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The Insertion Reactions of Olefins into Metal-Ethyl Bonds in the Vanadium Compounds-Ethyl Aluminum Ziegler Catalyst System. A Proposed Mechanism for the Syndiotactic Polymerization of α-Olefin

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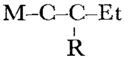
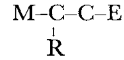
In order to clarify the mechanism of the syndiotactic polymerization of olefin, the insertion reaction of several olefins into metal-ethyl bonds in VCl_4-$AlEt_nCl_{3-n}$, $VOCl_3$-$AlEt_nCl_{3-n}$, and $V(AA)_3$-$AlEt_nCl_{3-n}$ systems were studied. Cyclohexene was easily inserted into metal-ethyl bonds in these catalysts to give a metal-ethylcyclohexyl bond at −70°C. Pentene-1 and 4-methylpentene-1 gave  $\text{M–C–}\underset{\displaystyle\text{R}}{\text{C}}\text{–Et}$ (I) and  $\text{M–}\underset{\displaystyle\text{R}}{\text{C}}\text{–C–Et}$ (II). At −70°C with VCl_4-$AlEt_2Cl$, where the syndiotactic polymerization of propylene proceeds, four times as much (II) as (I) was obtained. However, at 0°C or in the VCl_4-$AlEt_3$ catalyst system, the amount of (I) exceeded the amount of (II). With the $VOCl_3$-$AlEt_nCl_{3-n}$ or the $V(AA)_3$-$AlEt_3Cl_{3-n}$ system, the selectivity for the formation of metal-alkyl (II) was decreased. The above results lead to the conclusion that, in the course of syndiotactic polymerization, the secondary metal-alkyl bond (II) was an intermediate of the polymerization. By means of this mechanism every experimental result reported can be explained without difficulty.

A hypothesis for the mechanism of the syndiotactic polymerization of α-olefin was presented in a previous communication,[1] this hypothesis was based on the results of the insertion reactions of pentene-1 into metal-ethyl bonds in the VCl_4-$AlEt_2Cl$ catalyst system. In this paper, in order to generalize the hypothesis, the present authors will study the mode of the insertion reactions of several olefins into metal-ethyl bonds in various Ziegler-type catalysts containing certain vanadium compounds. Vanadium catalysts are known to be syndiospecific catalysts for propylene at low temperatures[2] and as good copolymerization catalysts for ethylene and propylene, producing random copolymers.[3] However,

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[1] Y. Takegami and T. Suzuki, This Bulletin, **42**, 848 (1969).

[2] G. Natta, I. Pasquon and A. Zambelli, *J. Amer. Chem. Soc.*, **84**, 1488 (1962).

[3] G. Natta, G. Mazzanti, A. Volvassori and G. Pajaro, *Chim. Ind.*, Milan), **39**, 733 (1957).

the reason for or the mechanism of the special properties of these catalyst systems has not yet been clarified.

Boor and Youngman[4] have suggested a mechanism for the syndiotactic polymerization of propylene, a mechanism in which the polymerization proceeds *via* a coordinate anionic mechanism and in which the steric interaction between substituents of the last-added monomer and the new monomer units plays a very important role in the stereo regulation. However, in this mechanism, in contrast to the isotactic polymerization, the necessity for the syndiotactic configuration is not satisfied.

Recently Zambelli *et al.*[5] have investigated the mode of the double-bond opening of deutero propylene in the course of the syndiotactic polymerization, and have demonstrated that the opening of the double-bond is *cis*, as in the case of the isotactic polymerization with the Natta catalyst.[6] They have also[7] suggested the use of bimetallic catalytic species for the polymerization.

In the course of the isotactic polymerization with a titanium catalyst ($TiCl_3$-$AlEt_3$), a primary metal-alkyl bond was predominantly formed as an insertion product of an α-olefin into metal-ethyl bonds in the catalyst.[8] It can be concluded that the primary metal-alkyl is the intermediate of the isotactic polymerization.

