water-white nonadiyne-2,4 showed n^{25}D 1.49148 and density (25°) 0.8165. Molecular refraction: To the value calculated for nonadiyne-2,4,[19] 40.34, should be added the increment for diyne conjugation exaltation, which value however could not be located in the literature. The observed molecular refraction was 42.67.

Anal. Calcd. for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 90.29; H, 9.96.

The ultraviolet absorption curve (Fig. 2) taken with a 1.42×10^{-3} M solution in 95% alcohol, showed maxima at 224.5 mμ (ϵ 366), 232 mμ (ϵ 294), 237 mμ (ϵ 335) and 252 mμ (ϵ 194). The infrared absorption curve (Fig. 1) was free of maxima at 3.03 μ (terminal acetylene) and at 5.15 μ and 11.71 μ (terminal allene), but did show peaks at 4.42 μ (2260 cm.$^{-1}$), 4.56 μ (2190 cm.$^{-1}$), 4.65 μ (2150 cm.$^{-1}$) and at 4.91 μ (2039 cm.$^{-1}$).

Isomerization of Nonadiyne-1,4 Followed by Ultraviolet Absorption.—A solution containing freshly distilled allene-free nonadiyne-1,4 (10.07 mg.) and potassium hydroxide in 8:1 (vol.) alcohol-water (total volume 10 ml.) was held in a thermostated water-bath at 25°. The concentrations of nonadiyne-1,4 and of alkali were 8.39×10^{-3} M and 12.1×10^{-3} M, respectively. Samples were removed at intervals by pipet, drained into an equal volume of 0.0282 N sulfuric acid in alcohol water (8:1) and diluted with aqueous alcohol (1:1 vol.) so that the optical density at 220.5 mμ was 0.27–0.43. Readings were taken against a solution made up in the same manner as the sample but without the nonadiyne-1,4. The accompanying table shows how the density at 220.5 mμ rose rapidly and then fell slowly. At 10,000 minutes and 11,400 minutes, the ultraviolet curves began to take on the shape of the curve for nonadiyne-2,4. The ultraviolet curves of samples removed between 20,100 and 26,000 minutes showed maxima at 225 mμ (ϵ 370–425), 232 mμ (ϵ 310–360), 236–237 mμ (ϵ 340–390) and 252 mμ (ϵ 207–229). The isomerization of skipped diyne I to allene II is at least 18 times as fast as the isomerization of allene II to conjugated diyne III; this estimate was arrived at by taking the ratio of the time required for the optical density at 220.5 mμ to reach a maximum to the time required for this maximum to become small.

Time, min.	Optical density[a]	Time, min.	Optical density[a]
7.5	6[b]	1400	43
71	34[c]	1800	34
140	55	2900	20
320	74	5700	7[d]
420	71		

[a] Of original solution. [b] Shoulder at 220.5 mμ. [c] Maximum at 220.5 mμ. [d] No maximum at 220.5 mμ.

Isomerization of Nonadiyne-1,4 Followed by Infrared Absorption.—A solution made up of allene-free nonadiyne-1,4 (3.720 g. or 0.0309 mole), 5.00 ml. of 4.72 N aqueous sodium hydroxide and enough absolute alcohol to bring the volume to 50.00 ml. was kept in a water-bath at 25°. At intervals, 10-ml. samples were removed and were drained into 40 ml. of petroleum ether (30–60°) and 40 ml. of water. Each sample was worked up in the usual manner to give 0.52–0.60 g. of vacuum distilled material (70–80% recovery). A trial recovery experiment with nonadiyne-1,4 performed as above but without alkali showed that the recovery with or without alkali was approximately the same. The compositions of the samples, estimated from the intensities of absorptions at 3.03, 5.15 and 4.91 μ, are given in the accompanying table. The infrared absorption curves (Baird) of the 22-hour and of the 49-hour sample were substantially the same as that of nonadiyne-2,4 in Fig. 1. The ultraviolet absorption curve of the 49-hour sample showed maxima at 224.5 mμ (ϵ 406), 232 mμ (ϵ 232), 237 mμ (ϵ 350) and 252 mμ (ϵ 203). In another experiment in which nonadiyne-1,4 was isomerized to nonadiyne-2,4, the isomerized material showed absorption maxima at 224.5 mμ (ϵ 382), 232 mμ (ϵ 308), 237 mμ (ϵ 340) and 252 mμ (ϵ 203).

