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The Insertion Reaction of Propylene into Metal-Ethyl Bonds in the Ziegler-Natta Catalyst

Yoshinobu Takegami, Toshimitsu Suzuki and Takuya Okazaki

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

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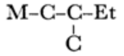
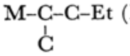
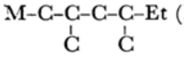
The insertion reaction of propylene into metal-ethyl bonds in $TiCl_4$-$AlEt_3$, $TiCl_3$-$AlEt_3$, $TiCl_3$-$AlEt_2Cl$, and $TiCl_3$-$ZnEt_2$ catalyst systems was studied. The insertion products were converted to the corresponding hydrocarbons by methanolysis, and then analysed by gas-liquid chromatography. From these hydrocarbons, the following three metal alkyls were considered to be formed in the reaction system;


$\mathrm{M{-}C{-}\underset{\substack{|\\ C}}{C}{-}Et}$ (I),

$\mathrm{M{-}\underset{\substack{|\\ C}}{C}{-}C{-}Et}$ (II), and

$\mathrm{M{-}C{-}\underset{\substack{|\\ C}}{C}{-}C{-}\underset{\substack{|\\ C}}{C}{-}Et}$ (III).

These metal alkyls were formed in the solid phase of the catalyst at first and were then transferred to the liquid phase of the catalyst. The amount of the metal alkyls formed in the reaction system was dependent on the catalytic system used. The active polymerization system $TiCl_3$-$AlEt_3$ gave a very small amount of metal alkyls, but the less active $TiCl_3$-$ZnEt_2$ and -$AlEt_2Cl$ systems gave a much greater quantity of the metal alkyls, (I) and (III). In the case of the $TiCl_4$-$AlEt_3$ system, metal alkyl formation was much affected by the Al/Ti molar ratio and the reaction time. Finally, it was concluded that the metal alkyls formed in the system were connected to the polymerization of propylene.

The initiation reaction of the Ziegler-Natta polymerization of α-olefins is considered to be the insertion reaction of the olefin into a metal-alkyl bond in the catalyst.[1] Only a few workers have however, studied the insertion reaction of olefins into metal-alkyl bonds in Ziegler-type catalysts. Vries studied the reaction of isobutene with methyltitanium trichloride. Isobutene was not polymerised by this catalyst, but the formation of neopentane was observed after the hydrolysis of the reaction mixture. In the case of ethylene, no insertion products were obtained and only high-molecular-weight polyethylene was obtained.[2] Azuma and his co-workers found that propylene was formed by the reaction of ethylene with bis(cyclopentadienyl)dimethyltitanium.[3] Shilov studied the reaction of heptene-1 with a soluble Ziegler catalyst ($(C_5H_5)_2TiCl_2$-$AlMe_3$) to give 2-methylheptene-1.[4]

These results apparently indicate that the insertion reaction of olefins into alkyl-titanium bonds occurs.

The present study deals with the insertion reaction of propylene in the presence of active polymerization catalysts, and discusses the course of metal-alkyl formation.

Experimental

Material. The titanium trichloride (HA grade; hydrogen-reduced $TiCl_4$ and activated by grinding) was obtained from the Stauffer Chemical Co. The titanium tetrachloride was distilled in the presence of a small amount of copper powder under an argon atmosphere.

The alkylaluminum compounds were obtained from the Ethyl Corporation and were used without further purification. The decalin was twice distilled under reduced pressure (bp 70—75°C/25 mmHg).

Reaction Procedure. A three-necked flask was equipped with a magnetic stirrer, a gas inlet, a self-sealing rubber cap, and a gas outlet connected to a mercury manometer and a vacuum system. The gas inlet was connected with a line for propylene, argon, or hydrogen.

To the reaction flask flushed with argon, titanium trichloride, a solvent, and an alkylaluminum compound were added in this order. The catalyst mixture was aged for ten minutes at a certain temperature, the

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[1] Leo Reich and A. Schindler, "Polymerization by Organometallic Compounds," Interscience Publ., New York (1966).

