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A Kinetic Study of Ethylene and 1-Hexene Homo- and Copolymerization Catalyzed by a Silica-Supported Cr(IV) Complex: Evidence for Propagation by a Migratory Insertion Mechanism

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Abstract: The surface organometallic fragment $(\equiv SiO)_2Cr{=}CHCMe_3$ initiates the polymerization of ethylene and 1-hexene at room temperature in the absence of organoaluminum or other activators. The kinetics at the gas−solid interface were studied by in situ IR spectroscopy in a constant volume, variable pressure reactor. At low pressures, the reaction is first order in $P(C_2H_4)$, first order in the number of moles of chromium, and linearly dependent on the Cr loading on silica. The second-order rate constant for polymerization is (177 ± 3) s^{-1} (mol Cr)$^{-1}$ at 21 °C, and is virtually unchanged upon subsequent additions of ethylene to the catalyst. The kinetic isotope effect, $k(C_2H_4)/k(C_2D_4)$, is a meagre 1.29. The temperature dependence of the second-order rate constants yields $\Delta H^{\ddagger}_{obs} = (30.2 \pm 0.9)$ kJ/mol and $\Delta S^{\ddagger}_{obs} = (-99 \pm 3)$ J/(K·mol). These values are consistent with a propagation mechanism of agostically assisted migratory insertion at an alkylchromium(IV) active site. They are inconsistent with an alternating alkylidene/metallacycle mechanism requiring rate-determining C−H cleavage. The rate of polymerization is accelerated by a factor of 3.2 in the presence of 18 mol % H_2. Homopolymerization of 1-hexene is only 4.7 times slower than that of ethylene, an effect attributed to weaker preequilibrium binding of the substituted olefin which is partially compensated by faster migratory insertion. Copolymerization of ethylene and 1-hexene is random. It results in slower incorporation of ethylene but faster incorporation of 1-hexene relative to their respective homopolymerization rates.

Introduction

The demand for catalysts to make new varieties of polyethylene has inspired an extraordinary effort from researchers in both industry and academia, due to the growing commercial importance of these materials. Global production currently stands at just over 40 million tons annually, making polyethylene by far the most widely used commodity polymer.[1] However, a major challenge remains in rationalizing and ultimately predicting the differences in activity manifested by various catalyst formulations, stemming partly from problems in obtaining and interpreting kinetic data for polymerizations. Reactions can be extremely rapid, and the fraction of propagation sites difficult to establish. While catalyst activities (integral rates) are relatively easy to obtain, they are highly dependent on the variable contributions of activation and deactivation processes, such that rate constants for the key propagation steps are not readily extracted.[2] Multiple equilibria involving active sites, as well as changes in the number of participating centers during the course of the reaction, are additional complications, even for so-called single-site catalysts.

Solid rather than soluble catalysts are preferred for production-scale polyolefin processes, in large part because polymer morphology replicates that of the catalyst particles.[3] Supporting molecular complexes on solid oxide surfaces has been used successfully to create supported catalysts based on group IV metallocenes and their derivatives.[4] However, such complexes show high activity only in the presence of a cocatalyst such as an organoaluminum compound; in the resulting two-component systems, the interaction between the catalyst and the activator is complex and remains incompletely understood.[5] Nevertheless, and by analogy with well-behaved single-component homogeneous catalysts,[6] a consensus has emerged that propagation occurs by migration of an alkyl ligand at the Group IV metal to the (not necessarily precoordinated)[7] olefin.

Solid polymerization catalysts can also be made by supporting early transition metal oxides (of V, Cr, Mo, and W) on silica and related oxide supports. Of these, by far the most active combination is Cr/silica,[8] which accounts for about one-third[9] of current production of high-density polyethylene. These “one-component” systems, including the Phillips[10] and Union Carbide[11] families of catalysts, polymerize ethylene in the absence of activators, and are thus simpler in composition than Ziegler−Natta catalysts, although methods for their preparation do not yield well-defined materials.[12] Phillips-type catalysts can be made from almost any Cr salt in almost any oxidation state, impregnated on silica followed by high-temperature calcination

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to give the catalyst precursor described as CrO_3/SiO_2.[13] This ease of preparation and physical robustness (the individual components as well as their mixture are thermally and air stable) confer an important technological and economic advantage, relative to the comparatively more fragile organometallic Group IV catalysts. In addition, polyethylene properties can be varied over a wide range by minor differences in catalyst activation protocols.[12]

Catalytic activity depends on the fraction of metal atoms which are active propagation sites. The number of such sites on various Phillips-type catalysts is low, on the order of 0.01 to 10% of total Cr.[12,14] All oxidation states between (II) and (V) may coexist and have been proposed at various times as "the" active valence for Cr/silica catalysts.[10,15] The nature of the Cr propagation centers is (still!) one of the most hotly debated issues in the catalysis literature.[12,16] The controversy persists because the average valence is not necessarily the active one(s).[17] Also, there is quite plausibly a difference between the initial oxidation state of the propagation sites and the oxidation state that is prevalent during polymerization.[12]

The nature of the initiation step is also unresolved. Proposals for initiation by in situ-generated (but not directly observed) hydrido-, alkyl-, allyl-, or vinylchromium complexes are extant in the literature,[10,17,18] and most researchers have interpreted the behavior of Cr catalysts in terms of a migratory insertion mechanism,[17] by analogy with d^0 catalysts based on alkylmetal complexes from Groups III and IV. However, Cr catalysts are potentially different because the active sites almost certainly have d^n ($n \neq 0$) configurations. Although olefin binding is more favorable,[19] the barrier to migratory insertion of the growing polymer chain may be elevated for catalysts based on d^n metal complexes.[20] Various carbene/alkylidene active sites have also been proposed.[21-26] Ethylene has been suggested to coordinate to Cr(II) sites, then rearrange to ethylidene on the propagation centers.[25,27] Although similar rearrangements have been documented for molecular compounds,[28,29] the involvement of alkylidene complexes in ethylene polymerization over Cr/silica catalysts remains to be convincingly demonstrated.

We showed previously that a bis(neopentyl)chromium(IV) fragment bound to a silica surface, represented as $(\equiv SiO)_2Cr(CH_2CMe_3)_2$, **1**,[30] undergoes clean intramolecular α-H abstraction in vacuo at 70 °C to give a new chemisorbed surface species identified as a site-isolated Cr(IV) neopentylidene complex, **2**, eq 1.[31,32]

$$\underset{\mathbf{1}}{(\equiv SiO)_2Cr(CH_2CMe_3)_2} \xrightarrow{70\ °C} \underset{\mathbf{2}}{(\equiv SiO)_2Cr{=}CHCMe_3} + CMe_4 \quad (1)$$

2 is a one-component olefin polymerization catalyst (i.e., it is active in the absence of organoaluminum or other activators).[31] The mechanism of its polymerization of ethylene is of interest since, unlike metal catalysts with alkyl ligands, **2** is not suited to undergo migratory insertion. An alternating alkylidene/metallacycle mechanism has been suggested as the propagation sequence for heterogeneous catalysts with chromium(IV) alkylidene active sites.[26,33] However, the absence of H/D scrambling during polymerization of partially labeled ethylene was deemed inconsistent with such a mechanism,[34] and the sole example to date of a high-valent molecular alkylidene complex of Cr was reported not to react with ethylene.[35] Nevertheless, complexes of the heavier Group VI congeners (Mo, W) with alkylidene ligands are highly effective olefin metathesis catalysts,[36] via metallacyclobutane intermediates. As we will show, **2** has much in common with the Phillips catalyst. Thus the nature of olefin polymerization by **2** is of great interest.

