Reaction of Vanadium Tetrachloride with Aluminum Trialkyls/Alkyl Chlorides: Formation of Intermediates in Ziegler Polymerization

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ABSTRACT: The kinetics of the rapid reaction of VCl_4 (1) and ethylaluminum sesquichloride (2) (seconds at 0 °C) have been measured in a continuous flow experiment. These reaction mixtures lead to a Ziegler olefin polymerization catalyst. Polymerization experiments indicate that only a single polymerization catalyst species is ultimately formed in near-quantitative yield under our experimental conditions. Continuous flow experiments are useful for studying the intial stages of the reaction, and we find that (a) initial reaction products are catalytially inactive, (b) the reaction has a 1:1 stoichiometry, and (c) 1 reacts independently, in first-order processes, with the dissociated monomer and the dimers of 2. Kinetic reaction constants for each of the constituent reactions have been obtained for the reaction of 1 with 2 and a group of closely related aluminum alkyl chlorides. The rate of reaction of 1 with monomer and dimers of aluminum alkyls is affected by the substitution on the aluminum. Highly alkylated aluminum compounds with small alkyl groups (Me > Et > *i*-Bu) react faster: the effect is more dramatic for dimers than for the monomers. This study provides an insight into the mechanism of reaction of early transition metal halides and aluminum alkyls—a process which is at the heart of many useful catalyst syntheses.

Introduction

Ziegler–Natta catalyst systems consisting of mixtures of early transition metal compounds (e.g., vanadium and titanium chlorides) and aluminum alkyl halides are widely used[1] for the coordination polymerization of olefins. The resulting polymers include polyethylene and polypropylene as well as the copolymers of ethene and α-olefins. The chemical reaction of these two transition metal compound components generally produces a range of products, only some of which are polymerization catalysts. These catalysts differ in their polymerization characteristics depending on the nature of the reaction components and may produce very different polymers (distinguishable by molecular weight, molecular weight distribution, and composition) under identical polymerization conditions. The selection of the reaction procedures which lead to the largest concentration of the most desirable catalyst (usually defined in terms of polymerization activity, polymer characteristics, and catalyst lifetime) is thus important. This requires a control of the chemical reaction between the transition metal halide and the alkylaluminum halides. These, usually empirical, procedures would be easier to develop if we had quantitative information about the nature of the reaction. Unfortunately, for most of the useful cases, in spite of several attempts, the details of the reaction are not well understood.[2] Simple chemical characterization tools and kinetic techniques are defeated by the rapid reaction rates, multiplicity of products, and partly heterogeneous reaction mixtures characteristic of Ziegler–Natta catalyst compositions. In this study we have used a continuous flow reactor to quantitatively estimate the rate, stoichiometry, and mechanistic features of the reaction of vanadium tetrachloride and alkylaluminum halides. These catalyst components are widely used for copolymerizing ethene and α-olefins.

Historically, quantitative estimates about the Ziegler catalyst formation reactions are inferred from a careful analysis of the reaction products. Thus identification of the products of ligand exchange reactions between the catalyst components indicates the type of interaction, while spectroscopic analysis (e.g., ESR and UV–vis) of the reaction mixtures indicates the extent of formation of new transition metal species. Characterization of polymer from controlled polymerization reactions has been a useful guide in estimating the concentration of Ziegler catalyst species. Natta[2e] was able to estimate the composition and relative concentration of several different ethene polymerization catalysts derived from $TiCl_3$ and VCl_3 by a careful analysis of the resulting low molecular weight polyethylene. Tait[3] has described the formation of a polymerization catalyst from VCl_3 and $Al(i\text{-}Bu)_3$ (i-Bu = i-C_4H_9) as an absorption process followed by alkylation of the transition metal compound. These experiments are, however, unable to provide either a detailed mechanistic understanding of the interaction of the catalyst components or a direct observation of the reacting species.

A significant exception to these procedures is the series of independent but closely related experimental observations on the reaction of aluminum alkyls with discrete biscyclopentadienyl complexes of vanadium,[4] titanium,[5,6] zirconium,[7] and scandium[8] halides. These reaction mixtures are models for Ziegler catalysts, although the activity of these mixtures differs widely. Results, in particular the ESR spectroscopy of Evans et al.[4] and the ^{13}C NMR and the plug flow reactor design of Fink et al.,[6] indicate a combination of a soluble reaction mixture, a catalyst system with only a few transition metal byproducts, and experimental equipment capable of studying the rapidly reacting species (e.g., a plug flow reactor) is needed to measure rates for the fundamental processes in the formation of a Ziegler catalyst. Most of these studies showed certain common features: (i) alkylation of the transition metal–halide bond by transfer of alkyl groups from the aluminum compound occurs readily, (ii) alkylation proceeds more readily with the dissociated monomeric aluminum alkyl halide, (iii) bimetallic complexes of the transition metal and aluminum were usually formed prior to alkylation and persisted through the reaction, and (iv) small changes in reaction conditions lead to a very different product distribution. The most detailed of these investigations were for compounds (titanium and vanadium) which are not active polymerization catalysts; thus it is unclear which reaction products/conditions are necessary to promote catalytic activity. These investi-

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Table I
GPC and Fractionation Results for Ethene–Propene Copolymers Made with 1 and 2 in a CFSTR

		GPC results			fractionation results: compositions[b]		
polymn temp (°C)	polymer compn[b]	M_n	MWD	polymer/1[a]	frac 1	frac 5	frac 8
-10	0.27	43 200	2.1	0.95	0.25	0.27	0.27
0	0.31	42 100	1.9	1.02	0.30	0.31	0.31
10	0.34	45 400	2.0	1.01	0.34	0.34	0.35
20	0.39	40 900	2.1	1.03	0.38	0.39	0.40
30	0.43	37 800	2.0	1.02	0.42	0.43	0.43
40	0.47	32 000	2.3	1.16	0.51	0.47	0.46

[a] Polymer/1 is the ratio of the moles of polymer made to the moles of 1 used per minute. [b] Polymer composition is the weight percent ethene content in the polymer.

gations are attempts at understanding the formation and structure of analogues of olefin polymerization catalysts. However, they are limited to the biscyclopentadienyl compounds of transition metals. The logical extension of these efforts, which is the subject of this work, would be a study of a widely used, active polymerization catalyst to correlate chemical transformations of the transition metal compounds to catalytic activity.

We have examined the interaction of vanadium tetrachloride (VCl_4, 1) and ethylaluminum chlorides of the empirical formula $Et_xAl_2Cl_{6-x}$, where $x = 6$–2, at molar ratios between 1/5 and 1/30 and temperatures between −5 and +30 °C in hexane. Ethylaluminum sesquichloride (2, $x = 3$) is of particular interest since the combination of 1 and 2 at these reaction conditions leads to a soluble olefin polymerization catalyst which is widely used for solution copolymerization of ethene and α-olefins.[1d] Ethylaluminum chlorides of the above general formula with $x = 1$ and 0 could not be used since they are not soluble in hexane. The reaction of 1 with $Me_4Al_2Cl_2$ and $(i\text{-}Bu)_4Al_2Cl_2$ has also been studied: these experiments provide insight into a possible mechanism for the reaction. The reaction is conducted in a continuous flow reactor at a vanadium concentration of 0.4–2 mM (vide infra) and monitored by observing the disappearance of 1 since 1 in hexane solution has a strong absorbance[9] at 412 nm (log $\epsilon = 3.12$). We have incorporated several of the most important conclusions of earlier studies[4-8] in designing these experiments.

Results

Reaction System. In this study hexane is used as the solvent since interactions of either the reactants or the products with olefinic (which polymerize in the presence of 1 and 2), aromatic (complexes with 1),[10] or chlorinated alkane solvents (with aluminum alkyls)[11] have been reported. Polar solvents such as THF form stable addition complexes with 1 and 2: they are thus unsuitable. Purity (usually <2 ppm in moisture and oxygen combined) and the isomer distribution of hexane are described in the Experimental Section.