	Approximate per cent. of		
Hours	Nonadiyne-1,4	Nonadien-1,2-yne-4	Nonadiyne-2,4
0.0	100	0	0
0.5	<10	>40	40
1.25	<10	20–40	60– 80
3	0	<10	90–100
22	0	< 1	100
49	0	0	100

Isomerization of Nonadien-1,2-yne-4.—A reaction mixture made up of nonadien-1,2-yne-4 (1.533 g. or 0.0128 mole), 5.00 ml. of 4.72 N aqueous sodium hydroxide with enough absolute alcohol to bring the total volume to 50.00 ml. was thermostated at 25°; 17-ml. samples were removed at intervals, quenched in a mixture of 10% sulfuric acid (5 ml.), water and ice, extracted with pentane and worked up as usual. No absorption peak at 3.03 μ (terminal acetylene) appeared after 3, 21 or 45 minutes. Judging from the absorptions at 4.91 and 5.15 μ, very little change occurred after 3 minutes. At 45 minutes nonadiene-1,2-yne-4 and nonadiyne-2,4 were present in approximately equal amounts.

Boston, Massachusetts
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[Contribution from the Polychemicals Department, Research Division, E. I. du Pont de Nemours & Co., Inc.]

The Polymerization of Ethylene by Lower Valent Compounds of Titanium

By D. B. Ludlum, A. W. Anderson and C. E. Ashby

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Ethylene is polymerized at atmospheric pressure to a high molecular weight, linear polymer by the products obtained from the reaction of titanium tetrachloride with various organometallic alkylating agents. Rates of polymerization have been followed at constant temperature and pressure, and catalytic activity has been related to: (a) the titanium tetrachloride concentration, (b) the ethylene concentration, (c) the nature of the alkylating agent, (d) the alkylating agent-to-titanium tetrachloride mole ratio, and (e) the temperature of polymerization. The weight of polymer produced after a given length of time is directly proportional to the titanium tetrachloride and ethylene concentrations. Although there is usually a decrease in rate of polymerization during the reaction, catalytic activity remains constant under conditions where very low molecular weight, soluble polymer is produced. A mechanism which involves propagation by a lower valent alkyltitanium or alkyltitanium halide is proposed to explain these results.

Introduction

Numerous publications[1–3] have appeared recently describing the polymerization of ethylene to a high molecular weight, linear polymer by the reaction products of $TiCl_4$ and organometallic alkylating agents. Following the independent discovery in this Laboratory[4,5] that ethylene, α-

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[1] K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, **67**, 541 (1955).

[2] G. Natta, P. Pino, *et al.*, *Chimica e industria*, **39**, 19 (1957).

[3] G. Natta, I. Pasquon and E. Giachetti, *Angew. Chem.*, **69**, 213 (1957).

[4] E. I. du Pont de Nemours & Co. British Patent 776,326 (June 5, 1957).

[5] A. W. Anderson and N. G. Merckling, U. S. Patent 2,721,189 (October 18, 1955).

olefins and certain bicyclic olefins could be polymerized at atmospheric pressure by these reaction products, an extensive program was undertaken to determine the mechanism of polymerization. As part of this program, the kinetics of ethylene polymerization were followed in a batch reactor at constant temperature and pressure. Although interpretation of these data is complicated by the fact that insoluble polymer is formed in most cases, they help to clarify the nature of the active catalyst and to elucidate the mechanism of polymerization.

Experimental

Materials.—Reagents of the highest purity were required in order to obtain reproducible results. Purified ethylene containing approximately 1 p.p.m. oxygen, 3 p.p.m. water and 3 p.p.m. carbon dioxide was stored in a cylinder and admitted to the polymerization system as required through a glass-packed tower of molten sodium. Du Pont "Decalin" decahydronaphthalene solvent was purified by repeated passage through long columns of silica gel activated at 200–250°, followed by distillation from lithium aluminum hydride. Solvent was stored under nitrogen until needed to prevent peroxide formation.

