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Roles of the Electron Donors in the Three-Component Polyolefin Catalysts

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The reactions of the three-component polyolefin catalysts consisting of titanium trichloride (α-type), triethylaluminum, and various electron donor compounds have been investigated. Electron donors in a certain range of reactant ratios were found to accelerate the alkylation of the titanium ion remarkably at a temperature suitable for the polymerization of α-olefins. The roles of the electron donors have been discussed on the basis of the reaction behavior of the catalyst components and of the properties of the complexes which are thought to be the reaction intermediates.

Various electron donor compounds, such as amines and ethers, are known to have characteristic effects on the Ziegler-Natta catalyst in the polymerization of α-olefins: they promote the polymerization rate, and improve the stereospecificity and the molecular weight of the polymer.[1-4] The present author and Aishima also found similar pronounced effects of various alkylantimony compounds.[5] In order to clarify the roles of the electron-donor compounds, several attempts have been made by several authors, and several mechanisms have been proposed.[6-8] Razuvaev *et al.* have supposed that the coordination of the electron donors to the catalyst facilitates the insertion of a monomer molecule into the growing polymer chain.[6] Pigrov and Chirkov have also proposed that the coordinated complexes between titanium trichloride and the electron donors contribute to the polymerization.[7] Boor has reported that the donor molecules which are chemisorped to the surface chlorine atoms of the crystalline titanium trichloride activate the polymerization sites.[8] However, the detailed mechanism has not been proved exactly, since the chemistry of these three-component catalysts is very complex.

The present author has found that the reactions among the three catalyst components occur rapidly, with the evolution of large amounts of gas; he has taken this fact as an important key to understanding the role of the electron donors.

It is well known that the electron donors form coordinated complexes with both titanium trichloride[9-11] and triethylaluminum.[12-14] The present author has also previously studied the

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1) J. Boor, Jr., *J. Polymer Sci.*, **C1**, 257 (1963).

2) Y. Atarashi and H. Kodama, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **64**, 1140 (1961).

3) R. L. McConnel, M. A. McCall, G. O. Cash, Jr., F. B. Joyner and H. W. Coover, Jr., *J. Polymer Sci.*, **A3**, 2135 (1965).

4) S. Murahashi, S. Nozakura and K. Hatada, This Bulletin, **34**, 939 (1961).

5) Y. Takashi and I. Aishima, unpublished.

6) G. A. Razuvaev, K. S. Minsker, G. T. Fedoseeva, and U. K. Bykhovskii, *Polymer Sci., USSR.*, **2**, 299 (1961).

7) O. N. Pigrov and N. M. Chirkov, *Vysokomol. Soed.*, **7**, 491 (1965).

8) J. Boor, Jr., *J. Polymer Sci.*, **A3**, 995 (1965).

9) G. W. A. Fowles and R. A. Hoodless, *J. Chem. Soc.*, **1963**, 33.

10) H. Schlafer and R. Götz, *Z. anorg. u. allgem. Chem.*, **328**, 1 (1964).

11) R. J. H. Clark, J. Lewis, D. J. Machin and R. S. Nyholm, *J. Chem. Soc.*, **1963**, 379.

12) K. Ziegler, "Organometallic Chemistry," ed. by H. Zeiss, Reinhold Publishing Corp., New York (1960), p. 202.

13) Y. Takashi and I. Aishima, to be published.

14) R. D. Bushick and R. S. Stearns, *J. Polymer Sci.*, **A4**, 215 (1966).

complex-forming reactions between each binary combination of the three catalyst components, namely, the reactions of typical electron-donor compounds with titanium trichloride(16,17) and with triethylaluminum;(18) he has reported some of the foundamental properties of these complexes. It is obvious that at least one of these two types of donor complexes is involved in the vigorous reactions of the three-component systems, because no remarkable reaction is observed in the binary system of titanium trichloride and triethylaluminum.(15)

It the present paper, the reactions within the ternary catalyst systems are investigated, and a mechanism to explain the marked effects of the electron donors on the polymerization of α-olefins is discussed.

Results and Discussion

Three catalyst components consisting of titanium trichloride(α-type), triethylaluminum, and an electron-donor compound, such as triethylamine, pyridine, or triethylstibine, were found to react vigorously within a certain range of molar ratios at 60°C. On the other hand, no remarkable reaction took place in the absence of any electron-donor compound. Figure 1 shows some typical examples of gas evolution during the reactions. The gaseous products consisted mainly of ethane, along with small quantities of ethylene, hydrogen, and C_4 hydrocarbons. The color of titanium trichloride changed from violet to black as the amount of gas liberated increased.

