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Transition Metal Catalysts. IV. Role of Valence in Low Pressure Catalysts[1]

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Examination of several low-pressure ethylene polymerization catalysts based on both vanadium and titanium compounds showed that the transition metal compound was reduced to a low valence species in every case. In those catalysts based on vanadium compounds, catalytic activity was only observed when part of the vanadium had been reduced to the divalent state, thus suggesting that the appearance of at least some of the divalent species may be a necessary prerequisite for catalytic activity with this metal. Theoretical analysis of the role of transition metal valence and some other essential parameters supports a polymerization mechanism involving propagation from a transition metal center by the two-step process of (1) coördination of the olefin to the transition metal to provide activation followed by (2) a rearrangement reaction to incorporate the coördinated monomer into the growing polymer chain.

Introduction

In the group of new organometallic mixed catalysts for olefin polymerization, literally hundreds of combinations have been reported over the last few years which are claimed to polymerize ethylene and other olefins to high molecular weight polymers under very mild conditions.[2,3] In general, the polyethylene prepared with these catalysts is linear, and the poly-α-olefins often have stereoregular structures. Since these features are not ordinarily associated with the classical radical, carbonium ion or carbanion catalysts, the new catalysts may be sufficiently unique to be considered as a fourth general class of vinyl polymerizations. Since the various catalysts in this group show great differences in structure, solubility, general physical character, nature of the metals involved and in the structure and properties of the polymers produced,[2] one can convincingly say that these catalysts are not identical. However, if one only considers the narrow question of the propagation reaction and the related initiation reaction, it may be seen that certain similarities exist which allow generalizations to be made that apply to the entire group. In this paper a common propagation mechanism for the organometallic mixed catalysts is proposed, and the structure and valence of the active transition metal center is discussed.

Experimental

Determination of Biphenyl Formation in the AlX_3–VX_n–$Sn(C_6H_5)_4$ Catalyst.—A dry 200-ml. bottle was charged with 1 g. (2.3 mmoles) of tin tetraphenyl and about 120 ml. of boiling cyclohexane and sealed under nitrogen ($\simeq$ 75–80°) with a rubber serum bottle stopper. The bottle was weighed before and after addition of the solvent and the exact volume was calculated from the density. By way of hypodermic syringes 2.1 g. (7.9 mmoles) of aluminum bromide and various specific amounts of vanadium halide (see Fig. 1) quickly were added as cyclohexane solutions. When the aluminum and vanadium halides were added, the solution turned an intense red color which quickly faded to a stable light pink color. After a reaction period of about 10 minutes the samples were quenched by the addition of 20 ml. of a cold saturated solution of dry hydrogen bromide in cyclohexane (or by simply bubbling dry hydrogen bromide through the solution) to cleave all carbon–metal bonds. This was followed by the addition and mixing of 20 ml. of deaerated 1 *N* sulfuric acid to extract the inorganic components into the aqueous layer. The infrared spectra of the hydrocarbon layers of samples prepared in this way show only those absorptions due to biphenyl (12.87, 13.6, 14.35 μ) and benzene (14.85 μ) in the 12–15 μ region. Analysis showed that all the vanadium was in the aqueous phase. Quantitative analyses for diphenyl in the hydrocarbon layer were carried out by infrared absorption at 13.6 μ using a calibration curve for this absorption based on measurements with solutions of known biphenyl concentrations. The exact concentration of divalent vanadium in the aqueous phase was measured by polarography as described below.

Polarographic Determination of Vanadous Ion.—Lingane[4] has investigated the polarographic behavior of the various vanadium valences and has defined the polarographic, halfwave potentials for the appropriate oxidation or reduction reactions. In this work, vanadous (V^{+2}) ion concentration was determined by a quantitative calibration of the anodic diffusion current from the oxidation of vanadous to vanadic ion.

Standard solutions of vanadous ion were prepared by reduction of ammonium metavanadate in 1 *N* sulfuric acid with zinc amalgam (10% mercury), or by dissolving solid vanadium dichloride in 1 *N* sulfuric acid and storing the resulting solution in contact with zinc amalgam. The actual vanadium content of the solutions was determined by chemical analysis[5] and the absence of higher valence compounds was established by the fact that only an anodic wave was present in the polarograms. With a series of known samples, a plot of diffusion current *vs.* vanadium concentration was found to be linear with a slope (Q) of 2.09 ± 0.07 μa./mg. of vanadium (vanadous ion). Meites[6] has discussed in detail the care required in the preparation and handling of a vanadous ion solution.

