JOURNAL OF CATALYSIS 47, 197–209 (1977)

A Soluble Chromium-Based Catalyst for Ethylene Trimerization and Polymerization

R. M. MANYIK, W. E. WALKER, AND T. P. WILSON

Union Carbide Corporation, Research and Development Department,
South Charleston, West Virginia 25303

Received September 3, 1976; revised December 31, 1976

The catalyst formed by the interaction of chromium (III) 2-ethylhexanoate or related compounds with partially hydrolyzed triisobutyl aluminum, in paraffinic solvents, polymerizes ethylene to linear polyethylene at ethylene turnover numbers of the order of 30 sec^{-1} atm^{-1}. The polyethylene appears to be formed by what has come to be considered a conventional Ziegler olefin polymerization mechanism [Novaro *et al.*, *J. Catal.* 41, 91 (1976)]. Hexene-1 can also be produced, at rates comparable to those of polyethylene formation. The mechanism of hexene-1 formation differs from that of polyethylene formation, as shown by differences in the pressure and temperature dependence of the two rates and by the inhibition of hexene-1 formation, but not polyethylene formation, by small quantities of dienes. Some mechanistic implications of the hexene-1 formation kinetics are discussed. Information relating to the structure of poly(isobutyl aluminum oxide) is also presented. Some structures for the catalytically active centers are proposed, and reactions by which such structures could be produced are suggested.

INTRODUCTION

A recent paper on oligomerization of α-olefins with Ziegler–Natta catalysts by Novaro *et al.* (*1*) gives the results of a detailed quantum mechanical study of the mechanism whereby α-olefin oligomers are formed from ethylene in the presence of a soluble, Ti^{3+}-containing, complex catalyst. Their arguments and calculations, following on those of Cossee (*2*) and Armstrong *et al.*, (*3*) provide a detailed picture of the chain growth and chain termination processes by which such catalysts produce polymers with α-olefinic unsaturation from ethylene. A related, soluble, chromium-based catalyst was investigated by the authors some years ago (*4*). That catalyst made polyethylene with vinyl end groups, at a rate proportional to the ethylene pressure. Chain termination occurred by chain transfer to monomer, as shown by the presence of vinyl end groups and the lack of effect of pressure on the polymer molecular weight. Thus the polymer fits into the pattern described by Novaro *et al.* (*1*), Ballard (*5*), Hogan (*6*), Henrici–Olivé and Olivé (*7*) and others. In addition to high molecular weight polymer, the catalyst could produce substantial quantities of ethylene oligomers, predominantly hexene-1. Its ability to produce hexene-1 from ethylene is apparently unique among the myriad of catalysts, formed by the interaction of aluminum alkyls with transition metal compounds, whose characteristics have been reported. The purpose of this communication is to point out that hexene-1 must be produced in this chromium-based catalyst system by a mechanism different from that described by Novaro *et al.* (*1*).

ISSN 0021-9517

The process of catalyst formation and the kinetics of high polymer formation are discussed briefly as background for the discussion of hexene-1 formation.

EXPERIMENTAL METHODS

Catalyst Preparation

Catalyst preparation is described in some detail in the issued patents (*4*), especially U. S. 3,300,458. In general, the procedure used was to add a solution of a trivalent chromium compound such as chromium (III) 2-ethylhexanoate, in a light paraffinic solvent from which water, oxygen, and oxidation products had been eliminated, to a solution of a poly(alkyl aluminum oxide). The latter was best prepared by the addition of water to a hydrocarbon solution of tri-isobutyl aluminum (TIBA). Soluble divalent chromium compounds gave active catalysts of comparable characteristics (*8*) but were less convenient to handle. Alkanoates and acetylacetonates of other transition and rare earth metals, specifically those of V, Ti, Zr, Ce, and U, also gave moderately active catalysts in these recipes, although the catalyst preparation procedures were not optimized for those compounds. Of these five metals, only uranium gave yields of hexene-1 comparable to those obtained with chromium.

The poly(isobutyl aluminum oxide), PIBAO, formed by the reaction:

$$(i\text{-Bu})_3\text{Al} + \text{H}_2\text{O} \rightarrow \frac{1}{n}\,(i\text{-Bu AlO})_n + 2\,\text{H}(i\text{-Bu}),$$

was most active if obtained by mixing solutions containing no liquid water phase. Addition of water as a liquid to a dilute solution of tri-isobutyl aluminum also gave good results if done slowly and if the reaction mixture was well agitated and carefully cooled. As prepared, the solution produced was clear, colorless and fluid, even when made starting with 25 vol% aluminum alkyl. The PIBAO was best used within an hour or two of its preparation but retained some activity for periods of up to 1 year if stored in the absence of air or water. The polymeric nature of the PIBAO was most directly demonstrated by ultracentrifuge measurements of its molecular weight, which varied from 1000 to 10,000 in different samples.