Consistent results in these solution experiments depend on the concentration of the transition metal. At concentrations less than 0.2 mM the adventitious moisture and polar impurities in hexane are a significant fraction of the total vanadium concentration. This is the lower limit of vanadium concentration for reliable results. However, at vanadium concentrations above 10 mM the chemical reactions involved in the formation of the polymerization catalyst are too rapid for convenient study. These concentration ranges thus define the limits of these experiments. Vanadium concentrations between 0.4 and 2.0 mM are studied since they are widely used for polymerization reactions and they are within the limitations of our experimental procedures.

Polymerization Experiments: A Single Catalyst. The number of active catalyst sites is determined by a hexane solution copolymerization of ethene and propene to make copoly(ethene–propene) copolymer with <70 mol % ethene in composition. These polymers are amorphous and soluble in hexane at temperatures above −10 °C. If (a) all of the reaction components including the resulting polymer are soluble and (b) agitation of the reaction mixture is sufficient to prevent nonuniform diffusion of monomers to the catalyst site, then polymers of statistically the same monomer composition and distribution will be formed by the single-sited catalyst.

Polymerization experiments were conducted in a 1-L continuous flow stirred tank reactor (CFSTR) as described in the Experimental Section. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of these polymers (Table I) were obtained by gel permeation chromatography (GPC). Since sufficient monomer is available to react with each catalyst molecule formed by the interaction of 1 and 2, the moles of polymer will equal the moles of 1 used if all of 1 forms the catalyst and there is no chain transfer. The molecular weight distribution of the polymer lies in a narrow range of values between 1.9 and 2.2: these numbers are, within experimental error, equal to 2.0, which is expected for a polymerization with a single-sited catalytic species.

Intermolecular compositional distribution in the CFSTR and plug flow reactor polymers was measured by fractional precipitation as described in the Experimental Section. These solvent–nonsolvent separations are useful for detecting the presence of polymeric fractions which differ in composition (ethene/propene ratio) or molecular weight. Several fractions (typically eight) of approximately equal weight are collected and analyzed for composition (ratio of polymerized ethene/propene) by IR. The largest differences in composition are expected between the first and last fraction, with the intermediate fractions having an intermediate composition. This analytical data is shown in Table I as the ratio of the measured ethene content for the extreme fractions (fractions 1 and 8) and an intermediate fraction (fraction 5). The difference in composition for the polymer fractions is small, irrespective of the polymerization conditions used. The largest difference in ethene compositions is about 2% difference in the absolute ethene content. This indicates the presence of a single polymerization catalyst.

We conclude based on these two results (compositional uniformity and polymer chains/vanadium) that at reaction temperatures of −10 to +30 °C, where most of our data are collected, reaction of 1 with an excess of 2 produces a stoichiometric amount of an olefin polymerization catalyst. Alternate reaction pathways which do not lead to an active catalyst or a catalyst with different polymerization properties are not significant.

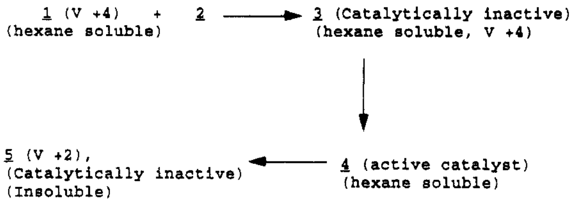


Figure 1. Proposed reaction scheme for the interaction of 1 and 2. This study investigates transformation of 1 to 3.

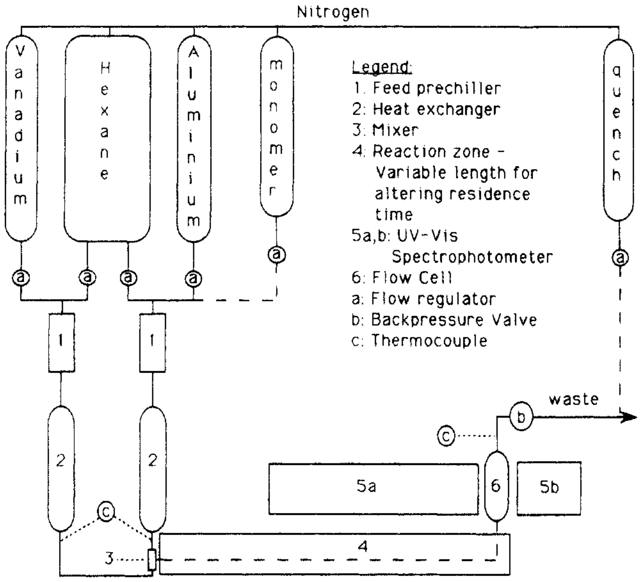


Figure 2. Schematic diagram of the continuous flow spectroscopy/polymerization equipment. Operational procedures are given in the Experimental Section.

Solubility of Reaction Products. The observation of the reaction products of 1 and 2 by UV–vis spectroscopy is quantitatively possible if all reactants and products are soluble in hexane. We know that 1 and 2 are while 5 (Figure 1) is not soluble.[13] We will show later that there is convincing spectroscopic evidence that, at least in the time scale of the observations, 3 (Figure 1) is soluble. This solubility is independent of the presence of polymerizable monomer.

Continuous Flow Spectroscopy. All experiments were performed in a continuous flow reactor shown in Figure 2. We have used the continuous flow reactor in preference to other experimental designs (e.g., stopped flow) for the following reasons. Continuous flow systems are less affected by impurities (e.g., moisture, oxygen) retained on the walls because of short contact times and large reactant volume/reactor surface area. Changes in the temperature/concentration (by dilution) of the reactants and the uniform dispersion of additional reactive components (e.g., polymerizable olefins) to mixtures of 1 and 2 are rapidly accomplished. We found it necessary to design our own continuous flow reactor since commercially available continuous flow reactors[14] with capillary lines as reactor zones are rapidly contaminated by particles of insoluble products. Our reactor is made of stainless steel tubing (SS 304) with an inner diameter of 0.213 cm in the reaction zone: flow rates of 6–15 mL/s ensure a turbulent flow with a Reynolds number[15] of 7800–19700, respectively. At these flow conditions there is rapid radial but very little axial mixing: thus the velocity profile for the fluid flow across a cross-section of the tube is essentially uniform. The kinetic analysis of reaction data is simple: the distribution of residence times in the reaction zone is narrow,[16a,b] and the average residence time (the time between initiation of the reaction and the observation) is the reaction time in the kinetic equations. A single-pass flow cell of 0.35-mL volume was used as the sample cell: detection of events differing by 0.05 s is possible with this particular experimental design. We recognize that mixing of rapidly reacting components in a turbulently flowing stream is neither simple nor instantaneous and results are affected by fluctuations in flow patterns and unanticipated "dead zones" in the reactor design. Careful design of the flow path and consistent time averaging of data were found to be essential in removing inconsistencies.

Reaction of 1 and 2. Panels a and b of Figures 3 show spectra in the range 300–600 nm of reacting solutions of 1 and 2 using a vanadium concentration of 0.59 mM and an Al/V molar ratio of 8 for a range of residence times of 0–47 s at −5 °C. Figure 3a shows that reaction of 1 and 2, monitored by the loss of absorbance at 412 nm, occurs for the spectra recorded between 0 and 22.7 s. Further changes in the spectra do not occur between residence times of 22.7 and 29 s. We interpret this to indicate complete transformation of 1 to form an adduct 3 in 22.7 s, and the spectra at 22.7 and 29 s, which have an absorption maximum at 322 nm, are spectra of 3. Isosbestic points at 320 and 376 nm in the spectra of reaction mixtures of 1 and 2 indicate that 3 is soluble in hexane and is the only vanadium-containing product formed from 1. The absorbance at 412 nm in these solutions is the linear sum of the absorbances of 1 and 3. Assuming a 1:1 transformation between 1 and 3, V_t, the concentration of 1 at residence time t, is easily calculated from this absorbance. These values of V_t are shown for the residence times in the region 0–47 s in Table II.

Further reactions of 3 occur at residence times greater than 29 s (Figure 3b). This is shown by the diminished absorption (in the region 300–450 nm) for the spectra at 34 s and greater. We believe that these reactions of 3 lead to the formation of 4 and insoluble 5. This appears as gradually increasing baseline absorptions above 500 nm at these residence times. The extent of reaction of 3 is probably much greater at these residence times than indicated by the diminution of the absorbance at 322 nm: scattering of the radiation by the particulates of 5 results in artificially enhanced absorbances at smaller wavelengths (300–400 nm). The presence of 5 contaminates the spectroscopic data and renders quantitative analysis impossible. The complementary experiment where 1 is reacted with increasing concentrations of 2 at a single residence time of 6.2 s was also performed—this produced similar results, and the spectral changes are similar to those reported in Figures 3.