Polarographic analyses were carried out using a Sargent model 21 recording polarograph. The polarographic cell was kept under an atmosphere of nitrogen, and traces of oxygen in the nitrogen sweep were removed by first bubbling the stream through gas washing bottles containing an acid solution of vanadous ion in contact with zinc amalgam. The standard vanadous ion solution was added to the cell from a buret which also had a layer of zinc amalgam at the bottom. Sufficient 1 *N* sulfuric acid then was added to bring the total volume of liquid in the cell to 20 ml. Polarograms were obtained over the -0.1 to 1.1 volt range.

Suitable aliquots of the *N* H_2SO_4 acid layer in the catalyst samples, prepared as described above, were removed and polarograms obtained for the purpose of measuring the anodic diffusion current due to vanadous (V^{+2}) ion (Figs. 2, 3 and 4). The other metals in the catalyst solutions were

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[1] Part of this work was presented as paper No. 47 Polymer Division, 133rd Meeting of the American Chemical Society, San Francisco, Calif., April, 1958, and the remainder was presented as paper No. 4, Polymer Division, 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

[2] N. G. Gaylord and H. F. Mark, "Linear and Stereoregular Addition Polymers," Interscience Publishers, Inc., New York, N. Y.,

[3] Soc. Chem. Ind., Reports on the Progress of Applied Chemistry, Vol. 42, pp. 436–444, 1957.

[4] J. J. Lingane, THIS JOURNAL, **67**, 182 (1945).

[5] W. F. Hillebrand, G. E. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 461.

[6] L. Meites, *J. Chem. Ed.*, **27**, 458 (1950).

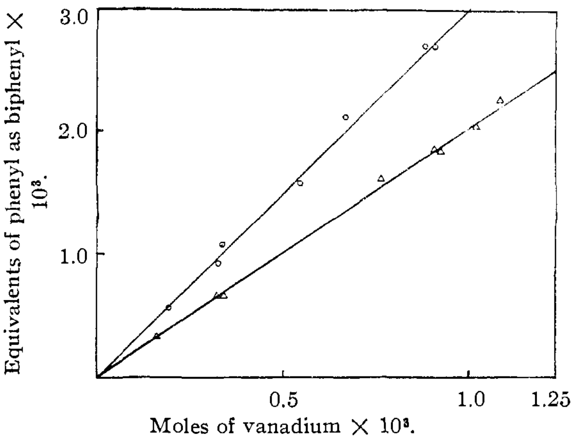

Fig. 1.—Formation of biphenyl as a function of vanadium concentration in the $AlBr_3$-VX_n-$Sn(C_6H_5)_4$ catalyst; Δ, VCl_4; O, $VOCl_3$.

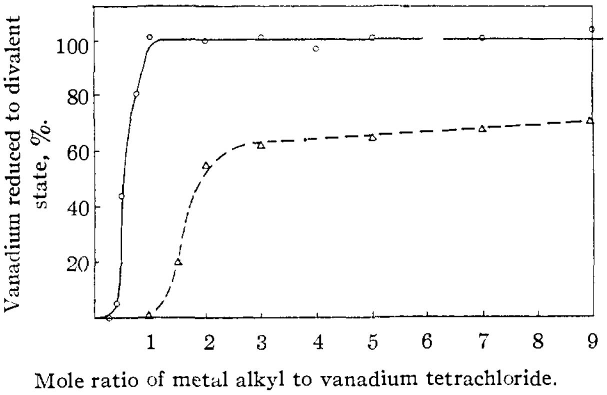

Fig. 2.—Reduction of vanadium tetrachloride with triisobutylaluminum (O) and diphenylzinc (-Δ-); 15-minute reaction time at room temperature and 25 millimoles per liter total reagent concentration.

shown in separate experiments to have negligible effect on the polarograms.

The reaction of triisobutylaluminum (5 mmoles) with biscyclopentadienylvanadium dichloride (1.2 mmoles) in 150 ml. of cyclohexane for 3 hours at room temperature caused reduction of 8% of the vanadium to the divalent state.

The reaction of triisobutylaluminum (5 mmoles) with finely ground vanadium trichloride (3 mmoles) in 150 ml. of cyclohexane for 24 hours at room temperature caused reduction of 5% of the vanadium to the divalent state.

