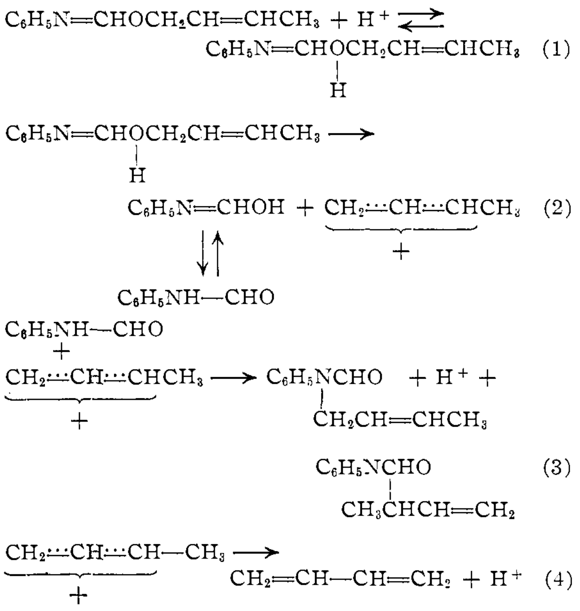
and the higher boiling isomeric N-substituted anilines by fractional distillation. In these reactions in which unsubstituted formanilide was produced, significant amounts of volatile products were evolved during the exothermic reaction. These were collected in a cold trap and were found to be 1,3-butadiene, from α- and γ-methylallyl esters, and isoprene, from β,γ-dimethylallyl ester.

Mixtures containing approximately the same proportion of isomeric N-α-methylallylformanilide and N-γ-methylallylformanilide were produced from both α-methylallyl N-phenylformimidate and γ-methylallyl N-phenylformimidate, with the primary allylic isomer predominating in a ratio of about 4:1. The mixture of isomers obtained by acid-catalyzed rearrangement of β,γ-dimethylallyl N-phenylformimidate also apparently contained the primary allylic isomer in predominant amount, but the characterization of this mixture was not rigorous.

Mechanisms of the Thermal and Acid-catalyzed Rearrangements.—The mechanism of the thermal rearrangement of the allylic N-phenylformimidates is obviously the same as that of the benzimidates, which was described by Mumm and Möller[4] as involving a pseudo-cyclic transition state analogous to that of the *ortho*-Claisen rearrangement. The rearrangement is practically free of side reactions, like that of the aryl N-phenylbenzimidates, but takes place at a much lower temperature. This probably reflects the lower energy of a transition state with a six-membered ring compared to a four-membered ring.[2]

The observed differences in the rearrangements of the allylic N-phenylformimidates produced by the addition of sulfuric acid; *e.g.*, (1) more rapid and exothermic reaction at lower temperatures, (2) production of mixtures of allylic isomers and (3) decomposition into diene and formanilide, are all inconsistent with an intramolecular mechanism and suggestive of carbonium ion or ion-pair intermediates. A mechanism which appears to be reasonable for the reactions in the presence of acid is outlined, using γ-methylallyl N-phenylformimidate as an example.



$$C_6H_5N{=}CHOCH_2CH{=}CHCH_3 + H^+ \rightleftarrows C_6H_5N{=}CH\underset{H}{\underset{|}{O}}CH_2CH{=}CHCH_3 \quad (1)$$

$$C_6H_5N{=}CH\underset{H}{\underset{|}{O}}CH_2CH{=}CHCH_3 \longrightarrow C_6H_5N{=}CHOH + \underbrace{CH_2\text{⋯}CH\text{⋯}CHCH_3}_{+} \quad (2)$$

$$C_6H_5N{=}CHOH \rightleftarrows C_6H_5NH{-}CHO$$

$$C_6H_5NH{-}CHO + \underbrace{CH_2\text{⋯}CH\text{⋯}CHCH_3}_{+} \longrightarrow C_6H_5\underset{CH_2CH{=}CHCH_3}{\underset{|}{N}}CHO + H^+ + C_6H_5\underset{CH_3CHCH{=}CH_2}{\underset{|}{N}}CHO \quad (3)$$

$$\underbrace{CH_2\text{⋯}CH\text{⋯}CH{-}CH_3}_{+} \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + H^+ \quad (4)$$

AUSTIN 12, TEXAS

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO.]