Rate studies were carried out initially with lithium tetra-*n*-heptylaluminum as alkylating agent. This compound was prepared by the reaction of heptene-1 with lithium aluminum hydride[6] and was purified by recrystallization from cyclohexane. Solutions of *n*-hexyllithium were prepared by the reaction of pure lithium metal with distilled *n*-hexyl chloride in Decalin solvent, followed by filtration to remove precipitated lithium chloride. Tri-*n*-hexylaluminum was prepared from these solutions by reaction with the equivalent amount of sublimed aluminum chloride, again followed by filtration. The same two reactions were used to prepare triisobutylaluminum, although this compound is now available commercially. The triisobutylaluminum was purified by vacuum distillation through a short Vigreux column before being used. Triethylaluminum was prepared by sodium reduction of diethylaluminum bromide[7] and was distilled before use. Commercially available titanium tetrachloride was used throughout and, again, this compound was distilled before being used.

Solutions of titanium tetrachloride and all organometallics were made up to approximately 0.1 *M* in Decalin. These were stored in glass stoppered flasks fitted with small rubber stopples[8] through which samples could be withdrawn by hypodermic syringes. All solutions, except those of *n*-hexyllithium which were stored in a refrigerator, were stable at room temperature.

Rate Measurements.—Polymerizations were carried out at constant temperature and pressure in a 500-ml. round-bottom flask connected to a gas buret and mercury manometer. The system was completely closed to the atmosphere through mercury bubblers, and adequate agitation was provided by a heavy, glass encased magnetic stirrer whose efficiency was improved by creasing the reaction flask. The entire flask was submerged in an oil-bath thermostated to within ±0.5° of the desired reaction temperature. Ethylene pressure could be varied from 0.5 to approximately 1.5 atmospheres.

Rates were followed by measuring the volume of gas polymerized as a function of time. To make sure that transfer of ethylene from the gas phase to the solvent was not a rate-determining step, polymerizations were carried out at rates well below the maximum which could be attained. At these lower rates, the reaction was not dependent on degree of agitation, as long as this was maintained above a certain minimum level.

In an actual polymerization, the flask, buret and manometer were first flushed throughly with purified ethylene. The system was then isolated by stopcocks and the required volume of solvent, usually 100 ml., was introduced with a syringe through a rubber stopple on the reaction flask. About half a milliliter of titanium tetrachloride solution (50 micromoles) was added next and the mercury leveling bulb was adjusted to atmospheric pressure. Then, with full stirring, the desired amount of organometallic was added dropwise over a period of about two minutes. Zero time was taken when the first organometallic was added and the volume of gas polymerized was followed as a function of time for two or three hours thereafter. A typical volume *versus* time curve is shown in Fig. 1.

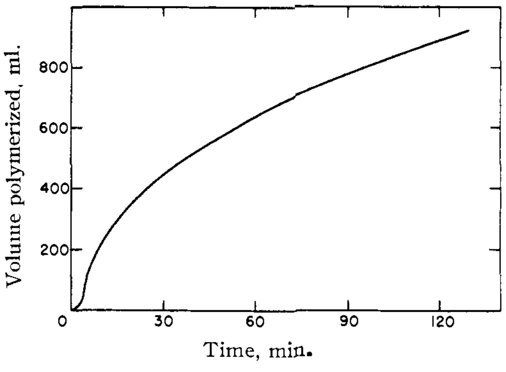

Fig. 1.—Typical polymerization with a $TiCl_4$–AlR_3 catalyst at 100°; 49 micromoles of $TiCl_4$ and 180 micromoles of AlR_3 in 100 ml. of Decalin.

Experimental Results

Treatment of Data.—A complete kinetic interpretation of curves such as the one shown in Fig. 1 is difficult. We must first assume that the catalyst forming reaction is relatively fast; then, observed changes in dv/dt, the instantaneous rate of ethylene absorption, are related to the polymerization step and not to additional changes in the catalyst composition. This assumption was checked experimentally by: (a) carrying out the catalyst-forming reaction in an adiabatic calorimeter where it appeared to be complete in less than a minute, and (b) polymerizing with catalysts which had been aged five or ten minutes in a helium atmosphere. The rate of polymerization with these aged catalysts was the same as with those made in the presence of ethylene, indicating that no changes in catalyst activity occurred over the period of aging.

In the present article the shape of these volume *versus* time curves has not been considered in detail, but instead a single parameter has been chosen as a measure of catalytic activity. The volume of gas polymerized after two hours at 100° has been chosen for this purpose, although volumes polymerized at much shorter time intervals correlate well with those obtained after two hours. Where catalyst activities are compared at different temperature the initial rate of polymerization, which is unaffected by differences in the solubility of the polymer, was used to measure activity. Initial rates were not used throughout because they are generally less reproducible than the volume of gas polymerized after a given time interval.