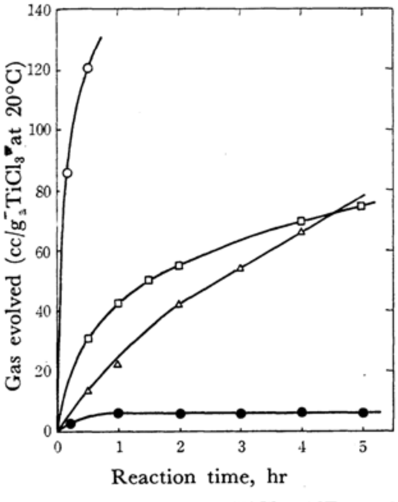

Fig. 1. Reactions between $TiCl_3$, $AlEt_3$ and various electron donor compounds (60°C).

○ Pyridine (Donor/$AlEt_3$ molar ratio=0.50)
△ Triethylamine (1.0)
□ Triethylstibine (1.0)
● No electron donor

The black solid products evolved a large amount of hydrogen when hydrolyzed. This fact indicates the presence of the bivalent titanium ion in these products; hence, the titanium trichloride might have been reduced through an ordinary alkylation step as follows:

$$\rangle\mathrm{Ti{-}Cl} + \rangle\mathrm{Al{-}Et} \rightarrow \rangle\mathrm{Ti{-}Et} + \rangle\mathrm{Al{-}Cl} \tag{1}$$

$$\rangle\mathrm{Ti{-}Et} \rightarrow \mathrm{Et}\cdot + \rangle\mathrm{Ti}\cdot \tag{2}$$

$$\mathrm{Et}\cdot + \gtrdot\mathrm{C{-}H} \rightarrow \mathrm{EtH} + \gtrdot\mathrm{C}\cdot \tag{3}$$

Although no stoichiometric relationship between the amount of the ethane evolved during the reactions and the amount of hydrogen evolved on the hydrolysis of the solid products was observed, as is shown in Table 1, it may be concluded that an appropriate amount of an electron-donor compound remarkably accelerates the alkylation of titanium trichloride in these reaction systems.

Figure 2 shows the reactivity of the three catalyst components as a function of the molar ratios of the electron donors to triethylaluminum. The behavior of pyridine is especially characteristic. That is, a vigorous reaction took place at Py/$AlEt_3$ molar ratios lower than unity, but a slight excess of pyridine over triethylaluminum inhibited the alkylation of titanium trichloride almost completely. With the addition of a slight excess of pyridine over triethylaluminum, the color of titanium trichloride did not change, and the powder X-ray diffraction pattern of the solid product showed the characteristic lines of α-titanium trichloride only. As the amount of excess pyridine was increased, the weight of the solid increased, and the IR spectrum of the solid showed the bands characteristic of the pyridine

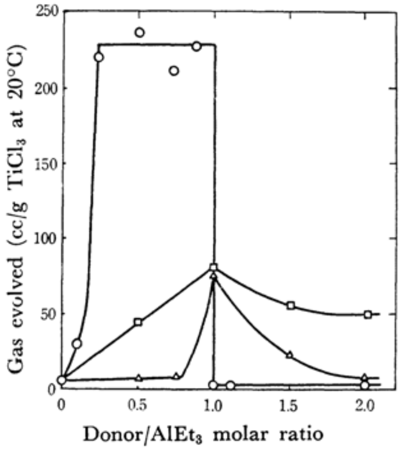

Fig. 2. Gas evolved during the reactions between $TiCl_3$, $AlEt_3$ and various electron donors. (60°C×5.0 hr; $AlEt_3/TiCl_3$ molar ratio=3.0)

Donor compounds: ○, Pyridine; △, Triethylamine; □, Triethylstibine

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

TABLE 1. REACTIONS BETWEEN THE THREE-COMPONENT CATALYSTS (60°C×5.0 hr)