Reactions of 1 with other aluminum trialkyls and aluminum alkyl halides were also performed under similar conditions. The rates of reaction are very different for different aluminum alkyl compounds. This will be explored in a later section. In all cases adducts similar to 3 were observed; they differed little in the position of the absorption maxima. Very little change was observed in the absorbance at 412 nm for these analogues of 3. Thus calculations for V_t are only slightly affected by changes in the aluminum alkyl compound.

Reaction Stoichiometry and Products. The stoichiometry of the reaction of 1 and 2 was determined using low-temperature titration (at −10 °C) while monitoring the disappearance of 2 at 412 nm (Figure 4) using a residence time of 25 s and a 3.1 mM concentration of 1. In this experiment progressively greater amounts of 2, in the range of 0–2 molar equiv, react with a constant amount of 1. The stoichiometry for the reaction of 1 and 2 is 1:1.2 in Figure 4: this can be approximated to be a 1:1 reaction.

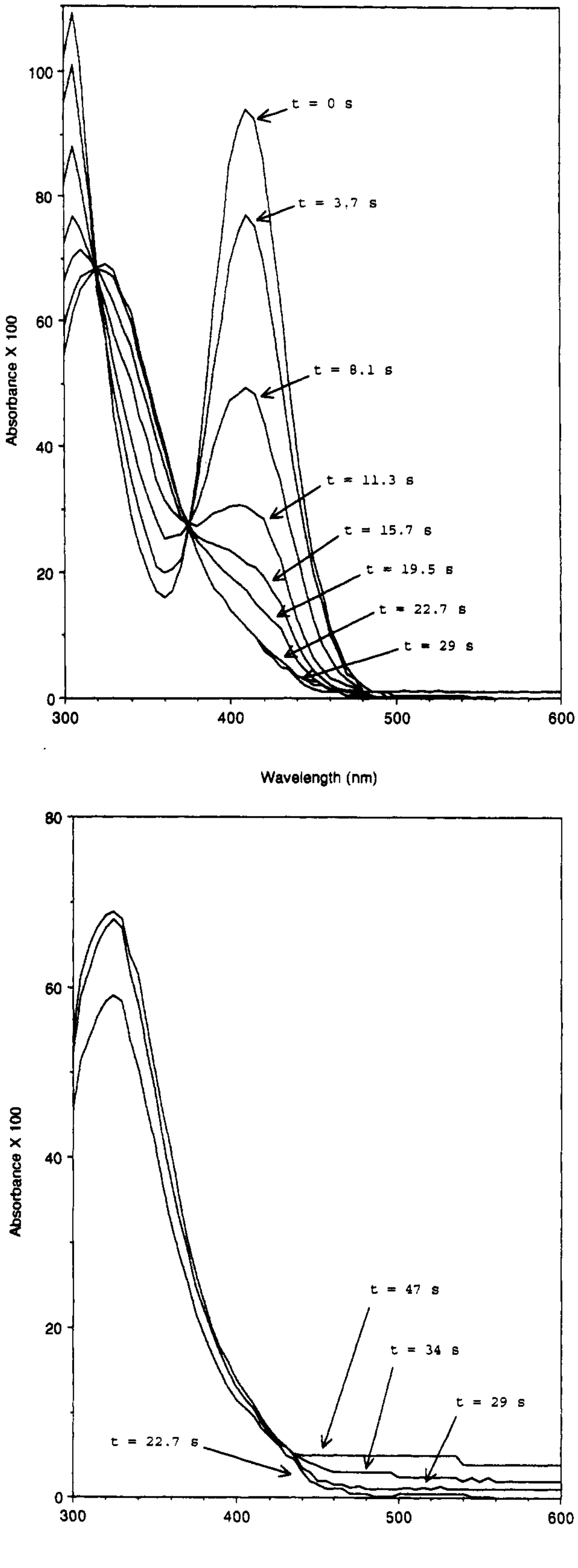


Figure 3. (a, Top) Absorbance spectra between 300 and 600 nm for a 0.59 mM solution of 1 reacting with 2 (Al/V = 8) at -5 °C for residence times of 0–29 s. Note isosbestic points at 320 and 375 nm. (b, Bottom) Absorbance spectra between 300 and 600 nm for a 0.59 mM solution of 1 reacting with 2 (Al/V = 8) at -5 °C for residence times of 22.7–47 s. Increasing baseline absorbance at 500–600 nm indicates solids precipitation.

Table II
Reaction of 1 and 2 to 3 + 4 in a Continuous Flow Reactor at -5 °C Using an Al/V Molar Ratio of 8

spectroscopy results		polymerization results[a]	
residence time (s)	V_t (mM)	3 (mM)	4 (mM)
0	0.59		
3.7	0.47	0.12	
8.1	0.27	0.32	
11.3	0.14	0.45	0.01 (2%)
15.7	0.07	0.52	0.02 (4%)
19.5	0.04	0.55	0.01 (2%)
22.7	0.01	0.58	0.04 (4%)
29.0		0.59	0.07 (4%)
34.0			0.12 (8%)
47.0			0.26 (30%)

[a] Figure in parentheses is the percent of the original concentration of 1 appearing as a polymerization catalyst.

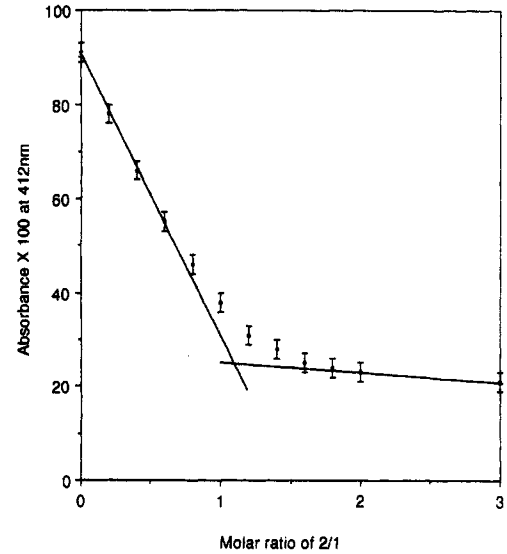


Figure 4. Spectral titration of 1 with 2 at 412 nm at -20 °C. Equivalence is at 1.2 mol of 2/mol of 1. Vertical bars are the expected errors in the absorbance data.

IR spectra of the solutions of 3, obtained by the reaction of 1 and an excess of 2 at -10 °C for 25 s, showed new absorbances at 712 cm^{-1}. This is consistent[17] with the presence of vanadium alkyl bonds in 3: however, these IR signals could also arise from the aluminum alkyl compounds[18] complexed to a vanadium center. Hydrolysis of 3 at low temperature (-15 °C) with an acidic mixture of 2-propanol and water yields a blue solution with an absorbance in the visible spectra at 650 nm: this is characteristic of V in a +4 oxidation state.[9] Further characterization of 3 was hampered by our inability to isolate this material: 3 is unstable with an estimated half-life of a minute at -15 °C. In conclusion, 3 is a soluble adduct containing vanadium in the +4 oxidation state formed by the interaction of equimolar amounts of 1 and 2. We are unable to determine whether the adduct 3 contains a dimer or dissociated monomer of 2.

