total amount of gas was liberated. The solid was collected under nitrogen, washed with methanol and ether, and dried.

Anal. Calcd. for $Ni(CH_2{=}CHCN)_2$: Ni, 35.62; acrylonitrile, 64.38.

Acrylonitrile was determined by careful thermal decomposition of the nickel complex in a high vacuum apparatus. The volatile fraction was weighed and identified by infrared analysis as pure acrylonitrile.

Found: Ni, 35.3, 35.6; acrylonitrile, 63.3, 60.2.

Preparation of the Complex of $PdCl_2$ with Acrylonitrile.—Palladium dichloride (1 g.) was dissolved in hot acrylonitrile, and the solution was filtered. Diethyl ether was added, and the solution was cooled to about −40°, whereby yellow crystals appeared. The complex is not very stable and loses acrylonitrile slowly at room temperature.

Anal. Calcd. for $PdCl_2(NC{-}CH{=}CH_2)_2$: Pd, 37.5; Cl, 25.0. Found: Pd, 37.5; Cl, 26.3.

Preparation of Bis-acrylonitrile Nickel Triphenylphosphine.—Freshly prepared bis-acrylonitrile nickel (2.5 g.) was suspended under nitrogen in a solution of 4 g. of triphenylphosphine in 40 ml. of ether and was refluxed for 3 hours. The red starting material was slowly converted into a yellow powder. This was filtered, washed with ether, and dried under exclusion of oxygen. When heated in a sealed tube, it decomposed into acrylonitrile, triphenylphosphine and nickel at 185°.

Anal. Calcd. for $Ni(CH_2{=}CHCH)_2P(C_6H_5)_3$: Ni, 13.75; P, 7.3; N, 6.3. Found: Ni, 13.8, 13.9; P, 7.3; N (Kjeldahl), 6.1.

Preparation of Heptatrienenitrile with Bisacrylonitrile Nickel as Catalyst.—The conditions were essentially the same as described by Cairns, *et al.*,[1] except that the bisacrylonitrile nickel was employed as catalyst. The reaction was carried out at 75° and 13.5 atm. and required no induction period. The resulting heptatrienenitrile boiled at 53° (2–3 mm.). Its infrared and ultraviolet spectra were identical with those reported for heptatrienenitrile.[3]

Anal. Calcd. for C_7H_7N: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.92; H, 6.72; N, 13.19.

Cycloöctatetraene from Acetylene and Bisacrylonitrile Nickel.—Freshly prepared bisacrylonitrile nickel (1 g.) was suspended in 50 ml. of dry tetrahydrofuran and was allowed to react under the usual precautions,[7] in a stainless steel rocker bomb (500 ml.) at 80–85° and 20.4 atm. acetylene pressure for 18 hours. The lowest boiling fractions (after filtration from a polymeric resin-like material (polyacetylene) and removal of the solvent) consisted mainly of cyclooctatetraene as evidenced by comparison of the infrared spectra with an authentic sample and vapor-phase chromatography. A small amount of a higher-boiling fraction was found to consist of a complicated mixture (vapor-phase chromatography) and was not examined further.

Infrared analysis was performed on a Beckman IR 4 Instrument.

Compound	State	—C≡N, cm.$^{-1}$	Vinyl absorption (900–1000 cm.$^{-1}$)
Acrylonitrile	Liquid	2245	Present
$Ni(CH_2{=}CHCN)_2$	Solid (in Nujol)	2220	Absent
$Ni(CH_2{=}CHCN)_2P(C_6H_5)_3$	Solid (in Nujol)	2180	Absent
$PdCl_2(NCCH{=}CH_2)_2$	Solid (in Nujol)	2290	Present

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(7) W. Reppe, "Neue Entwicklungen auf dem Gebiet der Chemie des Acetylens und Kohlenoxyds," Springer, 1949, pp. 137–138.