Polymerization of Ethylene with Bis-(cyclopentadienyl)-titanium Dichloride and Diethylaluminum Chloride

BY WENDELL P. LONG AND DAVID S. BRESLOW

RECEIVED AUGUST 31, 1959

The reaction which takes place between bis-(cyclopentadienyl)-titanium dichloride (I) and diethylaluminum chloride has been examined. Spectroscopic evidence has been obtained for the existence of three complexes: $(C_5H_5)_2TiCl_2{\cdot}(C_2H_5)_2AlCl$ (II), $(C_5H_5)_2C_2H_5TiCl{\cdot}C_2H_5AlCl_2$ (III) and $(C_5H_5)_2TiCl{\cdot}C_2H_5AlCl_2$ (IV). A correlation of spectral changes with catalytic activity has indicated that complex III, or some species readily derived from it, is the active catalyst for the polymerization of ethylene.

Introduction

Bis-(cyclopentadienyl)-titanium dichloride, $(C_5H_5)_2TiCl_2$ (I), reacts with alkylaluminum compounds to form soluble catalysts for the low temperature, low pressure polymerization of ethylene.[1-3] Previous reports have described the systems derived from dimethylaluminum chloride[4] and from methylaluminum dichloride.[5] The present paper is concerned with a more detailed study of the diethylaluminum chloride system. From a mechanistic point of view this appears to be the most important system, inasmuch as the reaction of the "sandwich" dichloride (I) with diethylaluminum chloride appears to be essentially independent of the presence of ethylene. The methylaluminum systems, on the other hand, undergo quite different reactions in the absence of monomer, but appear to parallel the diethylaluminum chloride system in the presence of ethylene. Although the Ziegler polymerization of ethylene with heterogeneous catalysts may differ in some details from the polymerization with these soluble catalysts, it is believed that the fundamental mechanism is the same.

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(1) D. S. Breslow, U. S. Patent 2,827,446 (1958).

(2) D. S. Breslow and N. R. Newburg, THIS JOURNAL, **79**, 5072 (1957).

(3) D. S. Breslow and N. R. Newburg, *ibid.*, **81**, 81 (1959).

(4) J. C. W. Chien, *ibid.*, **81**, 86 (1959).

(5) W. P. Long, *ibid.*, **81**, 5312 (1959).

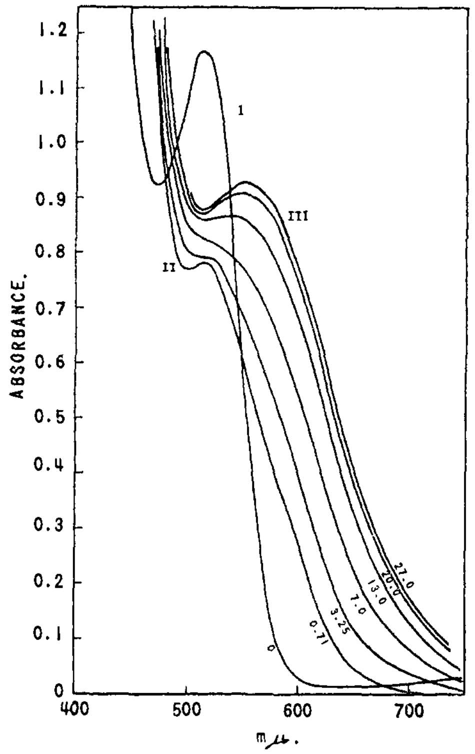

Fig. 1.—Change of spectra with time of 5 millimolar $(C_5H_5)_2TiCl_2$ and 7.5 millimolar $(C_2H_5)_2AlCl$ at 2.3°. Numbers represent time in minutes after mixing.