In this paper, we report the kinetics of the reactions of **2** with ethylene and 1-hexene to give homo- and copolymers. Our approach, using differential rates, is rarely applied to heterogeneous (or even homogeneous) polymerization catalysts, but it has the potential to be more precise and informative about the reaction mechanism than measurements of overall conversion. Polymerizations initiated by **2** are kinetically well-behaved and its active sites are compositionally homogeneous. The results of our study clearly distinguish between two contending mechanisms for α-olefin polymerization by Cr/silica catalysts.

Experimental Section

The syntheses and characterization of **1** and **2** on silica surfaces have previously been described in detail.[30,32] Since porosity of the catalyst support and its ensuing fragmentation in the course of polymerization[3] may introduce additional complications in kinetics studies, a nonporous silica (Degussa Aerosil-200, surface area 200 m^2/g) was used as the oxide support in all our experiments. High-purity C_2H_4 (Matheson), H_2 (Air Products), and C_2D_4 (98% D, Cambridge Isotopes) were further purified by passing each one through a trap containing a mixture of BTS Deoxo Catalyst (Fluka) and 3 Å molecular sieves (Aldrich), then stored in glass high-vacuum bulbs. The desired gas was transferred into the in situ reactor containing the catalyst through a high vacuum line (base pressure $<10^{-4}$ Torr) equipped with a capacitance manometer reading absolute pressures. All IR experiments were performed in a high-vacuum in situ reactor equipped with IR-transparent KCl windows.

Studies of gas-phase olefin polymerization kinetics were undertaken in closed reactors under constant volume conditions. Since **2** is highly air-sensitive, and we used no organoaluminum scavenger for impurities, strict standards of high-vacuum protocol and purification of reagents

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were necessary to obtain reproducible results. Addition of olefins containing traces of water or oxygen results in inhibition of polymerization. (We note that the commercial Phillips catalyst is also highly sensitive to such impurities, after activation.)

In general, 400 to 600 mg of compacted (pressed into pellets then ground in a mortar) silica were pretreated at 200 °C then modified with tetraneopentylchromium,[30] to give samples containing 0.3−1.3 wt % Cr (note that a loading of 1.0 wt % corresponds to 0.6 Cr/nm^2). The modified silica was heated to generate **2**,[31] then divided into 70 to 80 mg portions and sealed under vacuum in glass tubes equipped with breakseals. Each tube containing catalyst was welded directly onto a glass reactor for in situ measurements. The desired pressure of olefin was introduced into the reactor, which was placed inside the dry-air purged sample compartment of a Mattson Research Series spectrophotometer such that only the gas phase inside the cell was sampled by the IR beam. Once aligned, the reactor was not moved for the duration of the experiment. The breakseal sidearm containing the catalyst was placed in either a water bath or a preheated ceramic tube furnace thermostated at the desired temperature (±1 °C). The breakseal was broken under vacuum, using a glass-encased metal rod, to initiate polymerization. The amount of ethylene present in most kinetics experiments, ca. 1 mmol, was a 100-fold excess relative to the amount of Cr, typically 10 μmol.

The gas-phase IR absorbance spectrum was recorded at regular time intervals, without moving the reactor, to obtain differential rate data. The quantity of unreacted olefin present in the reactor was determined by integration of either the ν(CH) spectral region, 3200−2800 cm^{-1}, or the ν(CD) region, 2300−2000 cm^{-1}, as appropriate, to give an intensity I which is directly proportional to the pressure of olefin in the reactor. Nonlinear least-squares fits were performed with three variable parameters (I_0, I_∞, and k) to the first-order integrated rate equation $I_t = I_0 + (I_\infty - I_0)e^{-kt}$. Activation parameters were derived from a linear fit to a plot of ln(k/T) versus $1/T$. The errors in the activation parameters were calculated from error propagation formulas derived from the Eyring equation.[37]

Measurements of magnetization were made at 3000 G on samples sealed under vacuum in quartz tubes. Data collection was performed on a Quantum Design MPMS5S SQUID magnetometer. Background subtraction was effected by making the same measurement on a tube containing only silica. The slopes of plots of the corrected magnetic moment vs $1/T$ were used to calculate the Curie constant C and thence μ_{eff}.[38]

Results

There is no gas−solid reaction between the silica-supported bis(neopentyl)chromium(IV) complex, **1**, and low pressures of ethylene (ca. 60 Torr) at room temperature, regardless of Cr loading. However, when the temperature was slowly raised from 20 to 70 °C, a sudden rapid consumption of gas-phase ethylene was observed, Figure 1, and polyethylene was formed. The substantial induction period before the reaction with ethylene commences is associated with heating. Thus when **1** was first transformed, by thermolysis,[31] to **2**, then exposed to 60 Torr of ethylene at room temperature, we observed an immediate consumption of ethylene without an induction period, Figure 2a. After a few minutes, the orange catalyst was covered by a white film, confirmed by IR and NMR to be polyethylene.[39] An initially fragile, transparent silica pellet became rigid and opaque as it was transformed into a hard polymer disk. Ethylene disappeared completely from the gas phase, although traces of oligomers[40] were detected by GC/MS. The properties of the polyethylene formed closely resemble those of the HDPE produced by the Phillips catalyst.[41]

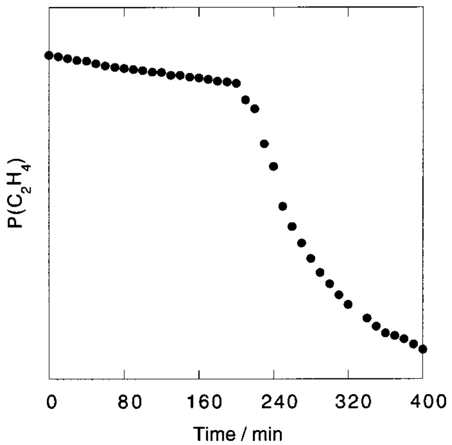

Figure 1. Time-resolved consumption of $C_2H_{4(g)}$ during polymerization initiated by solid $(\equiv SiO)_2Cr(CH_2CMe_3)_2$, **1**, at 0.89 wt % Cr loading. The temperature of the catalyst was ramped from 20 to 70 °C during the course of the experiment.