DAYTON 7, OHIO

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

Complexes of Aluminum Chloride and Methylaluminum Dichloride with Bis-(cyclopentadienyl)-titanium Dichloride as Catalysts for the Polymerization of Ethylene[1]

BY WENDELL P. LONG

RECEIVED MAY 4, 1959

The interactions of bis-(cyclopentadienyl)-titanium dichloride, $(C_5H_5)_2TiCl_2$, with aluminum chloride and with methylaluminum dichloride have been followed spectrophotometrically. In each case two complexes are formed, the first at a ratio of one Al per Ti and the second at a higher ratio. Only acid-catalyzed polymerization was observed with $(C_5H_5)_2TiCl_2$ and aluminum chloride, whereas linear polyethylene was obtained with methylaluminum dichloride. The initial rate of polymerization paralleled the spectroscopic concentration of the first complex. The active catalyst is discussed.

A few years ago Ziegler[2] gave great impetus to the field of low-pressure, ordinary temperature polymerization of 1-olefins. Since his release of information there has been a heavy concentration of effort to commercialize such polymerizations; considerable effort also has been made to explain the mechanism of this type of reaction.

As ordinarily used, the Ziegler process involves activated catalyst particles dispersed in an inert medium. Activity is subject to many factors: the metals used, their valence states and ligands; the catalyst history; the temperature and pressure; and the monomer. For mechanism studies, the most difficult variable is the solid surface of the catalyst. For the present study, this problem has been avoided by the choice of a completely soluble catalyst based on bis-(cyclopentadienyl)-titanium dichloride (I), $(C_5H_5)_2TiCl_2$.

The catalyst based on I was first reported by Breslow.[3] Natta[4] and his co-workers have used the compound and some of its derivatives in their mechanism studies. In the presence of triethylaluminum or diethylaluminum chloride, I is reduced rapidly to complexes of trivalent titanium. The high degree of catalytic activity for ethylene polymerization associated with the compound is dependent on the presence of a transitory complex of tetravalent titanium[3a]; the trivalent state is very much less active.

Complexes of I with methylaluminum compounds are much more stable than the corresponding ethyl derivatives. For this reason, the methyl derivatives have been used for the study reported here. Information has been obtained which correlates catalyst structure with catalytic activity.

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(1) Presented in part before the Delaware Science Symposium, Newark, Del., February 14, 1959, and at the Symposium on Stereospecific Polymerization at the 135th National Meeting of the American Chemical Society, Boston, Mass., April 5–10, 1959.

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

(3) (a) D. S. Breslow, Belgian Patent 551,283 (1957), U. S. Patent 2,827,446 (1958); (b) D. S. Breslow and N. R. Newburg, THIS JOURNAL, **79**, 5072 (1957); **81**, 81 (1959).

(4) G. Natta, P. Pino, G. Mazzanti, U. Giannini, E. Mantica and M. Peraldo, *Chim. e ind. (Milan)*, **39**, 19 (1957); *J. Polymer Sci.*, **26**, 120 (1957).

Experimental

Materials.—Bis-(cyclopentadienyl)-titanium dichloride was prepared by the method of Wilkinson and Birmingham.[5] Baker and Adamson anhydrous sublimed aluminum chloride was ball-milled in *n*-heptane in steel mills and used as the dispersion. Methylaluminum dichloride was prepared in *n*-heptane solution by addition of aluminum chloride to trimethylaluminum obtained from Rocky Mountain Research; the analysis of four solutions, normalized to Al, was 1.00 Al, 2.01 ± 0.08 Cl, 0.99 ± 0.03 CH_3. Toluene was treated as described by Chien[6]; it was transferred by hypodermic syringe. Phillips research grade ethylene analyzed to be 99.96^+ % pure was used throughout. Linde Seaford grade nitrogen was used directly.

Bis-(cyclopentadienyl)-methyltitanium Chloride (VI).[7]—Into a nitrogen-filled, 200-ml. capped Pyrex centrifuge bottle containing 5.00 g. (20 mmoles) of I was injected 10 ml. (20 mmoles) of a 2.0 *M* solution of methylmagnesium chloride in ether. The bottle was shaken overnight. After centrifugation, the liquor was removed and taken to dryness to give 4.33 g. of crude product. The product was recrystallized from heptane and then from methylcyclohexane. The compound is stable in air at room temperature for several weeks.