Isolation of Precipitate from the Interaction of Triisobutyl aluminum and Vanadium Tetrachloride.—A dry centrifuge bottle was charged with 200 ml. of cyclohexane, 0.8 g. of vanadium tetrachloride and 5.0 g. of triisobutylaluminum and sealed, under nitrogen, with a rubber serum bottle stopper. This mixture was aged for 2 hours at room temperature, centrifuged to separate the precipitate, and the supernatant discarded. The precipitate was washed three times by reslurrying with cyclohexane followed by centrifugation and then dried under vacuum. The dry precipitate weighed 0.960 g. During these operations, a nitrogen atmosphere was maintained over the precipitate at all times to prevent any preliminary oxidation or hydrolysis.

At the end of the experiment, the dry, black precipitate was dissolved in dilute sulfuric acid, and the solution was analyzed for total aluminum, vanadium and chlorine by standard methods. The results are shown on Table I.

Determination of Divalent and Trivalent Titanium.—The catalyst solutions were prepared by the interaction of titanium tetrachloride and triisobutylaluminum in cyclohexane solution in sealed bottles as described above. The analytical procedure is essentially the same as that described by Tabakova and Soloveva[7] and is only summarized here. A sample of the reduced titanium compounds was added to a solution of ferric alum, and the total reducing power was measured by titration with potassium permanganate. A second sample of the reduced halides of the same size was added to dilute hydrochloric acid, followed by addition of ammonium sulfate solution to stabilize the trivalent state and dilute sulfuric acid (1:20) to oxidize any divalent titanium to the trivalent state. Ferric alum then was added, and the reducing power was again titrated with potassium permanganate. The concentration of divalent titanium can be calculated from the difference between these two titers, and twice the second titer minus the first titer is equal to the trivalent titanium concentration.

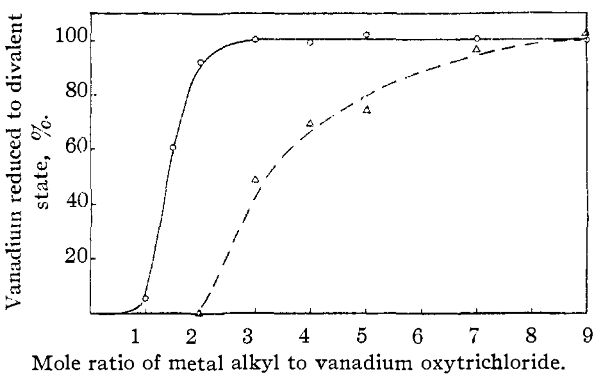

Fig. 3.—Reduction of vanadium oxytrichloride with triisobutylaluminum (O) and isobutylaluminum dibromide (-Δ-); 15-minute reaction time at room temperature and 25 millimoles per liter total reagent concentration.

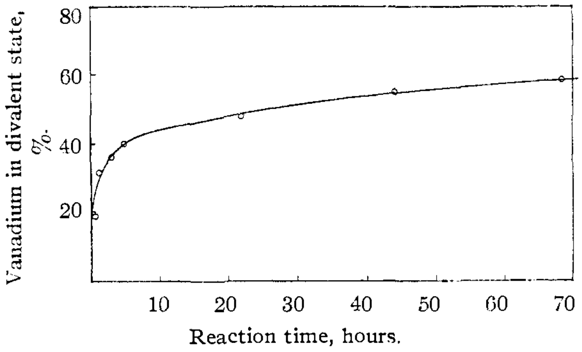

Fig. 4.—Reduction of *n*-propyl vanadate by triisobutylaluminum, 0.5 millimole of $(n\text{-}C_3H_7O)_3V{=}O$, 3.5 millimoles of $(C_4H_9)_3Al$, 150 ml. of cyclohexane, room temperature.

Ethylene Polymerization Tests with Vanadium Halides and Mixtures of Vanadium Halides and Aluminum Bromide.—Polymerization tests were carried out with ethylene at 65° and atmospheric pressure in cyclohexane, using the procedure that has been described already.[8] In separate experiments ethylene was bubbled into solutions of vanadium tetrachloride or vanadium oxytrichloride, and slurries of vanadium trichloride or vanadium dichloride containing 20 millimoles of the vanadium compound per liter of cyclohexane. No polymerization to form solid polyethylene occurred in an hour. However, addition of tetraphenyltin to the mixture of aluminum bromide and vanadium halide forms a very active catalyst as previously described.[8]

Results and Discussion

Aluminum bromide reacts with vanadium halides to form colored solutions in cyclohexane, indicating the presence of compound or complex formation between the two species. Further evidence for

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(7) E. G. Tabakova and Z. V. Soloveva, *Zavodskaya Lab.*, **22**, No. 12, 1417 (1956).

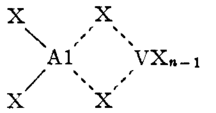
(8) W. L. Carrick, R. W. Kluiber, E. F. Bonner, L. H. Wartman, F. M. Rugg and J. J. Smith, THIS JOURNAL, **82**, 3883 (1960).

