cule of the vanadium compound can catalyze the formation of hundreds of polymer molecules, termination of a growing molecule must take place by some chain transfer or oxidation–reduction process in which the active site is regenerated with retention of its function. The molecular termination process is very likely a combination of two reactions since not all the polymer molecules have the same end groups. The mechanism by which the active vanadium center is regenerated is still under investigation and will be discussed further at a later date.

A kinetic treatment of vinyl polymerizations, assuming any of the conventional termination reactions, ordinarily leads to a predicted weight average to number average molecular weight ratio of between one and two,[23] when the reaction is carried out under equilibrium conditions. In this case the M_w/M_n ratio of about 1.5 is probably not sufficiently exact to argue for a specific mechanism on kinetic grounds; however, the low value of the M_w/M_n ratio is good evidence that this catalyst system has only a *single active species.* The M_w/M_n ratios of 15–30 observed for polymers produced with the AlR_3–$TiCl_4$ catalyst suggest that this system has several different active sites, each producing its own characteristic polymer. For this reason, the heterogeneous catalyst is much more difficult to investigate from a mechanistic point of view.

Acknowledgment.—The authors are indebted to Miss P. Payton and Mr. E. G. Hendricks for the osmotic and cryoscopic molecular weight determinations, and to Mr. W. E. Wright for assistance with some of the polymerizations.

BOUND BROOK, N. J.

---

(23) Paul J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VIII.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE PLASTICS CO., A DIVISION OF UNION CARBIDE CORP.]

Transition Metal Catalysts. II. Formation and Catalytic Activity of Organovanadium Compounds Formed by Interaction of Diphenylmercury and Vanadium Halides[1]

BY WAYNE L. CARRICK, WALTER T. REICHLE, FILLIPO PENNELLA AND JOSEPH J. SMITH

RECEIVED AUGUST 24, 1959

The organovanadium compounds $C_6H_5VOCl_2$ and $C_6H_5VCl_3$ are formed by the interaction of diphenylmercury and vanadium oxytrichloride or vanadium tetrachloride in cyclohexane solution. These compounds are unstable and spontaneously decompose giving a quantitative yield of biphenyl and the lower valence vanadium halide according to the equation: $C_6H_5VX_n \rightarrow {}^1/_2C_6H_5C_6H_5 + VX_n$. This reaction is a concerted process and does not involve the intermediate formation of phenyl radicals. Ethylene polymerization tests with these compounds at room temperature and atmospheric pressure were negative. However, other tests using mixtures believed to contain di- or trivalent organovanadium compounds produced a low yield of high molecular weight polyethylene. These results are interpreted as support of the theory that the active catalyst species in low-pressure, organometallic, olefin polymerization catalysts contains an organic derivative of a transition metal in a low valence state.

Introduction

Catalysts for the polymerization of ethylene and other olefins to high molecular weight polymers are formed by the interaction of certain reactive organometallic compounds and transition metal halides.[2,3] Reactions between these species presumably lead to the intermediate formation of alkyl or aryl transition metal compounds; therefore a definition of the role of such intermediates would significantly advance our understanding of these polymerization catalysts. Investigation of the structure and properties of the alkyls of the catalytically active Groups IV–VI transition metals is difficult due to the inherent instability of these compounds.[4] The only authentic examples of the catalytic behavior of such compounds, in which there is a carbon to transition metal single bond are phenyl titanium triisopropoxide[5] and methyl titanium trichloride.[6] Phenyl titanium triisopropoxide has been reported to polymerize styrene, presumably by a free radical mechanism, but its catalytic behavior toward ethylene or other α-olefins was not mentioned. Methyl titanium trichloride is reported to form a catalyst for the low pressure polymerization of ethylene,[7] but its activity is appreciable only after partial thermal decomposition.

An additional feature of organometallic catalysts which has not been rigorously investigated is the influence of valence on the stability and reactivity of the various transition metal species. Theoretical treatments have shown that a metal center should become less electronegative with a decrease in valence,[8,9] and the stability of its organometallic compounds should also increase with decreasing electronegativity of the metal center.[10] Therefore, the most stable organotransition metal compounds should be those in the lowest valence states. The more polar character of the C–M bond in the low valence species may also be important in

---

(1) This work was presented in part before the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 13 to 18, 1958, Polymer Division.

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

(3) Soc. Chem. Ind., Reports on the Progress of Applied Chemistry, **42**, 436 (1957).