Catalytic Properties of 3. 3 is not a catalyst for polymerization of α-olefins. A mixture of ethene and propene (molar ratio 1/9) with 450 equiv of olefin/mol of 1 was injected into a solution of 3. Higher ratios of ethene/propene lead to formation of only partially soluble polymer: this introduces errors into the experimental procedure. 3 was formed by reacting a 0.59 mM solution of 1 with an 8-fold molar excess of 2 at -5 °C. Injection of the ethene–propene mixture was at residence times of 11.3, 15.7, 19.5, 22.7, 29, 34, and 47 s (cf. Figure 3). The polymerization reaction was quenched by injection of a stream of 2-propanol in hexane at a molar excess of 50:1 (based on the amount of vanadium and aluminum present) 1.5 s after the monomer addition. The quench terminates the polymerization. The molecular weight of the resulting polymer was determined by GPC, and the molecular weight distribution (M_w/M_n) was unimodal and usually less than 1.5. The data in Figure 3 indicate that the composition of the catalyst components remains approximately constant during the 1.5-s polymerization interval. Thus this polymerization is an instantaneous "snapshot" of the catalytic properties of the reaction mixture. Correlation of the polymer molecular weight with the the amount of 1 used (Table II) in the experiment showed that only 2% of the vanadium atoms were active as olefin polymerization catalysts at 15.7 s. The fraction of vanadium atoms which are polymerization catalysts is 2% and 4% at residence times of 19.5 and 22.7 s, respectively. Table II indicates that the transformation of 1 to 3 is about 93% and >99% at these residence times. Note that much higher fractions of vanadium atoms (close to 100%) are eventually catalytically active in these solutions. Decomposition of 3 has already started at a residence time of 34 s where the fraction of catalytically active vanadium atoms increases to 12%, and the largest observed amount of active vanadium atoms in this experiment is 26% at an even longer residence time of 47 s. Thus catalytic olefin polymerization properties are not correlated to the concentration of 3 and in fact appear most intensely when 3 has decomposed. This indicates that the actual polymerization catalyst is 4 which is derived from 3.

Rate of Reaction of 1 with Aluminum Alkyl. 1 reacts rapidly with trialkylaluminums or aluminum alkyl chlorides of the general formula $Et_xAl_2Cl_{6-x}$: The reaction of 1 with these compounds having integral values of $x = 6$, 5, 4, 3, and 2 is reported here. Aluminum ethyl chlorides with $x < 2$ are hexane insoluble. Experiments with $Me_4Al_2Cl_2$ and $(i\text{-}Bu)_4Al_2Cl_2$ generated data for comparison to diethylaluminum chloride. The residence time for the reaction was adjusted so that not more than 10% of the aluminum alkyl was consumed. This requires 0.2–2 s, depending on the aluminum alkyl, at our experimental reactant concentrations. We have restricted ourselves to this initial reaction region for the following reasons: (i) the minor changes in the aluminum alkyl composition which occur during the course of the complete reaction with 1 even at large molar excess of aluminum lead to large differences in the rate, (ii) degradation of the adduct 3 and its analogues competes with the formation at long residence times, and (iii) the concentration of aluminum alkyl can be assumed unchanged at the initial concentration. The rate of the reaction has been monitored by following the disappearance of 1.

The reaction is first order in 1 for all aluminum compounds. For reactions with 2 ($x = 3$ above) at temperatures between −25 and 15 °C using a residence time of 0.2–3.9 s, vanadium concentrations between 0.32 and 4.2 mM, and a constant aluminum concentration of 40.4 mM, the initial rate of reaction of 1 depends only on the initial concentration of 1. Less detailed experiments were conducted with other aluminum alkyls ($x = 6$, 5, 4, and 2 above): these results do not show significant deviation from the first-order rate dependence on the concentration of 1.

Table III
Values of ln (V_0/V_t)[a] for $R_xAl_2Cl_{6-x}$ Compounds and Corresponding [Al] Concentrations

[Al] (mmol/L)	ln (V_0/V_t)					
	R = Et				R = Me	R = *i*-Bu
	$x = 6$[b]	$x = 4$	$x = 3$	$x = 2$	$x = 4$[c]	$x = 4$
0.25	0.08				0.10	0.05
0.5	0.15	0.15	0.07	0.04	0.17	0.07
0.75	0.21				0.25	0.09
1.0	0.26	0.27	0.14	0.07	0.32	0.11
1.25	0.31				0.40	0.12
1.5	0.36	0.36	0.18	0.10	0.47	0.14
2.0	0.46	0.46	0.23	0.12	0.61	0.16
2.5	0.56	0.56	0.27	0.14	0.75	0.18
3.0		0.64	0.3	0.16	0.89	0.20
4.0		0.80	0.36	0.19		0.24
5.0		0.96	0.41	0.22		0.27
7.0		1.25	0.50	0.27		0.33
10.0			0.62	0.34		0.41

[a] All data are for $t = 1$ s except as noted below. [b] Data for Et_6Al_2 are for $t = 0.25$ s. [c] Data for $Me_4Al_2Cl_2$ are for $t = 2.5$ s.

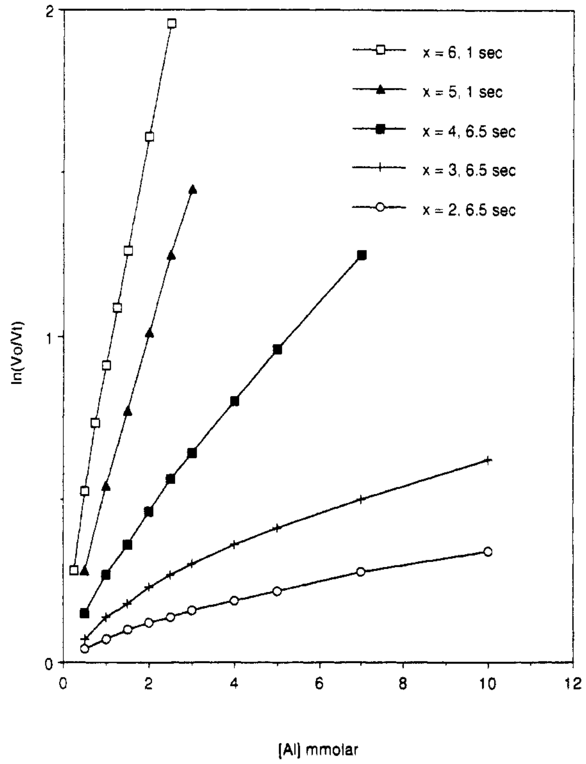


Figure 5. Plot of ln (V_0/V_t) for 1 at −5 °C with aluminum triethyl/ethyl chlorides $Et_xAl_2Cl_{6-x}$ at residence time $t = 1$ s for $x = 6$ and 5 and $t = 6.5$ s for $x = 4$, 3, and 2. Lines between data points are a visual aid only.

The reaction rate is a more intricate function of the concentration of aluminum alkyl than the concentration of 1 (Table III). In Figure 5 the first-order reaction rate for 1 integrated over t seconds of residence time—ln (V_0/V_t), where V_0 is the initial concentration of 1 and V_t is the concentration of 1 after a residence time of t seconds—is compared to the initial concentration of the aluminum alkyl/alkyl halide, expressed as the aluminum concentration. Data for $x = 4$, 3, and 2 are for a residence time of 6.5 s, while the data shown for $x = 6$ and 5 are for a residence time of 1 s. Note that more than 10% of the aluminum alkyl has been consumed for some of the data points for $x = 5$ or 6. This, along with the difference in residence times between these two sets of data, illustrates the decrease in the reaction rates with decrease in the degree of alkylation for aluminum alkyls. Data obtained at a residence time of 0.25 s for $x = 5$ and 6 were used for the kinetic analysis. Figure 5 shows that, although the extent of the reaction of 1 increases with the initial concentration of the aluminum alkyl, these increases are nonlinear. Faster increases are noted at lower concentrations of the aluminum compound than at higher concentrations. These nonlinearities are most pronounced in the case of the reaction of 1 with ethylaluminum chlorides with values of $x = 3$ and 2.