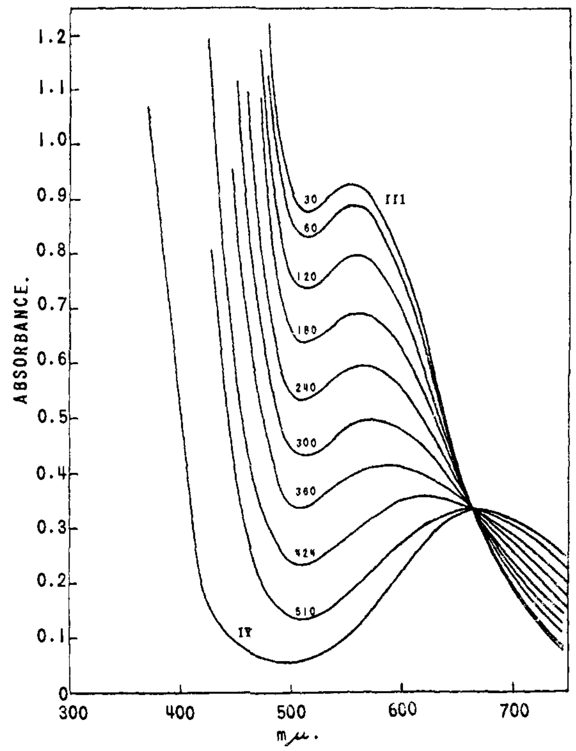

Fig. 2.—Change of spectra with time of 5 millimolar $(C_5H_5)_2TiCl_2$ and 7.5 millimolar $(C_2H_5)_2AlCl$ at 2.3°. Numbers represent time in minutes after mixing.

Experimental

Reagents.—Bis-(cyclopentadienyl)-titanium dichloride was prepared according to the procedure of Wilkinson and Birmingham,[6] and was recrystallized from methylene chloride. Diethylaluminum chloride was prepared according to the procedure of Grosse and Mavity.[7] Solvents were purified as described previously. Phillips Petroleum Co. research grade ethylene was used throughout.

Bis-(cyclopentadienyl)-ethyltitanium Chloride.—To 5.0 g. (20 millimoles) of powdered bis-(cyclopentadienyl)-titanium dichloride as a slurry in 50 ml. of methylene chloride under nitrogen at −30° was slowly added 8 ml. (16 millimoles) of 2 *M* ethylmagnesium chloride in ether; an excess of Grignard should be avoided. The reactants were stirred for 1–2 hours as the temperature was allowed to rise to about 20°. The slurry was centrifuged to remove salts and the solution transferred; solvent was removed and the residue was extracted with heptane to recover product (about 60% yield). The product could be recrystallized readily from aliphatic hydrocarbons, m.p. 92–94°. It may be handled in the air at room temperature, but is best stored at −80°.[8]

Anal. Calcd. for $C_{12}H_{15}TiCl$: C, 59.4; H, 6.23; Ti, 19.7; Cl, 14.6. Found: C, 59.3; H, 6.43; Ti, 19.0; Cl, 14.6.

Spectra.—All spectra were obtained on a Cary model M14 recording spectrophotometer in toluene using 1-cm. cells as described previously.[5]

Interaction of Bis-(cyclopentadienyl)-titanium Dichloride (I) with Diethylaluminum Chloride.—The cell compartment was thermostated either at 30° or at 2.3°. The solution of I in toluene was placed in the cell and allowed to come to thermal equilibrium. Then the solution of $(C_2H_5)_2AlCl$ was injected and the spectrum was scanned repeatedly. Alternatively the spectrophotometer could be set to follow the change at a given wave length. Typical families of curves are given in Figs. 1 and 2.

Comparison of Spectra with Catalytic Activity.—A 3-millimolar solution of bis-(cyclopentadienyl)-titanium dichloride in toluene was treated with diethylaluminum chloride at 0° so that the Al:Ti ratio was 2.5. At various time intervals samples were removed and the concentration of intermediate III was determined by measuring the absorbance at 670 mμ. Simultaneously, samples were pressured with ethylene and the initial polymerization rate was determined. These experiments were carried out during the time interval in which intermediate III was being formed. An identical series was carried out at 30° during the time in which intermediate III was decomposing to IV using the absorbance at 520 mμ. The results of both sets of experiments are shown in Fig. 3.

