THE VAPOR PHASE POLYMERIZATION OF ETHYLENE ON AN ORGANOTITANIUM CATALYTIC SURFACE¹

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ABSTRACT

The polymerization of ethylene has been studied in the gas phase on a solid catalyst formed by the reaction of an organotitanium vapor with a solid crystalline titanium compound deposited on the walls of a reaction vessel.

The rate of polymerization of ethylene was found to be, initially, of first order but as the reaction proceeded departure from the first-order case was observed. Experiments conducted under the condition of constant pressure as well as the usual

constant-volume state enabled us, with the aid of an analogue computer, to devise a mathematical model which explained the experimental results in an unique fashion.

A measure of the rate constant for catalyst decay was also obtained as well as the activation energy for the overall propagation step in the polymerization of ethylene.

The discovery of stereospecific polymerization processes capable of leading, by polyaddition of olefinic units, to high yields of sterically regulated polymers has created a tremendous surge of interest in polymer chemistry.

In spite of all the effort which numerous investigators have expended upon the study of coordination catalysis no adequate description of the mechanism of action of the catalyst nor complete kinetic analysis of the polymerization process has been formulated to date.

The catalyst systems themselves are many and varied. The majority of catalysts do involve a complex of a transition metal and a metal organic compound. Nonetheless even the most cursory survey of what is now an immense patent literature concerning these systems will indicate the diversity of materials capable of the polymerization of alpha olefins. There are very few of the elements in the periodic table which cannot be found playing some role in some system of what is now rather loosely termed coordination catalysis.

The work which we are about to describe deals with the study of one of the more common types of catalyst, the system of transition metal and metal organic compound previously mentioned, but differs from the majority of such systems in that the active species contains but one metal element. The choice of a single-metal system was made in order to simplify so far as possible the mechanism of the catalytic function.

All the polymerizations studied have been carried out by the reaction of a gaseous monomer at a solid catalytic surface under conditions of constant temperature and either constant volume or constant pressure.

EXPERIMENTAL

Apparatus The apparatus, illustrated in Fig. 1, was in essence a simple two-manifold high-vacuum system provided with a high-capacity two-stage rotary vacuum pump; liquid nitrogen cooled traps; a reaction vessel, to be described later, immersed in a water bath the temperature of which was controlled within $\pm 0.1^{\circ}$ C; glass

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FIG. 1. Apparatus. A, to gas chromatograph; B, reaction vessel; C, to pump; D, mixing bulb; E, hydrogen; F, ethylene; G, to mercury manometer.

bulbs for the storage of monomer and other gaseous reactants; storage facilities for catalyst components; an all-glass pressure-measuring device; mercury manometer and automatic apparatus which could be used to maintain the pressure of the system constant.

The reaction vessel was a pyrex glass bulb into which was sealed, through uranium glass, a tungsten electrode of the sort found in fluorescent light fixtures. Entrance into the reaction vessel from the vacuum manifold was through a Springham greaseless stopcock fitted with a Viton A diaphragm and O ring. Exit from the vessel into an automatic gas chromatograph was made by means of a Hoke A431 all-metal bellows valve attached by a kovar glass to metal seal. Similar Hoke valves were used in those places where catalyst contact with greased stopcocks was deemed to be undesirable.

Since the catalyst has been found to be photochemically unstable to room lighting all transparent parts of the reaction line with which catalyst came in contact were externally blackened with a dispersion of colloidal graphite.

Pressures were automatically recorded to a precision of ± 0.05 cm of Hg by means of a small glass spiral used in a differential fashion and accurately calibrated against a mercury manometer. This pressure measuring device, previously described by Edgecombe and Jardine (1), was constructed in such a way that pressure changes within the system varied the capacitance of a simple plate condensor. These capacitance variations were in turn fed to a capacitance transducer which transposed them into a voltage, a form suitable for amplification and strip chart recording.

The course of the polymerization could also be followed by gas chromatography. An automatic gas chromatograph was devised (2) which could remove at regular intervals very small samples of gaseous monomer from the system and record their concentration.