TABLE I

ANALYSIS OF SOLID CATALYST

	$Al(i\text{-}Bu)_3$ (g.) +	$VCl_4 \xrightarrow[200\ ml.]{C_6H_{12}}$		Precipitate (g.)
A	5.0	0.800		0.960
B	5.0	1.600		1.500
	Vanadium, g. (mole ratio)	Aluminum, g. (mole ratio)	Chlorine, g. (mole ratio)	Isobutyl, g. (mole ratio)
A	0.201	0.071	0.234	0.455
	(1)	(0.67)	(1.67)	(2.05)
B	0.351	0.099	0.570	0.480
	(1)	(0.53)	(2.32)	(1.22)

complex formation is the fact that the insoluble, low valence halides such as VCl_2 become partially soluble in cyclohexane by reaction with an excess of aluminum bromide. Such complexes likely have the four-membered ring structure previously shown to exist in aluminum halides,[9] aluminum alkyls[10,11] and other electron-deficient molecules.[12,13]



X = halogen
n = vanadium valence

Typically, a dilute cyclohexane solution of a combination of aluminum bromide and vanadium oxytrichloride (Al/V = 20) is purple in color. Addition of this solution to a solution of tetraphenyltin causes the appearance of a fleeting red color which quickly fades to a faint pink, and the solution contains an active catalyst for the polymerization of ethylene. Obviously, each of these color changes indicates the presence of a new chemical species and illustrates the complexity of the catalyst-forming reactions.

The presence of significant concentrations of biphenyl in the hydrocarbon layer of the quenched, and acid-washed, catalyst system pointed to the formation of unstable organovanadium compounds in the AlX_3–VX_n–$Sn(C_6H_5)_4$ system which decompose according to the equation

$$C_6H_5VX_n \longrightarrow {}^1/_2C_6H_5 - C_6H_5 + VX_n \qquad (1)$$

Since all routes for reduction of the vanadium are believed to proceed through this step, the amount of biphenyl formed was related to the vanadium concentration and initial valence of the vanadium compound in the catalyst system. The data of Fig. 1 show the results of such a study when both vanadium tetrachloride and vanadium oxytrichloride were used as the initial halide. Two equivalents of phenyl were converted to biphenyl when vanadium tetrachloride was the cocatalyst and three equivalents were converted to biphenyl when vanadium oxytrichloride was the cocatalyst. This relationship holds over at least a 10-fold range in vanadium concentrations, and in both cases the biphenyl formation corresponds exactly to reduction of the vanadium to the divalent state. Specific analysis for vanadous ion by polarography confirmed the valence measurement by biphenyl formation within an experimental error of about 3%.

The reduction was complete in 1–3 minutes at 70° at the lower vanadium concentrations and only required 5–10 minutes at the higher vanadium concentrations. Completion of the reaction can be judged by the disappearance of the intense purple or red color of the complex formed between aluminum bromide and the higher valence vanadium halides. The speed of the reaction was established by the fact that no more biphenyl was formed when longer periods for reaction, than those noted above, were allowed before quenching with HBr.

There is a possibility that the tin compounds might oxidize the reduced vanadium species as

$$Sn^{+4} + V^{+2} \longrightarrow Sn^{+3} + V^{+3} \qquad (2)$$

If this reaction occurs, the trivalent vanadium species would again be phenylated and reduced with the formation of more biphenyl. Aging the unquenched solutions an additional hour did not cause the formation of any more biphenyl, so it may be concluded that there is no oxidation–reduction interaction between the tin and vanadium compounds.

In separate experiments in which the aluminum compound was excluded from the system no biphenyl was formed, thus showing that tetraphenyltin alone does not reduce the vanadium compound under these conditions. Under more extreme conditions with temperature above 100° and with prolonged contact time, tetraphenyltin does reduce vanadium tetrachloride or vanadium oxytrichloride very slightly.

When the vanadium halide concentration was increased to the range of one mole per mole of tetraphenyltin, other conditions remaining constant, the linear relationship between vanadium concentration and biphenyl formation no longer held. At these relatively higher vanadium concentrations there are not enough available phenyl groups to reduce all the vanadium to the divalent state. By progressively increasing the vanadium concentration with the same fixed charge of aluminum bromide and tetraphenyltin, the quantity of biphenyl formed approached a limit which was lower than the total quantity of phenyl added as tetraphenyltin. For example, a mixture of 6 millimoles of aluminum bromide, 2 millimoles of tetraphenyltin and 5 millimoles of vanadium oxytrichloride gave only *four* millimoles of phenyl as biphenyl. This shows that only two of the four phenyl groups on tetraphenyltin are easily removed and available for the reduction process.