One characteristic of PIBAO which is deserving of note was discovered by Whipple (*9*) in some nmr studies of the material. He found that PIBAO, TIBA and the product of the reaction of 0.5 mole of water/mole of TIBA each have a characteristic nmr spectrum. A mixture of PIBAO and TIBA, in benzene, exhibited the spectra of both the materials originally present, for periods of days at room temperature. There was no indication from the nmr spectrum that the half-hydrolyzed product was being formed. This implies a high degree of stability for PIBAO, somewhat analogous to that well known for dialkyl aluminum dialkylamides and alkoxides (*10*).

Catalyst concentration levels appropriate for use at 50–90°C and 10 atm (1 atm $= 101{,}325\ \text{N m}^{-2}$) total pressure were found to be 1–5 mmoles of aluminum, as PIBAO, and 3–10 μmoles of chromium/liter of final solution. In laboratory batch polymerizations it was frequently necessary to add 1 mmole of TIBA/liter to the system, as a scavenger for residual traces of unidentified poisons in the solvents and on the walls of the reactor, in order to get the reaction to go at all. The TIBA was not necessary in continuous polymerizations with clean solvents. Its use had side effects on the polymerization, which are discussed below.

Equipment and Procedures

The reactor used in the batch experiments to be described was a 1-liter Autoclave Engineers Magnedash autoclave, equipped with thermocouple, gas inlet and outlet and a separate catalyst injection port. This was purged with N_2 and then loaded with solvent containing a small quantity of TIBA. It was then heated to reaction temperature, purged and brought to pressure with ethylene. Catalyst solution was forced into the autoclave from a reservoir under nitrogen pressure. New autoclaves required conditioning with catalyst solution before polymerization would occur.

Continuous laboratory polymerizations were carried out in a modified 2-liter Autoclave Engineers Magnedrive autoclave equipped with turbine-type stirrer and a standpipe to control the liquid level. Catalyst solutions were metered in with Milton-Roy Minipumps, and ethylene inlet flow was monitored on a Fischer-Porter rotameter. Reactor pretreatment was less critical in the continuous unit than in the batch reactor. Gas and polymer slurry were vented to a vapor–liquid separator whose pressure was controlled by a Grove back-pressure regulator. The separator contained a small quantity of water to quench the reaction. Slurry was vented manually to an atmospheric pressure receiver as required, and ethylene outlet flow was measured.

The polyethylene normally formed as a fluid slurry. This characteristic made possible meaningful rate measurements on the system.

RESULTS

Catalyst Formation

A reaction occurs between the chromium compound and PIBAO when these catalyst components are mixed. This was most clearly demonstrated in a series of experiments in which a solution of the chromium compound was added to concentrated PIBAO (1 mmole Al/ml in benzene) in a uv-visible spectrometer cell. The characteristic two-band pattern of chromium (III) 2-ethylhexanoate faded rapidly at room temperature but never disappeared completely even at an Al/Cr ratio of 300. In its place, a strong charge transfer type of band appeared in the ultraviolet, extending into the blue portion of the visible spectrum. On addition of 2-ethylhexanoic acid, the 590 nm band of Cr^{3+} was regenerated essentially quantitatively. The 440 nm band was apparently not completely regenerated, but this could have been due to a strong background absorbance remaining in that region. Chemical determination of the chromium valence in a similar mixture also showed that the chromium was not reduced.

When chromium (II) 2-ethylhexanoate was used in place of the chromium (III) compound, the single 440 nm band of the starting material disappeared completely at Al/Cr = 100. Again a charge transfer-type band appeared in the ultraviolet. On addition of excess 2-ethylhexanoic acid, the chromium (II) 2-ethylhexanoate was regenerated in part, along with some of the chromium (III) compound, presumably formed as a result of inadvertent admission of air to the system. This sensitivity to air is, of course, characteristic of Cr^{2+} compounds. It can easily account for the similarity noted between catalysts made from Cr^{2+} and Cr^{3+}. At the micromole per liter level used in polymerizations with these catalysts, oxidation would be virtually impossible to avoid. The fact that the Cr^{2+} compound reacts completely with PIBAO, while the Cr^{3+} compound does not, presumably reflects the well-known difference in lability of compounds of these two ions.