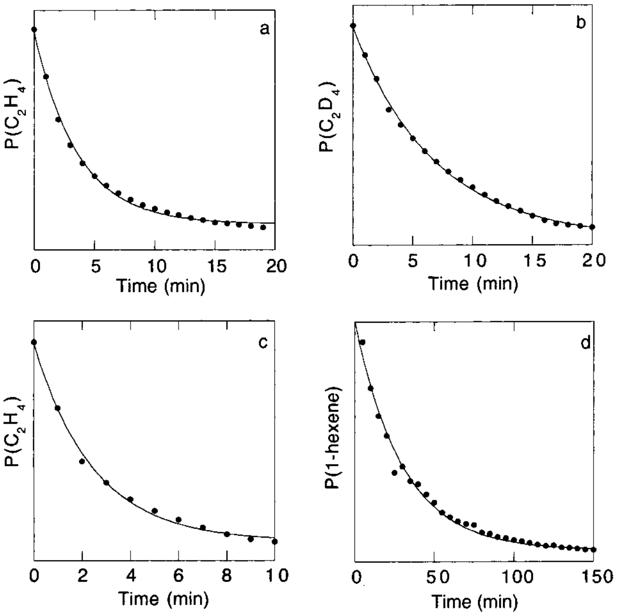

Figure 2. Time-resolved consumption of α-olefins during polymerization initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$, **2**, at constant $T = 21$ °C. (a) Polymerization of C_2H_4; (b) polymerization of C_2D_4; (c) polymerization of C_2H_4 in the presence of 18 mol % H_2; (d) polymerization of 1-hexene. The solid curves are three-parameter fits to the first-order integrated kinetic rate equation.

Kinetics of Polymerization. A powdered sample of **2** was thermally equilibrated in a reactor equipped for in situ IR spectroscopy immersed in a 21 °C water bath. Following addition of ethylene, the IR spectrum of the gas phase was recorded at timed intervals. By integration of the IR intensity in the ν(CH) region (which decreases as ethylene is consumed), we inferred the progress of the polymerization reaction occurring on the surface. A typical data set is shown in Figure 2a. The decrease in ethylene pressure is described by a single-

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(39) IR (in situ, cm^{-1}): 2924 $\nu_{as}(CH_2)$, 2850 $\nu_s(CH_2)$, 1471, 1466 (sh) $\delta(CH_2)$, 730, 718 $\rho(CH_2)$. After extraction into hot 1,2,4-trichlorobenzene: ^{1}H NMR (δ, ppm) 1.33, s; ^{13}C NMR (δ, ppm) 30.13.

(40) The oligomers are even-numbered olefins, such as butenes, hexenes, octenes, etc., as well as odd-numbered olefins which contain the neopentylidene ligand.

(41) The polyethylene produced over catalyst **2** is high-density, 0.967 g/cm^3, based on its T_m of 410 K as measured by DSC (Cowie, J. M. G. *Polymers: Chemistry and Physics of Modern Materials*; Blackie: London, 1991). It has less than two branch/end groups per 1000 C, from ^{13}C NMR. Its estimated crystallinity is 76%, from the relative intensities of the methylene rocking modes in the IR at 718 and 730 cm^{-1} (Koenig, J. L. *Spectroscopy of Polymers*; Wiley: Washington, DC, 1992).

Table 1. Pseudo-First-Order Rate Constants for C_2H_4 Polymerization Initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$

temp/°C	wt % Cr	m_{Cr}/mg	k_ψ/min$^{-1\,a}$
21	0.99	0.687	0.139 ± 0.006
21	0.45	0.756	0.149 ± 0.008
21	0.45	1.035	0.211 ± 0.006
21	0.62	1.048	0.208 ± 0.008
21	0.78	1.303	0.277 ± 0.008
48	0.35	0.343	0.257 ± 0.003
48	0.62	0.572	0.425 ± 0.002
48	0.78	0.741	0.566 ± 0.002
80	0.35	0.202	0.377 ± 0.002
80	0.62	0.281	0.542 ± 0.003
80	0.78	0.468	0.925 ± 0.004

[a] Errors are from the three-parameter nonlinear least-squares fit to one time series dataset.

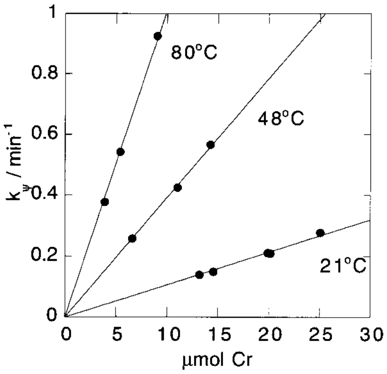

Figure 3. Dependence of the pseudo-first-order rate constants k_ψ for ethylene homopolymerization initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$, **2**, on the quantity of Cr, at the temperatures indicated.

Table 2. Second-Order Rate Constants for C_2H_4 Polymerization Initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$ at Different Temperatures

temp/°C	k/min^{-1} (μmol Cr)$^{-1}$
21	0.0106 ± 0.0002
48	0.0392 ± 0.0004
80	0.1010 ± 0.0002

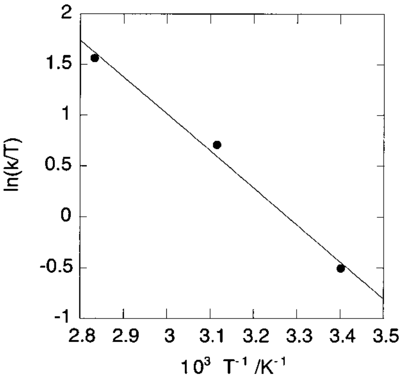

Figure 4. Eyring plot of the temperature dependence of second-order rate constants for ethylene polymerization initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$, **2**.

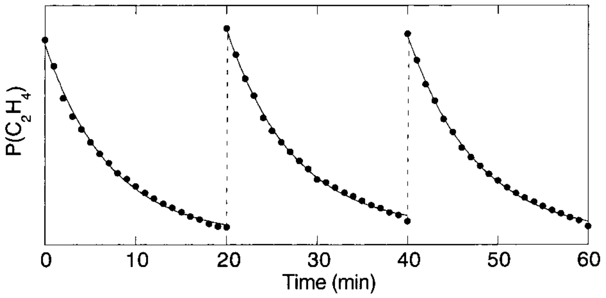

Figure 5. Activity comparison for $(\equiv SiO)_2Cr{=}CHCMe_3$ (13.2 μmol Cr, 0.99 wt % on silica) in sequential additions of ca. 65 Torr of ethylene at 21 °C. Solid lines are three-parameter fits to the first-order integrated kinetic rate equation.

Table 3. Pseudo-First-Order Rate Constants for C_2D_4 Polymerization Initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$ at 21 °C

wt % Cr	m_{Cr}/mg	k_ψ/min^{-1}
0.52	0.294	0.146 ± 0.004
0.77	0.420	0.204 ± 0.008
0.99	0.547	0.249 ± 0.010

exponential function. The value of the pseudo-first-order rate constant k_ψ is $(4.6 \pm 0.1) \times 10^{-3}$ s^{-1} in the presence of 1.30 mg of Cr supported on 167 mg of SiO_2 (i.e., 0.78 wt % Cr).