Experimental

Materials. Commercial vanadium tetrachloride and vanadium oxytrichloride were used without further purification and were diluted with olefin-free *n*-octane. Vanadium(III) acetylacetonate ($V(AA)_3$) was synthesized from VCl_3 and acetylacetone under a stream of dry NH_3 and was sublimed under reduced pressure; it was produced as a greenish-brown powder. Toluene, ethylbenzene, and *n*-octane were purified by distillation over dispersion sodium under an argon atmosphere. Commercial pentene-1 and 4-methylpentene-1 were dried by means of calcium hydride, and their purity was determined by gas chromatography.

Procedure. A three-necked flask equipped with a magnetic stirrer, a gas inlet, a gas outlet connected to an argon line and a vacuum line, and a self-sealing rubber cap was flushed with argon, and then a solvent, vanadium salt, an olefin, and an alkyl aluminum were introduced (in this order) at the reaction temperature. After a certain reaction time the reaction mixture was taken off with the use of a hypodermic syringe, quenched with cold methanolic hydrochloric acid, and washed with cold water to remove any methanol and hydrochrolic acid. The metal alkyls thus formed in the catalytic system were converted to the corresponding hydrocarbons and gas chromatographed.

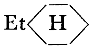
A Hitachi model F6D gas liquid chromatograph with a Golay Z45 and an R45 column was employed for the qualitative and quantitative analyses.

Results and Discussion

Cyclohexene. It is well known that this olefin is not homopolymerized with a Ziegler-Natta-type catalyst, but, as has been shown in previous papers,[9] the insertion reaction into metal-ethyl bonds in the catalyst occurred and the amount of the insertion product is correlated with the amount of the metal-ethyl bond in the catalyst system.

To estimate the amount of the metal-ethyl bond in the vanadium catalyst, cyclohexene was reacted with the VCl_4-$AlEt_nCl_{3-n}$ catalyst system at various temperatures. The results are summarized in Table 1. The results show that, at −70°C, a relatively large amount of ethylcyclohexane was obtained ; in the titanium catalyst systems, on the other hand, below 0°C a very small amount of ethylcyclohexane was obtained.[*1]

TABLE 1. INSERTION REACTION OF CYCLOHEXENE IN VCl_4-$AlEt_nCl_{3-n}$

AlR_3	Reaction		 (mmol)	Remarks
	Temp. (°C)	Time (min)		
$AlEt_2Cl$	−70	120	0.010	anisole 1.0 mmol added
		240	0.021	
		360	0.009	
	−70	60	0.091	
		120	0.124	
		240	0.082	
		360	0.027	
	−30	60	0.089	
	0	60	0.091	
$AlEt_3$	−70	60	0.040	
	0	60	0.095	
	30	60	0.146	

VCl_4 1.0 mmol solvent (*n*-heptane 15 m*l*)
AlR_3 3.0 mmol cyclohexene 10 mmol

In contrast to the titanium system, the amount of ethylcyclohexane was slightly affected by the reaction time, and it rather decreased with an increase in the reaction time. This may show that, in this catalyst, the formation of the metal-ethyl bond is very rapid at −70°C and that this metal-ethyl bond is very reactive toward the insertion reactions of an olefin. As the elimination of ethylcyclohexene or other decomposition products from metal-ethylcyclohexyl bond was not observed, the decrease in

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[4] J. Boor, Jr., and E. A. Youngman, *J. Polym. Sci., Part A-1*, **4**, 1861 (1966).

[5] A. Zambelli, M. Giongo and G. Natta, *Makromol. Chem.*, **112**, 183 (1968).

[6] T. Miyazawa and T. Ideguchi, *J. Polym. Sci., Part B-1*, 389 (1963).

[7] A. Zambelli, I. Pasquon, R. Signorini and G. Natta, *Makromol. Chem.*, **112**, 160 (1968).

[8] Y. Takegami, T. Suzuki and T. Okazaki, This Bulletin, **42**, 1060 (1969).