Polymerization

The effects on the ethylene polymerization reaction of varying catalyst component concentration and ethylene pressure were studied in a series of batch polymerizations. The catalyst components whose concentrations were varied were chromium (III) 2-ethylhexanoate, PIBAO and TIBA. The data from one such series are shown in Table

TABLE 1

Changes in Polymerization Rate with Catalyst Component Concentration

Concn[a]			Rate of solid polymer formation (g liter^{-1} hr^{-1})	k[b]
[Cr^{3+}]	[TIBA]	[PIBAO]		
0.0044	1.52	1.60	67[c]	5.1[c]
0.009	0.96	1.60	54	4.6
0.018	0.96	1.60	142	6.0
0.009	1.92	1.60	32	5.4
0.018	1.92	3.20	126	5.3
0.026	1.68	1.60	108	5.6
0.026	1.20	1.60	146	5.4
0.013	1.60	1.60	58	5.5
0.013	1.60	2.40	98	6.2
0.013	1.60	3.20	120	5.7
0.013	1.60	0.80	31	5.9

[a] All concentrations in mmoles/liter of heptane solvent; total pressure = 7.8 atm except where noted; temperature = 70°C.

[b] As defined in Eq. (1) in the text. Units are moles C_2H_4 polymerized (moles Cr)$^{-1}$ sec^{-1} atm^{-1}. Chromium turnover number = k[PIBAO]/TIBA].

[c] Total pressure = 28.2 atm.

1. The rates conform to the relationship:

$$\text{rate} = k \frac{[\text{Cr}][\text{PIBAO}]}{[\text{TIBA}]} P_{C_2H_4}, \quad (1)$$

with a maximum deviation of 14%. Equation (1) is to be considered strictly empirical, and applicable only over the range of variables covered by these particular experiments. Other experiments showed that if either the [Cr] or the [PIBAO] was held constant, and the other increased without limit, a maximum rate of polymerization was attained beyond which further additions made no difference. With batch-prepared PIBAO, the maximum turnover number, or rate per chromium atom present, was obtained at Al/Cr ratios of the order of 200. Equivalent or higher rates could be obtained at Al/Cr ratios <100 if the PIBAO was prepared and used continuously.

The [TIBA] term in the denominator of Eq. (1) must be considered as a special case of what would probably be a term of the form (1 + a[TIBA]) in a more broadly applicable equation. Clearly the rate does not go to infinity in the absence of TIBA. Another way of reducing or eliminating the inhibiting effect of TIBA was found to be to add isobutene to the reacting system. This effect and the tendency of the PIBAO concentration effect to be nonlinear are shown in Fig. 1. Isobutene had no effect on the polymerization in the absence of TIBA. The higher turnover numbers attainable without added TIBA or with both TIBA and isobutene present are comparable to those reported elsewhere (*5*, *6*) for the most active ethylene polymerization catalysts.

The effect of adding isobutene is presumed to be due to its reversal of the diisobutyl aluminum hydride formation reaction (*11*, *12*).

$$\text{Al}(i\text{-Bu})_3 \rightleftharpoons \text{HAl}(i\text{-Bu})_2 + i\text{-}C_4H_8. \quad (2)$$

The hydride is much more extensively dimer- or trimerized than is TIBA (*12*) presumably in good part because of steric problems with TIBA. This would be expected also to be a factor in associations with other relatively hindered metal centers.

In spite of differences in apparent turnover number, polymer prepared with different catalysts differed little in properties. It would appear that the active centers produced differed in number but not in kind from one catalyst to another, so long as impurity effects were minimal. This is not to suggest that only one type of active center is formed, but rather that the distribution of centers formed changes very little. Characterization of the polymers produced shows them to have $\bar{M}_w/\bar{M}_n$ ranging from 5 to 15 or more. If only a single type of site were present, $\bar{M}_w/\bar{M}_n$ should be about 2.

When ethylene quality was good the catalyst activities obtained initially remained constant, at temperatures up to 85°C, for periods in excess of 1 hr. In one experiment, the rate of polymerization was