(4) F. A. Cotton, *Chem. Revs.*, **55**, 551 (1955).

(5) D. F. Herman and W. K. Nelson, THIS JOURNAL, **75**, 3877, 3882 (1953).

(6) Belgian Patent 553,477.

(7) (a) Belgian Patent 553,478; (b) C. Beermann and H. Bestian, *Angew. Chem.*, **71**, 618 (1959).

(8) M. Haissinsky, *J. Phys. Radium*, **7**, 7 (1946).

(9) T. L. Allen, *J. Chem. Phys.*, **26**, 1644 (1957).

(10) H. H. Jaffe and G. O. Doak, *ibid.*, **21**, 196 (1953).

polarizing the double bond in the monomer. This concept is particularly important if the propagation reaction occurs by an ionic mechanism, as some investigators have proposed.[11–13]

Many of the catalyst studies carried out by this group have been based on vanadium compounds. There have been no simple organovanadium compounds reported in the literature. However, preliminary investigation showed that such compounds can be prepared in cyclohexane solution by the interaction of diphenylmercury and a vanadium halide, preferably a soluble vanadium chloride. This paper discusses the significance of these organovanadium compounds in regard to the mechanism of olefin polymerization by organometallic mixed catalysts.

Experimental

Potentiometric Titration of Vanadium Valences.—Vanadium analyses were carried out by potentiometric titration using permanganate as the oxidizing agent. The titrations were carried out in dilute sulfuric acid and the potential of the solution was measured using a platinum indicator electrode and a calomel reference electrode with a Beckman *p*H meter adjusted to read in millivolts.

The partial reactions in acid solution are[14]

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{++} + 4H_2O \qquad E^0 = 1.52$$

$$V^{++} \longrightarrow V^{+++} + e^- \qquad E^0 = 0.255$$

$$H_2O + V^{+++} \longrightarrow VO^{++} + 2H^+ + e^- \qquad E^0 = -0.361$$

$$3H_2O + VO^{++} \longrightarrow V(OH)_4^+ + 2H^+ + e^- \qquad E^0 = -1.00$$

As expected from the normal potential values of the partial reactions, it is possible to oxidize quantitatively the lowest valence state first, before the higher valence states are oxidized. Consequently, more than one break is found in the titration curve when a valence state lower than +4 is present (Fig. 1).

In the titration of vanadium with permanganate, equilibrium is reached slowly, especially near the equivalence point. It was found that the potential assumed a constant value more rapidly if the titration was carried out at 70–80°.

It is necessary to carry out the titration in an inert atmosphere to avoid oxidation of the lower valence states by atmospheric oxygen. Therefore, nitrogen was bubbled through the acidified water, before dissolving the vanadium salts precipitated when diphenylmercury and VCl_4, or $VOCl_3$, were allowed to react. The solution was preheated to 80° and held at this temperature, under nitrogen, until the titration was complete. The nitrogen stream also provided stirring of the solution.

It is difficult to obtain an accurate determination of the concentration of vanadous ion (V^{+2}) under these conditions, since this species is oxidized to vanadic ion by water. The trivalent ion is also unstable in water solutions; however, the spontaneous oxidation of trivalent ion to the tetravalent state is slow and a relatively accurate determination of V^{+3} can be obtained by titration with permanganate at room temperature. In view of these facts, the necessity of carrying out the titration as rapidly as possible is apparent. A high acidity is also desirable for accurate results. Generally, about 1 ml. of 1:1 aqueous sulfuric acid was added per 50 ml. of solution.

The color changes during the titration are those characteristic of the vanadium ions. The violet color of V^{+2} turned green upon addition of a few drops of permanganate solution. During the titration of the +3 oxidation state the green color changed to blue, but long before the equivalence point was reached. A green color reappeared again when V^{+4} was oxidized to V^{+5}, then the solution slowly turned colorless. After the last jump in potential one or two drops of permanganate still must be added to obtain a pink color.