[9] Y. Takegami, T. Suzuki and K. Hamada, *Kogyo Kagaku Zasshi*, **72**, 1720 (1969); *Shokubai* (*Catalyst*), **7**, 11 (1965).

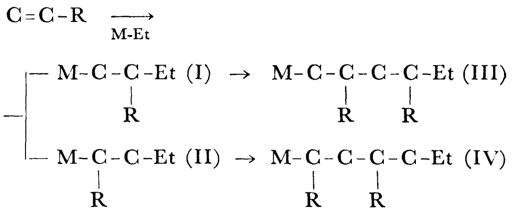
[*1] 0.2—0.5 mol % of $TiCl_3$.

the amount of ethylcyclohexane with an increase in the reaction time may be explained by the fact that cyclohexene is inserted into the metal-ethylcyclohexyl bond, on account of the high activity of the vanadium alkyl bond in the catalyst system. However, the formation of cyclohexylethylcyclohexane was not confirmed.

With $AlEt_2Cl$, the amount of ethylcyclohexane was not affected by an increase in the reaction temperature. On the other hand, in the case of the catalytic system containing $AlEt_3$ the amount of ethylcyclohexane increased with an increase in the reaction temperature. These results suggest that there are different types of metal-ethyl bonds in the $AlEt_2Cl$ and $AlEt_3$ systems, as will be descibed below. With $AlEt_2Cl$ a metal-ethyl bond which is relatively thermally unstable may be formed.

Pentene-1 and 4-Methylpentene-1. According to Zambelli *et al.*,[7] the mechanism of the anionic coordinated polymerization of propylene to the syndiotactic polymer can be explained by the fact that the bimetallic catalyst complex plays an important role. However, the bimetallic catalyst structure proposed by them has not well been elucidated, for the differences in the syndiotactic and the isotactic polymerizations remain unexplained.

As has been shown in a previous communication,[1] in the VCl_4-$AlEt_2Cl$ catalyst system at −70°C pentene-1 was inserted into the metal-ethyl bond to give, predominantly, secondary metal alkyl (II). The insertion processes of an α-olefin into the metal-ethyl bond can be formulated as follows:



$$C{=}C{-}R \xrightarrow[\text{M-Et}]{} \begin{cases} M{-}C{-}\underset{R}{C}{-}Et\ (I) \rightarrow M{-}C{-}\underset{R}{C}{-}C{-}\underset{R}{C}{-}Et\ (III) \\ M{-}\underset{R}{C}{-}C{-}Et\ (II) \rightarrow M{-}\underset{R}{C}{-}C{-}\underset{R}{C}{-}C{-}Et\ (IV) \end{cases}$$

On the other hand, in the case of the isotactic polymerization catalyst systems, containing $TiCl_3$ or $TiCl_4$, only the insertion reactions occurred to give the primary metal alkyl (I) and (III); From the behavior of the primary metal alkyls (I) and (III), these substances were considered to be intermediates of the isotactic polymerization of the