[2] H. DE Vries, *Rec. trav. Chim.*, **80**, 866 (1961).

[3] K. Shikata, K. Nishino and K. Azuma, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **68**, 352 (1965).

[4] A. E. Shilov, A. K. Shilova and B. N. Bobkov, *Vysokomolekul. Soedin.*, **4**, 1688 (1962).

remaining argon was pumped off, and propylene was introduced to start the reaction. After a certain reaction time, the residual propylene was pumped off and the reaction mixture was cooled to $-70°C$ to prevent any unexpected side reactions (isomerization or a transfer reaction). The reaction mixture was then transferred to the precipitation tube, which had previously been purged by argon, under an argon atmosphere, and separated into solids (titanium trichloride and an insoluble polymer) and liquids (the solvent and alkylaluminum compounds) by means of a centrifuge.

The two phases thus obtained were treated with cold methanolic hydrochloric acid. By this treatment the metal-alkyl bonds formed in the system were converted to the corresponding hydrocarbons. The polymers were filtered off, and the filtrate was subjected to gas-chromatographic analysis.

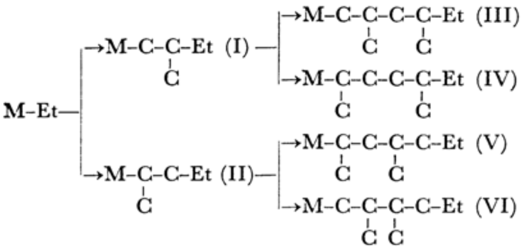
A Hitachi model F6D gas-liquid chromatograph equipped with a hydrogen flame ionization detector was employed for the quantitative and qualitative analyses of the reaction products. The operating conditions are presented below:

Column	Golay Z45 (SE30)	Golay R45 (PEG)
Size	$0.5\,\text{mm}\phi \times 45\,\text{m}$	$0.25\,\text{mm}\phi \times 45\,\text{m}$
Temperature	40°C	60°C
N_2 flow rate	$1.5\,\text{m}l/\text{min}$	$0.6\,\text{m}l/\text{min}$
Split ratio	1/80	1/150
Sample size	$2\mu l$	$5\mu l$

Results and Discussion

It is well known that the titanium on the solid surface of the Ziegler-Natta catalyst is ethylated and complexed with alkylaluminum compounds.[5] This metal-ethyl bond is considered to be very reactive, and olefins are easily inserted.

The insertion processes of propylene into metal-ethyl bonds may be formulated as follows:



From the end-group analysis of a polymer chain, using ^{14}C-labeled triethylaluminum with titanium trichloride catalyst, it has been said that one end of the polymer chain is an ethyl group,[6] while the other end is a vinylidene double bond as a result of chain transfer to the monomer.[7] These findings lead to the conclusion that the polymerization may proceed *via* primary metal alkyls, (I), (III), and so on.

Identification of the Products. The metal alkyls (I)—(VI) in the catalyst system were converted to the corresponding saturated hydrocarbons by the methanolysis of the reaction mixture. These hydrocarbons were analysed by gas chromatography.

First of all, as a blank test, the catalyst mixture itself ($TiCl_3$-$AlEt_3$ or $TiCl_4$-$AlEt_3$) was decomposed by methanol and then gas-chromatographed. Besides ethane (from ethylaluminum), several small peaks were observed; these were considered to be ethylene oligomers. Three small peaks, which have retention times of 4—5 min were also observed; these have the same retention times as those of isopentane, *n*-pentane, and isopropyl chloride respectively. However, the concentrations of these products were too low for them to be identified more precisely. After the reaction with propylene, three rather remarkable peaks and complex peaks (CP) with retention times of 25—27 min were observed. These peaks were absent in the propylene-free system. Mixing with authentic samples confirmed the formation of isopentane, *n*-pentane, and 2,4-dimethyl-hexane. These hydrocarbons correspond to the methanolysis products of the metal alkyls (I), (II), and (III) respectively. The possibilities of the formation of the metal alkyls (IV), (V), and (VI) were carefully examined in the region of (CP). However, these hydrocarbons were not detected by the gas chromatography.