Interaction of Diphenylmercury and Vanadium Halides.—The reaction between diphenylmercury and vanadium tetrachloride, or vanadium oxytrichloride, was carried out in a nitrogen atmosphere using either 10 or 20 millimoles of each compound in 500 ml. of purified cyclohexane. Immediately upon mixing, the solutions turned dark red and a precipitate of phenylmercuric chloride deposited. This precipitate was identified by its melting point and comparison of its infrared spectrum with that of a known sample of phenylmercuric chloride. In some experiments the precipitate was removed by filtration or by centrifugation of a small part of the sample. Whether the precipitate was removed or not, the color of the solution slowly faded, and after a few hours the solution became clear, indicating complete decomposition of the color-producing species. As decomposition progressed, dark precipitates of lower valence vanadium compounds were deposited. These precipitates were digested in *N* sulfuric acid, and the vanadium valence was determined by permanganate titration. When the mercury-to-vanadium ratio in the original mixture was unity, the vanadium in the precipitate was one unit lower in valence than the original halide. Higher mercury-to-vanadium ratios gave reduction of more than one valence unit, and potentiometric titration revealed the presence of more than one vanadium valence state, thus showing that the product, in these cases, was never a single species. Evaporation of the cyclohexane from the clear hydrocarbon supernatant gave only biphenyl as a residue. This compound was identified by comparison of its melting point and infrared spectrum with those of a known sample of biphenyl.

Infrared Measurements.—Spectrophotometric examination of the various solutions was carried out using a Perkin–Elmer model 21 infrared instrument with matched sodium chloride cells of either 1 or 3 mm. path length. A cell of equivalent path length and filled with solvent was placed in the reference beam in all cases. Cyclohexane was chosen as solvent for this work because it contains no intense absorptions from 12.5–15μ, the region used to measure the aromatic compounds in solution. The concentration of biphenyl in the various solutions was determined by comparison of the absorption at 13.6μ with a calibration curve based on prepared cyclohexane solutions containing known concentrations of biphenyl.

Infrared spectra of solid samples were obtained using pressed disks of the sample mixed with powdered potassium bromide.

Kinetic Study of the Rate of Decomposition of $C_6H_5VOCl_2$.—The primary reaction vessel consisted of a flask equipped with a mechanical stirrer, inlet for an inert atmosphere, and a serum bottle stopper for adding and withdrawing samples by way of hypodermic syringes. The entire apparatus was immersed in a constant temperature bath maintained at 29.8 ± 0.01°. An atmosphere of argon, purified by passage through Linde 4-A molecular sieves and then through liquid sodium–potassium (25% Na) alloy, was maintained over the system throughout the experiment. Cyclohexane was purified by refluxing over concentrated sulfuric acid, water washing to remove acid, drying over magnesium sulfate, and a final distillation. For each experiment, a sample of this solvent then was redistilled over sodium–potassium alloy into a calibrated receiver, under argon, and added directly to the reaction flask without exposure to air. Twenty millimoles of diphenylmercury, recrystallized once from chloroform–ethanol and once from hot cyclohexane, was added through one neck of the reaction flask and allowed to dissolve. Vanadium oxytrichloride was obtained as a pale yellow liquid from Union Carbide Metals Co. and was used as received. Twenty millimoles of the pure liquid was injected into the reactor by way of a hypodermic syringe to start the reaction.

The rate of decomposition of the resulting organovanadium compound was followed by removing 10-ml. samples, at intervals, by hypodermic syringes, and injecting them into a 50-ml. volumetric flask immersed in a Dry Ice-bath. This flask contained enough dry hydrogen bromide dissolved in cyclohexane to cleave the carbon-to-metal bonds and convert the phenyl groups to benzene. Additional pure cyclohexane was added to bring the solution to the proper volume, and the biphenyl concentration was determined by the infrared absorption at 13.6μ.

---

(11) G. Natta, *J. Polymer Sci.*, **34**, 21 (1959).

(12) D. B. Ludlum, A. W. Anderson and C. E. Ashley, This Journal, **80**, 1380 (1958).

(13) W. L. Carrick, *ibid.*, **80**, 6455 (1958).

(14) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952.

Decomposition of $C_6H_5VOCl_2$ in the Presence of Carbon Monoxide.—A solution of 20 millimoles of diphenylmercury in 500 ml. of cyclohexane was brought to a boil under an atmosphere of nitrogen. A stream of carbon monoxide, purified by passage through columns of Ascarite and Drierite, was admitted to the system, and then 20 millimoles of vanadium oxytrichloride was added from a hypodermic syringe. At the end of 25 minutes the reaction was stopped. Infrared examination showed that all the diphenylmercury had reacted, yet only 50% of the theoretical amount of biphenyl was obtained. Since there was no absorption between 5.8 and 6.1μ, it was concluded that no ketones were present.