The gradual decrease in activity which continues all during the polymerization is caused by occlusion of catalyst sites with insoluble or adsorbed polymer. When the polymerization is carried out with a catalyst composition which gives a very low molecular weight soluble polymer, no decrease in rate is observed for as long as three hours after certain initial changes are complete. This fact indicates that there is no true termination and that the reac-

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[6] K. Ziegler, *Angew. Chem.*, **64**, 323 (1952).

[7] A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

[8] C. F. Roth and J. Mitchell, Jr., *Anal. Chem.*, **28**, 1502 (1956).

tion is indeed catalytic. In this respect, this polymerization is very similar kinetically to the polymerization of ethylene by trialkylaluminums alone.[9]

Dependence of Activity on $TiCl_4$ and Ethylene Concentrations.—The range of ethylene concentrations is limited in the glass system described above, but over a pressure range of 1 to 1.5 atmospheres, rates were proportional to ethylene concentration. These results are shown in Fig. 2 where the rate of polymerization at increased pressure relative to the rate at one atmosphere is plotted against the ethylene pressure. Similar results were obtained when pressure was changed during a polymerization and d*v*/d*t* compared immediately before and immediately after the pressure change as when the entire polymerization was run at increased pressure. In interpreting these data, the assumption is of course made that Henry's law is followed over this dilute concentration range, and that ethylene concentration is proportional to the partial pressure of ethylene.

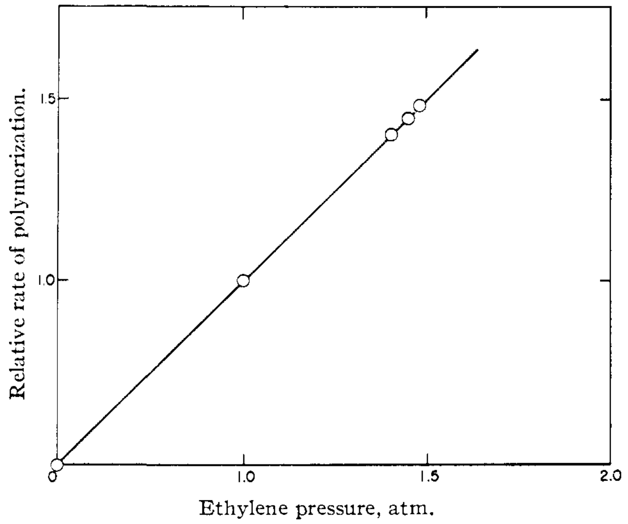

Fig. 2.—Dependence of activity on ethylene concentration: $TiCl_4$–$LiAlR_4$ catalyst system.

Experiments in which the concentration of $TiCl_4$ was varied are presented in Fig. 3. These experiments were performed at 100° with a tri-*n*-hexylaluminum catalyst at an Al/Ti ratio of 3.7. A similar first-order dependence on $TiCl_4$ concentration was obtained with catalysts based on other organometallic compounds.

Dependence of Activity on Catalyst Composition.—At a given temperature, the nature of the alkylating agent and the mole ratio of alkylating agent to titanium tetrachloride in the catalyst exert a major influence on activity. Catalyst activity as a function of composition is shown in Fig. 4.

In this figure, activity is plotted against mole ratio for catalysts prepared from titanium tetrachloride and (a) *n*-hexyllithium, (b) lithium tetra-*n*-heptylaluminum, (c) triisobutylaluminum and (d) triethylaluminum. In all cases, activity rises to a maximum at a given ratio and then decreases when more alkylating agent is employed.

It should be noted that the experimental procedure described above was carefully followed in all of these experiments. In particular, the catalyst-forming reaction was carried out by adding a solution of the alkylating agent to the titanium tetrachloride solution. Somewhat lower activities usually were obtained with the reverse order of addition.

Effect of Temperature.—The complex effect of temperature on catalyst activity is shown in Fig. 5. In this figure, the logarithm of the initial rate of polymerization, corrected for differences in ethylene solubility, is plotted against the reciprocal of the absolute temperature. The catalysts whose activities are shown in this figure were prepared from triisobutylaluminum and titanium tetrachloride. However, for all catalyst systems studied, activity first increased with an increase in temperature and then fell off sharply at higher temperatures. The optimum temperature depends on the alkylating agent and the mole ratio used in making the catalyst.