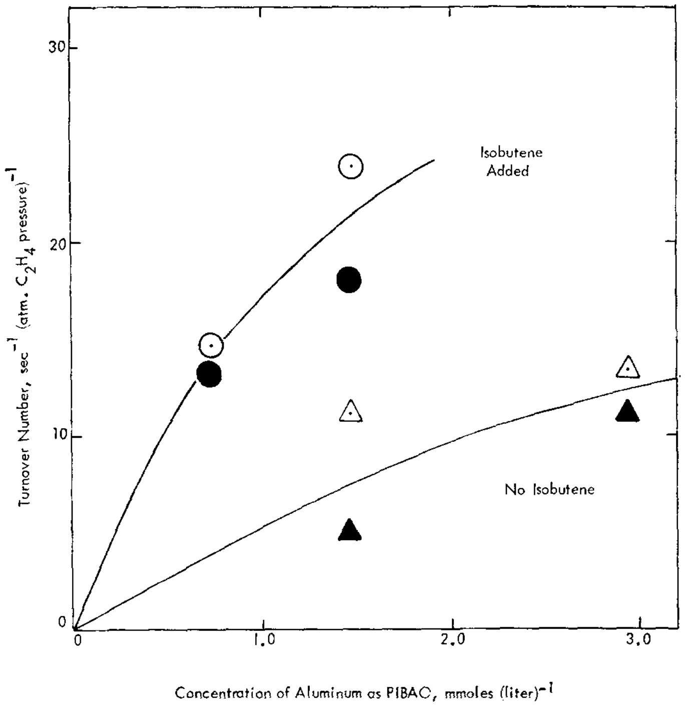


FIG. 1. Ethylene turnover number dependence on PIBAO concentration. Bath polymerizations at 7.8 atm, 70°C in 500 ml heptane with 0.96 mmole TIBA added (○) 20 mmole isobutene added; (△) no isobutene added. Open points: 4.1 μmoles Cr; solid points: 8.2 μmoles Cr.

measured first at 70°C, then at 82°C and then again at 70°C. The first and last measurements in this experiment agreed within 10%. The activation energy calculated from the two rates was 17 kcal/g-mole. This is in reasonable agreement with values reported for other ethylene polymerization catalysts (*13*).

*Kinetics of Hexene-*1 *Formation*

The pentane solvent from a typical batch ethylene polymerization at 73°C and 11.2 atm total pressure was analyzed for dissolved products by vapor chromatography. Relative weights of the lower olefins shown to be present are given in Table 2. The actual hexene-1 concentration in this sample was 1.1 wt%. Clearly hexene-1 is the predominant oligomeric product formed. Enough is present under these operating conditions to copolymerize to a significant degree with the ethylene present. The result is the production of polymer of reduced density (~0.955 g/ml) and stiffness. The compounds categorized as branched decenes were identified only as a characteristic trio of peaks appearing between octene-1 and decene-1 in the chromatograms obtained from Perkin-Elmer R-2 or N-5 columns. These appeared only when hexene-1 was present in the solvent. The branched decenes and at least part of the decene-1 are presumably formed by the olefin trimeriza-

TABLE 2

Relative Weights of Ethylene Oligomers Produced

Olefin	Wt found (butene-1 = 1)
Butene-1	1
Hexene-1	25
Octene-1	0.3
Branched decenes	0.5
Decene-1	0.03

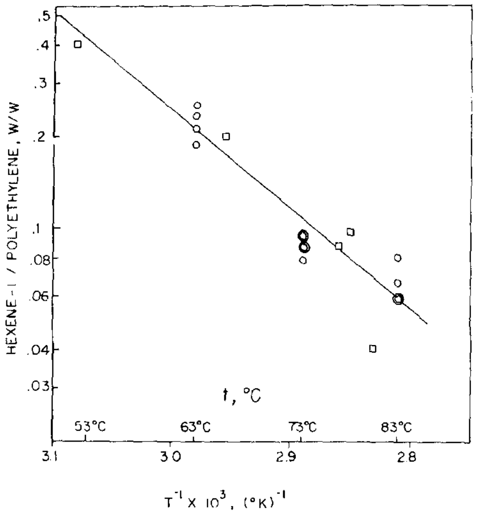


FIG. 2. Effect of temperature on hexene-1 production.

tion reaction, starting with two ethylene molecules and a hexene-1. The sequence in which those three molecules combined was not investigated.

The ratio of hexene-1 to polyethylene produced could be varied in at least three ways: by varying reaction temperature, by varying ethylene pressure or by introducing selective poisons. The effect of reaction temperature is shown graphically in Fig. 2. As the temperature was raised from 53 to 83°C at 7.8 atm, the ratio of hexene-1 to polyethylene produced varied from 0.4 down to 0.04. The variation in ratio with temperature corresponds to a difference of about 17 kcal/mole in the activation energies for the two reactions, the polymerization evidently having the greater activation energy. Within the accuracy of the experimental data, the difference is the same as the absolute activation energy for the polymerization process, hence the trimerization reaction has a near-zero activation energy.

TABLE 3

Approximate Rate Constants

Rate constant[a]	Value at 75°C	ΔE_a/kcal g-mole^{-1}
k_p	30	17
k_t	0.4	36
k_h	0.1	0

[a] k_p = rate of addition of ethylene to the polymer chain, atm^{-1} sec^{-1}; k_t = rate of chain termination by chain transfer, atm^{-1} sec^{-1}; k_h = rate of hexene-1 formation, atm^{-2} sec^{-1}. All rate constants given as moles consumed, or moles of product, per mole of chromium present, i.e., turnover number.

Rate constants for polymer formation, chain transfer to monomer and hexene-1 formation by an active catalyst of this type are collected in Table 3, along with the respective activation energies.