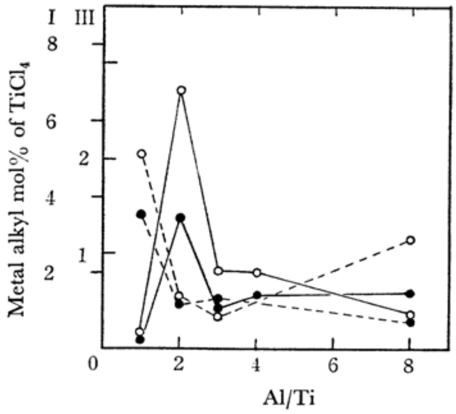


Fig. 1. Effect of Al/Ti molar ratio.
○ metal alkyl (I) ● metal alkyl (III)
bold line at 3 min
dashed line at 15 min
$TiCl_4$ 2.5 mmol, propylene 50 mmol, decalin 50 ml, at 0°C.

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[5] L. A. M. Rodriguez and H. M. Van Looy, *J. Polymer Sci.*, *Al*, **4**, 1951, 1971 (1966); J. C. W. Chien, *ibid.*, *A*, **1**, 425 (1963).

[6] G. Natta, *ibid.*, **34**, 21 (1959).

[7] G. Natta and G. Mazzanti, *Advances in Catalysis*, **11**, 1 (1959).

In the presence of aluminum trichloride, propylene gave many C_6-C_8 hydrocarbons, some of which were also observed in the case of titanium-containing catalyst systems. (CP) seemed to be the products from propylene in the presence of a cationic catalyst. This is also supported by the fact that the more acidic $TiCl_4$-containing system gave much (CP).

$TiCl_4$-$AlEt_3$ System. In this catalyst system the polymerization activity of propylene is remarkably affected by the molar ratio of Al/Ti.[8] The amount of the metal alkyls formed in the initial stage (3 or 15 min) is plotted against the molar ratio of Al/Ti in Fig. 1. At 3 min, the quantity of metal alkyls reached a maximum at the Al/Ti molar ratio of 2.0. At 15 min, however, we could not observe the maximum of the metal-alkyl formation at the Al/Ti molar ratio of 2.0. The amounts of the metal alkyls (I) and (III) are almost parallel at any Al/Ti molar ratio at each reaction time.

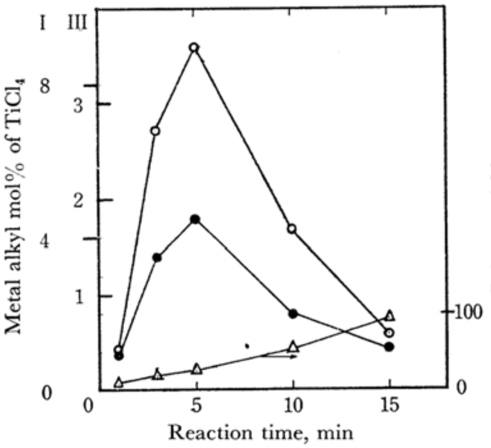

Fig. 2. Metal alkyls *vs*. reaction time.
○ metal alkyl (I) ● metal alkyl (III)
$TiCl_4$ 2.5 mmol, $AlEt_3$ 5.0 mmol,
propylene 50 mmol decalin 50 m*l*, at 0°C

The influence of the reaction time on the course of metal-alkyl formation at the Al/Ti molar ratio of 2.0 is shown in Fig. 2. The amount of the metal alkyls in the solid phase reaches a maximum after about 5 min and then gradually decreases, while the yield of the isotactic polymer increases. In this system transfer reactions of metal alkyls in the solid phase to the liquid phase were also observed (see the next section).

In this catalyst system, the formation of the primary metal alkyls (I) and (III) was observed, while the formation of secondary metal alkyls or cross-inserted metal alkyls was not observed. On the other hand, the insertion reactions of such internal olefins as cyclohexene[9] or pentene-2[10] into metal-ethyl bonds in the Ziegler-Natta catalyst occur under severe conditions. Therefore, we can not rule out the possibility of the formation of secondary metal alkyls in the course of the propylene polymerization; actually, a small amount of the secondary metal alkyl (II) was indeed found in the propylene-polymerization system. Therefore, it becomes an important problem which of these metal alkyls is connected with the isotactic polymerization of propylene.