Discussion

When a solution of bis-(cyclopentadienyl)-titanium dichloride (I) in toluene is treated with diethylaluminum chloride, a series of color changes takes place; the initial orange solution immediately turns red, and then more slowly brown, green and finally blue. It has been demonstrated that the final blue solution contains a complex of $(C_5H_5)_2$-Ti(III)Cl with an alkylaluminum chloride.[3] A plausible mechanism for the reduction might be

$$\underset{I}{2(C_5H_5)_2TiCl_2} + [(C_2H_5)_2AlCl]_2 \rightleftharpoons \underset{II}{2(C_5H_5)_2TiCl_2\cdot(C_2H_5)_2AlCl} \quad (1)$$

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[6] G. Wilkinson and J. M. Birmingham, This Journal, **76**, 4281 (1954).

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

[8] Methylene chloride is an excellent solvent for this reaction. In ether the reaction invariably led to reduction to $(C_5H_5)_2Ti(III)Cl$, while in toluene the yields were low and irreproducible. The reason for the solvent effect is not obvious. Bis-(cyclopentadienyl)-dimethyltitanium appears to undergo an autocatalytic decomposition,[9] and the diethyl compound would be expected to be even less stable. Methylene chloride may either prevent dialkylation or react with the diethyl compound to convert it into the monoethyl derivative. Another alternative is that the decomposition of the ethyl compound is catalyzed by trivalent titanium; $(C_5H_5)_2Ti(III)Cl$ has been found to be oxidized by methylene chloride.

[9] T. S. Piper and G. Wilkinson, *J. Inorg. & Nuclear Chem.*, **3**, 104 (1956).

$$(C_5H_5)_2TiCl_2\cdot(C_2H_5)_2AlCl \rightleftharpoons \underset{\text{III}}{(C_5H_5)_2C_2H_5TiCl\cdot C_2H_5AlCl_2} \quad (2)$$

$$(C_5H_5)_2C_2H_5TiCl\cdot C_2H_5AlCl_2 \longrightarrow \underset{\text{IV}}{(C_5H_5)_2TiCl\cdot C_2H_5AlCl_2} + C_2H_5\cdot \quad (3)$$

In Fig. 1, curve I is the spectrum of uncomplexed bis-(cyclopentadienyl)-titanium dichloride with a maximum at 515 mμ; the compound has a more intense maximum at 388 mμ which was not used in this work. Curve II shows the spectrum scanned 0.7 minutes after mixing the two reagents at 2.3°; even in this short a time most of the original "sandwich" compound has disappeared and a new colored material has been formed. Curve II is at least an approximation of the spectrum of intermediate II. The formation of a complex between the "sandwich" dichloride and diethylaluminum chloride shown in equation 1 is presumably an acid–base reaction and, as such, should be very rapid. If a mixture of the two components is quenched with diethyl ether within a minute of mixing, bis-(cyclopentadienyl)-titanium dichloride is regenerated; diethyl ether is apparently a stronger base than the "sandwich" dichloride and displaces it from the complex. Spectroscopically, curve II cannot represent a mixture of the "sandwich" dichloride and the species whose spectrum is represented by curve III because, if it were, curve II should not fall below that of III in the 500–530 mμ region. Over a period of about 30 minutes at this temperature, curve II is transformed into curve III shown in Fig. 1. The species responsible for curve III is relatively stable at low temperatures and is slowly converted into still another complex whose spectrum is shown by curve IV in Fig. 2. The evidence that curve III is the spectrum of complex III is as follows. Addition of diethyl ether at this point in the reaction gives a material whose spectrum is essentially the same as that of bis-(cyclopentadienyl)-ethyltitanium chloride. Furthermore, addition of ethylaluminum dichloride to bis-(cyclopentadienyl)-ethyltitanium chloride gives a complex whose spectrum is very close to curve III.