Anal. Calcd. for $(C_5H_5)_2CH_3TiCl$: C, 57.7; H, 5.73; Cl, 15.51; Ti, 20.95. Found: C, 57.3; H, 5.64; Cl, 15.47; Ti, 20.2.

Spectra.—All spectra were taken with a Cary M14 spectrophotometer. The cells were fitted with a T-tube opening so that solutions could be introduced through rubber stopples with hypodermic syringes. A steady purge of nitrogen was maintained through the upper tube during use.

Interaction of Aluminum Chloride with I.—Compound I has a spectrum with absorption maxima at 388 and at 515 mμ, Fig. 1 (curve I). As aluminum chloride was added to the 5.0 millimolar solution in toluene, a new maximum at 580 mμ was produced, Fig. 1 (curve II). The change required approximately 1.2 Al:Ti for completion. At lower concentrations, a simultaneous change from the peak at 388 mμ to one at 410 mμ was also observed. Larger amounts of aluminum chloride gave another species having an absorption maximum at 475 mμ (Fig. 2, curve III).

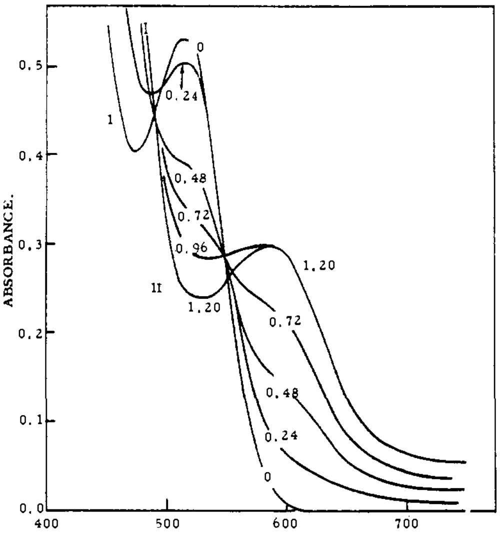

Fig. 1.—Interaction of 5.0 millimolar $(C_5H_5)_2TiCl_2$ with ≤ 1.2 $AlCl_3$ in toluene, 0.5-cm. cell; numbers indicate Al:Ti ratios.

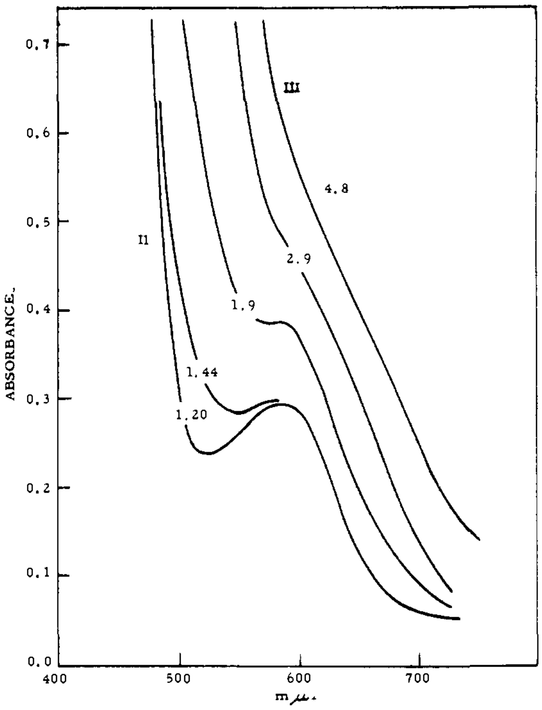

Fig. 2.—Interaction of 5.0 millimolar $(C_5H_5)_2TiCl_2$ with >1 $AlCl_3$ in toluene, 0.5-cm. cell; numbers indicate Al:Ti ratios.

In the case of aluminum chloride with I a brown flocculent precipitate slowly appeared. Spectra were taken within 3 minutes of the mixing of the components so that the precipitate would be entirely negligible. Addition of ether, even after much solid had formed, gave a clear solution with a spectrum identical with I.

Attempts to isolate the species II and III led only to dark-colored oils.