The behavior of the primary metal alkyls, (I) and (III), in Fig. 2 quite resembles that of the intermediate of a successive reaction. The decrease in metal alkyls with an increase in the reaction time may show that propylene is inserted into these metal alkyls and that the regeneration of these metal alkyl slows or the quantity of metal-ethyl bonds decreases. The same phenomenon was observed in the insertion reaction of isoprene into the metal-ethyl bonds in the $TiCl_4$-$AlEt_3$ catalyst system.[11]

The results obtained from the variation in the Al/Ti molar ratio can be explained by the fact that, at the Al/Ti molar ratio of 1.0, the rate of the insertion reaction of propylene into the metal-ethyl bond and into the metal alkyl (I) is slower than that at the Al/Ti molar ratio of 2.0. The maximum amount of these metal alkyls is about 10 mol% of the titanium used; if all of these metal alkyls are intermediates of the polymerization, this value is too large. As will be discussed below, some of them must be deactivated by being transferred to alkyl-aluminum compounds in the liquid phase and contaminated with an insoluble polymer in the solid phase.

The isotacticity of the polymer obtained in this catalyst system is 50 to 60%. However, no formation of corss-inserted metal alkyls (IV or VI) was detected. This shows the good selectivity of an olefin orientation to a metal-alkyl bond. In the present study we have paid close attention to the structure of the metal alkyls; as Natta has pointed out,[12] the stereospecificity are not a structural problem but a configurational problems in the metal alkyls. Therefore, our findings are not inconsistent with the fact that even in the case of a low-stereospecific catalyst, no cross-inserted metal alkyls were found.

$TiCl_3$-$AlEt_3$ System. In our experiments the

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[8] G. Natta and P. Pino, *Gazz. Chim. Ital.*, **87**, 549 (1957).

[9] Y. Takegami, T. Suzuki and T. Okazaki, *Shokubai* (*Catalyst*), **7**, 11 (1965).

[10] Y. Takegami, T. Suzuki and T. Okazaki, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **71**, 1719 (1968).

[11] Y. Takegami, T. Suzuki and T. Okazaki, *idid.*, **70**, 195 (1967).

[12] G. Natta, A. Valvassori, G. Ciampelli and G. Mazzanti, *J. Polymer Sci.*, *A*, **3**, 1 (1965).

rate of the polymerization is almost constant throughout the reaction, and no deactivation of the catalyst is observed.[13] The concentration of the metal alkyls is higher in the solid phase than in the liquid phase. The metal aklyls in the liquid phase are considered to be as a result of the chain-transfer reaction of the metal alkyls formed in the solid phase to alkylaluminum compounds in the liquid phase. This consideration is supported by the fact that after the catalyst mixture had been separated by a centrifuge, and after to the liquid phase thus obtained, propylene had been added and the mixture had then been treated with methanol and submitted to analysis, no metal alkyl formation was observed. The role of metal-ethyl bonds in the solid phase was examined. The solid phase of the catalyst was washed with decalin and centrifuged three times to remove alkylaluminum compounds and then to this solid phase decalin and propylene was added. After the methanolysis small amounts of polypropylene and the metal alkyl (I) were observed in the solid phase of the reaction mixture, but the metal alkyl (III) was not found. These findings indicate that the amount of the metal alkyl (I) in the solid phase is connected with the polymerization.