When it was necessary to carry out the polymerization under conditions of constant pressure two procedures were used. In the first instance the pressure of monomer in the reaction vessel was manually returned to the initial pressure after a short period of polymerization and this process repeated so that the record of pressure change with time as recorded on the strip chart recorder gave a sawtooth pattern. At a later stage of our investigation a more refined method was used to maintain a constant pressure. This device took the form of an automatic gas burette and is described elsewhere (3). It consisted essentially of a servo actuated screw raising the level of a container of mercury which was connected to a calibrated gas burette. Control was obtained by using the pressure-measuring device described previously and the pressure of the system could be maintained constant to within less than 0.01 cm of the initial pressure of 10 cm of Hg. The device was also capable of providing a continuous record of the time rate of volume change within the system.

Preparation of Materials

Ethylene

The ethylene used was a chemically pure grade supplied by Matheson Inc. and was taken directly from its cylinder by a suitable feed system and stored in a large bulb on the vacuum line. Although high-sensitivity gas chromatography could detect no impurity in the stored material several experiments were carried out in which the ethylene to be used was first passed through a purification train consisting of a 10-ft column of silica gel, a 2-ft column of ascarite, two washings with triisobutyl aluminum, and a 2-ft column of alumina. Ethylene thus treated reacted in no way different from that taken directly from the cylinder.

The hydrogen used in the reaction for the formation of titanium trichloride was of chemically pure grade and was not subjected to further purification.

The helium used as a carrier gas in the gas chromatographic system was of very high purity and was not treated in any way before use.

Titanium Tetrachloride

Fisher certified reagent grade titanium tetrachloride was used in the catalyst formation. It was distilled from a trap on the vacuum line immediately before use.

Titanium Trichloride

The titanium trichloride used in the catalyst preparation was formed within the reaction vessel by the action of $TiCl_4$ vapor and hydrogen at a tungsten filament heated to bright red. The reaction may be represented as

$$2\text{TiCl}_4 + \text{H}_2 \xrightarrow{\text{neat}} 2\text{TiCl}_3 + 2\text{HCl}.$$

The HCl vapor was immediately pumped off. The TiCl₃ formed was the alpha variety, i.e. purple TiCl₃. Experiments have shown that the TiCl₃ is laid down each time on the walls of the reaction vessel in a consistent pattern and if similar voltages are applied to the filament for identical periods of time reproducible quantities of TiCl₃ are produced.

A study was carried out in which the TiCl₃ deposit was carefully washed out of the reaction vessel with dilute nitric acid and a Volhard analysis performed to determine the chloride content. The amount of TiCl₃ deposited for a 35-minute reaction period with a voltage of 22 v a-c. applied to the filament from 1 cm pressure of TiCl₄ in a volume of 400 ml was determined to be 7.95×10^{-5} mole (average of 17 experiments).

Dimethyl Zinc

Dimethyl zinc was used in the formation of the catalyst precursor CH_3TiCl_3 . It was prepared in the following manner. Anhydrous zinc chloride was melted in a glass container and then cooled in an atmosphere of dry nitrogen. The fused zinc chloride was powdered in a mortar and transferred in the nitrogen atmosphere to a three-neck round-bottom flask purged with nitrogen. One neck of the flask was closed off. A condenser was fitted into one of the remaining necks and a dropping funnel containing trimethyl aluminum adapted to the third neck.

The entire system was purged with nitrogen. A stream of nitrogen was directed over any openings to the atmosphere in the system. Trimethyl aluminum was slowly added to the zinc chloride and the mixture heated to 50° C until it was evident that a reaction had commenced. The heat was removed and the reaction

$(CH_3)_3Al + ZnCl_2 \rightarrow (CH_3)_2Zn + CH_3AlCl_2$

continued, the material refluxing under its own heat of reaction. When all signs of reaction had disappeared the vessel was cooled in a dry ice – acetone mixture and transferred to a spinning band column through which the $(CH_3)_2Zn$ was distilled into a cooled glass container and finally redistilled into a storage trap on the vacuum line.