TABLE 2. INSERTION REACTION OF PENTENE-1 IN VX_n-$AlEt_nCl_{3-n}$

Run No.	VX_n	AlR_3	Reaction Temp. (°C)	Reaction Time (min)	Products I (mmol)	Products II (mmol)	Products Olefin[a]	Remarks
1	VCl_4	$AlEt_2Cl$	−70	5	0.0105	0.0422	0	
				10	0.0126	0.0392	0	
				360	0.0040	0.0142	0	
2	VCl_4	$AlEt_2Cl$	−70	10	0.0137	0.135	0	anisole 1.0 mmol
				40	0.0150	0.115	0	
				360	0.0022	0.103	0	
3	VCl_4	$AlEt_2Cl$	0	5	0.0289	0.0242	0	
				10	0.0284	0.0177	0	
				120	0.0360	0.0206	0	
4	VCl_4	$AlEt_3$	−70	5	0.0730	0.0502	0.037	
				40	0.0725	0.0505	0.048	
				120	0.0710	0.0505	0.033	
5	VCl_4	$AlEt_3$	0	5	0.0502	0.0232	0.032	
				30	0.0502	0.0233	0.033	
				60	0.0495	0.0208	0.034	
6	VCl_4	$AlEt_2Cl$	−70	5	0.0104	0.0431	0	
				5+5	0.0046	0.0191	0	C_3H_6 10 mmol
7	$V(AA)_3$	$AlEt_2Cl$	−70	120	~0	~0	0	
8	$V(AA)_3$	$AlEt_2Cl$	0	30	0.0502	0.0214	0.022	
9	$V(AA)_3$	$AlEt_3$	−70	10	0.0600	0.0061	0.025	
10	$V(AA)_3$	$AlEt_3$	0	10	0.0466	0.0050	0.020	
11	$VOCl_3$	$AlEt_2Cl$	−70	10	0.0199	0.0338		
				60	0.0237	0.0223		
12	$VOCl_3$	$AlEt_2Cl$	0	10	0.0393	0.0281		
13	$VOCl_3$	$AlEt_3$	−70	10	0.0910	0.0428	0.096	
14	$VOCl_3$	$AlEt_3$	0	10	0.0407	0.0292	0.021	

VX_n 1.00 mmol, AlR_3 3.00 mmol, Solvent: toluene 10 m*l*, pentene-1 5.0 mmol

I; 3-methylhexane, II; *n*-heptane, a) heptene-3

TABLE 3. INSERTION REACTION OF 4-METHYLPENTENE-1 IN VX_n-$AlEt_nCl_{3-n}$

Run No.	VX_n	AlR_3	Reaction		Products		Remarks
			Temp. (°C)	Time (min)	I (mmol)	II (mmol)	
15	VCl_4	$AlEt_2Cl$	−70	10	0.0158	0.0665	
				30	0.0179	0.0655	
				60	0.0044	0.0031	
16	VCl_4	$AlEt_2Cl$	−70	10	0.0165	0.0795	anisole 1.0 mmol
				30	0.0162	0.0799	
				60	0.0193	0.0805	
17	VCl_4	$AlEt_2Cl$	0	5	0.0223	0.0121	
				30	0.0199	0.0135	
				60	0.0225	0.0135	
18	VCl_4	$AlEt_3$	−70	10	0.0835	0.0565	a
				30	0.0782	0.0503	
				60	0.0800	0.0503	
19	VCl_4	$AlEt_3$	0	10	0.0640	0.0341	a
				30	0.0582	0.0322	
				60	0.0572	0.0325	
20	$V(AA)_3$	$AlEt_2Cl$	0	10	0.0801	0.0295	a
				30	0.0845	0.0365	
				60	0.0502	0.0203	
21	$V(AA)_3$	$AlEt_3$	−70	10	0.0504	0.0106	
				30	0.0500	0.0011	
22	$VOCl_3$	$AlEt_2Cl$	−70	10	0.0188	0.0186	
23	$VOCl_3$	$AlEt_2Cl$	0	10	0.0500	0.0691	
24	$VOCl_3$	$AlEt_3$	−70	10	0.0755	0.0330	
25	$VOCl_3$	$AlEt_3$	0	10	0.0870	0.0353	

VX_n 1.00 mmol; AlR_3 3.00 mmol; Solvent: ethylbenzene 10 m*l*, 4-methylpentene-1 5.0 mmol
a : olefins were formed. I: 2,4-dimethylhexane, II: 2-methylheptane

α-olefin.

When propylene was reacted with the VCl_4-$AlEt_2Cl$ catalyst at −70°C, the metal alkyls (I) and (II) were not detected after the methanolysis of the reaction mixture. However, at an elevated temperature a small amount of metal alkyl (I) was obtained and the polymer showed an IR absorption at 997 cm^{-1} which can be assigned to the isotactic band. These facts strongly support the idea that the formation of the primary metal-alkyl bond is connected with the isotactic polymerization. There are two possible reasons why, at −70°C metal, neither alkyl (I) or (II) was detected. One is that a steady-state concentration of the metal alkyls is very low ; that is, the second step of the insertion process is very rapid. The other possibility is that the syndiotactic polymerization proceeds without any insertion process. However, the latter reason can be ruled out on the basis of Natta's experimental finding.*2 Therefore, in the case of propylene the concentration of any metal-alkyl bond formed by propylene insertion should be low.