TABLE 1. THE EFFECT OF Al/Ti MOLAR RATIO ON THE FORMATION OF METAL ALKYLS

Al/Ti	Metal alkyls $\times 10^{-3}$ mmol I	II	III	Polymer yield mg
0.2[a]	0.9	0.1	0.38	190
0.5[a]	0.8	0.1	0.11	205
1.0[a]	1.7	0.2	0.82	205
2.0[a]	6.0	2.1	0.41	175
0.2[b]	1.9	—	0.68	80
0.5[b]	1.2	—	0.24	15
1.0[b]	0.9	—	0.11	40

a) 0°C, 5 min

b) −70°C, 1 min

$TiCl_3$ 13 mmol, $AlEt_3$ variable, decalin 50 m*l*, $P_{0\text{C}_3\text{H}_6}$ 710 mmHg (*ca.* 50 mmol)

TABLE 2. THE EFFECT OF REACTION TIME ON THE FORMATION OF METAL ALKYLS

Reaction time min	Metal alkyls $\times 10^{-3}$ mmol I	III	Polymer Yield mg	MW $\times 10^4$
1	0.5	0.31	120	45.2
5	1.0	0.35	380	66.8
15	0.6	0.32	400	58.6
30	2.3	1.09	600	80.4
60	2.6	1.58	960	105

$TiCl_3$ 13 mmol, $AlEt_3$ 6.5 mmol, decalin 50 m*l*, 0°C, $P_{0\text{C}_3\text{H}_6}$ 710 mmHg (50 mmol)

In Tables 1 and 2 the effect of the Al/Ti molar ratio and the reaction time on the amounts of the metal alkyls is shown. The Al/Ti molar ratio has little effect on the formation of metal alkyls. The metal alkyls do, however, increase slightly with an increase in the reaction time. Usually a few more metal alkyls are found in this system than in the $TiCl_4$-$AlEt_3$ system. This may be attributed to the low concenentration of the metal-ethyl bond and to the higher propagation rate. The $TiCl_3$-$AlEt_3$ system gives a polymer with a molecular weight of 400000 in a 1-min reaction, while the $TiCl_4$-$AlEt_3$ system gives only a 50000-molecular-weight polymer under the same conditions.

$TiCl_3$-$AlEt_3$-H_2 System. The addition of hydrogen to the Natta catalyst caused a remarkable reduction in the molecular weight of the polymer, suggesting that a chain termination by the hydrogenolysis of metal-polymer bonds occurred. The amount of metal alkyls in the solid phase increased slightly upon the addition of hydrogen, as is shown in Table 3. In this case much isopentane and much 2,4-dimethylhexane were observed in the liquid phase, suggesting that the metal alkyls formed are decomposed by hydrogen before methanolysis.

TABLE 3. EFFECT OF HYDROGEN ON THE CATALYTIC SYSTEM $TiCl_3$-$AlEt_3$

$P_{0\text{H}_2}$ mmHg	$P_{0\text{C}_3\text{H}_6}$ mmHg	Reaction time min	Metal alkyls $\times 10^{-3}$ mmol I	III	Polymer Yield mg	MW $\times 10^4$
0	210	1	0.9	0.41	96	43
500	210	1	4.3	1.40	73	24
0	210	5	1.3	0.39	132	51
500	210	5	4.9	1.92	106	27
640	70	1	3.5	1.51	32	14

$TiCl_3$ 13 mmol, $AlEt_3$ 6.5 mmol, decalin 50 m*l*, 0°C

The increase in the amount of the metal alkyls in the solid phase compared to that in the hydrogen-free system may be attributed to the decrease in the propagation rate and to the contamination of the liberated hydrocarbons in the solid phase.

$TiCl_3$-$AlEt_2Cl$ System. In this catalyst system, the so-called settling time[14] was observed. During the settling period the amount of the metal alkyls in the system (in both the liquid and the solid phase) increased with an increase in the polymerization rate (Fig. 3).

The effect of the reaction temperatures on the formation of the metal alkyls is shown in Table 4;

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[13] T. Keii, *Chem. High Polymer* (Tokyo), **22**, 242 (1965).

[14] G. Natta and I. Pasquon, *Makromol. Chem.*, **24**, 258 (1957).