Formation of Catalyst

Five millimeters of Hg pressure of dimethyl zinc contained in a 4-liter mixing bulb was condensed and isolated in a cold finger surrounded by liquid nitrogen. The bulb was next pumped out and 10 mm of Hg pressure of titanium tetrachloride vapor distilled into it. The $(CH_3)_2Zn$ in the cold finger was quickly warmed to slightly above room temperature and was expanded into the bulb, where it mixed and reacted with the TiCl₄. The reaction represented by the following equation takes place:

$$Zn(CH_3)_2 + 2TiCl_4 \rightarrow 2CH_3TiCl_3 + ZnCl_2.$$

 CH_3TiCl_3 is a vapor and $ZnCl_2$ a solid. The $ZnCl_2$ settles out leaving CH_3TiCl_3 , which has been shown by infrared spectroscopy to be free of zinc compounds and unreacted $TiCl_4$.

 CH_3TiCl_3 was then expanded into the evacuated reaction vessel upon which a layer of $TiCl_3$ had been deposited. The reaction between CH_3TiCl_3 and $TiCl_3$ was allowed to proceed for a fixed time after which the residual CH_3TiCl_3 and the $TiCl_4$ produced by the reaction was pumped out.

$CH_{3}TiCl_{3} + TiCl_{3} \rightarrow TiCl_{4} + CH_{3}TiCl_{2}$

CH₃TiCl₂ is the active catalyst and is thought of as an alkylated TiCl₃ surface.

Infrared Instrumentation

In the discussion reference will be made to several infrared analyses. A Perkin–Elmer Model 221 doublebeam spectrophotometer fitted with sodium chloride optics was used to record the infrared spectra from 4000 to 650 cm⁻¹. A Perkin–Elmer single-beam, double-pass Model 112 spectrophotometer with cesium bromide optics was used for the region 650 to 290 cm⁻¹.

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The infrared gas cells used in this work were of pyrex, 10 cm in length and fitted with a vacuum stopcock. CsBr windows were sealed on with glyptal in such a manner that the cells were vacuum tight.

THE CATALYTIC SYSTEM

Before presentation of the kinetic data, a few comments on the catalytic system which we have used are in order.

The existence of methyl titanium trichloride has been known for some time. During the years 1955 and 1956 this laboratory carried out a rather exhaustive study of its physical and catalytic properties. It was found that CH_3TiCl_3 vapor alone was extremely stable in the dark at room temperature, Fig. 2, and that in the pure form either in



hydrocarbon solution or the vapor state possessed little or no catalytic activity. If, on the other hand, one partially decomposed CH_3TiCl_3 by photochemical or thermal means, a catalyst, active for the polymerization of ethylene, was formed. It was also found, by an infrared technique, that during the decomposition of CH_3TiCl_3 in cyclohexane solution $TiCl_4$ was formed, Fig. 3.

Van Heerden (4), discussing a paper by Natta, drew attention to a Hoechst patent (5) which mentioned that TiCl₃ forms an active system for polymerization when reacted with tetravalent alkyl titanium halides. Dr. Van Heerden further reported that in his own laboratory the combination of CH_3TiCl_3 and brown TiCl₃ formed by the thermal decomposition of CH_3TiCl_3 was an extremely active system. His explanation of the experimental results is applicable to the system which we are describing and consequently warrants repetition.

The Ti—C bond in the tetravalent titanium alkyl halide seems too stable to give a rapid "aufbau" reaction under the mild conditions of low-pressure ethylene polymerization. The unique character of the Ti—C bond has become apparent in an infrared analysis (6) of CH_3TiCl_3 carried out in this laboratory and to be published shortly. It has become evident that the CH_3 group present in CH_3TiCl_3 does not possess the infrared character of the normal metal organic methyl group and therefore the Ti—C bond is

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FIG. 3. Decomposition of TiCl₃CH₃ in cyclohexane in the dark at 25° C.