Interaction of Methylaluminum Dichloride with I.—To 2.0 ml. of 3.0 millimolar I in a 0.5-cm. cell were added 0.030-ml. portions of methylaluminum dichloride solutions in toluene. The change from the 515 mμ band of I to the new peak at 575 mμ is shown in Fig. 3 (curve IV). As more methylaluminum dichloride was added, the spectrum

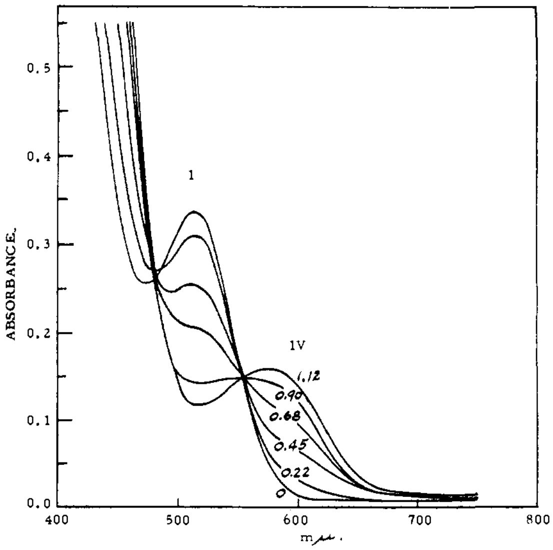

Fig. 3.—Interaction of 3.0 millimolar $(C_5H_5)_2TiCl_2$ with ≤ 1.1 CH_3AlCl_2 in toluene, 0.5-cm. cell; numbers indicate Al:Ti ratios.

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

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

(7) I am indebted to Dr. N. C. MacArthur for the preparation of this sample by a modification of the procedure described by Farbwerke Hoechst A.G.[8]

(8) German Patent DAS 1,037,446 (1958).

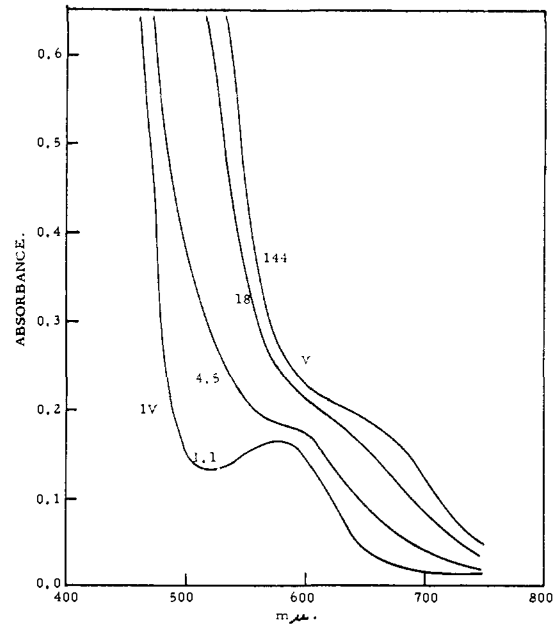


Fig. 4.—Interaction of 3.0 millimolar $(C_5H_5)_2TiCl_2$ with >1 CH_3AlCl_2 in toluene, 0.5-cm. cell; numbers indicate Al:Ti ratios.

changed to a new peak at approximately 480 mμ (Fig. 4, curve V). For this series there was a change in solvent from toluene to 30% heptane introduced by the stock solutions of methylaluminum dichloride in heptane. At concentrations of I more dilute than 3 millimolar larger ratios of Al were required for complete complex formation.

Interaction of Aluminum Chloride with VI.—Compound VI has no absorption maxima in the visible region (Fig. 5, curve VI). As aluminum chloride was added to a 5.0 millimolar solution of VI in toluene, an absorption maximum at 580 mμ was obtained at a ratio of 1 Al:Ti. With additional aluminum chloride the spectrum changed with formation of a band at 475 mμ.