The rate of hexene-1 formation is more sensitive to ethylene partial pressure than is the rate of polymerization. In one factorially designed set of experiments run at 73°C the polymer/hexene-1 weight ratio was found to be 10.3 ± 0.5 at 6.1 atm and 5.8 ± 0.5 at 11.2 atm. Since the rate of polymer formation was proportional to the ethylene pressure, the rate of hexene-1 formation must be dependent on the square of ethylene pressure. The same conclusion can be drawn from studies of the effect of ethylene partial pressure on polymer density which are not described here.

Effects of Dienes and Other Additives

The second order dependence of rate of hexene-1 formation on ethylene pressure suggested the possibility that two olefin-absorbing sites were present in the active centers responsible for that reaction. Addition of dienes, at very low levels, did in fact result in the inhibition of hexene-1 formation, as illustrated by the data in Table 4. Hexene-1 formation could be reduced by a factor of 10 by the addition of butadiene to the solvent at a concentration of the order of 1 mmole/liter. Isoprene and piperylene were about as effective as butadiene. Choroprene and 2-methoxybutadiene only had to be present at a level of approximately 50 μmoles/liter (5–10 times the chromium concentration) to have an equivalent effect. This is less than the number of molecules of polymer produced per hour by

TABLE 4

Inhibition of Hexene-1 Formation[a] by Dienes

Diene		Polymer (wt% in slurry)	Hexene-1 (wt% of products)	Polymer properties	
Name	mM			Melt index[b] (dg min^{-1})	Density (g m^{-1})
None	0.0	12.0	13.1	1.2	0.9552
Isoprene	0.08	12.4	4.1	1.2	0.9649
	0.20	11.9	0.8	0.8	0.9702
Piperylene	0.20	11.2	2.0	1.3	0.9688
2-Chlorobutadiene-1,3	0.016	13.7	5.7	0.2	0.9626
	0.04	11.2	1.3	1.2	0.9684
3-Ethylidenecyclohexene	0.07	9.7	8.4	0.2	0.9632

[a] Continuous flow polymerization, heptane solvent, 73°C, 11.0 atm total pressure, 1.2 hr average residence time. Cr = 7–8 μM, PIBAO = 2.3–2.7 mM (Al), H_2O/TIBA = 1.2, aging time = 20 min. Additive in chromium feed.

[b] ASTM D-1238-73, test condition E.

each atom of chromium present. At these levels there was no detectable incorporation of the dienes in the polymer produced, the rate of polymer formation was not changed and the polymer differed only in density from that produced in the absence of the dienes. The average polymer molecular weight and molecular weight distribution were essentially unchanged. The lack of effect of dienes on average molecular weight of the solid polymer produced is shown by the lack of variation of melt index in the data shown in Table 4. Melt index is approximately proportional to $(1/\bar{M}_w)^4$.

In other tests, cyclohexadiene and 3-ethylidenecyclohexene proved to be about as effective as butadiene in inhibiting hexene-1 formation, but cyclooctadiene-1,5 and cyclododecatriene were less effective. A high degree of bulky substitution on the diene, as in 1,4-diphenyl butadiene, reduced the compound's effectiveness. Phenyl acetylene appeared about as effective as butadiene but styrene was not.

A variety of other additives, both mono- and difunctional, were tested to determine their effects on the catalyst system and on the polymers produced. Compounds such as triphenyl phosphine, hexamethylphosphoramide, o-phenathroline, thiophene and furan did not significantly reduce the ratio of hexene-1 to polymer produced, but did cause an increase in polymer molecular weight (decrease in melt index). Dimethoxyethane and o-dimethoxybenzene, at the 50 μmole/liter level, had no effect on melt index but may have increased hexene-1 production. The dimethoxy compounds may simply have complexed preferentially with excess alkyl in the system rather than with the transition metal sites. Additions of unhydrolyzed TIBA decreased hexene-1 production but led to the production of polymer having a high wax content.

Poisons

Several compounds were found which stopped all ethylene polymerization completely when added in an amount equivalent on a molar basis to that of the chromium present. These included carbon monoxide, cyclopentadiene and α,α'-bipyridyl. Smaller quantities resulted in partial poisoning.

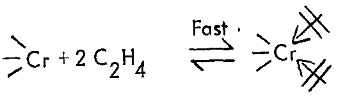
Acetylene was a temporary poison. Polymerization slowed drastically when it was added, but then slowly revived if the acetylene was purged out of the system and replaced with ethylene. During the time the polymerization was slowed down, the white slurry slowly turned dark, presumably due to the formation of the purplish polyacetylene. Butadiene, too, when added in large quantities, poisoned the ethylene polymerization reaction and was itself polymerized very slowly.