		Donor	Pyridine	Et_3N	$SbEt_3$
Reactant	$TiCl_3/AlEt_3/$Donor mole ratio		1.0/3.0/1.5	1.0/3.0/3.0	1.0/3.0/3.0
Gas evolved during the reaction	Total	cc/g $TiCl_3$	193.0	73.1	40.4
	Ethane	mol/mol $TiCl_3$	1.33	0.50	0.28
Solid product	Appearence		Black powder	Black powder	Black powder
	Elementary analysis	Ti wt% (mmol/g)	28.81(6.01)	28.76(6.00)	26.71(5.57)
		Al wt% (mmol/g)	8.42(3.12)	4.28(1.59)	2.43(0.90)
		Cl wt% (mmol/g)	29.03(9.00)	43.43(13.5)	50.05(15.5)
		C wt% (mmol/g)	21.64(18.0)	15.17(12.6)	6.49(5.40)
		H wt% (mmol/g)	2.83(28.3)	3.03(30.3)	1.19(11.9)
		N wt% (mmol/g)	0.96(0.69)	1.59(1.14)	—
		Sb wt% (mmol/g)	—	—	8.91(0.73)
		Total wt%	91.69	96.26	93.64
	Hydrolysis	Total cc/g	201.0	110.6	42.8
		H_2 mmol/g	7.82	4.90	1.82
		C_2H_6 mmol/g	0.74	0.05	0.08
		C_2H_4 mmol/g	0.40	0.02	0.01
		C_4-Hydrocarbons mmol/g	0.12	0.03	0.004
		$2H_2/Ti$ molar ratio	2.61	1.53	0.65

ligand.[16] Pyridine has been found previously to react readily with titanium trichloride, giving a coordinated complex, $TiCl_3\cdot 3Py$.[16] The pyridine present in excess in the three-component system, therefore, is thought to have coordinated with titanium trichloride.

To explain the rapid alkylation of the titanium ion, it could possibly be proposed that titanium trichloride reacts first with pyridine to form a coordinated complex, $TiCl_3\cdot 3Py$, and that then free triethylaluminum attacks this complex to alkylate the titanium ion. Such a mechanism would include the transfer of the pyridine ligand from triethylaluminum to titanium trichloride, since, at the beginning of the reaction, triethylaluminum, titanium trichloride, and the $AlEt_3\cdot Py$ complex may be present in the mixture containing excess triethylaluminum. At a pyridine/$AlEt_3$ molar ratio slightly higher than unity, this transfer would result in the formation of free triethylaluminum and, hence, the alkylation of the titanium ion. However, since practically no gas was evolved at a pyridine/$AlEt_3$ molar ratio higher than unity, the above mechanism is impossible; it has, therefore, been deduced that no complex between titanium trichloride and pyridine is involved as an intermediate in the alkylation of the titanium ion in this three-component system.

Alternatively, in view of the elemental reactions among the catalyst components, the alkylation of the titanium ion which was observed at pyridine/$AlEt_3$ molar ratios lower than unity can be explained by the following three-step mechanism: (1) First, pyridine reacts with triethylaluminum to give the ionic 1 : 1 complex, $AlEt_3\cdot Py$ (A^+B^-). It was previously found that this reaction proceeded instantaneously and quantitatively.[14,18]

(2) This complex forms a double salt with titanium trichloride on those parts of the crystalline surface where the titanium ion is exposed.

$$Ti^{3+}Cl^- + A^+B^- \rightarrow Ti^{3+}(B^-)Cl^-(A^+) \qquad (4)$$

The chlorine ion adjacent to the titanium ion coordinated with the B^- ligand may be expected to be more loosely bound to the titanium ion in this double salt than the chlorine ion in pure titanium trichloride.

(3) The loosely-bound chlorine ion in the double salt is replaced by an ethyl group bound to aluminum. This substitution may be caused by the intramolecular rearrangement of the double salt itself, or by the attack of free triethylaluminum or the $AlEt_3\cdot Py$ ionic complex. At present, the predominant path can not be discussed.

The facts that the alkylation of titanium trichloride is completely inhibited when pyridine is present in excess and that the complex between titanium trichloride and pyridine is formed, suggest that the coordination of pyridine to the bare titanium ion prevents the formation of the double salt (Eq. (4)).

In the other three-component systems, a mechanism similar to that described above can be supposed, although the reaction behavior is somewhat different from that of the pyridine system, as is illustrated in Fig. 2. The alkylation of the titanium ion was retarded by the presence of excess triethylamine or triethylstibine but, in contrast with the pyridine system, it was not inhibited completely. Since the coordination of titanium trichloride with

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[16] Y. Takashi, to be published.

triethylamine as well as triethylstibine is greatly hindered by the bulkiness of the alkyl groups,[16,17] the presence of such electron donors in a free state may not prevent the formation of the double salts (Eq. (4)) completely.