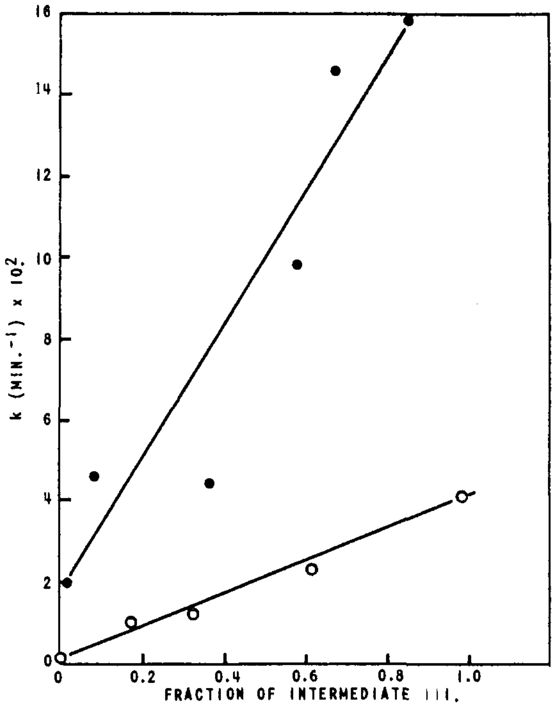

Fig. 3.—Initial polymerization rate as a function of intermediate III concentration: ○, formation at 0°; ●, decomposition at 30°.

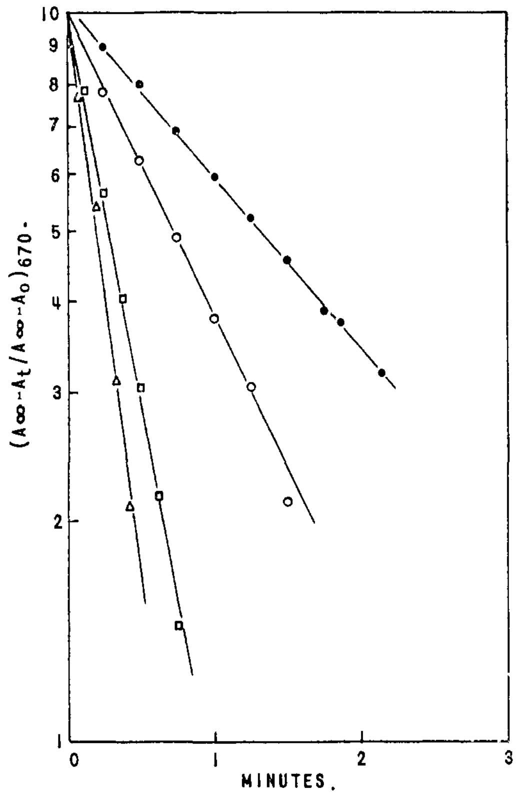

Fig. 4.—Rate of formation of intermediate III at 30°, $(C_2H_5)_2AlCl$ concn. 5.8 millimolar, $(C_5H_5)_2TiCl_2$ concn.: ●, 5.8 millimolar; ○, 2.9; ■, 1.45; △, 0.72.

The isosbestic point in Fig. 2 indicates that there are only two colored species present, one responsible for curve III and one for curve IV. The material responsible for curve IV is stable indefinitely at room temperature in the absence of oxygen. Addition of diethyl ether liberates $(C_5H_5)_2Ti(III)Cl$, and addition of either diethylaluminum chloride or ethylaluminum dichloride to the trivalent "sandwich" compound gives a complex whose spectrum is almost identical with curve IV. There can be little doubt, therefore, that curve IV represents either species IV or a complex of the trivalent titanium compound with some other alkylaluminum compound. Thus, the spectroscopic evidence indicates that there are only four colored materials present, and it seems reasonable to assign structures to them as shown in equations 1–3.