Oxygen was not a particularly potent poison, not nearly so deadly as CO for example. In view of the susceptibility of Cr^{2+} compounds to air oxidation and the relatively slow reaction of O_2 with dilute aluminum alkyls, the insensitivity of the catalyst to O_2 in the gas phase provides additional support for the view that the catalytically active species are not Cr^{2+} but are, at least predominantly, Cr^{3+}. Oxygen additions, if carried to the point where they reduced the polymerization rate, normally raised the average molecular weight of the polymer produced. The same effect could be obtained by adding isobutanol or aluminum isobutoxide in limited amounts.

DISCUSSION

The rate of hexene-1 formation by the Cr–PIBAO catalyst system described above is characterized by a second order dependence on the ethylene pressure, by a near-zero activation energy, and by a pronounced inhibition by dienes, especially those bearing electron-withdrawing groups. None of these characteristics are consistent with the oligomerization mechanism described by Novaro *et al.* (*1*). All of them can be understood if two molecules of ethylene are coordinated with the active transition metal ion in the activated complex involved in the rate-determining step. One possible sequence of reactions leading to hexene-1 formation, which is consistent with the information available, is the following:

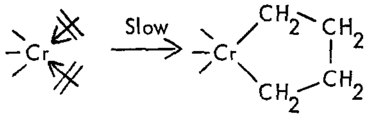
1. A chromium ion coordinates reversibly with two ethylene molecules,



(3)

The chromium is presumed to be trivalent, based on the chemical evidence that reduction does not occur, and three-coordinate because the series of reactions proposed will require coordination of this chromium with a total of three molecules of ethylene. Rapid displacement of a coordinated oxide or carboxylato ligand from Cr^{3+} by an olefin is not considered likely.

2. The coordinated olefins rearrange to form a metallocyclopentane in which the chromium is pentavalent:

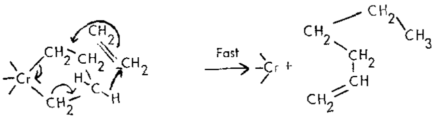


(4)

This is the reverse of the decomposition reaction observed by Grubbs and Brunck (*14*) in their work with a tungsten metallocycle. The rate of this step must determine the overall rate of hexene-1 formation to account for the dependence of that rate on the second power of the ethylene pressure. The zero activation energy found for hexene-1 formation would imply that the activation energy for rearrangement of the complex is equal numerically but opposite in sign to its heat of formation, so that the complex's rate of rearrangement increases and its concentration decreases as the temperature is increased.

3. The metallocycle reacts with ethylene, splitting out hexene-1 and regenerating the

original Cr^{3+} compound:

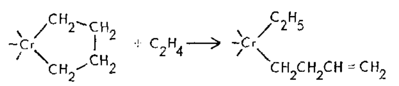


(5)

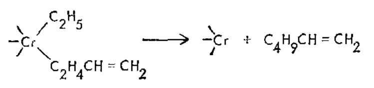
Inspection of models shows that this reaction could occur by a process resembling the one described by Novaro *et al.* (*1*) for chain transfer to monomer. A vacant coordination site is required if the ethylene is to be added in such a step. Such a site would only be available if the original chromium compound was three-coordinate.

Butadiene could coordinate with a three-coordinate chromium (III) compound and then react to form a metallocyclopentene. Coordination of butadiene should be enhanced over that expected for two ethylene molecules by the chelate effect, which could increase the stability of the resulting complex by a factor of 10^4 or more. Additional stabilization would result from use of a diene containing an electron-withdrawing group. Formation of the cyclic structure from the coordinated olefin would appear likely to be a facile reaction. Formation of hexadiene by addition of ethylene to that structure would appear unlikely, though, because it would require transfer of a vinylic proton to the incoming ethylene. Models show that these protons are not located in positions where that transfer could occur easily. Thus butadiene molecules should preferentially occupy the coordination sites necessary for the trimerization of ethylene, without themselves reacting.

An alternative to reaction (5) would be the stepwise process:



(6a)

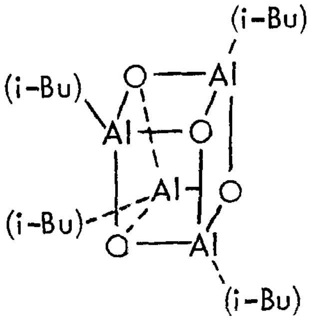


(6b)

This would be the direct analogue of Novaro's chain transfer to monomer process, involving only one end of the C_4 ring, followed by reductive elimination. There is no compelling reason evident for preferring reaction (5) over reaction (6), unless one of the other ligands on the chromium ion is an alkyl group. This possibility will be discussed following some speculations concerning the structures around the chromium ions.