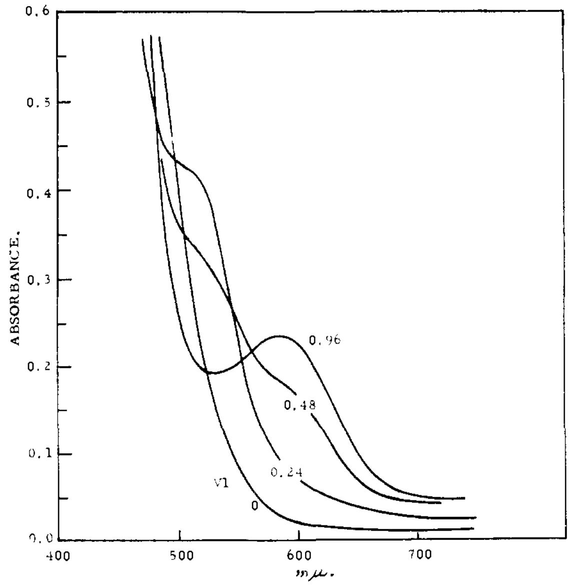


Fig. 5.—Interaction of 5.0 millimolar $(C_5H_5)_2CH_3TiCl$ with ≤1 $AlCl_3$ in toluene, 0.5-cm. cell; numbers indicate Al:Ti ratios.

Polymerization.—All polymerizations were run in 250-ml. magnetically stirred crown-neck bottles sealed by a metal cap with punched holes and a neoprene liner. An Ashcroft-type 1014 pressure gage coupled to a hypodermic needle was used to measure pressure. To the nitrogen-flushed bottle were added 50 ml. of toluene and the catalyst components as standard solutions in toluene or heptane. Nitrogen was removed and ethylene was introduced to the desired pressure. Rates were determined by the time required for pressure to drop a standard amount while flow was interrupted.

All attempts to polymerize ethylene with I and aluminum chloride resulted only in small amounts of oil.

Rates for polymerization with I and methylaluminum dichloride at 30° and 10 lb. per sq. in. of ethylene are given in Fig. 6. The runs were quenched with ethanol at 20 minutes reaction time; during this time the rate remained relatively constant or, for the very low catalyst concentrations, showed some increase. Reduced specific viscosity (r.s.v.) was determined for 0.1% solutions in decalin at 135°; the values of r.s.v. decreased with increasing Ti concentration; for the maximal points given in Fig. 6, the values were 0.3 millimolar Ti, 1.5; 1.0 millimolar, 0.9; 3.0 millimolar, 0.6; 8.0 millimolar, 0.4.

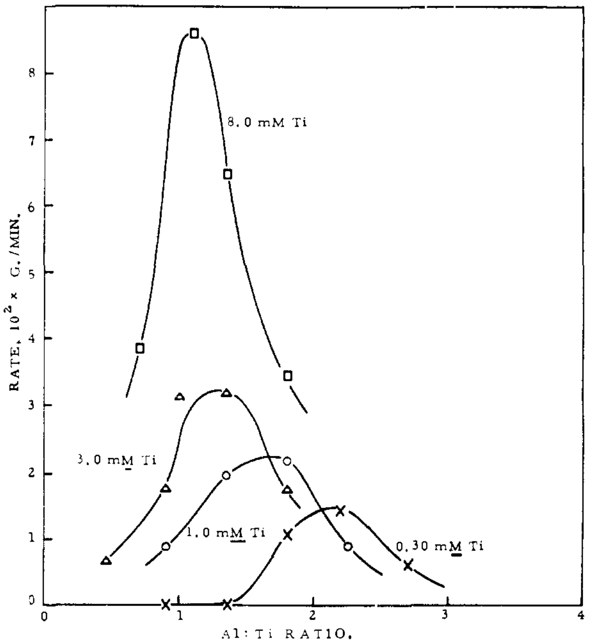


Fig. 6.—Rate of polymerization of ethylene in toluene at 30° with 10 lb. per sq. in. of ethylene; catalyst: $(C_5H_5)_2TiCl_2$-CH_3AlCl_2; Ti concentration: X, 0.30 millimolar; O, 1.0 millimolar; △, 3.0 millimolar; □, 8.0 millimolar.

The polyethylene produced was very highly linear. For an r.s.v. of 1.5, methyl content varied in the range 0.05-0.20 % and melting point was 134-136°.

Decrease in Methyl Concentration during Polymerization.—Bottles were prepared as previously, but at much higher than normal catalyst concentrations in order to obtain larger amounts of methane. At the preset quenching time, ethylene was pumped out of the bottle, nitrogen admitted, and then ethanol added. Evolved methane was determined by mass spectrometry. Data are given in Table I.