Since a mixture of tetraphenyltin and the vanadium halide results neither in significant valence reduction nor in catalytic activity, disproportionation reactions between the aluminum halide and tetraphenyltin obviously produce the essential reducing agent. The quantitative correlation between valence reduction and biphenyl formation argues strongly for the transitory formation of unstable, higher valence organovanadium compounds, and it is reasonable to assume that some divalent organovanadium compounds ultimately are formed which do not decompose further. Reduction of vanadium

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(9) K. J. Palmer and N. Elliott, THIS JOURNAL, **60**, 1852 (1938).

(10) L. O. Brockway and N. R. Davison, *ibid.*, **63**, 3287 (1941).

(11) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

(12) R. E. Rundle and P. H. Lewis, *ibid.*, **20**, 132 (1953).

(13) G. Natta, P. Corradini and I. W. Bassi, THIS JOURNAL, **80**, 755 (1958).

to the metal does not occur under the catalytic conditions.

Early in the work on the $AlBr_3$–VX_n–$Sn(C_6H_5)_4$ catalyst, it was observed empirically that high concentrations of the vanadium halide (VCl_4) formed *less effective* catalysts than those containing no more than a few mole per cent. of vanadium.[8] In the cases where the V/Sn ratio was > 1 the system had poor to nil catalytic activity. The reason for this is that at high vanadium concentrations much (or all) of the available organic groups are consumed in reducing the vanadium to the trivalent state and to such completely inorganic, divalent vanadium compounds as VCl_2 which were shown to be non-catalytic. Higher valence organovanadium compounds undoubtedly are formed in the reduction sequence; however, the fact that catalytic activity decreased when the concentration of such species was a maximum shows that these higher valence compounds probably are not catalysts. The necessity of strong reducing power and strong arylating ability to form the catalyst suggests that the active species contains an organic derivative of the transition metal in a low valence state, which may be complexed with one of the other metal compounds. This conclusion is in accord with the results on organovanadium compounds reported in the second paper of this series. Since only a single stable vanadium species is present, this suggests a single active catalyst site which is in accord with the narrow molecular weight distribution of the polymer.[8]

A number of other catalyst samples were prepared using different reducing agents with several vanadium compounds, and the percentage of vanadium reduced to the divalent state was determined by polarography. The data of Fig. 2 show that vanadium tetrachloride is partially reduced to the divalent state by diphenylzinc, and is exclusively reduced to the divalent state by triisobutylaluminum at Al/V ratios > 1 but is only partially reduced at Al/V ratios of 0.4–1. At Al/V ratios below about 0.4 no divalent vanadium was detected, and the system had poor to nil catalytic activity.

Reduction of the vanadium compound probably proceeds through transitory formation and decomposition of unstable organovanadium compounds as previously discussed. Therefore, one equivalent of alkyl (or aryl) is required to reduce the vanadium one unit in valence. In order to reduce vanadium tetrachloride (tetravalent) to the trivalent state, 0.33 mole of triisobutylaluminum (one equivalent of alkyl) is required as a minimum. This explains why no significant concentration of divalent vanadium was detected at Al/V ratios below 0.33. In the hydrocarbon slurries there actually may be divalent vanadium existing in the presence of a tetravalent compound; however, when water is added the reaction occurs

$$V^{+4} + V^{+2} \longrightarrow 2V^{+3} \qquad (3)$$

so no divalent vanadium will be detected by the analytical procedure used here, so long as an excess of tetra- or pentavalent vanadium compounds is present.

Vanadium oxytrichloride also is reduced readily to the divalent state by both triisobutylaluminum and isobutylaluminum dibromide (Fig. 3). The ease of reduction is again demonstrated by the appearance of vanadous ion at all Al/V ratios at which it is stoichiometrically possible.

That not all vanadium compounds are so readily reduced is shown by the data of Fig. 4 on the reduction of *n*-propyl vanadate by triisobutylaluminum. In this case, there is fairly rapid reduction of part of the vanadate during the first hour and then a very much slower reaction, and even after 72 hours, reduction to the divalent state was only about 60% complete. The rapid initial reduction followed by a much slower subsequent reduction probably means that some chemical change other than reduction is occurring in the system as time progresses.