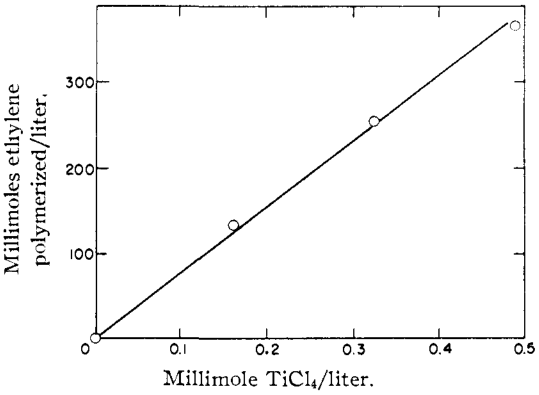

Fig. 3.—Catalytic activity *vs.* $TiCl_4$ concentration; millimoles of ethylene polymerized after two hours *vs.* millimoles $TiCl_4$ per liter.

In these experiments two separate factors enter into the rate of polymerization, and their interaction may well account for this unusual temperature dependence. Since the catalyst was formed at the temperature of polymerization, the difference in temperature may have changed the nature of the catalyst as well as the actual propagation rate in the polymerization step. In fact, as will be discussed further in the next section, we might expect that increasing the temperature would increase the degree of alkylation of the titanium tetrachloride and eventually result in reduction of the titanium past its catalytically active valence state.

Dependence of Activity on Average Valence State.—When it was realized that the catalyst-forming reaction involved reduction of the titanium to a lower valence state, experiments were performed to relate catalytic activity to average valence state. Complete elemental analysis of the reaction products of titanium tetrachloride and hexyllithium indicated, for example, that at an alkyllithium-to-titanium halide ratio of four where

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[9] G. Natta, P. Pino and M. Farina, Symposium on Macromolecular Chemistry, International Union of Pure and Applied Chemistry, Supplement to *La Ricerca Scientifica*, 120 (1955).

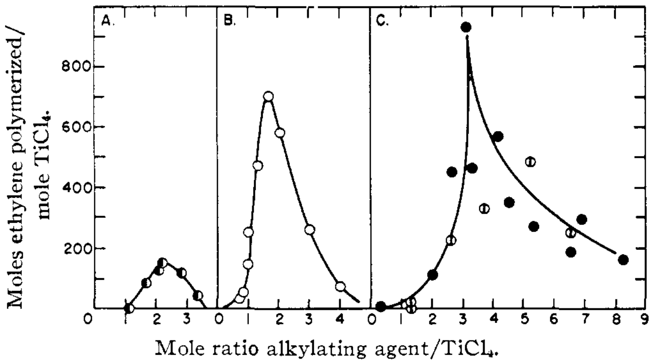

Fig. 4.—Catalytic activity *vs.* catalyst composition at 100°; moles of ethylene polymerized after two hours, per mole of TiCl$_4$ *vs.* mole ratio of catalysts: ◐, *n*-hexyllithium catalysts; ○, lithium tetra-*n*-heptylaluminum catalysts; ●, triisobutylaluminum catalysts; ⦶, triethylaluminum catalysts.

catalyst activity had declined to zero, the average valence state of titanium was zero. The peaked curve of activity *versus* catalyst ratio shown for this system in Fig. 4 suggests, therefore, that catalytic activity is associated with some compound of titanium in an intermediate valence state. The concentration of this compound increases as the alkyllithium-to-titanium halide ratio is increased to a certain point, and decreases thereafter.

Additional experiments were performed to relate average valence state of titanium to catalyst activity in the titanium tetrachloride–triethylaluminum system. It may be assumed, as will be discussed in a later section, that each mole of ethane released in the reaction of titanium tetrachloride and triethylaluminum corresponds to a reduction of one in the valence state of one mole of titanium. When this assumption is made, it is possible to calculate the average valence state of titanium from quantitative off-gas measurements in this catalyst system. These experiments were performed in boiling cyclohexane, and the results are indicated in Fig. 6. Average valence state decreases gradually as the alkylaluminum-to-titanium halide ratio is increased.

When these results are combined with the activity data in Fig. 4, we obtain the relationship between catalyst activity and average valence state shown in Fig. 7. This figure suggests strongly that maximum activity is associated with titanium in an average valence state of two. It should be noted that, although the analytical data of Fig. 6 are obtained at a slightly lower temperature than the activity data of Fig. 4, additional activity data at lower temperatures confirm this dependence of activity on average valence state.