TABLE I

METHANE IN QUENCH GAS OF BIS-(CYCLOPENTADIENYL)-TITANIUM DICHLORIDE-METHYALUMINUM DICHLORIDE POLYMERIZATION OF ETHYLENE

Quench time, min.	Rate at quench / Initial rate	CH_4 evolved / CH_4 evolved originally	Polymer G.	R.s.v.
0	1.0	1.0	..	..
4.0	0.73	0.58	1.53	0.5
20.3	.25	.14	5.03	0.5
85.0	.01	.04	7.62	1.0

Discussion

The simplest complexes of I with an aluminum compound are those with aluminum chloride. Although these are not catalysts for the low-pressure polymerization of ethylene, they do provide essential references. The reactions may be expressed by eq. 1 and 2. There is only simple complex formation; if ether is added, the complexes are destroyed and I is recovered. Because the aluminum compounds are transparent in the visible region, any change in the spectrum arises from a change in the bis-(cyclopentadienyl)-titanium chromophore. The proposed structures involve charge separation to make titanium more positive and aluminum less so. The extent of ionization is unknown, but sufficient change must occur to give the new chromophore.

$$\underset{\text{I}}{(C_5H_5)_2TiCl_2} + {}^1/_2Al_2Cl_6 \rightleftharpoons \underset{\text{II}}{{}^+[(C_5H_5)_2TiCl(AlCl_4)]^-} \quad (1)$$

$$\text{II} + {}^1/_2Al_2Cl_6 \rightleftharpoons \underset{\text{III}}{{}^{++}[(C_5H_5)_2Ti(AlCl_4)_2]^=} \quad (2)$$

A formula of $(C_5H_5)_2TiClAl_2Cl_7$ for II is undesirable because of the Al:Ti ratio required for the reactions; it also is undesirable for III because a distant change in the anion should not alter the cationic chromophore. However, there is no reason to exclude $(C_5H_5)_2Ti(Al_2Cl_7)_2$ for III.

When one chlorine on the aluminum is replaced by a methyl group, the spectroscopic behavior appears to be unchanged. There is first a 1:1 complex and then a higher one, as in eq. 3 and 4.

$$\underset{\text{I}}{(C_5H_5)_2TiCl_2} + {}^1/_2(CH_3)_2Al_2Cl_4 \rightleftharpoons \underset{\text{IV}}{{}^+[(C_5H_5)_2TiClCH_3AlCl_3]^-} \quad (3)$$

$$\text{IV} + {}^1/_2(CH_3)_2Al_2Cl_4 \rightleftharpoons \underset{\text{V}}{{}^{++}[(C_5H_5)_2Ti(CH_3AlCl_3)_2]^=} \quad (4)$$

Because of the equilibrium, at very low titanium concentrations, the maximum concentration of the 1:1 complex IV occurs at actual ratios higher than 1:1. The reactions are simple complex formations; addition of ether restores I. Cleavage by ether also indicates that no more than a few per cent. of the methyl groups have been transferred from aluminum to titanium. Had transfer occurred, ether cleavage would give $(C_5H_5)_2CH_3TiCl$, as in the preparation of this compound from I and dimethylaluminum chloride[8] or as in the preparation of methyltitanium trichloride from titanium tetrachloride and dimethylaluminum chloride.[9]

The chromophore is quite sensitive to the ligands. There is a pronounced spectral shift even in the halide derivatives. Substitution of a methyl for chlorine on the titanium completely changes the spectrum. A methyl bridge in IV or V would be unlikely to produce the same spectrum as II or III. If the complexes II through V involve bridging, the bridges are Ti–Cl–Al.

If the original situation is reversed so that the methyl starts on the titanium, a new system results. Only at a ratio of 1:1 aluminum to titanium does the mixture become similar to the 1:1 material prepared from I with methylaluminum dichloride.

As a polymerization catalyst, the combination of I with methylaluminum dichloride is very effective under typical low-pressure conditions. As shown in Fig. 6, for a given titanium concentration there is an optimum Al:Ti ratio to produce maximum initial rate. The pronounced rate maxima occur very close to the maximum concentration of IV in the spectrum (Table II). This close correspondence shows that the species responsible for the polymerization either is IV or is readily derived from it.