The dependence of k_ψ on the quantity of Cr was evaluated by varying the amount of catalyst present at constant Cr loading, and also by varying the Cr loading. The results are shown in Table 1. At 21 °C, k_ψ is directly proportional to the total amount of chromium present regardless of loading, Figure 3. The rate law for polymerization of ethylene at low pressure can therefore be expressed as

$$-\mathrm{d}P(C_2H_4)/\mathrm{d}t = k\, n_{Cr}\, P(C_2H_4) = k_\psi\, P(C_2H_4) \qquad (2)$$

where n_{Cr} is the number of moles of Cr present in the catalyst. The second-order rate constant for polymerization of ethylene initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$ at 21 °C is $k = (177 \pm 3)$ s^{-1} (mol Cr)$^{-1}$.

Similar kinetics experiments were performed at temperatures of 48 and 80 °C. The rate constants k_ψ are shown in Table 1. The second-order rate constants were extracted from the dependence of k_ψ on n_{Cr} at each temperature, Figure 3, and are summarized in Table 2. These values were used to construct the Eyring plot in Figure 4. Its slope and intercept yield $\Delta H^\ddagger_{obs} = (30.2 \pm 0.9)$ kJ/mol and $\Delta S^\ddagger_{obs} = (-99 \pm 3)$ J/(K·mol).

The catalyst is not significantly deactivated during the polymerization of ethylene. Sequential additions of 67, 69, and 65 Torr of C_2H_4 at 21 °C to a catalyst sample of **2** containing 13.2 μmol of Cr gave pseudo-first-order rate constants of (2.32 ± 0.10), (2.26 ± 0.07), and (2.18 ± 0.05) × 10^{-3} s^{-1}, respectively, Figure 5.

Kinetic Isotope Effect. The polymerization of C_2D_4 was also studied. The rate constants for polymerization initiated by **2** at 21 °C were measured as described above, but with integration of the absorbance in the ν(C−D) region to monitor the consumption of monomer. The polymerization of C_2D_4 is pseudo-first-order, Figure 2b. The rate constants k_ψ are given in Table 3. The second-order rate constant for polymerization of C_2D_4 at 21 °C is (137 ± 3) s^{-1} (mol Cr)$^{-1}$, from the slope of Figure 6c. Polymerization of C_2D_4 is thus slower than that of C_2H_4 by a factor of $k(C_2H_4)/k(C_2D_4) = (1.29 \pm 0.05)$.

Effect of H_2. A mixture of 10 Torr of H_2 and 47 Torr of C_2H_4 was added to samples of **2** at 21 °C and the decrease in intensity in the gas-phase IR spectrum of C_2H_4 was monitored as a function of time. The polymerization followed pseudo-first-order behavior, Figure 2c, with the rate constants k_ψ given in Table 4. The magnitude of k_ψ once again exhibited a linear dependence on the amount of Cr present, Figure 6a. The second-order rate constant is (505 ± 13) s^{-1} (mol Cr)$^{-1}$. The presence of 18 mol % H_2 thus causes the rate of polymerization of ethylene to accelerate by a factor of 3.2.

Kinetics of Homo- and Copolymerization of 1-Hexene. 1-Hexene (200 Torr) was polymerized by **2** at 21 °C. The

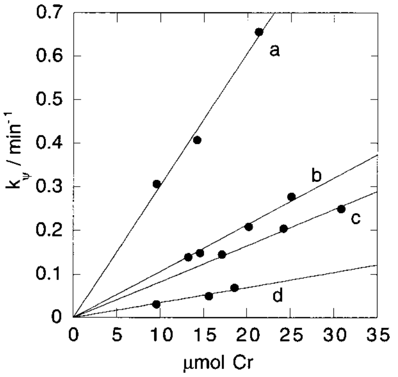

Figure 6. Dependence of the pseudo-first-order rate constants k_ψ at 21 °C for polymerization of (a) C_2H_4 in the presence of 18 mol % H_2, (b) C_2H_4, (c) C_2D_4, and (d) C_2D_4 in the presence of 80 mol % 1-hexene, initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$, **2**, on the quantity of Cr.

Table 4. Pseudo-First-Order Rate Constants for C_2H_4 Polymerization Initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$ in the Presence of 18 Mol % H_2 at 21 °C

wt % Cr	m_{Cr}/mg	k_ψ/min^{-1}
0.56	0.479	0.307 ± 0.002
0.81	0.739	0.407 ± 0.002
1.27	1.10	0.639 ± 0.003

Table 5. Pseudo-First-Order Rate Constants for 1-Hexene Polymerization Initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$ at 21 °C

wt % Cr	m_{Cr}/mg	k_ψ/min^{-1}
0.52	0.268	0.0118 ± 0.0004
0.77	0.390	0.0162 ± 0.0003
0.81	0.516	0.0211 ± 0.0010
0.99	0.761	0.0333 ± 0.0009

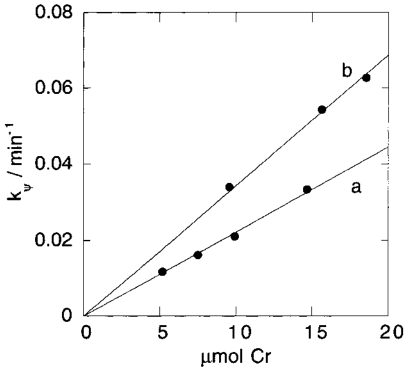

Figure 7. Dependence of the pseudo-first-order rate constants k_ψ for (a) 1-hexene homopolymerization and (b) 1-hexene copolymerization with 20 mol % C_2D_4 at 21 °C initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$, **2**, on the quantity of Cr.

Table 6. Pseudo-First-Order Rate Constants for Copolymerization of C_2D_4/1-Hexene Mixtures Initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$ at 21 °C

		k_ψ/min^{-1} [a]	
wt % Cr	m_{Cr}/mg	C_2D_4	1-hexene
0.56	0.494	0.031 ± 0.007	0.034 ± 0.001
0.89	0.813	0.050 ± 0.008	0.055 ± 0.002
0.99	0.965	0.069 ± 0.007	0.063 ± 0.001

[a] Rate constants were derived from nonlinear least-squares fits to data from the first two half-lives only.

Table 7. Summary of Measured and Derived Second-Order Rate Constants for Olefin Polymerization Initiated by $(\equiv SiO)_2Cr{=}CHCMe_3$ at 21 °C

reagent mixture	k/s^{-1} (mol Cr)$^{-1}$
C_2H_4	177 ± 3
C_2D_4	137 ± 3
0.82 C_2H_4 + 0.18 H_2	505 ± 13
1-hexene	38 ± 2
0.20 C_2D_4 + 0.80 1−hexene	C_2D_4: $k_E = 58 \pm 3$ $k_{21} = 38 \pm 5$[a] 1-hexene: $k_H = 57 \pm 2$ $k_{12} = 133 \pm 18$[a]

[a] Calculated from k_E and k_H.

consumption of 1-hexene is pseudo-first-order, Figure 2d, with rate constants shown in Table 5. They depend linearly on the amount of Cr, Figure 7a. The second-order rate constant at 21 °C is (38 ± 2) s^{-1} (mol Cr)$^{-1}$. The rate of homopolymerization of 1-hexene is therefore 4.7 times slower than the homopolymerization of ethylene.