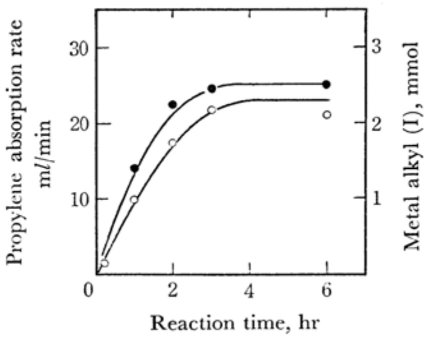

Fig. 3. Metal alkyl and polymerization rate *vs.* reaction time.
○ metal alkyl (I) ● propylene absorption rate
$TiCl_3$ 13 mmol, $AlEt_2Cl$ 6.5 mmol
$P_{C_3H_6}$ 710 mmHg, decalin 50 m*l*, 0°C

TABLE 4. EFFECT OF REACTION TEMPERATURE IN THE CATALYTIC SYSTEM $TiCl_3$-$AlEt_2Cl$

Reaction		Metal alkyls $\times 10^{-3}$ mmol		Polymer yield mg
Temp. °C	Time nim	I	III	
−70	15	0.7	trace	trace
0	15	2.9	0.78	21
30	15[a)]	5.3	1.01	105
30	120[b)]	25.0	12.0	1350
55	15	68.8	5.91	275

$TiCl_3$ 13 mmol, $AlEt_2Cl$ 6.5 mmol, decalin 50 m*l*.
$P_{C_3H_6}$ 710 mmHg const.
a) propylene absorption rate 4.3 m*l*/min
b) propylene absorption rate 13.8 m*l*/min

with a remarkable increase in the polymer yield, the amount of metal alkyls increases.

The electron paramagnetic resonance study of this catalyst[15)] has established that the liquid phase of this catalyst contains Ti^{3+} species. The catalyst mixture was separated into liquid and solid phases in the manner described above. To the liquid phase propylene was then added, and after methanolysis, the products were analysed. In this case, contrary to the case of the $TiCl_3$-$AlEt_3$ system, the metal alkyls (I) and (III) were found in the reaction mixture.

TABLE 5. FORMATION OF METAL ALKYLS IN THE CATALYTIC SYSTEM $TiCl_3$-$ZnEt_2$

Reaction		Metal alkyls $\times 10^{-3}$ mmol		Polymer	
Temp. °C	Time min	I	III	Yield mg	MW $\times 10^4$
−70	15	19.2	5.98	—	
0	1	39.2	7.35	—	
0	15	55.2	4.06	trace	
30	15	7.3	4.60	9	2.8
30	240	284	107	786	4.1

$TiCl_3$ 13 mmol, $ZnEt_2$ 6.5 mmol, decalin 50 m*l*,
$P_{C_3H_6}$ 710 mmHg const.

The titanium contents in the liquid phase were determined by colorimetry. The amount of metal alkyls in the liquid phase corresponds to the amount of titanium in the liquid phase.[*1]

These findings indicate that, in this catalyst system, the active site for the polymerization is connected with some complex in the liquid phase.

$TiCl_3$-$ZnEt_2$ System. This catalyst system has a very low activity with regard to the polymerization of propylene, while the amount of the metal alkyls formed in the solid phase is rather large. The large amount of the metal alkyls found also in the liquid phase of the reaction mixture indicates that the diethylzinc has a high ability to make chain transfers.[16)]

The last two catalytic systems have low activity in the polymerization of propylene at the initial stage of the reaction, but with an increase in the polymerization activity, the metal alkyls increase. The $AlEt_2Cl$ system is usually considered to be a transfer-free polymerization system,[5)] however, and it is difficult to confirm our finding. In our opinion this transfer reaction is connected with the activation of the catalyst.

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15) Y. Ono and T. Keii, *J. Polymer Sci.*, *Al*, **4**, 2441 (1966).

[*1] When 13 mmol of $TiCl_3$ and 6.5 mmol of $AlEt_2Cl$ in 20 m*l* of a solvent are used at 30°C, the reaction mixture gives a liquid phase containing 0.06 mmol of titanium. After a 60-min reaction with propylene, this liquid phase gives 0 05 mmol of the metal alkyls (I)+(III).

16) G. Natta, *J. Polymer Sci.*, **34**, 531 (1959).