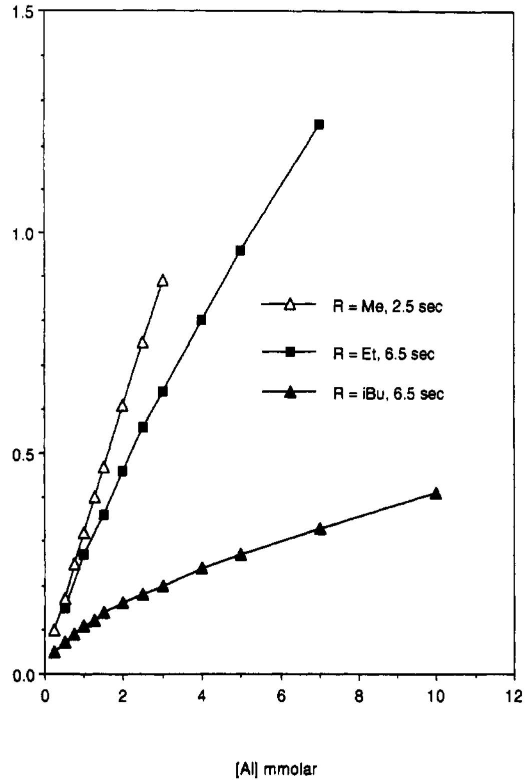


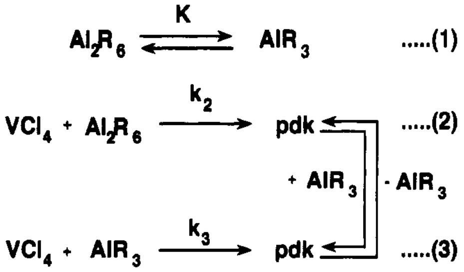
Figure 6. Plot of ln (V_0/V_t) for 1 at −5 °C with aluminum dialkyl chlorides $R_4Al_2Cl_2$ at residence time t = 2.5 s for R = Me and t = 6.5 s for R = Et and *i*-Bu. Lines between data points are a visual aid only.

Table IV
Thermodynamic Parameters and Calculated Equilibrium Concentrations for the Dissociation of Al_2R_6 to AlR_3 in Alkane Solvents

Et_6Al_2	ΔH = 16.9 kcal mol^{-1}	ΔS = 32 cal mol^{-1} °C^{-1}
for all others	ΔH = 20.0 kcal mol^{-1}	ΔS = 32 cal mol^{-1} °C^{-1}

	Et_6Al_2		all other Al alkyls	
total [Al] (mol/L)	monomer concn (mol/L)	dimer concn (mol/L)	monomer concn (mol/L)	dimer concn (mol/L)
0.25	1.11E−5	1.19E−4	6.79E−7	1.25E−4
0.5	1.58E−5	2.42E−4	9.61E−7	2.50E−4
0.75	1.94E−5	3.65E−4	1.17E−6	3.75E−4
1.0	2.25E−5	4.89E−4	1.35E−6	5.0E−4
1.25	2.51E−5	6.13E−4	1.52E−6	6.25E−4
1.5	2.76E−5	7.37E−4	1.66E−6	7.50E−4
2.0	3.19E−5	9.85E−4	1.92E−6	1.00E−3
2.5	3.57E−5	1.23E−3	2.15E−6	1.25E−3
3.0			2.35E−6	1.50E−3
4.0			2.72E−6	2.0E−3
5.0			3.04E−6	2.5E−3
7.0			3.59E−6	3.5E−3
10.0			4.30E−6	5.0E−3

Parallel data for the disappearance of 1 were generated for the comparative reactions with $R_4Al_2Cl_2$ where R = Me, Et, and *i*-Bu. These are shown in Figure 6. Note that data for R = Me are for 2.5 s of residence time while the remaining data are for a residence time of 6.5 s. This illustrates the difference in the rate of reaction of these very similar compounds with 1. The specific rate of reaction with 1 slowly decreases with increasing concentration of the aluminum alkyl: the effect is very noticeable for R = Et and R = *i*-Bu.



$$Al_2R_6 \underset{}{\overset{K}{\rightleftarrows}} AlR_3 \quad .....(1)$$
$$VCl_4 + Al_2R_6 \xrightarrow{k_2} pdk \quad .....(2)$$
$$VCl_4 + AlR_3 \xrightarrow{k_3} pdk \quad .....(3)$$

Figure 7. Proposed reacton scheme for reaction of 1 with monomer/dimer of aluminum alkyls.

Reaction of 1 with Monomer/Dimer of Aluminum Alkyl. An explanation for the observed nonlinearity in the increases of the reaction rate with increasing concentration of aluminum alkyl resides in the known dimer–monomer equilibrium of alkylaluminum chlorides and trialkylaluminums in alkane solution.[19] The kinetic data can be explained with two assumptions: (i) the monomer–dimer equilibrium for trialkylaluminum and alkyl aluminum halides is faster than the reaction with 1 and (ii) 1 reacts independently with the monomer and dimer at very different rates. The postulated reaction scheme is shown in Figure 7. This leads to the following differential reaction rate:

$$-\mathrm{d}(VCl_4)/\mathrm{d}t = k_2[VCl_4][Al_2R_6] + k_3[VCl_4][AlR_3] \quad (4)$$

which can be integrated for the case of the initial reaction over t seconds where the change in $[Al_2R_6]$ and $[AlR_3]$ is small

$$\ln (V_0/V_t) = \{k_2[Al_2R_6] + k_3[AlR_3]\}{*}t \quad (5)$$

R represents either a chloride or an alkyl group in these and subsequent expressions.

The rate of dissociation of Al_2R_6 dimers in alkane solvents has been studied for a few cases using vapor pressure measurements, IR spectroscopy, and ^1H and ^{13}C dynamic NMR.[19] In all cases exchange of the spectroscopically distinct terminal and bridging groups has been observed in the NMR time scale. This is believed to occur through dissociation of Al_2R_6 followed by association of the resulting AlR_3 monomers. The rate of scrambling of the R groups is thus equal to the rate of dissociation of Al_2R_6 dimers. Reaction rates of 10–15 times per second have been determined for this process at 0 °C for both Al_2Me_6 and $Et_3Al_2Cl_3$. These rates are much faster than the reaction of Al_2R_6 with 1, where less than 10% of Al_2R_6 is consumed in this time period: thus the equilibrium concentrations of dimeric Al_2R_6 and monomeric AlR_3 are maintained unchanged during the reaction time.

Several studies[19] in the gas phase and in alkane solution have attempted to determine the thermodynamic parameters for the dissociation of aluminum alkyls and aluminum alkyl halides. Differential solvation of Al_2R_6 and AlR_3 in weakly coordinating aromatic solvents such as benzene promotes the dissociation: these are not considered. A consistent experimental data set for the dissociation for all the aluminum alkyls and aluminum alkyl halides used in this study is not available. Table IV lists the ΔH and ΔS that we have used for the dissociation of Al_2R_6 to two AlR_3 monomers (eq 1 in Figure 7). Table IV also gives the concentrations of Al_2R_6 and calculated relative amounts of AlR_3 at each experimental initial concentration ([Al] in Figures 5 and 6 and Table III) of aluminum trialkyl or aluminum alkyl halide. Al_2R_6 concentrations are half the difference of [Al] and AlR_3 throughout the table. The dissociation of Et_6Al_2 has been well investigated,[19h] and consistent, reliable estimates are available: this is shown in Table IV. The dissociation parameters for Et_5Al_2Cl are unimportant for reasons explained later: these have not been reported. Values of ΔH and ΔS for the dissociation of Al_2R_6 dimers of the remaining aluminum compounds, all of which have dimers bridged with a pair

Table V
Values[a] of k_2 and k_3 for the Reaction of 1 with Aluminum Alkyls at −5 °C

	concn of 1 (mM)					
	0.34		0.59		1.08	
aluminum alkyl	k_2	k_3	k_2	k_3	k_2	k_3
Et_6Al_2	1500 (110)	18000 (2300)	1300 (68)	18000 (2000)	1600 (180)	17000 (3500)
$Et_4Al_2Cl_2$	23 (3.0)	14000 (2700)	37 (2.5)	17000 (2100)	47 (7)	12000 (3100)
$Et_3Al_2Cl_3$	8 (2.2)	12000 (2000)	6.4 (1.9)	15000 (2800)	5 (1.5)	13000 (1500)
$Et_2Al_2Cl_4$	3 (1.1)	5500 (700)	4.1 (1.0)	7600 (1200)	3.5 (1.1)	7000 (900)
$Me_4Al_2Cl_2$	240 (87)	18000 (3500)	210 (7)	18000 (3500)	180 (32)	20000 (3500)
$(i\text{-Bu})_4Al_2Cl_2$	3.3 (0.5)	12000 (2000)	3.0 (0.42)	11000 (460)	2.5 (.20)	10000 (720)

[a] Units for k_2 and k_3 are L mol^{-1} s^{-1}. Figures in parentheses are 95% confidence intervals.

of chloride ligands, are believed to be similar, with values for ΔH differing by less than 1.5 kcal/mol. This uncertainty is greater than the inherent uncertainty in the value of ΔH (~2–5 kcal/mol); hence a single set of ΔH and ΔS values is used for all these compounds. The difference in ΔH values for the Al_2R_6 dimers between those which have ethyl bridging groups (Et_6Al_2) and chloride bridging groups (other Al_2R_6 dimers) is about 3 kcal/mol. This reflects the lesser ability of the ethyl group, compared to a chloride, to participate in a three-center, two-electron bond with two aluminum atoms. The ΔS values of 32 cal mol^{-1} °C^{-1} for all of the dissociation reactions is the average of the experimental values for this dissociation.

