerization, DP, was determined by taking $\langle M_n \rangle/28$ and a corrected $\langle M_n \rangle$ was obtained from DP x 32. S. D. Smith, Personal communication.

(10) A similar rationale has been used to explain inverse isotope effects for reactions where a ground state M−H(D) bond is replaced by a stronger C−H(D) bond in the transition state. The isotope effects reported for these systems ranged from 3 to 3.5: (a) Jacobsen, E. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2023. (b) Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119. (c) Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 4685. (d) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335.

(11) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

Scheme 2

(or d_5-**3**) in which the agostic C−H(D) bond has been converted to a terminal C−H(D) bond. Integration of the P(OMe)$_3$ ^{1}H

(1)

1a
d_5 - **1a**

3
d_5 - **3**
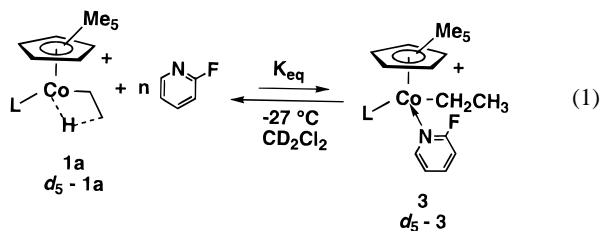
NMR resonance for **1a** (3.57 ppm) relative to that of **3** (3.73 ppm) at −27 °C yields K = 14.7 for **1a** ⇌ **3** and 25.4 for d_5 - **1a** ⇌ d_5-**3**, corresponding to an inverse equilibrium isotope effect of *ca.* 0.59. Taking into account temperature effects, this equilibrium isotope effect is significantly less than the kinetic isotope effect observed in the polymerizations. In the model system **1a** $J_{C_\beta - H_a}$ = 65 Hz, whereas in the alkyl-substituted resting state **1b** $J_{C_\beta - H_a}$ of the major isomer is a remarkably low 38 Hz.[12] These values imply that the zero point energy difference between Co---H- - -C$_\beta$ and Co- - -D- - -C$_\beta$ should be substantially greater in **1a** relative to **1b**, and likely account for the larger value of K_H/K_D relative to k_H/k_D.

To probe the kinetic isotope effect due to the incoming monomer, solutions of **1a** (25 mL, 6.92 × 10^{-4} M) were

---

(12) Brookhart, M.; Lincoln, D. M.; Volpe, A. F., Jr.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212.

Table 1. C$_2$D$_4$ Content (mol %) in the Monomer Feed and the Resultant C$_2$D$_4$ Content (mol %) in the Polyethylene Produced (700 mm Hg Total Initial Pressure, Chlorobenzene, 23 °C)

monomer	polymer
75	78
50	52
25	27
15	17

exposed to mixtures of C$_2$H$_4$ and C$_2$D$_4$. Reactions were stopped at low conversion (<20%) so that the relative amounts of C$_2$H$_4$ and C$_2$D$_4$ were essentially constant throughout the reaction. The molar ratios of hydrogen and deuterium in the resulting polymer (as analyzed by IR spectroscopy)[13] matched the molar ratios of C$_2$H$_4$:C$_2$D$_4$ in the monomer feed for all ratios examined (Table 1). These results clearly indicate that there is no selectivity[14] of **1** for the binding and insertion of C$_2$H$_4$ versus C$_2$D$_4$ and that there is no kinetic isotope effect due to the incoming monomer. The previously inserted monomer and its agostic interaction with the metal center are responsible for the observed inverse isotope effect.

The experiments described for this Co(III) system demonstrate that an inverse isotope effect may arise for olefin polymerization catalysts whose resting states involve an agostic interaction, provided no such interaction is present in the transition state. This is in contrast to normal isotope effects (k_h/k_d > 1) in many d^0 systems where the sole agostic interaction is proposed to be in the transition state. It is interesting to note that in d^0 alkyl systems (where β-agostic interactions have been observed),[11,15] a β-agostic resting state interaction and an α-agostic transition state interaction could offset each other. Furthermore, the lack of an observable difference in the selectivity of incorporation of C$_2$H$_4$ versus C$_2$D$_4$ into polyethylene despite the presence of a kinetic isotope effect points out a potential pitfall in assessing isotope effects using the more easily performed intermolecular competition experiments.

Supporting Information Available: Experimental details and results (7 pages). See any current masthead page for ordering and Internet access instructions.

---

(13) IR spectra were obtained from KBr presses of the powdered polyethylene samples. The C−H (ν = 2920 and 2850 cm^{-1}) and C−D (ν = 2195 and 2090 cm^{-1}) bands were integrated. A calibration curve, obtained from IR spectra of known mixtures of polyethylene and polyperdeuterio-ethylene homopolymers, allowed calculation of the deuterium content of the copolymer.

(14) While no selectivity for incorporation of C$_2$H$_4$ vs C$_2$D$_4$ occurs for the polymer sample as a whole, the fraction of C$_2$D$_4$ should be greater in higher molecular weight fractions while the fraction of C$_2$H$_4$ should be greater in lower molecular weight fractions. For quantitative analysis of the C$_2$H$_4$:C$_2$D$_4$ distribution as a function of the degree of polymerization, see ref 4b, particularly footnote 17.

(15) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.