Discussion

The catalyst-forming reactions described above are probably special cases of a more general alkylation reaction. A standard method of preparing new organometallic compounds[10] involves the reaction of an organometallic compound of a more electropositive element with the chloride of a less electropositive element. When this reaction is applied to titanium tetrachloride, however, no pure organotitanium compounds are ordinarily obtained; instead, yellow-brown to black precipitates of variable composition result. Chemical characterization of these precipitates is extremely difficult because they are insoluble in hydrocarbon media and because they lose their catalytic activity, and perhaps their identity, in more polar solvents.

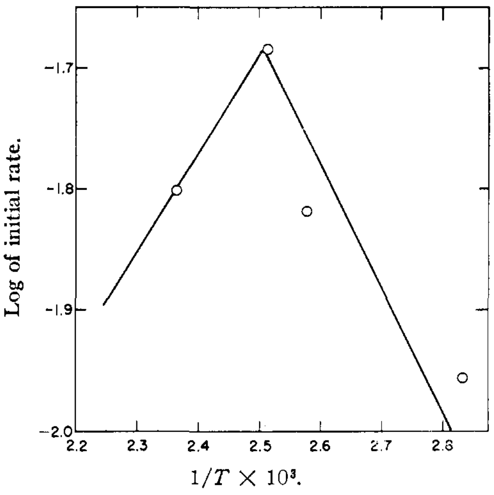

Fig. 5.—Dependence of activity on temperature; logarithm of initial rate in moles/liter-min., corrected to ethylene solubility at 125° *vs.* reciprocal of absolute temperature; TiCl$_4$–AlR$_3$ catalysts with [TiCl$_4$] = 0.2 mmole/liter, Al/Ti = 3.0.

Because of the difficulty in obtaining direct chemical information on these catalysts, the rate studies described above were undertaken to elucidate the mechanism of polymerization. These data support the mechanism described below which involves polymerization by a lower valent alkyltitanium compound. They are not, however, sufficient to determine completely the nature of the active catalytic species.[11]

The catalyst-forming reactions probably are least complex in the case of TiCl$_4$ and LiR. Here, we propose that catalyst formation involves an alkylation reaction such as

$$TiCl_4 + nLiR \longrightarrow nLiCl + TiCl_{4-n}R_n$$

where *n* is 1, 2, 3, or 4. It is further proposed that the more highly alkylated species decompose by a free radical mechanism to give such compounds as RTiCl, which may be the actual catalytic species. Similar reactions are postulated between TiCl$_4$ and AlR$_3$ or LiAlR$_4$.

When triethylaluminum is used as an alkylating agent, the organotitanium compounds formed initially would release ethyl radicals to form ethane. Hydrogen would be supplied to the ethyl radical by the solvent. This postulated series of reactions,

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[10] R. C. Jones and H. Gilman, *Chem. Rev.*, **54**, 835 (1954).

[11] Kinetic data published by Natta[3] on the polymerization of propylene with catalysts based on TiCl$_3$ and AlR$_3$ are in close agreement with our data, showing a first-order dependence of rate on propylene and TiCl$_3$ concentration. Natta believes, however, that the chain is actually growing from the Al rather than the Ti atom. Although this point cannot be proved by the kinetic data available at present, the similar kinetic behavior of catalysts produced with different alkylating agents makes us favor an organotitanium compound as the active site.

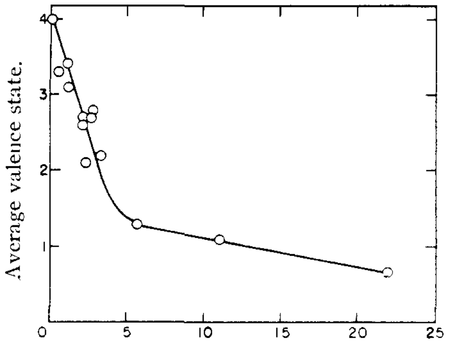


Fig. 6.—Dependence of average valence state of titanium on catalyst composition; catalysts prepared from $TiCl_4$ and triethylaluminum at 80° in cyclohexane.