The dimer and monomer concentrations for aluminum compounds in Table IV are used in a solution of eq 5. ln $(V_{0.0}/V_{0.25})$ data for the reaction with Et_6Al_2, ln $(V_{0.0}/V_{2.5})$ data for $Me_4Al_2Cl_2$, and ln $(V_{0.0}/V_{6.5})$ data for other aluminum compounds from Table III (Figure 5) were used for the extent of reaction of 1. In addition, a data point corresponding to the origin in Figures 5 and 6 was included. A two-parameter, multiple regression analysis (see Experimental Section) for eq 5 is used to determine k_2 and k_3 for each aluminum compound. All data points shown in Table III were considered for these calculations, and the residual errors are small. This indicates an acceptable fit of the data to the parameter set described in eq 5.

Reaction data for 1, similar to those reported in Table III and shown in Figures 5 and 6, were also collected at 0.34 and 1.08 mM concentrations of 1 for all of the aluminum trialkyls/alkyl halides indicated above. The same range of aluminum concentrations was used for this extension of the original study; however, the residence time for the reaction had to be changed. Dilute solutions of 1 needed to have a larger residence time in order that the absolute change in the concentration of 1 was experimentally significant. Concentrated solutions of 1 had to have a shorter residence time so that the extent of reaction of the aluminum alkyls was less than 10% of the original amount. Rate constants, k_2 and k_3 were determined at each of the concentrations of 1 by the method outlined above. The values of k_2 and k_3, along with confidence limits and test parameters for the regression analysis for each of the vanadium concentrations, are shown in Table V for all aluminum compounds except Et_5Al_2Cl. Values of k_2 and k_3 are similar, within the limits of experimental accuracy, for the range of concentrations of 1. This supports the proposed mechanism.

Rate Constants for $Et_xAl_2Cl_{6-x}$ for $x = 3$ or 5. Calculated values of k_2 and k_3 are not reported for Et_5Al_2Cl since they do not have a simple physical explanation. The dissociation equilibrium of the unsymmetrically bridged dimer Et_5Al_2Cl to Et_3Al and Et_2AlCl, according to the reaction scheme in Figure 7, is complicated by the competing association of these monomeric aluminum compounds to corresponding symmetrically bridged dimers. Thus there are three competing equilibria to consider. The difference in the ΔH of dimerization (ethyl bridges versus chloro bridges, Table III) to the three possible dimers indicates that a much larger amount of Et_3Al than Et_2AlCl monomer exists at equilibrium in dilute alkane solutions. This is reflected in the data in Figure 5, where the rate of reaction of 1 with Et_5Al_2Cl is shown to be similar to the rate of reaction with Et_6Al_2. The Et_3Al/Et_2AlCl ratio changes with changes in the total concentration of aluminum alkyl. Any deduction of k_2 and k_3 from the results in Table IV, where the rate of reaction of 1 is compared to the changes in the aluminum concentration, is dubious. Similar, though less severe, problems of interpretation arise for $Et_3Al_2Cl_3$, where the dissociated monomers are Et_2AlCl and $EtAlCl_2$. In this case all of the competing dimeric aluminum compounds ($Et_xAl_2Cl_{x-6}$ with $x = 4, 3,$ and 2) are symmetrically bridged with two chloride groups. The ΔH and ΔS of dissociation for these Al_2R_6 compounds are similar (Table III). This suggests that the concentrations of the monomeric aluminum species are equal. Further, the relative amounts of the monomeric species are unchanged by changes in the total aluminum concentration. Therefore k_2 and k_3 can be calculated for $x = 3$ and are measures of the reactivity of an equimolar mixture of Et_2AlCl and $EtAlCl_2$.

Rate Constants k_2 and k_3. Values of k_2 and k_3, as shown in Table V, show distinctive trends. The rate of reaction of 1 with aluminum compounds decreases with the decrease in the number of alkyl groups associated with the aluminum alkyl dimer. This change is particularly prominent for k_2, where the difference in the rate constant between Et_6Al_2 and $Et_2Al_2Cl_4$ is a factor of 500. Aluminum compounds with intermediate composition have intermediate reaction rates. These systematic changes in k_2 indicate that the initial attack of the aluminum compounds on 1 proceeds through the aluminum–carbon bond. This is shared with the electron-deficient center of 1 in a three-center, two-electron bond between 1 and the aluminum alkyl. 1 acts as the electron acceptor and the aluminum alkyl as the electron donor. Systematic replacement of ethyl groups in $Et_xAl_2Cl_{6-x}$ with electron-withdrawing chloride ligands, as in the sequence $x = 6$ to 2, inhibits this interaction not only by decreasing the number of aluminum–carbon bonds available for this reaction but also by decreasing the available electron density at the aluminum–carbon bond. Changes in the composition of the aluminum alkyl halide from $Me_4Al_2Cl_2$ to $Et_4Al_2Cl_2$ and finally to $(i\text{-Bu})_4Al_2Cl_2$ also lead to a progressive decrease in the value of k_2. This is consistent with the above postulate since the decreasing ability of the larger alkyl groups to participate in a three-center, two-electron bond because of either steric or electronic reasons is a rate-determining factor in the interaction between 1 and aluminum alkyls. It is unclear why the interaction of 1 and aluminum alkyl chlorides does not occur through an initial halide bridge, particularly since chloride is an excellent bridging ligand. It is possible that these interactions do occur but are reversible. This would lead to a degenerate chlorine for chlorine exchange between the vanadium and aluminum centers which is undetectable in the spectroscopic experiment.

The reactions of 1 with the dissociated aluminum alkyl monomer are much faster than those with the aluminum alkyl dimer (k_3 is larger than k_2). This is true for ethylaluminum chlorides as well as for the corresponding Me and *i*-Bu compounds. The trend of lower reaction rate with decreasing amount of alkyl substitution on the aluminum which was seen for k_2 is also noted for k_3 but the differences are much less. Thus, the k_3 for $EtAlCl_2$ is 60% that of Et_3Al. We speculate that the monomeric aluminum alkyls/alkyl chlorides with a vacant coordination site are much more reactive than the dimers and steric or electronic constraints which affect the reaction rate with dimers are much less important here.

Discussion

Reaction Pathway. The intent of this study has been to understand the interaction of 1 and 2 in dilute alkane solution as a first step in understanding the formation of Ziegler polymerization catalysts.

We represent our current understanding of the reaction of 1 and 2 in Figure 1. 3, 4, and 5 are vanadium-containing compounds, and there may be other redistribution or dissociation reactions of 2. The formation of the adduct 3 is spectroscopically clean, and we have described the stoichiometry and the kinetics of formation. 3 is not a Ziegler–Natta *olefin polymerization catalyst since catalyst* activity in reacting solutions of 1 and 2 is not correlated to the concentration of 3. We speculate that the actual polymerization catalyst, 4, is derived from 3, probably by reaction with additional amounts of 2. Similar suggestions have been made by others.[4,6] The formation of significant amounts of 4 cannot be separated from the appearance of the final, insoluble decomposition product 5. Therefore our spectroscopic data for the stoichiometry and kinetics of the transformation of 3 to 4 are unreliable. 5 is catalytically inactive for copolymerization of ethylene and α-olefins. The formation of 3, 4, and 5 occurs rapidly on mixing 1 and 2; at 1 mM concentration of 1 and using a 10-fold molar excess of 2, the conversion of 1 to insoluble 5 is essentially complete in 20 s.