not a normal metal carbon bond. (Rodriguez's (7) work using D_2O to hydrolyze methyl titanium trichloride also emphasizes this last fact since he found all of the mixed CDH groups present in his products.) Van Heerden's studies also show that a solution of CH_3TiCl_3 in the absence of TiCl_3 does not give the aufbau reaction or at least the rate of such a reaction is very small in comparison with the polymerization rate in coordination catalyst systems. De Vries' (8) work in the same laboratory as Van Heerden found that only those alkyl titanium chlorides are unstable which can decompose in a bimolecular reaction by the disproportionation of two alkyl groups to an olefin and an alkane, i.e. those compounds having an H atom on a β -C atom in the alkyl group. CH_3TiCl_3 lacking H atoms on β carbon atoms is consequently stable.

Arlman and De Jong (9) discussed the work of Beerman and Bestian (10) regarding the decomposition of CH_3TiCl_3 . The decomposition appeared autocatalytic and the addition of extra $TiCl_3$ increased the rate of decomposition. It was suggested that the reaction takes place predominantly at the surface of $TiCl_3$ crystals.

The preparation of the catalyst system used in our study is described in detail in the section of this paper dealing with experimental methods. The CH_3TiCl_3 vapor is reacted with a deposit of purple TiCl_3, i.e. the alpha form prepared in a pure state. An infrared examination of the formation of this catalyst has shown that TiCl_4 is formed during the reaction of the vapor and the solid. If the surface is pumped for an hour or more to remove any remaining TiCl_4 and then a small quantity of moist helium is brought into contact with it, methane is formed and has been detected by gas chromatography. No ethane has been found in the system.

From the foregoing discussion we postulate the following reaction to explain the formation of a catalyst active for ethylene polymerization:

 $TiCl_3 + CH_3TiCl_3 \rightarrow CH_3TiCl_2 + TiCl_4$,

 $CH_{3}TiCl_{2}$ being the active species. The active site might well be a chlorine vacancy in the crystal lattice, a mechanism well described by Cossee (11).

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KINETICS

The literature which has been built up since the advent of the polymerization of olefines by coordination catalysts contains many discussions of the kinetics of ethylene polymerization. A large variety of catalytic systems has been studied and numerous postulations made as to the factors controlling the rate of reaction. The majority of such investigations have dealt with polymerization in hydrocarbon solution and have involved catalysts generally formed *in situ*. Relatively few investigations have been carried out in the absence of solvent and the investigation of Eden and Feilchenfeld (12) represents one of these. It should be mentioned that we do not consider the fixed bed catalysts such as the chromium oxide system of Phillips Petroleum and the nickel, cobalt, and molybdenum oxide systems of Standard Oil as belonging to the class of coordination catalysts which we are considering.

Most investigations dealing primarily with catalysts formed by the reaction of aluminum alkyls and titanium or vanadium halides have shown that the rate curves for ethylene polymerization are complex. Ludlum, Anderson, and Ashby (13) divide their observed rate curve into three regions. Fukui (14) and his co-workers, using a somewhat different system than Ludlum, have delineated four regions in their overall rate curve. Badin (15) and Chien (16) have two regions and Gilchrist (17) by virtue of the time period of his observations finds but one. Most authors do, however, in spite of their divisions of the rate curve, observe a region in which the rate of polymerization of ethylene is first order in ethylene. Several people, among them Fukui (14) and Gilchrist (17), have found second-order dependence but often it is possible to postulate ethylene being a necessary substituent in the catalyst-forming step of their reaction scheme. It is commonly observed that the rate eventually departs from first order, and several explanations to be discussed later have been postulated to explain this fact.

Figure 4 represents the change in ethylene concentration with time for a constantvolume system in which gaseous ethylene is polymerized on the alkylated TiCl₃ surface previously described. Figure 5 is the same experiment plotted as a first-order reaction. It is evident that the rate of reaction obeys the first-order rate law during the first 50 minutes but then departs from that law and must be expressed in some different form.