TABLE II

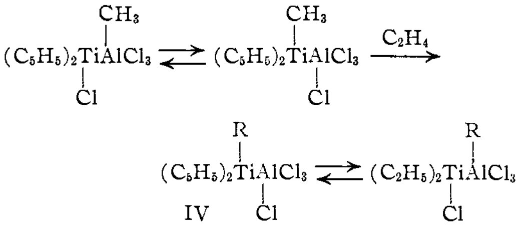
COMPARISON OF Al:Ti RATIOS FOR MAXIMUM RATE AND MAXIMUM CONCENTRATION OF IV

Ti, mmoles/l.	Al:Ti for max. rate	Al:Ti for max. concn. of IV
0.3	2.2	..
1.0	1.8	2.1
3	1.35	1.2
5	..	1.1
8	1.1	..

The data of Table I indicate that IV is not the active catalyst. Because the propagation step in the polymerization is rapid, were IV the same as any propagating site the methyl content should decrease to zero almost immediately. Instead, it falls gradually. Therefore, the true catalyst is in equilibrium with IV, but is present to only a small extent. Comparison of spectrum IV with II, allowing for the difference in concentration and for the formation of solids, shows that the two are essentially identical. Concentration of another species would be limited to the range covered by experimental error and would be of the order of 1 to 2%.

Trimethylaluminum and dimethylaluminum chloride alkylate I very readily. Methylaluminum dichloride should also alkylate I, although the extent would be small and, in this work, spectroscopically undetectable. It is suggested that the active catalyst present in equilibrium with IV is an alkylated titanium of the type $[(C_5H_5)_2CH_3TiAlCl_4]$.

The methyl content of the catalyst does decrease more rapidly than does the rate of polymerization (Table I). An exchange reaction as expressed in eq. 5 is indicated. An exchange of this type has been studied by Chien[3] for the catalyst composed of I and dimethylaluminum chloride. Catalyst is formed in equilibrium with IV and may grow to long chains in the presence of ethylene. The chain may be transferred to an inactive but unterminated position on aluminum; however, it may return to titanium to continue to grow again.



$$(C_5H_5)_2\underset{\text{Cl}}{Ti}\overset{\text{CH}_3}{Al}Cl_3 \rightleftharpoons (C_5H_5)_2\overset{\text{CH}_3}{Ti}\underset{\text{Cl}}{Al}Cl_3 \xrightarrow{C_2H_4} \underset{\text{IV}}{(C_5H_5)_2}\overset{\text{R}}{Ti}\underset{\text{Cl}}{Al}Cl_3 \rightleftharpoons (C_2H_5)_2\underset{\text{Cl}}{Ti}\overset{\text{R}}{Al}Cl_3 \quad (5)$$

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[9] Farbwerke Hoechst A.G., Belgian Patent 553,447 (1957).

Acknowledgment.—The author is indebted to Mr. R. E. Homer for his assistance in carrying out the experimental work and to members of the Research Center staff for their discussions of the work and their aid in the preparation of this manuscript.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE INSTITUTE FOR CHEMICAL RESEARCH, KYOTO UNIVERSITY, JAPAN]

Kinetics of the Reaction of the Ethylene–Mercuric Acetate Addition Compound with Anisole

BY KATSUHIKO ICHIKAWA, KOICHI FUJITA AND HAJIME OUCHI

RECEIVED APRIL 17, 1959

The kinetics of the reaction of the ethylene–mercuric acetate addition compound with anisole to form β-(*p*-methoxyphenyl)-ethyl mercuric acetate in acetic acid under perchloric acid catalysis has been found to be second order in both reactants. It is concluded that the essential role of the catalyst is not specific attack on the addition compound but its acidity.