Decomposition of $C_6H_5VOCl_2$ in the Presence of Azobisisobutyronitrile.—A solution of 15 g. of azobisisobutyronitrile in 500 ml. of cyclohexane was brought to a boil (80°) under an atmosphere of nitrogen. Then a solution of 20 millimoles of diphenylmercury and 20 millimoles of vanadium oxytrichloride in 300 ml. of cyclohexane that had been aged for 12 minutes at room temperature was added to the boiling solution of azobisisobutyronitrile over an 8-minute interval. The final solution was allowed to reflux an additional 11 minutes, and most of the solvent was removed by distillation. The residue was saponified with 60 g. of potassium hydroxide in 500 ml. of an ethanol–water mixture, and the solvent was evaporated. The residue was extracted with ether to remove biphenyl, etc., acidified, and again extracted with ether to remove the acids. Evaporation of this ether layer gave a residue that showed strong infrared absorption between 5.85–5.95μ, indicating the presence of organic acids, but no absorption between 13–15μ where a phenyl derivative would absorb.

Ethylene Polymerization Tests.—Ethylene polymerization tests were carried out under the same conditions as described in the previous paper.

Results and Discussion

Various aryl and alkyl organometallic compounds react with transition metal halides in inert solvents.[4,15,16] Here, diphenylmercury was chosen as the arylating agent for the preparation of organovanadium compounds from vanadium halides because it is available in pure form, and is readily soluble in cyclohexane, while the disproportionation product phenylmercuric chloride is not soluble. In addition, diphenylmercury reacts rapidly and cleanly with vanadium halides and has little tendency to form interfering complexes. Stronger alkylating reagents cause extensive reduction of all of the vanadium to the divalent or metallic state and often lead to highly complex products. Metal alkyls which are strong Lewis acids tend to form bimetallic complexes with lower valence transition metal compounds.[13,17] In order to characterize the organovanadium compounds at different valence levels, it was desirable to exclude the interfering influences of complex formation or excessive valence reduction in this phase of the investigation.

Interaction of Diphenylmercury and Vanadium Oxytrichloride.—The addition of vanadium oxytrichloride to a cyclohexane solution of diphenylmercury at room temperature forms a deep red solution with the precipitation of phenylmercuric chloride according to the equation

$$(C_6H_5)_2Hg + VOCl_3 \rightleftarrows C_6H_5VOCl_2 + C_6H_5HgCl\downarrow \quad (1)$$

This reaction is very rapid, and precipitation of phenylmercuric chloride is essentially complete in 10 minutes at room temperature. More than 95% of the theoretical amount of phenylmercuric chloride was recovered by centrifugation. The clear red solution contained all of the vanadium, in the pentavalent state, and half of the phenyl groups originally charged. The organovanadium compound so formed is unstable and decomposed over a period of about one hour at 30° giving a quantitative (97–100%) conversion to biphenyl and vanadyl chloride, as

$$C_6H_5VOCl_2 \longrightarrow {}^1/_2C_6H_5C_6H_5 + VOCl_2\downarrow \quad (2)$$

Vanadyl chloride separates as a dark precipitate while biphenyl remains in solution. Figure 2

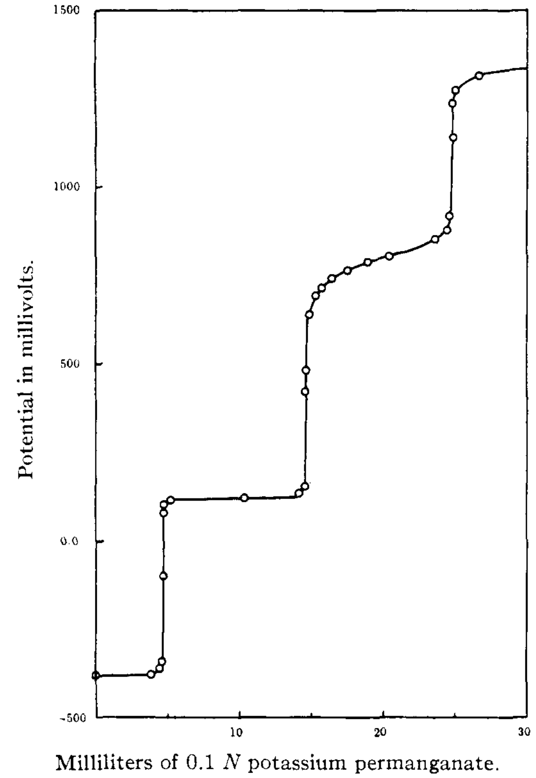


Fig. 1.—Potentiometric titration of 1 millimole of a vanadium chloride sample containing about equal concentrations of di- and trivalent vanadium.