Kinetic data indicate that the reactions are not so simple as outlined in equations 1–3. It is possible to determine the rate of formation of complex III by the increase in absorbance at 670 mμ. The choice is convenient in that the absorption of any decomposition product is the same as that of

TABLE I

RATE OF FORMATION AND DECOMPOSITION OF INTERMEDIATE III IN TOLUENE AT 30°

[Ti] $\times 10^3$, moles/l.	[Al] $\times 10^3$, moles/l.	Al:Ti ratio	$t_{1/2}$ (form.), sec.	$k_{obs} \times 10^2$, sec.$^{-1}$	$k_1 \times 10^2$, sec.$^{-1}$	$k_2 \times 10^2$, sec.$^{-1}$	$t_{1/2}$ (dec.), min.
2.97	1.8	0.6	54.6	1.27	1.27	..	19.5
2.96	3.3	1.1	54.0	1.28	1.28	..	10.7
2.96	3.3	1.1	69.0	1.01	1.01	..	8.2
2.94	5.8	2	39.0	1.78	..	0.67	13.1
2.88	11.6	4	21.0	3.30	..	.73	9.8
2.83	16.0	6	14.4	4.82	..	.74	8.7
5.80	5.8	1	78.0	0.89	0.89	..	24.5
2.90	5.8	2	42.6	1.63	..	0.52	10.9
1.45	5.8	4	20.4	3.40	..	.76	5.0
0.72	5.8	8	12.6	5.50	..	.63	4.7
				Av.	1.11	0.68	

the intermediate complex being followed. Its decomposition to the trivalent titanium complex IV can be followed conveniently at 520 mμ or at 750 mμ.

Table I shows the effect of varying the aluminum concentration at constant titanium concentration and the effect of varying the titanium concentration at constant aluminum concentration. The rate of formation of complex III appeared to be strictly first order with respect to the appearance of colored species; typical results are shown in Fig. 4. It is quite apparent that the formation of intermediate III is accelerated by increasing amounts of diethylaluminum chloride. The reaction follows the over-all rate equation

$$\frac{d\,[\mathrm{III}]}{dt} = k_1[\mathrm{II}] + k_2[\mathrm{II}]\,\frac{[\mathrm{Al_{ex}}]}{[\mathrm{Ti_0}]}$$

where $[\mathrm{Al_{ex}}]$ is the concentration of diethylaluminum chloride over and above that required to form a 1:1 complex, and $[\mathrm{Ti_0}]$ the initial concentration of bis-(cyclopentadienyl)-titanium dichloride. Inasmuch as these terms are constant during a run, it is apparent that the individual runs should follow first-order kinetics. Thus it appears that intermediate III can be formed by two simultaneous reactions. One involves a transfer of ethyl from aluminum to titanium in complex II, while the second involves a reaction of complex II with the excess diethylaluminum chloride; this might be analogous to an SN2 reaction.[3] Although the data are quite imprecise, probably as a result of the extreme sensitivity of the reagents to impurities, an attempt was made to evaluate the two rate constants. The observed rate constants, calculated from the first order half-lives, would be equal to k_1 at Al:Ti ratios of one or less if the complexing were essentially complete. This assumption appears to be justified by the k_{obs} of the one run carried out below a 1:1 ratio; it is unfortunate that more data were not obtained at low ratios. The average k_1 of the four runs indicated in Table I, 1.11×10^{-2} sec.$^{-1}$, was then used to calculate k_2 from the relationship $k_2 = (k_{obs} - k_1)\,([\mathrm{Ti_0}]/[\mathrm{Al_{ex}}])$; the constancy is about as good as can be expected from the data. The average k_2, 0.68×10^{-2} sec.$^{-1}$, indicates that the alkylation by the two routes occurs at comparable rates, the bimolecular reaction becoming more important at higher Al:Ti ratios.

The titanium term in the denominator is required to account for the increase in rate with decreasing titanium concentration. There are several possible explanations for the unusual dependence on the titanium concentration. It has been found that solutions of bis-(cyclopentadienyl)-titanium dichloride in toluene do not obey Beer's law, indicating perhaps a degree of association or ionization which is dependent on concentration. A second factor was discovered during the investigation of the reaction of bis-(cyclopentadienyl)-titanium dichloride with dimethylaluminum chloride, which is not complicated by a reduction step. Here it was found that the complexes analogous to II and III undergo dissociation to a certain extent, so that there are present, in addition to the complexes, $(C_5H_5)_2TiCl_2$, $(C_5H_5)_2CH_3TiCl$, $(CH_3)_2AlCl$ and CH_3AlCl_2. Although the dissociated materials in the diethylaluminum chloride system are apparently present in concentrations too low to be determined spectroscopically there can be little doubt that they are present. It is not surprising, therefore, in view of the numerous compounds present and equilibria involved, that the kinetic equation for the formation of complex III is not a simple one.