As has been known, higher olefins, such as pentene-1 and 4-methylpentene-1, were not polymerized with the syndiospecific catalyst.[4] However, cyclohexene was inserted easily into the metal-ethyl bond in the catalyst. From the mode of the insertion reactions of these higher olefins, the insertion process of propylene can be guessed at. As has been shown in Tables 2 and 3, at −70°C these olefins gave the metal alkyls (I) and (II). However, no polymer was obtained at this temperature. The amount of the secondary metal alkyl (II) was larger than that of the primary metal alkyl (I) (runs 1, 2, 15, and 16) ; these facts are quite different from the results obtained in the case of titanium-containing catalyst systems.[8] On the other hand, at an elevated temperature (runs 3 and 17) or with $AlEt_3$ (runs 4, 5, 18 and 19), the amount of metal alkyl (I) increased and a small amount of a solid polymer containing an isotactic fraction was obtained. This means that, as has been described above in the case of propylene, at 0°C the polymerization proceeds *via* the primary metal alkyl (I), just as in the case of titanium-containing systems.[8] These results show that two types of vanadium-ethyl bonds can be produced ; one has a tendency to form a secondary metal-alkyl bond, and the other has a tendency to form a primary metal-alkyl bond. At a low temperature the former vanadium-ethyl bond will be formed mainly. In the case of pentene-1 or 4-

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*2 When radioactive $Al(^{14}C_2H_5)_2Cl$ is used, the polymer obtained also has radioactivity.

methylpentene-1, the secondary metal alkyl (II) has the bulky substituent closely attached to vanadium; this substituent causes steric hindrance between the next-coming monomer and the active center.

The vanadium-ethyl bond to form a primary metal-alkyl bond will be formed as a minor product and will be less reactive toward the insertion reaction of olefins. Thus, the polymerization of higher olefins does not occur at low temperatures.

On the contrary, in propylene, if the secondary metal alkyl (II) is formed, the steric hindrance between the growing chain and the next-coming monomer is not so large that propylene can attack the secondary metal alkyl (II) from the less hindered side of the active center. By this alternating-monomer attack on the secondary metal alkyl bond from the less hindered side, the syndiotactic configuration may be obtained. This mechanism is also supported by the results of the copolymerization experiment reported by Zambelli *et al.*[10] In their report, the alternate copolymers of ethylene and propylene, and of ethylene and butene-1, were obtained at the higher molar ratios of propylene or butene-1 to ethylene. These results can be explained by our mechanism thus: first, a higher olefin, which has a high concentration compared to that of ethylene, is inserted into a metal-ethyl bond, and the secondary metal-alkyl bond is formed. Into this secondary metal-alkyl bond ethylene can then be easily inserted, because higher olefin has much steric hindrance. Thus, the primary metal-alkyl bond is regenerated, and into this primary metal-alkyl bond a higher olefin can be inserted. The repetition of the above insertion reaction leads to the formation of the ethylene and α-olefin alternating copolymer.

This theory is also supported by run 6 of our experiment. In this experiment, after reacting pentene-1 with VCl_4-$AlEt_2Cl$ at $-70°C$, a small amount of propylene was introduced into the reaction mixture. The amounts of the metal alkyls (I) and (II) decreased compared with run 1, in which propylene was not introduced. This fact shows that propylene was inserted into the metal alkyls (I) and (II).