Vanadium trichloride and bis-cyclopentadienylvanadium dichloride are extremely stable compounds because one is a crystalline solid (VCl_3) and the other is an aromatic "sandwich" compound, but even these very stable molecules are attacked by triisobutylaluminum with partial reduction (5–10%) in a few hours. In the latter case the polarographic wave for vanadous ion is similar to that obtained from reduction of the simple halides, thus indicating that the sandwich structure has been destroyed.

In all of this work the vanadium compounds that were easiest to reduce made the most active catalysts, and those that were difficult to reduce made catalysts which ranged from weak to very poor in activity. For example, mixtures of aluminum alkyls and vanadium tetrachloride or vanadium oxytrichloride[14,15] are very active catalysts at low temperature and low pressure with the maximum catalytic activity occurring when the vanadium is largely divalent. Combinations of triisobutylaluminum with *n*-propyl vanadate or bis-cyclopentadienylvanadium dichloride are very feeble catalysts under these conditions and hardly produce their own weight of polymer in an hour. In all the catalysts tested, significant activity was only observed in conjunction with the appearance of at least some of the divalent species.

Isolation of the Precipitate Formed by the Reaction of Vanadium Tetrachloride and Triisobutylaluminum.—*In order to gain more direct evidence* regarding the structure of the active catalyst, the black precipitate formed from the interaction of vanadium tetrachloride and triisobutylaluminum in cyclohexane solution was isolated and analyzed. This material reacted vigorously with air, evolving much heat and giving off both white and yellow fumes. The simple vanadium halides, even vanadium dichloride, react only sluggishly with air and moisture, indicating that this precipitate is more complex than a simple halide. The yellow fumes may possibly be vanadium pentoxide arising from combustion of an organovanadium compound. The precipitate then was analyzed for V, Al and Cl, and the residue was assumed to be isobutyl groups. Since the vanadium was shown to be divalent, this precipitate must be a mixture or complex of or-

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(14) (a) G. Mazzanti, A. Valvassori and G. Pajaro, *Chim. e. ind. (Milan)*, **39**, 825 (1957); (b) G. Natta, L. Parri, A. Mazzei, *ibid.*, **41**, 116–122 (1959); (c) G. Mazzanti, A. Valvassori and G. Pajaro, *ibid.*, **39**, 743–748 (1957).

(15) W. L. Carrick, F. J. Karol, G. L. Karapinka and J. J. Smith, THIS JOURNAL, **82**, 1502 (1960).

ganoaluminum compounds with divalent vanadium compounds, probably containing some of an organovanadium derivative as one component.

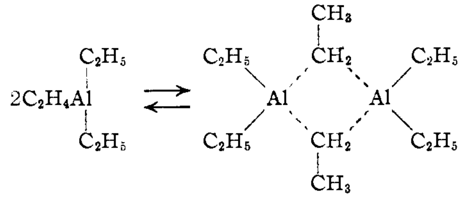
Valence Reduction in a Titanium Catalyst.—Since the principal or sole vanadium species present in the better organometallic catalysts based on this transition metal is divalent, a similar analysis of valence in the triisobutylaluminum + titanium tetrachloride catalyst was carried out. The data of Table II show that as the Al/Ti ratio was increased from 0.5 to 4, the concentration of divalent titanium increased from 6 to 100% in samples that were aged three hours at room temperature. Other investigators have reported measurements of the average valence of titanium[16,17] under other conditions and have discussed the catalytic activity of the various samples.[18] The data reported here are in qualitative agreement with the earlier work; however, somewhat more divalent titanium was found in the present case. It is interesting that at the lowest Al/Ti ratios there is divalent titanium formed even though not all of the tetrachloride has been reduced.

TABLE II

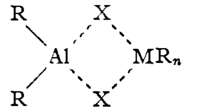
REDUCTION OF $TiCl_4$ BY $Al(i\text{-}Bu)_3$

Al/Ti ratio	Ti^{+2}, %	Reduced titanium, g.	Total titanium, g.
0.5	6	0.013	. . .
1	6	.033	0.041
2	28	.023	.025
3	69	.013	.013
4	100	.023	.022

Discussion of Propagation Mechanism.—The discovery that ethylene will add to aluminum triethyl to form hard paraffin-like polymers at moderate temperatures and pressures[19] was the first significant advance toward the newer organometallic mixed catalysts. Since aluminum triethyl and other aluminum alkyls are partially dimeric,[11,20] some investigators proposed that the dimer is essential for this "growth reaction,"[21,22] and extrapolated this theory to suggest that similar bimetallic complexes in which one of the metals is a transition metal are essential for the catalytic function of the mixed catalysts. Since large aluminum alkyls are known to be monomeric[20] under the optimum conditions of the growth reaction,[19,23] the assumption that a dimer is necessary does not seem well founded. Ziegler[24] recently has presented additional evidence showing that the growth reaction occurs at an aluminum alkyl monomer, and those compounds that are specifically dimeric do not add ethylene. The fact that only monomeric aluminum alkyls are active was interpreted to mean that a vacant orbital on aluminum is necessary to activate the olefin.