We attribute the disappearance of 1 to the alkylation of the vanadium center. The reaction of 1 with 2 (and, by extension, with other aluminum alkyl chlorides of this study) has a 1:1 stoichiometry. The products of this reaction—3 and its analogues—are unstable and rapidly decompose, which prevents isolation. Further, characterization is hindered by the dilute solutions used for the spectroscopic study. 3 is less stable in concentrated solutions. We speculate that concentrated solutions lead to an enhancement of further reaction of 3 with aluminum alkyl chlorides. The monomer and dimer of the aluminum compound react in parallel with 1. These two distinct pathways lead to initially different vanadium-containing compounds: however, since they are interconvertible by a fast association/dissociation reaction of the aluminum alkyl halide component, the ultimate reaction product is presumably the same. This reasoning is consistent with (i) the known kinetics of dimerization of aluminum trialkyls/alkyl halides and (ii) the formation of a single catalytically active vanadium component from the reaction of 1 and 2. Thus the intermediate in this reaction is a bimetallic dimer of aluminum and vanadium: we have no information whether these bimetallic structures persist in 3.

Polymerization Results. The results of the Ziegler polymerization from CFSTR and plug flow polymerizations show that in our experiments 1 is converted quantitatively into a single olefin polymerization catalyst. If different polymerization catalysts had been formed from the interaction of 1 and 2, they should differ either in the relative reactivity toward ethene the propene or in the molecular weights of the polymer. These differences should appear either as intermolecular compositional distributions (i.e., a mixture of polymers with different ethene contents) in the polymer or as broad ($M_w/M_n > 2$) molecular weight distributions. None of these perturbations were observed. The results of the polymer analysis assist the kinetic interpretation of the spectroscopy results since in the absence of this assumption the kinetic analysis is invalid.

These experimental observations may be consistent with an explanation which does not involve the stoichiometric formation of a single polymerization catalyst from 1. This requires two opposing but exactly equal factors—(i) some 1 does not form a polymerization catalyst and (ii) chain transfer reactions in all of the polymerization sites exactly compensate for the deficit in the number of polymer chains. Transfer reactions typically occur when the polymer chain undergoes β-hydrogen elimination near the transition metal to liberate the polymeric olefin followed by subsequent addition of the V–H bond across the olefin double bond of a polymerizable olefin to reinitiate a polymer chain. The absence of transfer reactions in combinations of 1 and 2 under our experimental conditions was shown by Ver Strate et al.,[12] who conducted a hexane solution plug flow copolymerization experiment using ethene and propene as the polymerizable monomers. They found that (a) a single polymerization catalyst is formed and, more importantly, (b) chain transfer reactions alluded to in (ii) above cannot be expermentally detected below about 10 °C. Plug flow polymerization reactions (in contrast to CFSTR polymerizations) are particularly sensitive to the chain transfer reactions since they lead to large increases in both the compositional distribution and the molecular weight distribution of the polymer (normally 1.1 to 1.3). Polymers made with the plug flow reactor technique cannot be fractionated by solvent–nonsolvent techniques to yield significant (>5% by weight) fractions with a composition different than the mean.

Solubility of Intermediates. There is some controversy as to whether the vanadium-based olefin polymerization catalysts (4 in Figure 1) formed by the interaction of 1 and 2 are truly soluble: we believe they are. Parshall[13] claims that an analogous polymerization catalyst made from $VOCL_3$ and $(i\text{-}Bu)_4Al_2Cl_2$ is insoluble since insoluble aggregates are formed on mixing these two components. An explanation for the apparent controversy is our observation that Ziegler–Natta catalyst activity for these solutions (either solutions of 1 and 2 or Parshall's compositions) is very short-lived (seconds at 25 °C). Insoluble vanadium-containing aggregates are rapidly formed on mixing: however, their formation is correlated to the decay of catalyst activity.

Experimental Constraints. These experiments have been intentionally restricted to the aluminum alkyls and the aluminum alkyl chlorides which exist in well-defined monomer–dimer equilibria. 1 reacts with almost all aluminum alkyl compounds, including hydrides, alkoxides, amides, and other halides. These reactions were not considered for this study for the following reasons. First, aluminum alkyl compounds with ligands other than halogen or alkyl groups are oligomeric with very poorly defined monomer–oligomer equilibria: this makes rational treatment of the kinetic data difficult. For example, the rate of addition of olefins to aluminum diisobutyl hydride is a linear function of the cube root of the concentration[21] of the aluminum component. This implies a trimer as the stable species for this aluminum compound which dissociates to monomers in the rate-determining step. Second, aluminum alkyl compounds containing halide ligands other than a chloride may react with 1 by exchange of this ligand with the chloride on 1: this would lead to an additional reaction pathway for the disappearance of 1. Restriction of the composition of the aluminum component to aluminum alkyl chlorides allows only two reaction pathways: (i) a degenerate chloride for chloride exchange which is not observable in our experiment and (ii) an alkylation of 1 which we can measure. Third, the interest in aluminum alkyls containing alkoxide or amide ligands is minor: the olefin polymerization activity of solutions of 1 and these compounds is weak.

Rate Constants. The magnitude of the rate constant k_3 is dependent on the values chosen for the thermodynamic parameters, principally ΔH, of the dissociation reaction of aluminum dimers. With larger positive values for ΔH in eq 1 of Figure 7, implying that the dissociation reaction is less favored, a lower equilibrium concentration of the aluminum monomers (which are a small fraction of the total aluminum concentration) is obtained. This results in a larger value of k_3 (the reaction rate of aluminum monomer with 1) from the data correlation. The effect of small increases in ΔH on the calculated values of k_3 is dramatic: an increase of 1 kcal/mol leads to an increase in k_3 by a factor of 5. The effect of changes in the value of ΔH on k_2 is significantly smaller. Since most of the aluminum exists as dimers, the absolute changes in concentration of Al_2R_6 with small changes in ΔH are negligible. Values of ΔH for the dissociation of Al_2R_6 are only known with precision from the heat of dissolution for dilute solutions in alkane solvents for Et_6Al_2. The corresponding parameters for Me_6Al_2, which is believed to have a ΔH only 2–3 kcal more, cannot be measured by this technique and are only approximate. Similar problems arise for aluminum alkyl compounds which dimerize by stable bridging groups such as hydrides, alkoxides, or halides. Thermodynamic data for the dissociation of these compounds for these cases are derived from vapor pressure measurements, and the range of published values is much larger than the small differences in ΔH that can affect our results. We have assumed a single value for the ΔH of the dissociation of all chlorine-bridged Al_2R_6 dimers. In the absence of such an assumption the variation in the final results makes any analysis of variation of reaction rates with changes in the structural features of the aluminum component internally inconsistent. There is some reason to believe that in the series $Et_4Al_2Cl_2$, $Et_3Al_2Cl_3$, and $Et_2Al_2Cl_4$ the ΔH for the dissociation decreases due to removal of electron density from the bridging ligands by the terminal chloride ligands. This would imply progressively larger equilibrium levels of the dissociated monomers in this series: consequently, the calculated values of k_3 would be progressively smaller than our current calculations. This would support our hypothesis and affect the absolute magnitudes but not the general trend of these values. We have chosen to neglect these anticipated differences to avoid confusion. Our choice of the value of ΔH for these compounds is at the low end of the spectrum of possible suggested values. The reason for this choice is that to be self-consistent the reaction rates (both k_2 and k_3) for Et_6Al_2 should be the greatest of all of the aluminum compounds we have investigated. Larger values of ΔH for the chlorine-bridged Al_2R_6 dimers would decrease the equilibrium concentration of the monomers. This has the unfortunate effect that apparent values of k_3 would initially increase and then decrease as the ethyl groups of Et_6Al_2 were progressively substituted with chlorine. This is contradictory to our expectations.

This reaction scheme where 1 reacts independently with both the dissociated monomers and the dimers of aluminum alkyls/alkyl chloride has partial precedents in the literature. Particularly well-investigated examples are the chain growth reaction with alkynes and alkenes.[21] These occur by insertion of the olefin/alkyne into the aluminum–carbon bond of aluminum trialkyls. In both these cases the olefin insertion reaction occurs predominantly on the dissociated monomer of the aluminum compound. The rate of the reaction is proportional to the square root of the total aluminum concentration, which corresponds to a linear dependence on the concentration of the dissociated aluminum trialkyl monomer. Both of these reactions have been investigated for trialkylaluminum compounds: we are not aware of any similar detailed investigation regarding the reactivity of monomeric alkylaluminum halides.