To evaluate the selectivity for insertion of 1-hexene versus ethylene, an examination of the kinetics of copolymerization of a C_2D_4/1-hexene mixture was undertaken. Deuteration of one of the monomers allows us to monitor separately yet simultaneously the incorporation of each substrate into the polymer, evaluating the individual rate constants for copolymerization of each monomer rather than the apparent rate constant for incorporation of both. The consumption of 1-hexene was monitored by the change in absorbance in the ν(C−H) region of the gas-phase IR spectrum, while the consumption of C_2D_4 was monitored as the loss of ν(C−D) intensity. Experiments were performed with 50 Torr of C_2D_4 and 200 Torr of 1-hexene at 21 °C. The ratio of monomers was chosen such that rate constants for each are similar, Table 6, thereby maintaining the C_2D_4/1-hexene ratio for most of the experiment. To minimize errors arising from drift in the C_2D_4/1-hexene ratio during a given experiment, the rate constants were derived from nonlinear fits to data collected in the first two half-lives only.

Both sets of values of k_ψ are proportional to the amount of Cr present. The overall second-order rate constants for copolymerization (k_E for C_2D_4 and k_H for 1-hexene) are derived from plots of k_ψ vs n_{Cr}, Figures 6d and 7b. C_2D_4 is polymerized 2.4 times slower in the presence of 80 mol % 1-hexene than in its absence, whereas the polymerization of 1-hexene is 50% faster in the presence of 20 mol % C_2D_4 relative to its homopolymerization rate, Table 7.

Selectivity ratios for copolymerization were calculated from the measured rate constants. Four possible (1,2) insertion reactions and their rate constants are defined below:

$$[Cr]CH_2CH_2P + C_2H_4 \rightarrow [Cr]CH_2CH_2CH_2CH_2P; \quad k_{11} \quad (3)$$

$$[Cr]CH_2CHBuP + C_2H_4 \rightarrow [Cr]CH_2CH_2CH_2CHBuP; \quad k_{21} \quad (4)$$

$$[Cr]CH_2CHBuP + CH_2CHBu \rightarrow [Cr]CH_2CHBuCH_2CHBuP; \quad k_{22} \quad (5)$$

$$[Cr]CH_2CH_2P + CH_2CHBu \rightarrow [Cr]CH_2CHBuCH_2CH_2P; \quad k_{12} \quad (6)$$

where [Cr] represents an active site and P is a growing polymer chain, irrespective of composition. Since the monomers are consumed at overall rates which are proportional to their (constant) mole fraction, the propagation sites $[Cr]CH_2CH_2P$ and $[Cr]CH_2CHBuP$ are necessarily also present in a ratio corresponding to the relative abundances of the respective monomers. Thus for a 20:80 ethylene/1-hexene mixture, the

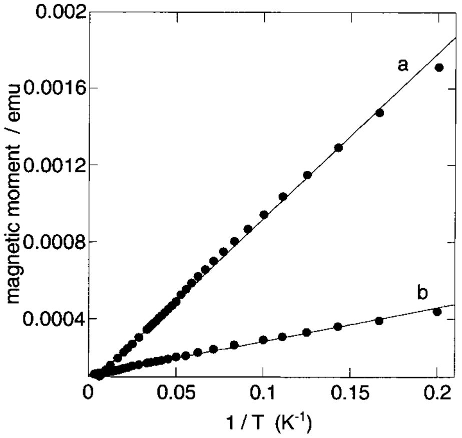

Figure 8. Curie plots for (a) 55.7 mg of $(\equiv SiO)_2Cr{=}CHCMe_3$, **2**, containing 0.3 wt % Cr and (b) 7.4 mg of polyethylene-encased **2**, containing 0.6 wt % Cr, prepared by room temperature polymerization of 20 Torr of C_2H_4 on the catalyst surface.

measured rate constants k_E and k_H are weighted averages of the homo- and crosspolymerization rate constants for each monomer:

$$k_E = 0.2\, k_{11} + 0.8\, k_{21} \tag{7}$$

$$k_H = 0.8\, k_{22} + 0.2\, k_{12} \tag{8}$$

Using the measured values of k_{11} and k_{22} (vide supra), $k_{21} = (38 \pm 5)\ s^{-1}\ (mol\ Cr)^{-1}$ and $k_{12} = (133 \pm 18)\ s^{-1}\ (mol\ Cr)^{-1}$ are derived. The perdeuterioethylene selectivity ratio r_1 is therefore $k_{11}/k_{21} = (3.6 \pm 0.6)$, while the 1-hexene selectivity ratio r_2 is $k_{22}/k_{12} = (0.29 \pm 0.05)$. From these ratios, the rates of polymerization for any mixture of the comonomers can be predicted.

Oxidation State of the Propagation Sites. The oxidation states of molecular $Cr(CH_2CMe_3)_4$,[42] of the surface complex $(\equiv SiO)_2Cr(CH_2CMe_3)_2$, **1**,[30] and of the alkylidene $(\equiv SiO)_2Cr{=}CH_2CMe_3$, **2**,[31] have all been shown to be (IV); moreover, the supported complexes are not mixtures. However, since redox processes may occur during initiation of polymerization, we reinvestigated the oxidation state of **2** after exposure to 20 Torr of ethylene, Figure 8. The effective magnetic moments of 2.8 μ_B/Cr before and 2.7 μ_B/Cr after polymerization are consistent with retention of mononuclear and noninteracting d^2 Cr(IV) surface organometallic complexes during polymerization. Upon subsequent additions of ethylene to the catalyst, polymerization occurs with the same rate constant (vide supra), therefore we conclude that Cr(IV) is the oxidation state active in ethylene polymerization in this system.

Discussion

The requirement for thermal activation of **1**, leading to the marked induction period prior to its reaction with ethylene, Figure 1, strongly suggests that **1** is first transformed into **2** which then initiates the polymerization. Indeed, reaction of preformed **2** with ethylene occurs at room temperature; this and subsequent polymerizations with the same catalyst sample show no detectable induction period. The catalyst is therefore “living” with respect to its propagation sites[43] (although it is not living with respect to individual polymer chains).[44] Kinetic studies of catalytic polymerization are greatly simplified when initiation is rapid compared to propagation, therefore all our kinetic analyses are based on the catalytic behavior starting with **2**. However, this does not imply that **2**, is the actual propagating center.