These same factors might account for the unusual kinetics observed in the decomposition of complex III, *i.e.*, its reduction to complex IV. From Table I it is obvious that at constant titanium concentration the rate of decomposition is essentially independent of the aluminum concentration, at least above Al:Ti ratios of one. At constant aluminum concentration, however, the rate of decomposition increases as the titanium concentration decreases. Furthermore, in the series of reactions there is a change in kinetic order; at high titanium concentrations the reaction is zero order in complex, while at low titanium concentrations the reaction is first order, as illustrated in Figs. 5 and 6.[10] Although equation 3 has been written as involving the unimolecular elimination of an ethyl radical, this is not necessarily valid. Cotton[11] has classified three types of cleavage of transition metal alkyls: unimolecular cleavage to give alkyl radicals, a bimolecular reaction to give disproportionated products, and a bimolecular reaction to give coupled products; presumably the last two do not involve the formation of free radicals. It has also been stated[12] that alkyltitanium trichlorides decompose only in a bimolecular reaction by disproportionation of the two alkyl groups to an olefin and an alkane. Natta, Pino, Mazzanti and Giannini[13] reported, in agreement with this statement, that the reaction of bis-(cyclopentadienyl)-titanium dichloride with triethylaluminum in the presence of a small amount of *n*-heptane yielded equimolar amounts of ethane and ethylene. We have found, however, that with diethylaluminum chloride the gas evolved is predominantly ethane and contains no ethylene.[3] Although

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(10) Plots of the data in Fig. 2 shows clean zero-order kinetics using the absorbance at any wave length between 487 and 750 mμ. Wave lengths above 700 mμ are especially meaningful, inasmuch as both species I and II show essentially no absorbance in this region.

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

(12) C. van Heerden, *J. Polymer Sci.*, **34**, 47 (1959).

(13) G. Natta, P. Pino, G. Mazzanti and U. Giannini, *J. Inorg. & Nuclear Chem.*, **8**, 612 (1958).

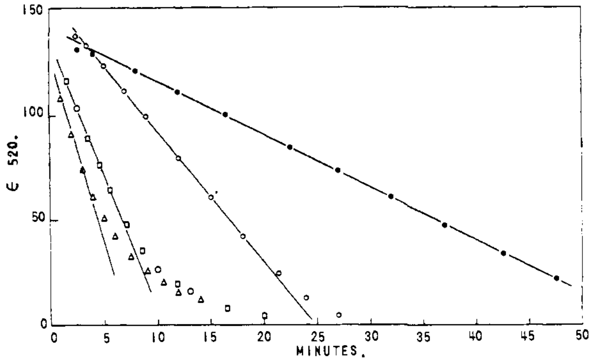

Fig. 5.—Zero-order plot of the decomposition of intermediate III at 30°, $(C_2H_5)_2AlCl$ concn. 5.8 millimolar; $(C_5H_5)_2TiCl_2$ concn.: ●, 5.8 millimolar; ○, 2.9; □, 1.45; Δ, 0.72.