Conclusion

We have shown that with the proper experimental equipment the reaction between early transition metal halides and aluminum alkyls is observable and quantifiable. The CFSTR polymerization and, more importantly, the use of the continous flow reactor results indicate that (i) 1 and 2 react to form a single polymerization catalyst and (ii) 1 reacts separately and independently with both the monomer and the dimers of the aluminum alkyl chlorides in first-order reactions. Large increases in the reaction rates are observed with (i) increase in the alkyl/chloride ratio of the aluminum alkyl and (ii) decrease in the size of the alkyl group. The product of the reaction is not an olefin polymerization catalyst but rather a precursor.

These results are similar to, but more quantitative than, the results for the reaction of biscyclopentadienyl transition metal complexes with aluminum alkyls, which are less definitive since multiple reaction products most likely were present in these earlier studies.[5,6] This work adds to understanding the nature of interaction in the formation of Ziegler polymerization catalysts.

Experimental Section

Materials. Experiments were carried out in polymerization grade hexane obtained from Phillips Petroleum Co. This grade of hexane is a mixture of saturated alkanes. A typical analysis by GC indicates the following composition: *n*-hexane, 84%; 2-methylpentane + 3-methylpentane, 9%; cyclohexane, 3%; heptane, 2%. Benzene concentration was less than 200 ppm in a typical solvent sample. The solvent was purified prior to use by passing it over silica gel (W. R. Grace Co., Davison Chemical Division, PA-400 20–40 mesh) and 4-Å molecular sieves (Union Carbide, Linde Division, 4-Å 1/16 pellets) to remove polar impurities which act as catalyst poisons. Dry solvent was deoxygenated by bubbling nitrogen for 15 min immediately prior to use. Solvent purity was measured by titration with a 0.01 M solution of sodium napthalenide in THF: levels of less than 1–1.5 ppm of water equivalent are routinely possible. The test is sensitive to the presence of active hydrogen impurities as well as oxygen. This concentration corresponds to 6–9% molar equiv of 1 (at 0.59 mM concentration) in the reaction zone of the continuous flow reactor: it is a much smaller fraction of the amount of aluminum alkyl/alkyl chlorides used in these experiments. Samples of 1 at a concentration of 0.59 mM are stable in this solvent for at least 1 h. Gaseous ethene (Liquid Carbonic, Specialty Gas Division) and liquid propene (Uniion Carbide, Linde Division) were purified by passing them over hot Cu_2O at 270 °C to remove oxygen followed by 4-Å molecular sieves for moisture removal. Aluminum trialkyls/alkyl halides were purchased as a 25% solution in hexane from Texas Alkyls; Et_5Al_2Cl was made by us by blending the commercially available symmetrical dimer products. 1 was obtained from Stratcor, Niagara Falls, or Metaux Speciaux S.A., Paris, France, and filtered free of suspended impurities (principally VCl_3 from the thermal decomposition of 1) prior to use: no difference in reactivity was observed between these samples.

Analysis. Molecular weight measurements were made by a combination of a Waters 150C GPC with an on-line light scattering KMX-6 Chromatix (Milton Roy). The procedures have been described.[12] The ethene content of the polymers was measured by infrared analysis using ASTM procedure D3900.

The intermolecular compositional distribution was measured as below. A sample (typically 5–7 g) of the polymer was dissolved in 600 mL of hexane at a concentration of 1.0–1.5 wt %. Aliquots of 2-propanol were added to the well-stirred solution of the polymer until a fraction of the polymer was precipitated. The precipitate was allowed to equilibrate with the supernatant for 1 h and removed by decantation followed by filtration through a 320-mesh stainless steel filter. The procedure was repeated with the filtrate to isolate several, typically eight, fractions of the polymer of approximately equal weight. The precipitated polymers at each stage were separately dried and analyzed for molecular weight and composition as described above.

Calculations. The values of k_1 and k_3 were obtained by a two-parameter regression analysis using the calculated concentration of the monomer and dimer of aluminum alkyl as the independent variables and the absorbance data for the disappearance of 1 as the dependent variable. Results are shown in Table V along with the 95% confidence interval for each data point.

CFSTR Polymerizations. Polymerizations were conducted in a 1-L CFSTR adiabatic reactor using hexane as the solvent. The residence time in the reactor was typically 9 min, and the pressure was maintained at 400 kPa. Hexane, ethene, and propene were metered into a single stream and cooled before introduction into the bottom of the reactor. Solutions of 1 and 2 were introduced continuously and separately into the reactor to initiate the exothermic polymerization. The temperature of the reactor was maintained by changing the temperature of the hexane feed. The solution of the polymer was withdrawn from the top, washed with dilute HCl to remove residues of 1 and 2, and then steam-distilled to isolate the polymer. In a typical polymerization experiment (as reported in Table I) the following flow rates were used: hexane, 59.4 g/min; ethene, 0.78 g/min; propene, 2.03 g/min; 1, 0.0063 g/min; 2, 0.036 g/min.

Continuous Flow Spectroscopy. Continuous flow spectroscopy for the reactions of 1 were conducted in the equipment described schematically in Figure 2. The flow of the reacting solutions, except for the "quench", is anticlockwise in this diagram. Accurately controlled nonpulsing flow of solvent and all reactants is essential to the success of this experiment and is obtained by maintaining a constant nitrogen pressure (about 200 kPa) on all feed containers and a backpressure of 30 kPa at valve "b" at the outlet of the equipment. Concentrated solutions of 1, usually about 5–10 mM, and aluminum alkyl, usually about 20–100 mM, are contained in the feed tanks (capacity 1600 mL) labeled "vanadium" and "aluminum", respectively. These, along with dilution hexane from the container "hexane", are accurately metered through Fischer–Porter rotameter valves "a" to the appropriate dilution, chilled to a few degrees (2–5 °C) less than the desired reaction temperature in the feed prechillers "1". The temperature of both feeds is then adjusted accurately by passage through a pair of core–shell heat exchangers "2", each with an internal volume of 350 mL. Temperature adjustment in the heat exchangers is with a Neslab 910 temperature control unit. The temperatures of the exiting solutions are monitored with thermocouples "c" and rapidly injection mixed in a mixer "3". The exiting reaction mixture enters the thermostated reaction zone "4", where the flow of solution is 6–15 mL/s. The reaction zone is made of lengths of stainless steel tubing with an inner diameter of 0.213 cm. Differences in residence time can be attained by using a combination of different flow rates and different lengths of tubing. The reacting solution enters the UV–vis spectrophotometer ("5a" and "5b") into the single-pass flow cell with a sample cell of 0.35-mL capacity "6" and exits the experimental setup through backpressure valve "b". Ethene or propene in hexane solution can be similarly introduced at any appropriate site in this experiment. Two changes are made to this experimental design for the polymerization experiments: (i) olefins are introduced into the appropriate region in "4" and (ii) "5", "5b", and "6" are replaced with an extension of the reactor. The polymerizing solution is quenched with a 50-fold molar excess—based on aluminum and vanadium—of 2-propanol, diluted in hexane, introduced into the reaction zone through a flow regulator valve "a". The polymer solution is collected at the exit of the reactor and isolated as described for the CFSTR polymers above.

UV–Visible Spectroscopy. UV–visible spectra were obtained in a Perkin-Elmer Lambda 7 spectrophotometer operating in conjunction with a Perkin-Elmer SPECCS data acquisition and storage system. Spectra were usually recorded between 220 and 900 nm; smaller sections of this interval were sometimes used as appropriate. 1 has a strong absorbance in this region at 412 nm ($\log \epsilon = 3.12$), and all spectral titrations (e.g., Figure 4) and the kinetic measurements for the reaction of 1 with alkylaluminum compounds were monitored at this wavelength. No corrections were applied to the spectral data for distribution of residence times that arise because of passage through the continuous flow reactor. This may affect the magnitude of the observed rate constants, but since all of the crucial experiments were conducted under identical flow conditions, our conclusions about the relative magnitude of the rate constants for the reaction of 1 with aluminum alkyl chlorides is unaffected.

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