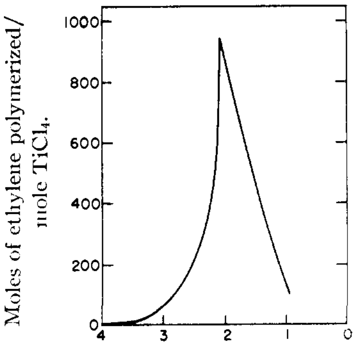
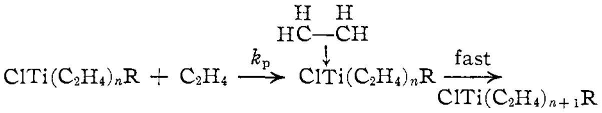


Fig. 7.—Dependence of catalytic activity on average valence state of Ti. Catalysts prepared from $TiCl_4$ and triethyl- or triisobutylaluminum.

which results in the formation of one mole of ethane when the valence state of one mole of titanium is decreased by one, is the basis for the valence state calculations mentioned in the Experimental section.

Polymerization occurs when an active catalyst (possibly RTiCl) complexes with ethylene and adds molecules stepwise until high molecular weight polymer is formed. The propagation reaction (assuming RTiCl to be the catalyst) would be



$$ClTi(C_2H_4)_nR + C_2H_4 \xrightarrow{k_p} \overset{\overset{\text{H}\ \ \text{H}}{\text{HC—CH}}}{\overset{\downarrow}{ClTi(C_2H_4)_nR}} \xrightarrow{\text{fast}} ClTi(C_2H_4)_{n+1}R$$

This reaction, involving coördination of ethylene with the active catalyst, has led to the term coordination polymerization for this process.

The propagation step proposed above leads to the differential rate equation

$$R_p = k_p[E][C] \qquad (1)$$

where R_p is the rate of polymerization, [E] is the concentration of ethylene in moles/liter, k_p is the propagation constant in liters/millimole minute and [C] is the concentration of active catalyst in millimoles/liter. For catalysts prepared under constant conditions of temperature and alkylating agent-to-titanium tetrachloride mole ratio, we would expect the active catalyst concentration to be proportional to the $TiCl_4$ concentration, C_0. If this proportionality constant is designated "f," the rate expression may be written

$$R_p = k_pf[E][C_0] \qquad (2)$$

Values of k_pf calculated from initial rates of polymerization are of the order of 1.4 liters/millimole minute at 100°. This product of k_p and f is about one twenty-fifth the propagation constant for the free radical polymerization of styrene.[12] Experiments now being carried out, which involve the partial poisoning of active catalyst with alcohol, may allow us to determine the factor, f, independently.

Application of the differential rate equation 1 to polymerization over an extended period of time is complicated unless the polymer remains in solution. If the polymer is insoluble, the effective catalyst concentration, C, decreases during the reaction in a manner which must be specified before equation 1 may be integrated. When the polymer remains in solution, however, [E] remains constant and equal to the solubility of the ethylene, [C] remains constant and proportional to [C_0], and from equation 2, the rate of polymerization remains constant with time.

In the special case where the polymer remains in solution, therefore, equation 2 predicts that catalyst activity, as measured by the volume of gas polymerized after a given time interval, is proportional to both ethylene and titanium tetrachloride concentrations. Experimentally, we have seen that we still have this second-order dependence when the polymer is partially insoluble.

Equation 2 also makes explicit the fact that a given catalyst preparation may be more active than another because (a) it has a higher propagation rate and, therefore, a higher value for "k_p" or because (b) there are more active sites per mole of $TiCl_4$ and f is, accordingly, larger. The alkylating agent employed may affect both k_p and f while the mole ratio of alkylating agent to titanium tetrachloride and the temperature of catalyst formation probably affect primarily the value of f.

The assumption that catalytic activity is associated with an intermediate valence state of titanium leads to predictions that catalyst activity will be affected by both temperature and catalyst ratio in the manner actually observed. An increase in either temperature or ratio of alkylating agent to titanium tetrachloride favors more extensive alkylation of the titanium tetrachloride. An increase in either factor will, therefore, increase activity until the average valence state is reduced to the optimum value. A further increase in either temperature or alkylating agent-to-titanium tetrachloride ratio will then lower activity because the titanium is concentrated in a lower and less active valence state. In data to be presented in a later publication, it will be shown that activity may then be restored by the addition of a mild oxidizing agent such as n-butyl chloride. For catalysts prepared from titanium tetrachloride and triethylaluminum at 100° our experimental data indicate that this optimum average valence state of titanium is two.

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(12) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 158.