Figure 6 shows the polymerization of ethylene under a condition approximating constant pressure; this condition was obtained in the manner previously described, i.e. returning the pressure to the initial value at frequent, regularly spaced intervals. It is obvious from this figure that the initial rate is changing. Figure 7 shows the polymerization of an alpha olefin under conditions of constant pressure using the automatic gas burette to control the pressure. The curve represents the volume change as a function of time. If one considers the general equation for a first-order process,

$$dn/dt = -k_1C,$$

where $n \equiv$ number of moles and $C \equiv$ number of moles/liter = n/V, assuming perfect gas n = PV/RT, C = P/RT it is easily shown that

$$dV/dt = -k_1,$$

i.e. for a first-order process the rate of change of volume should be constant. Since the result of the constant-pressure experiment is not a straight line it is evident





FIG. 4. The polymerization of ethylene. Ethylene concentration as a function of time. FIG. 5. The polymerization of ethylene. First-order plot.

that the reaction is not entirely first order. A consideration of a second-order process at constant pressure would give

$$dV/dt = -k_2P,$$

which would also be a straight line under the conditions of reaction.

The amount of curvature evident in the time rate of change of volume of Fig. 7 is a measure of the departure from either first or second order. From the constant-volume experiments it is evident that the rate deviates from the first-order case.

The initial attempt to explain our kinetic data was based on the following mathematical analysis. In the first approximation the following differential equations were said to govern the progress of the polymerization step. It is to be borne in mind that the catalyst is preformed and active. No initiation reaction is necessary.

$$[1] \qquad \qquad -dE/dt = k_1 E$$

$$[2] \qquad \qquad -dC/dt = k_2(E_0 - E)C$$

[3]
$$k_1 = k_3 C$$

 $E \equiv$ concentration of ethylene at time t, $E_0 \equiv$ initial concentration of ethylene, $C \equiv$ concentration of catalyst at time t, $C_0 \equiv$ initial concentration of catalyst.

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Equation [1] represents the first-order polymerization mechanism.

Equation [2] was derived in an intuitive fashion and represents the decrease in effective catalyst concentration (i.e. number of active sites) brought about by buildup of polymer around the site. This explanation for the decrease in polymerization rate has been suggested by Feilchenfeld and Jeselson (18) and also by Ludlum and his co-workers (13).

Equation [3] links the rate of polymerization with the concentration of catalyst.

Rewriting [1]

$$dE/dt = -k_3CE.$$

For ease in manipulation we shall make concentration and time terms dimensionless. Dividing by E_0 and letting E/E_0 be represented by Y

$$dY/dt = -k_3 CY.$$

 $= -k_3 C_0 X Y.$

Dividing by C_0 and letting C/C_0 be represented by X

$$[4] dY/dt$$

Transposing [2]

$$[5] dX/dt = -k_2 E_0 (1-Y)X.$$

At t = 0, $k_3C_0 = k_{1_0}$ (the initial rate constant) and X = Y = 1. Let $k_3C_0 \equiv \lambda$ and $\lambda t \equiv \tau$, and normalizing time, [4] becomes

$$[6] dY/d\tau = -XY$$

and [5] becomes

[7]

$$dX/d\tau = -\alpha(1-Y)X,$$

where $\alpha = k_2 E_0 / k_3 C_0$.

Equations [6] and [7] were then set up on an analogue computer and a family of solutions developed for various values of α . The solutions thus generated were then compared with the experimental curve and it was found that the solution obtained for an α value of 0.32 closely fitted the experimental results.

The experimental results just applied to the theoretical equations have been obtained from measurements made in a constant-volume system. If the theory is to be correct it should also apply to measurements made under constant pressure. The analogue computer was wired so as to perform a hypothetical constant-pressure experiment using the theoretical equations outlined previously. The results of this experiment showed that the theoretical equations were not adequate to describe the changing initial rate data found experimentally.

A new system of equations was then set up. The rate of catalyst decay was said to be proportional to the *rate* of ethylene polymerization. In this particular case equation [6] does not change but equation [7] becomes

$$dX/d\tau = -\alpha(XY)X.$$

It was found that the solutions generated using equations [6] and [8] fitted the constantpressure experiments, but failed to satisfy the constant-volume data.