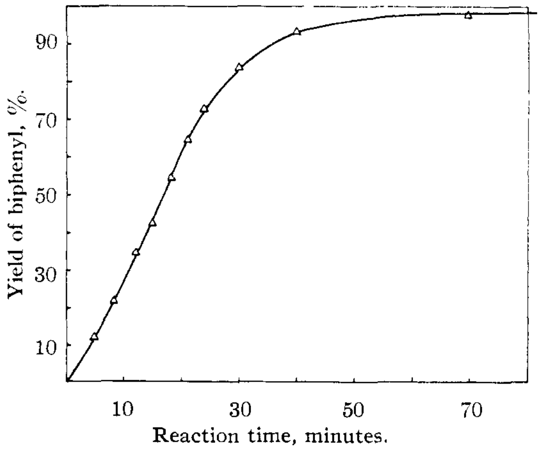


Fig. 2.—Appearance of biphenyl from the reaction of 20 millimoles of vanadium oxytrichloride and 20 millimoles of diphenylmercury in 500 ml. of cyclohexane.

(15) H. Gilman, R. G. Jones and L. A. Woods, THIS JOURNAL, **76**, 3615 (1954).

(16) C. C. Vernon, *ibid.*, **53**, 3831 (1931).

(17) G. Natta, P. Corradini and I. W. Bassi, *ibid.*, **80**, 755 (1958).

shows the rate of appearance of biphenyl as a function of time.

These experiments clearly established that an organovanadium compound is formed by the interaction of diphenylmercury and vanadium oxytrichloride; however, the structure of the compound was not rigorously established. Transition metals can form compounds containing a simple C–M single bond or they can also form π-bonded complex (sandwich) compounds with aromatic hydrocarbons[18,19] or with the cyclopentadienyl anion.[20,21] In order to distinguish between these possibilities, cyclohexane solutions of the organovanadium compound were examined by infrared spectrophotometry using sealed cells. Solvent absorptions and the general complexity of the system made the 2–12 μ region virtually useless; however, several distinct bands appeared in the 12–15 μ region. These bands are likely due to the C–H bending modes of the various aromatic compounds.

A solution of diphenylmercury in cyclohexane displayed strong absorptions at 13.8 and 14.35 μ, due to the C–H bending vibrations of the monosubstituted phenyl groups in this compound. A second examination after the addition of an equimolar amount of vanadium oxytrichloride and centrifugation to remove phenylmercuric chloride showed that the band at 13.8 μ was essentially unchanged, but the band at 14.35 μ had disappeared and a new band appeared at 14.9 μ. This shows that the diphenylmercury had reacted completely, and a new phenyl-containing compound was formed. Over the next 1–2 hours both absorptions at 13.8 and 14.9 μ disappeared and were in turn replaced by new absorptions at 12.87, 13.6 and 14.35 μ due to biphenyl. A very weak band at 14.9 μ, due to low concentrations of benzene, sometimes remains after decomposition is complete. Solutions of $C_6H_5VOCl_2$ can be quenched by the addition of dry gaseous hydrogen bromide at any time during the course of the experiment. After such treatment two aromatic compounds were detected in the solution, biphenyl and benzene. The biphenyl concentration was the same as was present at any instant without the addition of hydrogen bromide and the remainder of the phenyl groups appeared as benzene, undoubtedly from the reaction

$$C_6H_5VOCl_2 + HBr \longrightarrow C_6H_6 + VOCl_2Br \quad (3)$$

Since biphenyl was shown to exist, as such, in the unquenched solutions, this compound cannot be bound to the vanadium in a "sandwich" structure of the type that is known to exist in some of the chromium compounds.[18,22] Also hydrolysis gave benzene which is good evidence that the phenyl group in this organovanadium compound is still intact and is bound to the vanadium primarily by a C–V single bond. The strength of this bond is probably increased by some π-bond contribution, but this factor is believed to be secondary, not dominant.

Having established the presence of an unstable and reactive organovanadium compound, the question of its mode of decomposition then was considered. The literature concerning the reactions of such unstable transition metal organic compounds offers a confusing amount of evidence as to radical and non-radical routes, and the available data prove, at best, that the mechanism(s) of decomposition is neither simple nor obvious.[4] For example, silver methyl decomposes according to a first-order rate law to form ethane as the only hydrocarbon product, while copper methyl forms both methane and ethane.[23] In the latter case attempts to detect the presence of radicals were unsuccessful. Gilman, Jones and Woods[15] studied the hydrocarbons liberated when methyl and ethyl Grignard reagents were allowed to react with a variety of transition metal compounds and found that the relative amount of coupling *vs.* disproportionation or hydrogen abstraction varied widely in the different cases. They suggested that the decomposition may be unimolecular in some cases and bimolecular in others.