Rate Law and Activity. First-order behavior with respect to monomer pressure has previously been observed for polymerizations by heterogeneous Cr/silica catalysts,[11,17,45] although reports of other orders ranging from zero[46,47] to second[48] have also appeared; it has further been observed that the reaction order is pressure dependent.[17] Polymerizations initiated by **2** at low pressures are cleanly pseudo-first-order in monomer for the entire course of the reaction. Thus there is negligible diffusional restriction,[17] such that the reaction is always kinetically controlled, despite our observation that, in the case of ethylene, the catalyst particles become ensheathed in semicrystalline, high-density polymer as a consequence of the reaction.[41] First-order behavior implies that only one monomer is required to form the activated complex, although coordination of a second monomer which induces insertion of a pre-coordinated monomer (the trigger mechanism)[49,50] is kinetically indistinguishable, provided one of the two possible coordination sites is always filled.[50]

The polymerization reactions are also first-order with respect to total Cr, requiring that the fraction of active sites be reproducible, constant, and independent of catalyst loading.[51,52] In contrast, heterogeneous Cr/silica catalysts show increasing activity with decreasing Cr loading,[14] and the active site concentration appears to increase as polymerization proceeds.[22,51] Our observed first-order behavior in n_{Cr} rules out potential mechanisms that require two surface Cr sites for the activation of ethylene.[27,46,53,54] In addition, the magnetic properties of **2** indicate that the major, even exclusive, surface species is mononuclear.[30,31] We consider monomer-induced migration of active sites to be unlikely since the magnetic behavior of the still-active catalyst remains unchanged after polymerization. Our results further imply that (IV) is the resting oxidation state of Cr in the active catalyst.

To compare **2** quantitatively to other Cr-based one-component catalysts, the measured polymerization rate constant for ethylene at 80 °C (approximating the operating temperature of commercial reactors), $(1683 \pm 3)\ s^{-1}\ (mol\ Cr)^{-1}$, was converted to an activity, 5.9×10^6 g PE/(h·mol Cr·atm).[55] The maximum activity of CrO_3/SiO_2 operating at 80 °C was reported to be 5.0

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[44] The polydispersities of the polymers generated by **2** are high. The origin of the heterogeneity, which was unexpected given the homogeneity of the initiator, is the subject of a forthcoming publication.[57]

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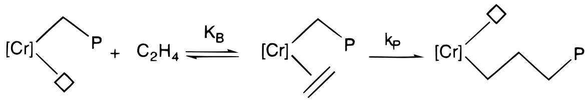
[55] The rate of formation of polymer, $dn(PE)/dt$, is expressed as $dn(PE)/dt = k\, n(C_2H_4)\, n(Cr)$. The activity, or rate of polymerization per mole of Cr, is $(dn(PE)/dt)/(n(Cr)) = k\, n(C_2H_4)$. At a pressure of 1 atm, the number of moles of ethylene in 1 L is 0.035. Therefore the activity is $(1683\ s^{-1}\ (mol\ Cr)^{-1})(3600\ s/h)(0.035\ mol\ of\ C_2H_4)(28\ g/mol) = (5.9 \times 10^6)$ g of PE/(h·mol Cr·atm). Burwell, R. L., Jr. *Adv. Catal.* **1977**, *26*, 351−392.

× 10^5 g PE/(h·mol Cr·atm).[56] A comparable activity was reported for $CrO_3/SiO_2-Al_2O_3$ at 0.001% Cr loading and 500 psi C_2H_4.[10] Clearly, the activity of **2** resembles that of the Phillips catalyst for which it is proposed as a model. The high activity of **2** even at relatively high Cr loadings and a low silica pretreatment temperature (200 °C) is likely a consequence of a higher fraction of active sites due to its relatively homogeneous nature (although the fraction does appear to be pressure-dependent).[50,57] In contrast, one-component homogeneous[58] and supported[4] Cr complexes (other than chromocene derivatives) show low or no activity unless treated with organoaluminum activators.[59]



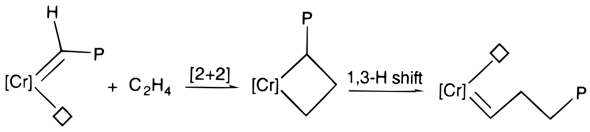
(9)

Propagation Mechanism. There are several mechanisms which are consistent with overall second-order kinetic behavior. Direct olefin insertion into a metal−carbon σ-bond would, of course, qualify, as would migratory insertion in an olefin−catalyst adduct,[60] eq 9. In the parlance of heterogeneous catalysis, these possibilities correspond to the Eley−Rideal (polymerization from the gas phase) and Langmuir−Hinshelwood (polymerization of adsorbed ethylene) mechanisms, respectively. In the latter case, the formation of an olefin adduct as a nonobservable preequilibrium intermediate follows saturation kinetics:

$$-\mathrm{d}P(\mathrm{C_2H_4})/\mathrm{d}t = K_\mathrm{B} k_\mathrm{P}\, n_\mathrm{Cr}\, P(\mathrm{olefin})/(1 + K_\mathrm{B}\, P(\mathrm{olefin})) \qquad (10)$$

where K_B is the binding constant of olefin to the active site and k_P is the rate constant for the rate-determining incorporation of the olefin into the growing polymer chain. If the binding constant K_B is small (as is typical of high-valent early transition metal complexes) and the olefin pressure low, the measured second-order rate constant k is a composite described by $k = K_Bk_P$.[61] Experimental rate laws which show this behavior are consistent with the failure to detect metal−olefin complexes in early transition metal catalyst systems.[6] At very high pressures, the dependence on P(olefin) should disappear as the rate law becomes zero-order in P(olefin), as reported for heterogeneous Phillips catalysts.[46,47,62] Unfortunately, such pressure ranges are beyond our current experimental capabilities to test.

A mechanism which is unlikely to display the observed overall second-order rate law is the alternating alkylidene−chromacyclobutane mechanism, eq 11. The observed first-order dependence on olefin pressure requires one of the unlikely[63] scenarios that cycloaddition be an unfavorable rapid preequilibrium step or rate-determining, rather than H-migration.



(11)

Propagation by repeated insertions into a metallacycle without regeneration of the alkylidene would, however, exhibit overall second-order kinetics, creating in the process a growing cyclic polymer chain with no end-groups. The failure to observe polymer chain termini by in situ IR[64] is unfortunately not conclusive for this mechanism because of their low abundance.[65] We conclude that olefin insertion into a Cr−C σ-bond is the mechanism most consistent with the observed kinetic behavior.

Interpretation of Activation Parameters. The enthalpic barrier for propagation of polymerization initiated by **2** is 30 kJ/mol. At low pressures and temperatures (<80 °C), the Phillips catalyst also shows an activation energy for ethylene polymerization of ca. 30 kJ/mol.[10] This value is much too low to be consistent with 1,3-H transfer within the chromacyclobutane intermediate, for which a barrier of over 200 kJ/mol has been calculated.[63]

For Ziegler−Natta catalysts, the activation barrier (typically 20−70 kJ/mol)[43] is presumed to be a composite reflecting both adsorption of ethylene on the active site and the barrier for the rate-determining propagation step. For the mechanism shown in eq 9, the temperature dependence of the polymerization rate constant is that described by eq 12:[66]

$$\ln(k/T) = \ln(R/Nh) + (\Delta S_\mathrm{B}{}^0 + \Delta S_\mathrm{P}{}^\ddagger)/R - (\Delta H_\mathrm{B}{}^0 + \Delta H_\mathrm{P}{}^\ddagger)/RT \qquad (12)$$

where $\Delta H_P{}^\ddagger$ and $\Delta S_P{}^\ddagger$ are activation parameters for the rate-determining propagation step and $\Delta H_B{}^0$ and $\Delta S_B{}^0$ are the enthalpy and entropy of olefin binding to the active site, respectively. The Eyring plot, ln(k/T) vs T^{-1}, is linear. Since olefin binding, if it occurs, is exothermic,[19] $\Delta H^\ddagger_{obs}$ is smaller than $\Delta H_P{}^\ddagger$ by $|\Delta H_B{}^0|$. Likewise, the negative value of $\Delta S^\ddagger_{obs}$ partly reflects the loss of entropy upon binding gas-phase ethylene to the catalyst, $\Delta S_B{}^0$.[67,68]