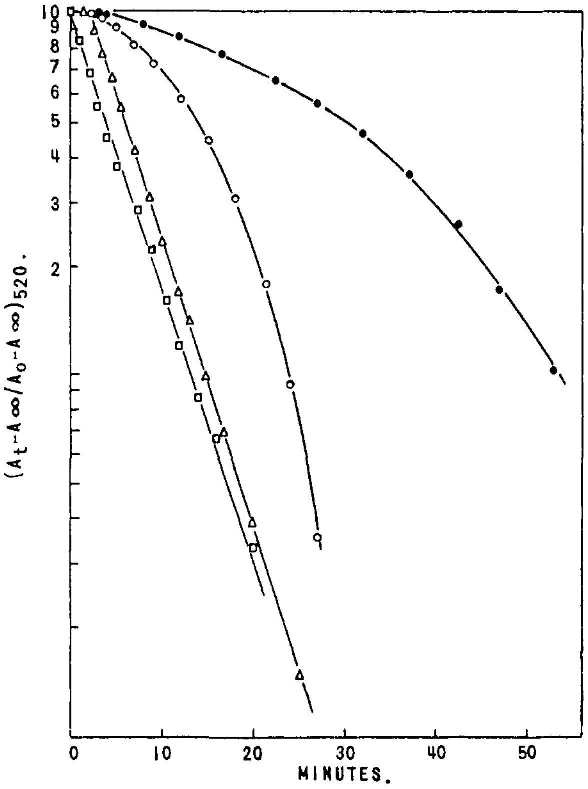

Fig. 6.—First-order plot of the decomposition of intermediate III at 30°, $(C_2H_5)_2AlCl$ concn. 5.8 millimolar; $(C_2H_5)_2TiCl_2$ concn.: ●, 5.8 millimolar; ○, 2.9; □, 1.45; Δ, 0.72.

ethylene, if formed, would undoubtedly have polymerized under our conditions, the amount of gas evolved using a large amount of toluene as a solvent was too great for the reaction to be exclusively one of disproportionation. Apparently the nature of the solvent and the experimental conditions have some effect on the course of the reaction.

Evidence had been presented in previous papers[2,3] that some tetravalent titanium must be present for soluble catalysts derived from bis-(cyclopentadienyl)-titanium dichloride to show their high activity. In an attempt to identify the active catalytic species, a comparison was made between the concentration of intermediate III and the initial rate of polymerization of ethylene. This was done both during the formation of complex III and during its decomposition (see Experimental section). As can be seen in Fig. 3, there is a reasonably good correlation between intermediate III concentration and initial polymerization rate, although there is considerable scatter in the decomposition curve. It seems reasonable to conclude from these results that the active catalyst in this system is complex III, to which we have assigned the structure $(C_5H_5)_2C_2H_5TiCl{\cdot}C_2H_5AlCl_2$, or some species in equilibrium with it or readily derived from it. If our assumption is correct that the mechanism of olefin polymerization is fundamentally the same with heterogeneous catalysts, the active ingredient in Ziegler polymerization is an alkylated transition metal compound complexed with a Lewis acid, such as $(C_2H_5)_2AlCl$, $AlCl_3$, $TiCl_4$, $TiCl_3$ and the like.

Acknowledgments.—We are indebted to Drs. H. M. Spurlin, H. G. Tennent and H. Boardman for many stimulating discussions.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Condensation of Phenylacetic Acid with Certain Ketones to Form α-Phenyl-β-hydroxy Acids by Alkali Amides. Equilibrium Factors[1]

BY PHILLIP J. HAMRICK, JR.,[2] AND CHARLES R. HAUSER

RECEIVED AUGUST 31, 1959

The disodio and dilithio salts of phenylacetic acid, prepared by means of two equivalents of sodium amide or lithium amide in liquid ammonia, were condensed with benzophenone and with cyclohexanone to form the corresponding α-phenyl-β-hydroxy acids. Yields up to 93% were realized for both acids, but a metallic cation effect was observed in the condensations with cyclohexanone in which the yield was better with lithium amide than with sodium amide. The monosodium salts of the β-hydroxy acids were cleaved in aqueous solution to regenerate the corresponding ketone and sodium phenylacetate. Consideration is given to the factors governing the condensation and cleavage.

It has previously been shown that phenylacetic can be alkylated[3] or added conjugatively to certain α,β-unsaturated carbonyl compounds[4] by means of sodium amide in liquid ammonia. Examples of

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(1) Supported by the Office of Ordnance Research, U. S. Army.

(2) Department of Chemistry, Wake Forest College.

(3) C. R. Hauser and W. J. Chambers, THIS JOURNAL, **78**, 4942 (1956).

(4) C. R. Hauser and M. T. Tetenbaum, *J. Org. Chem.*, **23**, 1146 (1958).