In regard to the $C_6H_5VOCl_2$ intermediate, two possible modes of decomposition are apparent. One is a simple homolytic cleavage of the C–V bond

$$C_6H_5VOCl_2 \longrightarrow C_6H_5\cdot + VOCl_2 \quad (4)$$

with rapid coupling of the resulting radicals to form biphenyl

$$2C_6H_5\cdot \longrightarrow C_6H_5C_6H_5 \quad (5)$$

and the other route is some complex concerted process which forms biphenyl directly from an organometallic intermediate.

When stoichiometrically equal amounts of diphenylmercury and vanadium oxytrichloride are allowed to react in dilute cyclohexane solution, biphenyl appears following a first-order rate law. The curved portion of the kinetic curve (Fig. 3) probably represents the time required for formation of $C_6H_5VOCl_2$ from its precursors (eq. 1). Since at time zero a stoichiometric quantity of $C_6H_5VOCl_2$ is not available for decomposition, but its concentration builts up as time progresses, one would expect a curved line and a lower decomposition rate during this early period. After the induction period of 10–12 minutes, the rate of appearance of biphenyl is strictly first order to a conversion of 80–90%. In numerous duplicate experiments the latter part of the curve was always linear on a first-order plot, but the slope of the line was not reproducible. One cause of the poor reproducibility is the extreme sensitivity of the reaction rate to the reagent charge ratio. In one series of experiments the slope of the line, such as in Fig. 3, varied linearly from 0.109 to 0.071 min.$^{-1}$ as the V/Hg ratio in the charge was increased from 0.985 to 1.025. When the V/Hg ratio was 2, the yield of biphenyl was only about 25% of the theoretical in 24 hours, and when the V/Hg ratio was 0.5, the decomposition was too fast to measure.

---

[18] H. H. Zeiss and M. Tsutsui, THIS JOURNAL, **79**, 3062 (1957).

[19] E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 655 (1955).

[20] P. L. Pauson, *Quart. Revs.*, **9**, 391 (1955).

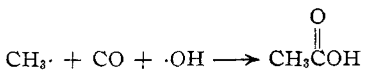
[21] G. Wilkinson and J. M. Birmingham, THIS JOURNAL, **76**, 4281 (1954).

[22] H. Zeiss and W. Herwig, *ibid.*, **79**, 6561 (1957).

[23] C. E. H. Bawn and F. J. Whitby, *Disc. Faraday Soc.*, **2**, 228 (1947).

The observation of unimolecular kinetics is in accord with the radical route shown as eq. 4; however, several other factors argue against this idea. A free phenyl radical is an exceptionally reactive species and would be expected to attack the solvent, cyclohexane.[24,25] For example, the thermal decomposition of benzoyl peroxide in hot cyclohexane did not give any biphenyl, but a 50% yield of carbon dioxide was obtained which shows that at least one phenyl radical was formed for each molecule of benzoyl peroxide.[24] In the decomposition of $C_6H_5VOCl_2$, both at 30 and 80°, the yield of biphenyl in several experiments was 93–100%, which points strongly to the absence of free phenyl radicals.

Several other attempts were made to capture phenyl radicals, if such were present, and all failed. When $C_6H_5VOCl_2$ and azobisisobutyronitrile were decomposed simultaneously, no phenylisobutyric acid was detected after saponification and acidification of the residue.[26] It is known that radicals react with carbon monoxide, for example[27]



$$CH_3\cdot + CO + \cdot OH \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}OH$$

However, when $C_6H_5VOCl_2$ was decomposed in an atmosphere of carbon monoxide, no benzophenone or other carbonyl compound could be detected in the residue by infrared examination.

These experiments seem to establish that *free* phenyl radicals are not produced in the decomposition of the above organovanadium compound. If phenyl radicals are formed but remain complexed with some other species ($VOCl_2$, $VOCl$, $VOCl_3$, etc.) then the increase in reaction temperature to 80° should have loosened them sufficiently to allow other side reactions. Since the $C_6H_5VOCl_2$ decomposition experiments at elevated temperatures resulted in 93–100% yields of biphenyl, this possibility must also be discarded.