Having shown that a three-coordinate Cr^{3+} compound could catalyze the formation of hexene-1 from ethylene, there remains the problem of explaining why the particular catalyst system employed should lead to the generation of Cr^{3+} in such an unusual coordination state. Three-coordinate Cr^{3+} has been reported by Kazanskii (*15*) to be present on the surface of chromium-impregnated silica gel, and by Alyea *et al.* (*16*) to be formed when Cr^{3+} is combined with sufficiently bulky monovalent ligands. Nevertheless, Cr^{3+} is normally octahedrally coordinated, and such compounds are kinetically inert. The PIBAO is also inert, at least to reaction with TIBA. Thus there are actually two obstacles to forming low coordination number Cr^{3+} ions from octahedrally coordinated Cr^{3+}—one being the low rate expected for the reaction of Cr(2-ethylhexanoate)$_3$ with PIBAO, and the other the ordinarily thermodynamically unfavorable reduction in coordination number. Little or no firm and conclusive evidence is available to show how the catalyst-forming reaction takes place, but rationalization is possible based at some points on known chemistry.

Since PIBAO is formed by the reaction of nearly equimolar quantities of water and TIBA, and since residual hydroxyl groups, if present, are there only in traces, PIBAO must have the empirical formula $(RAlO)_n$. This has been confirmed by carbon and hydrogen analyses. From the molecular weights measured by ultracentrifuge, n ranged from 10 to 100 in the samples studied. Its high degree of solibulity in aliphatic solvents distinguishes it from the EtAlO reported by Storr *et al.* (*17*). Evaporation of the solvent leaves a slightly tacky, glassy material which can be redissolved without change in molecular weight. In the light of those facts and the structures suggested for other aloxanes (*17*, *18*), it seems reasonable to believe that PIBAO is made up predominantly of aluminum atoms connected by oxide bridges in some three-dimensional fashion. The simplest and smallest such structure would be that shown as I.

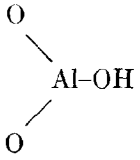


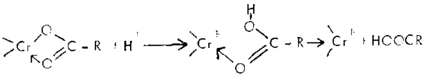
I

Obviously larger fused-ring systems are possible and are required to satisfy the molecular weights found for PIBAO. Solid structures consisting of six-membered ring building blocks would seem likely. The smaller clusters could couple through oxide linkages to build up higher molecular weight compounds.

The low viscosity of concentrated PIBAO solutions indicates that the fairly large molecules present are compact and do not interact chemically (gels are not formed). The solubility in aliphatic hydrocarbons suggests that the alkyl groups are exposed to the solvent. The insoluble nature of $(EtAlO)_n$ indicates that ethyl groups are not bulky enough to prevent interaction between the polar portions of the clusters. On the other hand, poly(*n*-hexyl aluminum oxide) is soluble and is nearly equivalent to PIBAO as a component of a chromium-based olefin polymerization catalyst system. The overall picture is one of a micellar structure, with isobutyl groups on the outside and aluminum and oxide ions inside the micelle. The aluminum must be largely four-coordinate to account for the stability of the structures produced.

Some hydroxyl groups do remain for long periods of time in hydrolyzed TIBA solutions. This was best shown by thermometric studies of the reaction. From these it was evident that the first alkyl group of TIBA reacted almost instantaneously with water in an aliphatic solvent, but that subsequent reaction proceeded at a much slower pace. The slow reaction could be followed for more than 1 hr by the techniques used. Residual hydroxyl groups present after 1 hr at room temperature would be a very few percent of the amount of water added, when equimolar quantities of TIBA and H_2O were allowed to react. Since PIBAO made continuously and used after 10 to 20 min was highly active there can be little doubt that the active material did contain hydroxyl groups. A similar low rate of reaction for the last few alkyl groups was found by Amdurski *et al.* (*19*) in their studies of triethyl aluminum hydrolysis. Presumably the rigidity of the aluminum–oxygen framework prevents the intramolecular reaction of isobutyl groups with a hydroxyl group in the same micelle, and steric hindrance prevents the properly oriented approach of separate micelles.

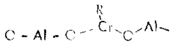
The presence of isolated hydroxyl groups in the PIBAO clusters must be the key to the rapid reaction of these clusters with compounds containing octahydrally coordinated Cr^{3+}. Two factors would then favor ligand exchange involving an  $\overset{O\diagdown}{\underset{O\diagup}{Al{-}OH}}$ grouping. In the first place, the low dielectric constant of the medium enhances dipole–dipole interactions, resulting in more than random contact between polar species. In addition, the special stepwise mechanism described by Basolo and Pearson (*20*) for acid-catalyzed hydrolyses of chelating ligands should be operative in the situation under discussion:



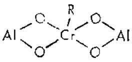
The carboxylic acid formed would react with an isobutyl group on the PIBAO to produce isobutane and an aluminum carboxylate. The chromium would then have exchanged a carboxylate ligand for an oxide ligand.