Agostic Assistance of Olefin Insertion. Two prominent candidates for propagation mechanisms, migratory insertion and alkylidene/metallacyclobutane alternation, should be readily distinguishable by the magnitudes of their kinetic isotope effects. The observed ratio $k(C_2H_4)/k(C_2D_4)$, at 1.29 ± 0.05, is clearly not consistent with the substantial primary kinetic isotope effect expected for C−H cleavage by 1,3-H shift, as required in the latter mechanism, nor is it consistent with simple migratory insertion, for which the effect is expected to be secondary but inverse, arising from rehybridization of the olefinic carbons.[69]

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(61) We note that a pseudo-first-order or second-order rate law does not require that all active sites polymerize ethylene at the same rate. If the rate is site-dependent, the measured rate constant is a weighted average of all the microscopic rate constants, i.e., $k = \sum_i K_{Bi}k_{Pi}$. However, all active sites must exhibit the same reaction order.

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(68) The true value of $\Delta S^\ddagger$ depends on the number of Cr sites which are active. The value reported here was calculated with the assumption that all sites are active. As a fraction of the Cr sites is inactive, the real activation entropy is greater than our reported value. We estimate the fraction of active sites at low pressures (e.g., 60 Torr) to be ca. 20%.

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Small positive kinetic isotope effects have been interpreted as evidence for agostic assistance of migratory insertion into metal−alkyl bonds.[70] Strong α-agostic interactions confer partial alkylidene character on the alkyl ligand,[7,71] stabilizing the electron-deficient transition state.[72] A secondary kinetic isotope effect of 1.25 was predicted for α-H vs α-D agostic transition states in migratory insertion.[72] Kinetic isotope effects of this magnitude have also been inferred from differences in the molecular weights of D- vs H-substituted polymers.[73] Such interactions have been documented for $[Cr_2(CH_2SiMe_3)_6]^{2-}$,[37] were calculated for the ethylene insertion transition state in $CrCl(H_2O)(CH_3)^+$,[74] and have precedent in some Group III and IV catalyst ground-state structures.[70,75]

H_2 Acceleration. The addition of H_2 during catalytic polymerization by CrO_3/SiO_2 moderates the molecular weight of polyethylene.[14] The origin of the effect is obscure, since it appears not to be exerted via acceleration of chain transfer,[12] as is the case for Cp_2Cr/silica and Group IV catalysts.[76] In contrast to the dramatic effect of H_2 on Cp_2Cr/silica,[11] Phillips-type catalysts generally exhibit only a minor response to H_2. In addition, the activities of Ziegler−Natta and chromocene catalysts are generally depressed in the presence of H_2,[77] whereas Phillips catalysts respond with an *increase* in catalyst activity.

The reason for the observed acceleration of ethylene polymerization initiated by **2** in the presence of H_2 is still not clear. One possibility is that H_2 revives deactivated sites. However, the evidence suggests that there is not much deactivation occurring under our reaction conditions, since readdition of ethylene to a used catalyst sample caused polymerization to recur with virtually the same rate constant. We suggest that H_2 causes propagation sites which are less active (or inactive) in its absence to become more active. It is conceivable that hydrogenolysis occurs to eliminate stalled polymer chains with branch points close to the metal center. The replacement of a polymer chain which is slow to undergo insertion by a more reactive hydride ligand could account for the observed rate acceleration. The origin of such chain branches in the homopolymerization of ethylene is discussed below.

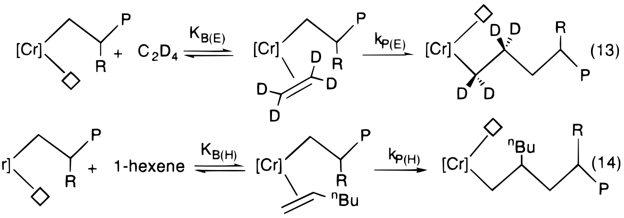
Polymerization of a Substituted Olefin, 1-Hexene. Heterogeneous Cr/silica catalysts polymerize substituted olefins provided there is no branch point closer than the 4-position,[10] although such reactions are slower than ethylene polymerization.[12] Homopolymerization of 1-hexene initiated by **2** yields poly-1-hexene. At low hexene pressures and 21 °C, the composite second-order rate constant for polymerization, $k = (38 \pm 2)\ s^{-1}\ (mol\ Cr)^{-1}$, is surprisingly only 4.7 times lower than the rate constant for ethylene incorporation into polyethylene.

In general, the binding of substituted olefins to metal complexes is weaker than that for ethylene; however, migratory insertion is faster.[78] We suggest that the slightly slower polymerization of 1-hexene initiated by **2** relative to ethylene reflects a compensation effect created by these opposing trends. CrO_3/SiO_2 catalysts, as well as **2**, generate traces of C_{2n} ethylene oligomers[23,79] during homopolymerization of ethylene. The subsequent incorporation of these higher α-olefins into the polyethylene chain is a plausible explanation for the origin of low levels of chain branching,[65,80] since these catalysts do not cause isomerization to give methyl branches.[12]

Copolymerization Behavior. CrO_3/SiO_2 is a catalyst for the copolymerization of ethylene with α-olefins, producing linear low-density polymers which are compositionally heterogeneous.[81] Copolymerization of ethylene with a small quantity of a substituted olefin, commonly 1-hexene, increases the frequency of chain branching (which enhances processability of the polymer) and decreases the average molecular weight.[10] The latter effect has been ascribed to an higher rate of termination of growing polymer chains containing β-substituents.[14]

The addition of an α-olefin other than ethylene sometimes results in an acceleration of the rate of ethylene polymerization.[82,83] The origin of this "comonomer effect" is poorly understood. Stronger coordination of the comonomer seems unlikely,[82] given the relative binding strengths discussed earlier.[84] No rate acceleration was reported for homogeneous catalysts in which there is no requirement for reduction by olefin during the induction period.[85] The absence of comonomer acceleration for **2** confirms that reduction of Cr(IV) is not required to generate the propagation sites. With regard to copolymerization, we conclude that **2** behaves more like a homogeneous than a heterogeneous catalyst.