An alternate mechanism which satisfies the unimolecular kinetics, without the production of radicals, is illustrated by the sequence

$$2C_6H_5VOCl_2 \rightleftharpoons (C_6H_5)_2VOCl + VOCl_3 \qquad (6)$$

$$(C_6H_5)_2VOCl \xrightarrow[\text{r. d.}]{} C_6H_5C_6H_5 + VOCl \qquad (7)$$

for which the kinetic expression for the appearance of biphenyl is

$$\text{rate} = k[(C_6H_5)_2VOCl] \qquad (8)$$

Since equation 6 represents an equilibrium reaction and the concentration of $VOCl_3$ is equal to the concentration of $(C_6H_5)_2VOCl$, the equilibrium expression may be written as

$$K = [(C_6H_5)_2VOCl]^2/[C_6H_5VOCl_2]^2 \qquad (9)$$

and

$$(C_6H_5)_2VOCl = K^{1/2}[C_6H_5VOCl_2] \qquad (10)$$

Substituting in equation 8 one obtains

$$\text{rate} = kK^{1/2}C_6H_5VOCl_2 \qquad (11)$$

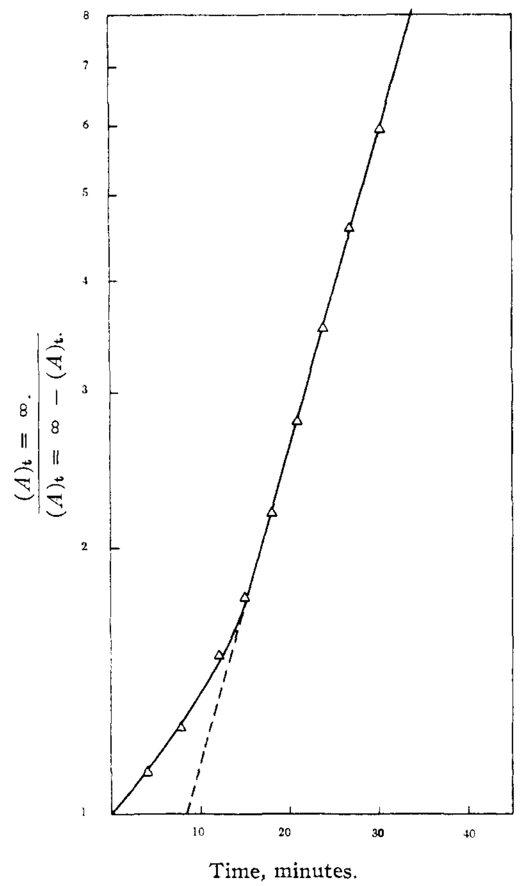


Fig. 3.—Semilog (first-order) plot of the appearance of biphenyl as a function of time from the decomposition of $C_6H_5VOCl_2$.

If decomposition proceeds through the discrete formation and then rate-determining decomposition of diphenylvanadium oxychloride, which is present in only low concentrations, all the available data are satisfied. The pronounced influence of the V/Hg ratio also becomes clear, since excess $VOCl_3$ inhibits decomposition by reversing the reaction illustrated by eq. 6 and excess diphenylmercury hastens decomposition by forming $(C_6H_5)_2VOCl$ directly. Obviously changes in the V/Hg ratio would change the kinetic order, but the decomposition mechanism probably would remain the same.

One assumption that must be made in this treatment is that the trivalent vanadium compound (eq. 7), formed in the decomposition step, must be immediately oxidized to the tetravalent state. This net reaction must be the reaction of one molecule of $VOCl$ and one molecule of $VOCl_3$ to give two molecules of $VOCl_2$, although the actual mechanism may be more complicated than this. This is necessary to satisfy the kinetic expression, and also because all of the vanadium at the end of the decomposition reaction has precipitated out of the solution and titration showed it to be tetravalent. The pentavalent compounds are soluble in cyclohexane, but no vanadium is left in solution at the end of the reaction. Because of the complexity of the over-all reaction sequence and the

---

[24] P. H. Hermans and J. Van Eyk, *J. Polymer Sci.*, **1**, 407 (1946).

[25] W. A. Waters, *J. Chem. Soc.*, 113 (1937).

[26] C. G. Overberger and W. B. Berenbaum, THIS JOURNAL, **73**, 4883 (1951).