At least some fraction of the oxide ligands acquired by chromium in this reaction would occupy only a single coordination site on the chromium. The net result would be a decrease in the coordination number of the chromium from 6 to 5. The other four coordination sites would be occupied by the two carboxylato ligands remaining at this stage. The energy necessary would come from the formation of isobutane.

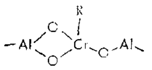
Once the chromium had become attached to a PIBAO micelle and had lost its octahedral configuration, it could confer lability on that PIBAO in which it found itself, or react with other micelles. Equilibration of the oxide and carboxylato ligands would ensue. The Al^{3+} ions, both because they are present in excess and because they are smaller than Cr^{3+}, should in most cases acquire all the carboxylato groups introduced with the chromium, leaving only oxide and alkyl groups for the Cr^{3+} ions. The electronegativities of Cr^{3+} and Al^{3+} are roughly equivalent, so the ratio of alkyl groups to oxide ions associated with the two types of metal ions should be nearly equal, i.e., there should be one alkyl group per metal atom, on the average. The RCr^{2+} grouping could exist in combination with the PIBAO in three (**II**), four (**III**), or five (**IV**) coordinate structures:



II



IV

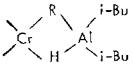


III

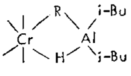
Any of these would meet the requirements for an active olefin polymerization catalyst, i.e., a transition metal ion with one alkyl ligand and a vacancy in its coordination sphere (*1*, *2*).

Only the three-coordinate structure would satisfy the demands of the hexene-1 production mechanism proposed above. Even then there is a question as to whether an alkyl group could be present on the hexene-1 producing center. Certainly it could not be there if the stepwise mechanism for hexene-1 formation from the chromium metallocycle is correct. An additional alkyl group would compete with the two formed by ethylene attack at one end of the tetramethylene portion of the ring [Reaction (6a)], resulting in a less specific production of hexene-1 and in much too frequent chain termination. Some thirty molecules of hexene-1 actually are produced per molecule of polymer under the operating conditions normally employed in these experiments. The concerted hexene-1 formation reaction could proceed leaving the polymer chain untouched.

Structures of the type discussed can also be used to rationalize the effects of $HAl(i\text{-}Bu)_2$, on the polymerization. All the active structures have vacant coordination sites. Coordination of the hydride with the active sites would be expected, leading to the formation of structures such as **V** from **II** of **VI** from **IV**:



V



VI

Structures similar to **V**, have been invoked by a number of writers (*11*, *21*, *22*) as the active species in olefin polymerization catalysts. Structure **VI** should no longer be an active catalyst, since no vacant coordination site is left. Thus if any sites such as **IV** were formed originally, some of these would be destroyed (reversibly) by coordination with $HAl(i\text{-}Bu)_2$. Thus the observed "poisoning" effect of TIBA could be due to elimination of some of the active species present. Of course, Structure **V** could also be less active than **II**.

The other point to note about Structure **V** is that it provides a mechanism for exchange of either H or *i*-Bu from the aluminum hydride molecules with the growing polymer chains. Thus it introduces another potential chain termination process. The number of alkyl groups associated with the usual TIBA additions (1 mmole/liter) was roughly comparable with the number of polymer molecules produced in the polymerizations without TIBA. If the complexing of $HAl(i\text{-}Bu)_2$ with all active catalytic sites is equal and is a rapid and reversible reaction, then in the hour over which the polymerizations were normally run, the polymer molecular weight should be reduced by a factor of two in the presence of TIBA. If some polymerization sites are affected by $HAl(i\text{-}Bu)_2$ while others are not, a polymer of high wax content would be produced, as observed when TIBA was added.

In summary, an ethylene polymerization catalyst which produces both high molecular weight polyethylene and hexene-1 has been described. The hexene-1 appears to be the product of a novel, highly specific ethylene trimerization reaction. A mechanism for the trimerization is proposed, based on three-coordinate Cr^{3+} as the catalytically active site. Some new information obtained on poly (isobutyl aluminum oxide), one of the catalyst components, is combined with information from the literature on aloxanes to develop the general outlines of the structure of that material. Elements of the proposed structure are then used to rationalize the reaction of PIBAO with soluble Cr^{3+} compounds based on monovalent, bidentate ligands to form low coordination number Cr^{3+} centers.

Note added in proof. The recent review of cobalt(I)-catalyzed cyclooligomerizations of acetylenes by K. P. C. Vollhardt (*Acc. Chem. Res.* **10**, 1 (1977)) indicates that they proceed through metallocyclopentadiene intermediates formed by reactions comparable to (4) above. The cyclopentadiene analogs could not readily undergo hydrogen transfer reactions comparable to reaction (5). Conversely, cyclopentane analogs should not undergo the Diels-Alder-type reactions which result in the formation of cyclic products from acetylenes.

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