In the more active polymerization catalysts based on transition metal compounds, there is considerable theoretical and experimental evidence that bimetallic complexes are formed between organoaluminum compounds and transition metal compounds at some time during the reaction.[13,25,26] Complexes also seem to be formed from the interaction of aluminum bromide or triisobutylaluminum and vanadium halides. However, even though the existence of such complexes is widely accepted, there is not yet agreement as to whether a complex is essential or incidental to the catalytic function.



X = halogen
R = halogen, alkyl or aryl

In considering the possible functions of bimetallic complexes it does not seem likely that the aluminum end of the complex is catalytic since this portion is structurally identical to one end of the aluminum alkyl or alkyl aluminum halide dimers which were shown to be specifically non-catalytic for the growth reaction.[24] It seems more reasonable that the active site is an alkylated transition metal center, whether it be complexed with another metal or not. Experimental evidence in support of propagation being governed by the transition metal center is the fact that the relative reactivity ratios of two monomers in copolymerization[15] changed when different transition metal compounds were used (indicates a change in the character of the active chain end), but were not affected by use of different reducing agents with a common transition metal compound. Additional evidence favoring propagation from a transition metal center is the fact that both titanium dichloride[27] and methyltitanium trichloride[28] have been claimed to polymerize ethylene without addition of other reagents, and in these cases only transition metal compounds are present.

Assuming propagation from a transition metal center, a reasonable mechanism involves preliminary coördination of the olefin to a vacant d-orbital of the transition metal and then a rearrangement to incorporate the polarized olefin into the growing polymer chain.[16,26,29]

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(16) D. B. Ludlum, A. W. Anderson and C. E. Ashby, THIS JOURNAL, **80**, 1380 (1958).

(17) (a) M. L. Cooper and J. B. Rose, *J. Chem. Soc.*, 795 (1959); (b) H. Martin and J. Stedefeder, *Ann.*, **618**, 17 (1958).

(18) E. J. Badin, THIS JOURNAL, **80**, 6545 (1958).

(19) K. Ziegler, *Brennstoff Chem.*, **33**, 193 (1952).

(20) (a) K. S. Pitzer and H. S. Gutowsky, THIS JOURNAL, **68**, 2204 (1946); (b) A. W. Laubengayer and W. F. Gilliam, *ibid.*, **63**, 477 (1941).

(21) F. Patat and H. Sinn, *Angew. Chem.*, **70**, 496 (1958).

(22) G. Natta, Manuscript of Paper Presented at International Meeting on Chemistry of Coordination Compounds, Rome, Italy, September, 1957.

(23) G. Natta, P. Pino and M. Farina, International Symposium on Macromolecular Chemistry, *Suppl. La Ricerca Sci.*, 120 (1955).

(24) K. Ziegler, *Angew. Chem.*, **71**, 623 (1959).

(25) D. S. Breslow and N. R. Newburg, THIS JOURNAL, **81**, 81 (1959).

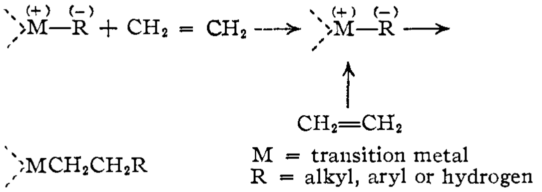
(26) W. L. Carrick, *ibid.*, **80**, 6456 (1958).

(27) British Patents, 778,639 and 777,538.

(28) (a) Belgian Patents 553,477 and 553,478; (b) Beermann and H. Bestian, *Angew. Chem.*, **71**, 618 (1959).

(29) C. C. Price and M. Osgan, THIS JOURNAL, **78**, 4787 (1956).