To elucidate the nature of the vanadium catalyst in the insertion reaction of olefin, the $VOCl_3$ and $V(AA)_3$-$AlEt_nCl_{3-n}$ systems were also investigated. With $VOCl_3$, even at $-70°C$ with $AlEt_2Cl$ (runs 11 and 22), the selectivity for the formation of the secondary metal alkyl (II) was not as high as in the case of VCl_4 in either olefin. With $V(AA)_3$-$AlEt_2Cl$ at $-70°C$ (run 7) very small amounts of the metal alkyls (I) and (II) were obtained and the tendency for the formation of the secondary metal-alkyl bond was not very large. With $V(AA)_3$-$AlEt_3$ (runs 9, 10 and 21) the formation of the primary metal-alkyl bond (I) is predominant, as in the titanium system. In the $V(AA)_3$ system at 0°C, even with the use of $AlEt_2Cl$, the formation of C_7 olefin is observed in the case of pentene-1 (run 8); the formation of olefin is also observed in the cases of VCl_4 and $VOCl_3$-$AlEt_3$ systems, even at $-70°C$. The structures of the olefins were not determined exactly, but judging from the retention time of the gas chromatogram they seemed to be heptene-3 (main) and 3-methylhexene-1. These olefins are eliminated from metal alkyls (I) and (II) by the β-hydrogen migration of the metal alkyl bond.

The elimination of olefin from a metal alkyl bond was observed in the case of the insertion reaction of cyclohexene into metal ethyl bonds in the $TiCl_4$-$AlEt_3$ and $AlEt_2Cl$ systems at a low Al/Ti molar ratio.[9] It was considered that the Ti(IV)-alkyl bond was unstable and that the elimination of the olefins was followed by a hydride shift. From the results obtained in vanadium systems, it may be shown that in rather lower valence states of vanadium, vanadium alkyl bonds will be more unstable than in titanium systems.

VCl_4, $V(AA)_3$, and $VOCl_3$-$AlEtCl_2$ systems were also investigated, but in these systems, on account of the strong cationic character of the catalyst, olefins were easily polymerized to a low-molecular-weight polymer and no insertion reactions were observed.

The addition of anisole is known to increase the syndiotacticity, but in the cases of the insertion reactions studied in this report, no remarkable changes were found. In the case of cyclohexene, the amount of the metal-ethylcyclohexyl bond decreased, in 4-methyl-pentene-1 no remarkable change was observed, and in pentene-1 the formation of the secondary metal-alkyl bond increased. However, in every case the stability of the metal-alkyl bond seemed to be increased.

From these results, it can be said that α-olefins are generally inserted into a vanadium-ethyl bond to form a secondary metal alkyl bond. Of the systems studied, the tendency to produce the secondary metal alkyl bond reaches its maximum with the catalytic system VCl_4-$AlEt_2Cl$ at $-70°C$. The hypothesis for the mechanism of the syndiotactic polymerization of α-olefin proposed in the previous communication,[1] that is, the secondary metal alkyl bond propagation mechanism, is strongly supported.

As has been reported by Natta,[11] V(III) species are present in the VCl_4-$AlEt_2Cl$ system at $-70°C$. Vanadium (III) has a $3d^2$ electronic structure and in the case of the titanium system the Ti(III) species has a $3d^1$ electronic structure. The difference between the electronic structure of the central

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10) A. Zambelli, A. Lety, C. Tosi and I. Pasquon, *Makromol. Chem.*, **115**, 73 (1968).

11) G. Natta, A. Zambelli, G. Lanzi, I. Pasquon, E. R. Mongnashi, A. L. Segre and P. Centola, *ibid.*, **61**, 161 (1965).

metal is considered to cause the marked difference in the insertion reactions of an α-olefin into the metal ethyl bonds. At an elevated temperature or with $AlEt_3$, the valency state of vanadium was reduced to V(II) and a $3d^1$ electronic structure. In this case, the formation of the primary metal alkyl bond is most likely. Naturally, the differences in the ligands of the vanadium and the valency states of the starting vanadium play an important role, as do the differences among the vanadium salts.

The contribution of the configuration of the active center of the syndiospecific catalyst can not be ruled out, either.