The reactivity of triethylaluminum-donor complexes toward titanium trichloride seems to be qualitatively related to the electrical conductivity of the donor complexes, as is shown in Table 2. This result supports the proposal that ionic species are involved in these reactions.

Recent studies of the mechansim of the Ziegler-type catalysis have supported the contention that the transition metal-alkyl bond in a suitable ligand field is likely to be an active site in the polymerization of α-olefins.[19-27]

TABLE 2. THE ELECTRICAL CONDUCTIVITY OF THE DONOR COMPLEXES OF TRIETHYLALUMINUM AND THE REACTIVITY OF THE DONOR COMPLEXES WITH TRIETHYLALUMINUM TOWARD TITANIUM TRICHLORIDE

Complex	Specific Conductance*[18]	Maximum volume of the gas evolved**	
	$\mu\mho$/cm	cc/g $TiCl_3$	Donor/$AlEt_3$ molar ratio
$AlEt_3\cdot$Pyridine	4.3	230	<1.0
$AlEt_3\cdot NEt_3$	3.6	78	1.0
$AlEt_3\cdot SbEt_3$	52.0	79	1.0
$(AlEt_3)_2$	$<10^{-3}$	6	—

* Measured at room temperature.

** Reaction was carried out without any solvent at 60°C for 5.0 hr using excess triethylaluminum.

The high activity of the three-component catalysts can be explained in two ways on the basis of the present results. First, the remarkably high rate of the alkylation of the titanium ion in these catalyst systems gives rise to an increase in the number of active sites. Second, the energetic contribution of the ligand field of the active sites is considered possible. As has been discussed before, the ethylation of titanium trichloride may be supposed to be preceded by the formation of a double salt of the titanium trichloride with the ion pair of the donor complex of triethylaluminum. If the polymer chain grows at this ethyl-titanium bond, the presence of the ligand at the adjacent position may affect the insertion of monomer molecules into the active site. Pigrov *et al.* have studied the kinetics of the polymerization of propylene, and have reported that both the frequency factors and the overall activation energies of the polymerization in the presence of a third component differ much from those of the bicomponent catalyst.[7] This result appears to support the idea of some energetic contribution.

For the isotactic α-olefin polymerization, a certain regular surface structure of the solid catalyst component is considered to be essential.[21-24,28,29] In the three-component catalyst, the special ligand which is coordinated at a position adjacent to the growing polymer end can be considered to improve the stereoregulariry of the polymer.

Experimental

Materials. All the reagents were purified in the manners described in previous papers.[16-18]

Analysis. The gaseous mixtures of hydrocarbons were analyzed by gas chromatography at room temperature, using a column, 5 m long×4.5 mm in diameter, packed with "C-2" (Shimadzu Seisakusyo) containing 25% liquid paraffin (for hydrocarbons) and with alumina containing 25% acetonylacetone (for hydrogen). The solid products were analyzed according to the usual method described elsewhere.[16,17]

Reaction of Titanium Trichloride and Triethylaluminum in the Presence of the Electron Donor. A mixture of triethylaluminum and an electron donor over a wide range of molar ratios was reacted with 1.0 g (6.5 mmol) of titanium trichloride (α-type) with stirring at 60°C under a nitrogen atmosphere. The gaseous products which were evolved during the reaction were then measured and analyzed. The solid product was washed repeatedly with dry *n*-hexane and dried *in vacuo*.

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17) Y. Takashi, to be published.
18) Y. Takashi, to be published.
19) C. D. Beerman and H. Bestian, *Angew. Chem.*, **71**, 618 (1959).
20) C. Van Heerden, *J. Polymer Sci.*, **34**, 46 (1959).
21) P. Cossee, *Trans. Faraday Soc.*, **58**, 1226 (1962).
22) P. Cossee, *J. Catalysis*, **3**, 80 (1964).
23) E. J. Arlman, *ibid.*, **3**, 89 (1964).
24) E. J. Arlman and P. Cossee, *ibid.*, **3**, 99 (1964).
25) K. Oita and T. D. Nevitt, *J. Polymer Sci.*, **43**, 585 (1960).
26) W. L. Carrick, *J. Am. Chem. Soc.*, **82**, 1502 (1960).
27) A. S. Matlack and D. S. Breslow, *J. Polymer Sci.*, **A3**, 2853 (1965).
28) J. Furukawa and T. Tsuruta, *Kagaku no Ryoiki (J. Japan Chem.)*, **12**, 85 (1958).
29) G. Natta, *Gazz. Chim. Ital.*, **89**, 52 (1959).