Although this reaction is written showing only one molecule of monomer coördinated to the transition metal, there may actually be two or more monomer molecules coördinated at one time. It is necessary that the –R group be hydrogen or hydrocarbon rather than halogen, oxygen, etc., to provide a low energy initiation reaction (M–R bonds are weaker than metal–halogen bonds), for a low-temperature process. In this mechanism, transition metal valence plays an essential role. With all transition metals there is a decrease in the electronegativity of the metal center with a decrease in valence. For example, the electronegativity of vanadium changes from 1.8 for the pentavalent state to 1.2 for the divalent state,[30] and titanium changes from 1.6 for the tetravalent state to 1.1 for the divalent state.[31] With each unit reduction in valence one more orbital becomes half-filled by the addition of one electron. These two factors operate in opposite directions. The progressive filling of the transition metal orbitals with increasing reduction should decrease the electron-attracting power of the metal for olefins, but at the same time the decreasing electronegativity makes the C–M bond more polar so that any coördinated (polarized) monomer is more readily incorporated into the growing chain by the rearrangement reaction. Therefore, optimum catalytic activity would consist of a proper balance between these two features. Experimentally, the best catalytic activity is observed with the low transition metal valences, which suggests that a very polar C–M bond is essential. High valence transition metal compounds have electronegativities of 1.6–1.8 which is in the same range as aluminum; therefore, if these compounds are catalytic at all, the rate of propagation should be low, as it is with aluminum alkyls alone. In addition, the organic derivatives of transition metals in their higher valences are unstable and would readily decompose, thus causing molecular termination if the organic derivative were a growing polymer molecule. Higher transition metal valences, if active at all, should then give lower molecular weight polymer. The lowest valence transition metal compounds would be the most stable with little thermal decomposition and should make polymer of the highest molecular weight. This is in substantial agreement with experimental observations.[18]



$$\overset{(+)}{\text{M}}-\overset{(-)}{\text{R}} + CH_2=CH_2 \longrightarrow \underset{\underset{CH_2=CH_2}{\uparrow}}{\overset{(+)}{\text{M}}-\overset{(-)}{\text{R}}} \longrightarrow \text{MCH}_2\text{CH}_2\text{R}$$

M = transition metal
R = alkyl, aryl or hydrogen

There have been reports that traces of oxygen significantly accelerate the rate of ethylene polymerization with some of the organometallic mixed catalysts, and this fact has been interpreted by some investigators as suggesting that tetravalent titanium is necessary for catalytic activity in at least one case.[25] The authors also have observed that oxygen often increases the rate of polymerization and otherwise affects the behavior of soluble catalysts, such as those described in references 8 and 26; however, in the catalysts examined in this work there has been no indication that titanium or vanadium valences > 3 are catalytically active. Studies on oxygen cocatalysis are still in progress in this group, and the data will be reported later.

[30] M. Haissinsky, *J. Phys. Radium*, **7**, 7 (1946).

[31] T. L. Allen, *J. Chem. Phys.*, **26**, 1644 (1957).

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Polarography of Organic Halogen Compounds. I. Steric Hindrance and the Half-wave Potential in Alicyclic and Aliphatic Halides[1,2]

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Alkyl and cycloalkyl bromides yield well-defined waves at the dropping mercury electrode with tetraethylammonium bromide as the supporting electrolyte in N,N-dimethylformamide. Qualitative correlation of the half-wave potentials with SN reactivity is present in the classic series of alkyl halides substituted at the carbon atoms alpha and beta to the halogen, as well as in the cyclic halides. Although the rate-determining step may involve transfer of a single electron, the results indicate that the reductive process can be likened to a nucleophilic substitution with noteworthy steric effects caused both by the bulk of the "attacking group" (the electrode) and by steric requirements of groups in the halide being reduced. The strong negative field of the electrode may be important both in orienting the halide as it approaches the electrode and in forcing an SN1 type of electroreduction in *t*-butyl bromide.

Introduction

Most qualitative and semi-quantitative interpretations of the significance of the half-wave potential in organic polarography have been concerned with correlating electronic effects in a series of related organic molecules with the $\Delta E_{1/2}$ between members of the series.[3] The importance of steric factors in the reduction of organic substances at a dropping mercury electrode has been given relatively little attention.[2,4] Indeed, in the cases cited of steric influence on the half-wave potential, the majority

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[1] (a) This work was initiated by a Research Corporation grant. A portion is abstracted from the M.A. thesis of K. K. The Research was completed at the California Institute of Technology while F. L. L. was a Science Faculty Fellow of the National Science Foundation, 1957–1958.

[2] For a preliminary report of part of the work, see *Chemistry & Industry*, 949 (1958).

[3] (a) *Cf.* the review of P. Zuman, *Chem. Listy*, **48**, 94 (1954), especially pp. 97–114 and 124–135; (b) more modern work in ref. 2, footnote 1.

[4] P. Zuman, ref. 3a, pp. 115–121, and in *Chem. Listy*, **53**, 154 (1959), points out several examples of steric effects not explicitly stated, or overlooked by the original investigators.