[27] R. Cramer, Abstracts 132nd Meeting of the American Chemical Society, 1957, 10-P, No. 5.

difficulty of measuring the concentration of any species other than the initial reactants and final products, further use of reaction kinetics to define the structure of the intermediates would be difficult.

The general instability of transition metal alkyls and aryls is thought to be due to the inherent weakness of the carbon to transition metal bond.[10] However, the data presented here show that the ready decomposition of $C_6H_5VOCl_2$ occurs, not by simple rupture of the C–V bond, but by some complex concerted route. Formation of a strong C–C bond (biphenyl) makes the reaction energetically possible and clearly shows that the C–V bond is much weaker than the C–C bond; however, even within these limits, the C–V bond may be inherently more stable than it has been considered to be *if the decomposition mechanism can be blocked.*

Interaction of Diphenylmercury and Vanadium Tetrachloride.—An equimolar mixture of diphenylmercury and vanadium tetrachloride in cyclohexane undergoes a reaction that is very similar to that described above for diphenylmercury and vanadium oxytrichloride

$$(C_6H_5)_2Hg + VCl_4 \rightleftarrows C_6H_5VCl_3 + C_6H_5HgCl \quad (12)$$

Phenylmercuric chloride (> 95% of theoretical) quickly precipitates and can be removed by centrifugation. The resulting organovanadium compound is very unstable and only exists for 10–20 minutes at room temperature before decomposing to give a near quantitative conversion (> 95%) to biphenyl and vanadium trichloride.

$$C_6H_5VCl_3 \longrightarrow {}^1/_2C_6H_5C_6H_5 + VCl_3 \quad (13)$$

Such rapid decomposition of the intermediate organovanadium compound prevented a more rigorous elucidation of its structure, although it is assumed to be similar to the compound formed from diphenylmercury and vanadium oxytrichloride.

Ethylene Polymerization Tests with $C_6H_5VOCl_2$ and $C_6H_5VCl_3$.—A cyclohexane solution of phenylvanadium oxydichloride, as prepared above, was tested as a catalyst for ethylene polymerization at 25 and 65° and atmospheric pressure. In one-hour polymerization tests, only 0.2 g. of solid, high molecular weight polyethylene (melt index $\simeq 0.1$)[28] was formed using an initial 20 millimoles of phenylvanadium oxydichloride in 1 l. of cyclohexane. Higher concentrations of the organovanadium compound or longer reaction times did not significantly increase the yield. When the cyclohexane solution from the above experiment was evaporated to dryness, only milligram quantities of oil and wax were obtained, thus showing that no significant amount of low molecular weight polymer was formed. Infrared examination of the clear cyclohexane solution at the end of the polymerization experiment showed considerable concentrations of biphenyl and benzene, as would be expected from decomposition and hydrolysis of phenylvanadium oxydichloride, and a new, but weak, absorption at 13.4 μ due to an unidentified product. Since mono-*n*-alkylbenzenes absorb at 13.4 μ, this absorption may be due to a hydrocarbon formed by the addition of ethylene to $C_6H_5VOCl_2$ or to a low concentration of phenyl radicals. No further attempt was made to isolate and identify the species more specifically because of its very low concentration and its apparent irrelevance to the reaction which forms high polymers.

The catalytic activity of $C_6H_5VCl_3$ was qualitatively similar to that of $C_6H_5VOCl_2$ with 20 millimoles of the compound producing 0.5 g. of high molecular weight polyethylene in one hour. Use of a higher ratio (2–10) of diphenylmercury to vanadium tetrachloride resulted in reduction of part of the vanadium to the divalent state, with an accompanying small, but steady, increase in catalytic activity as the vanadium valence was reduced. At Hg/V = 10, the system catalyzed the formation of 5 g. of polyethylene in one hour, and 15–20% of the vanadium was reduced to the divalent state. Vanadium dichloride and trichloride are not active polymerization catalysts under these conditions, so the active species must be some other reaction product. A reasonable interpretation of the low catalytic activity observed is that the active species is a trace concentration of a low valence "phenylvanadium chloride," such as C_6H_5VCl or $C_6H_5VCl_2$, probably deposited on a surface of vanadium di- or trichloride. On this basis, the contrast between the poor cocatalytic activity of diphenylmercury and the excellent cocatalytic activity of aluminum alkyls or aryls (with vanadium halides) may be attributed to the stronger alkylating ability of the latter.

Bound Brook, N. J.

---

[28] Melt index is a measure of melt viscosity and is inversely related to molecular weight. This sample has a molecular weight $\simeq$ 50,000.