The third case considered was that in which the catalyst decayed in a purely exponential fashion. In this instance equation [7] takes the form

9]
$$dX/d\tau = -kX$$

Once again, it was found that the solutions of the differential equations did not fit all of the experimental situations.

The mathematical expressions were again studied and it was found that if both constant-pressure and constant-volume conditions were to be met, another term would have to be introduced into equation [7]. The expressions

$$dY/d\tau = -XY$$

and

[8]

$$dX/d\tau = -\{\alpha(1-Y)X + \beta X\}$$

where βX represents exponential catalyst decay, gave a solution which satisfied all conditions. β is a constant equal to K/k_3C_0 in the normalized expressions given above, K being the decay rate constant.

The specific solution fitting the experimental measurements has a value of $\alpha = 0.38$ and a value of $\beta = 0.10$. It is evident from the expressions given above that in the initial stages of reaction the falloff in rate is due solely to catalyst decay, which has been shown to be slow from a study of experiments in which the catalyst was aged previous to the introduction of ethylene. As polymer builds up around the active site less monomer is able to reach it and the rate begins to drop.

The diffusion processes which have some influence on the chemical process are at present under study.

Estimation of the Rate Constant for Catalyst Decay

If we consider the initial stages of the polymerization and also assume that the only catalyst decay process of importance during that particular stage is normal exponential decay the constant-pressure experiments may be used to estimate the rate constant of this decay process. It is recognized that the above approximation is rather great but nonetheless the calculation is included since the method might find application to other processes.

Consider the curvature of the time rate of change of volume depicted in Fig. 7. Under conditions of constant pressure

$$[11] dV/dt = -k_E n_{\rm cat},$$

where $V \equiv$ volume, $t \equiv$ time, $k_E \equiv$ a rate constant for volume change, $n_{\text{cat}} \equiv$ number of moles of catalyst or number of active sites.

Making use of our aforementioned assumption involving first-order catalyst decay

$$dn_{\rm ext}/dt = -k_{\rm cat}n_{\rm cat}.$$

Integrate [12] and apply the condition that $n_{\text{cat}} = n_0$ at t = 0

[13]

$$n_{\rm cat} = n_0 \epsilon^{-k_{\rm cat}t}$$

Put [13] into [11]

$$dV/dt = -k_E n_0 \epsilon^{-k_{\rm cat}t}.$$

At t = 0

$$dV/dt = -k_E n_0.$$

Let $\phi = (k_E/k_{cat})n_0$, then at t = 0,

 $dV/dt = -k_{\rm cat}\phi.$

Also it may be shown that

$$\Delta V = (k_E/k_{\text{cat}})n_0[\epsilon^{-k_{\text{cat}}t}-1]$$

= $\phi[\epsilon^{-k_{\text{cat}}t}-1].$

Select any pair of values of ΔV and t. Find, by trial and error, various values of ϕ and k_{cat} which fit. Plot ϕ as a function of k_{cat} . Repeat for other values of ΔV and t which are widely separated.

The intersection of the family of curves, Fig. 8, denotes unique values of k_{cat} and ϕ . A value of $k_{cat} = 1.6 \times 10^{-2} \text{ min}^{-1}$ has been determined from a number of experiments.



FIG. 8. Estimation of rate constant for catalyst decay.

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The initial rate constant of polymerization of ethylene was measured at temperatures of 30° C and 40° C as well as 21° C. (The catalyst in all cases was formed at 21° C.) A plot of the log of the rate constant as a function of reciprocal absolute temperature was drawn. A straight line resulted and the activation energy for the overall polymerization reaction was calculated from the slope. This was found to be approximately 10 kcal/mole in agreement with Badin's (15) value of 10 kcal/mole for the polymerization of ethylene in the catalyst system $TiCl_4$ + (isobutyl)₃Al and Natta's (19) value of 11.7 kcal/mole for a cyclopentadienyl catalyst system.

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