The reactions of the ethylene–mercuric acetate addition compound (β-acetoxyethyl mercuric acetate) with aromatics to form β-arylethyl mercuric acetates were reported previously.[1] For example

$$\mathrm{AcOCH_2CH_2HgOAc + CH_3OC_6H_5 \longrightarrow CH_3OC_6H_4CH_2CH_2HgOAc + HOAc} \quad (1)$$

Since this is a new type of Friedel–Crafts reaction and proceeds under very mild conditions, it was desirable to study the kinetics in the hope of a quantitative approach to the reaction mechanism. This paper describes the results of a kinetic study of reaction 1 in acetic acid under perchloric acid catalysis. Under these conditions the reaction mixture is homogeneous.

It is well known that RHgZ can be titrated with thiocyanate. With the ethylene–mercuric acetate addition compound, however, these two reactions are possible

$$\mathrm{AcOCH_2CH_2HgZ + KSCN = AcOCH_2CH_2HgSCN + KZ} \quad (2)$$

$$\mathrm{AcOCH_2CH_2HgZ + 2KSCN = CH_2CH_2 + Hg(SCN)_2 + KOAc + KZ} \quad (3)$$

Reaction 2 cannot be used to follow the rate of reaction 1 because the thiocyanate consumption before and after the reaction is the same. Although the literature suggests that equation 3 could be used for analysis,[2] no quantitative data have been reported. To check this possibility, the ethylene–mercuric acetate addition compound solution in 75% acetic acid was titrated with 0.1 *N* potassium thiocyanate in the presence of nitric acid with the aid of ferric alum indicator. At room temperature, temporary appearance of the indicator color was observed, when an approximate equivalent amount of thiocyanate calculated by equation 2 was added. The reddish-orange color, however, soon disappeared and additional amounts of thiocyanate were added. This procedure was repeated until a permanent indicator color was observed. After about one hundred hours, the total amount of thiocyanate added was in accord with the calculated value (Fig. 1), and analysis is thus possible by reaction 3. To make this method practical for the purpose of the kinetic study, an excess of thiocyanate was allowed to react overnight, then a known amount of silver nitrate was added to react with the remaining thiocyanate and the excess silver nitrate was titrated again with thiocyanate. This modified method was shown to be satisfactory in the presence of perchloric acid. An attempt to shorten the reaction time by warming the reaction mixture resulted in erratic data, because of the decomposition of thiocyanate in the presence of perchloric acid.

Before the rate experiments, it was confirmed that the addition compound (0.5 *M* in 75% acetic acid) was stable in the presence of 1.5 *M* perchloric acid at 25° at least for ten hours, while this compound decomposes easily to give ethylene and mer-

TABLE I

SECOND-ORDER CONSTANTS FOR THE REACTION OF ETHYLENE–MERCURIC ACETATE ADDITION COMPOUND WITH ANISOLE AT 25.15°

Solvent acetic acid, wt. %	Perchloric acid, mole/l.	Initial concn. of anisole, mole/l.	Initial concn. of the addition compd., mole/l.	$k_2 \times 10^5$, l./mole sec.
75.0	1.60	1.007	0.0425	2.49
		0.9976	.0996	2.49
		0.9976	.2000	2.37
		1.007	.2178	2.42
		1.007	.2659	2.31
		0.9976	.3493	1.92
		0.9976	.4995	1.66
		1.007	.5318	1.48
		0.4989	.2001	2.37
		.7995	.2001	2.30
		.9976	.2001	2.37
	1.00	.9972	.2000	0.373
	1.32	.9972	.2000	0.992
	1.60	.9972	.2000	2.37
	1.99	.9972	.2000	8.43
	2.40	.9972	.2000	32.1
80.0	0.995	.9972	.2000	0.766
	1.60	.9972	.2000	4.58
	2.03	.9972	.2000	19.0
40.0	1.60	.1009	.0500	0.20
50.0		.1009	.0500	0.40
61.4		.1009	.0500	0.765
67.4		.0514	.0500	1.14
75.0		.9972	.2000	2.37
80.0		.9972	.2000	4.58
86.5		.9976	.0997	15.5
86.5		.9976	.2000	15.2

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[1] (a) K. Ichikawa, S. Fukushima, H. Ouchi and M. Tsuchida, THIS JOURNAL, **80**, 6005 (1958); (b) **81**, 3401 (1959).

[2] W. Manchot and Klug, *Ann.*, **420**, 170 (1920).