When two monomers such as ethylene and 1-hexene are present, they compete for the open coordination site on the supported Cr catalyst. The copolymerization mechanism for C_2D_4/1-hexene mixtures is shown in eqs 13 and 14, where P represents a growing polymer chain which may or may not contain a 2-butyl branch, i.e., R is H or ⁿBu. The rate laws for competing substrates are shown in eq 15 and 16:



(13)

(14)

$$-dP(C_2D_4)/dt = K_{B(E)}k_{P(E)}n_{Cr}P(C_2D_4)/(1 + K_{B(E)}P(C_2D_4)) \tag{15}$$

$$-dP(\text{1-hexene})/dt = K_{B(H)}k_{P(H)}n_{Cr}P(\text{1-hexene})/(1 + K_{B(H)}P(\text{1-hexene})) \tag{16}$$

As the value of each denominator approaches 1, the kinetics

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become pseudo-first-order with respect to each substrate, eqs 17 and 18.

$$-\mathrm{d}P(\mathrm{C_2D_4})/\mathrm{d}t = K_{\mathrm{B(E)}}k_{\mathrm{P(E)}}n_{\mathrm{Cr}}P(\mathrm{C_2D_4}) = k_{\psi(\mathrm{E})}P(\mathrm{C_2D_4}) \quad (17)$$

$$-\mathrm{d}P(\text{1-hexene})/\mathrm{d}t = K_{\mathrm{B(H)}}k_{\mathrm{P(H)}}n_{\mathrm{Cr}}P(\text{1-hexene}) = k_{\psi(\mathrm{H})}P(\text{1-hexene}) \quad (18)$$

Since pseudo-first-order behavior is indeed observed for each substrate during copolymerization, the olefin binding constants must be small, such that each substrate behaves kinetically *as if the other is absent*.

However, the presence of a comonomer does cause the magnitudes of the rate constants $k_{\psi(\mathrm{E})}$ and $k_{\psi(\mathrm{H})}$ to change. The ethylene polymerization rate decreases while the 1-hexene polymerization rate increases, relative to each homopolymerization rate. When deuterated ethylene inserts into a polymer chain whose most recent insertion was 1-hexene, the rate is 3.6 times slower compared to insertion into a chain which most recently inserted ethylene. For 1-hexene, insertion into a perdeuterioethylene-terminated chain is 5.3 times faster than into a 1-hexene-terminated chain. The explanation that 1-hexene adsorption prevents ethylene from binding at the active site[85] is not borne out by the kinetic behavior described by eqs 17 and 18.

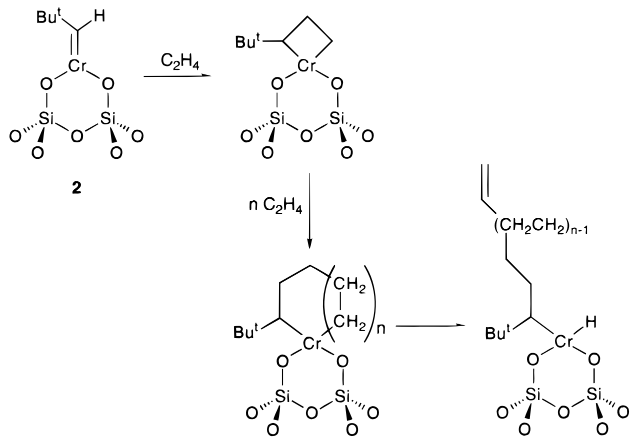
The second-order rate constants for homopolymerization (k_{11} and k_{22}) may differ from those for cross-polymerization (k_{12} and k_{21}) because of variations in k_{P} and/or K_{B}. The presence of a 2-butyl substituent in the growing polymer chain presumably exerts a steric effect which reduces both the binding constants and the insertion rate constants.

The selectivity of the catalyst based on **2** for perdeuterioethylene is low, $r_1 = 3.7$, in accord with the ability of Phillips-type catalysts to produce linear low-density polyethylenes. The selectivity for unlabeled ethylene is 177/38 = 4.7, assuming that only k_{11} and not k_{21} exhibits a significant kinetic isotope effect due to agostic interactions. For comparison, $\mathrm{MCl_4/Al^iBu_3}$ catalysts show much higher r_1 values, which for $\mathrm{C_2H_4/C_3H_6}$ mixtures range from 16 (M = V) to 76 (M = Hf).[86] $\mathrm{Cp_2Cr/SiO_2}$ catalysts show very poor propylene incorporation, with $r_1 = 72$.[11] The reactivity ratio for insertion of 1-hexene vs ethylene into an unlabeled polyethylene chain is $k_{12}/k_{11} = 0.75$, compared to 0.7 reported for incorporation of 1-butene vs ethylene by $\mathrm{CrO_3/SiO_2}$.[49]

Mechanism of Initiation of Polymerization by 2. The kinetic evidence accumulated thus far for α-olefin polymerization initiated by the alkylidene complex **2** points to a mechanism of agostically assisted migratory insertion at an alkylchromium(IV) active site, and is inconsistent with mechanisms that require regeneration of an alkylidene as a propagation step. Nevertheless, the first interaction of **2** with the α-olefin must be a reaction within the purview of transition metal alkylidene complexes, and is likely to be [2+2] cycloaddition to generate a chromacyclobutane.[85] In the case of the reaction of **2** with styrene, the metathesis product neohexene was observed, eq 19,[42] from which the metallacyclic intermediate is inferred.

$$(\equiv\mathrm{SiO})_2\mathrm{Cr{=}CHCMe_3} + \mathrm{PhCH{=}CH_2} \rightarrow (\equiv\mathrm{SiO})_2\mathrm{Cr{=}CHPh} + \mathrm{Me_3CCH{=}CH_2} \quad (19)$$

Scheme 1



In the case of reactions with α-olefins such as ethylene and 1-hexene, subsequent insertions into the metallacycle generate larger rings, for whom a likely fate is β-H elimination, Scheme 1. Hydridochromium(IV) complexes may then undergo α-olefin migratory insertion at Cr−H to generate the alkylchromium(IV) propagation center as required by the kinetics. The inability of the bis(neopentyl)chromium(IV) fragment **1** to initiate polymerization is attributed to steric hindrance at the metal center. Analysis of the volatiles produced during reactions with stoichiometric doses of ethylene suggests that insertion does not occur when there is a *tert*-butyl substituent in the α-position.[57]

This study has not addressed the important issue of how polymerization is initiated over the Phillips catalyst.[79] However, if ethylidene complexes of Cr(IV) are formed by the interaction of silica-supported Cr(II) with $\mathrm{C_2H_4}$,[25,26] then subsequent initiation reactions may resemble those in Scheme 1.

Conclusions

We have shown that the behavior of a well-defined silica-supported Cr(IV) polymerization catalyst resembles that of the activated Phillips catalyst, reproducing its activity, activation barriers, response to $\mathrm{H_2}$, and level of discrimination between ethylene and higher α-olefins. In addition, the polyethylene produced by **2** is similar in many of its properties to the polymer generated by activated $\mathrm{CrO_3/SiO_2}$, including its melting point, branching frequency, and end group identity. Indeed, the similarities manifested by catalysts based on a wide variety of Cr precursors suggest that all non-Cp-containing, silica-supported Cr catalysts ultimately tend toward a common propagating intermediate. Our results suggest that this intermediate is an alkylchromium(IV) fragment, bound to the silica surface via two covalent "siloxide" linkages. The absence of an induction period and the reproducibility of the rates of reactions of **2** with olefins have made possible a study of the kinetics of polymerization using methods usually not applicable to heterogeneous systems, hence new insight into the controversial propagation mechanism of a widely used catalyst.

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