SHORT COMMUNICATIONS

*Presence of a New Species of Titanium-Titanochloroform**

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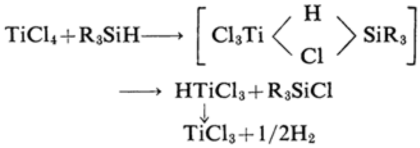
Titanochloroform or titanium hydrotrichloride[1], $HTiCl_3$, is one of the supposed intermediates in the olefine polymerization by Ziegler and Natta catalysts. Recently Cooper[2] proposed the possibility of the occurrence of titanochloroform as Eq. 1.

$$\text{R-ti} \rightleftarrows \text{Olefine} + \text{H-ti} \quad (\text{ti} = 1/4\ \text{Ti}) \qquad (1)$$

But the actual existence of this compound has not been proved so far. Recently we obtained titanochloroform as a solution and the presence was evidenced by the chemical analysis and the infrared spectrum. Moreover, we could find considerable amount of H-Ti bond remaining in the solid phase of some species of titanium trichloride, especially in the so-called active form prepared by aluminum reduction of titanium tetrachloride in benzene.

Previously, we found that propylene was polymerized by the methylhydropolysiloxane modified Ziegler catalyst system, and gave silicon containing polypropylene[3]. To clarify the process, the reaction of titanium tetrachloride with triethylsilane, triphenylsilane, triethoxysilane, methylhydropolysiloxane, or methylhydrodichlorosilane, were studied and the reaction mechanism was disclosed as Eq. 2.



$$TiCl_4 + R_3SiH \longrightarrow \left[Cl_3Ti \left\langle \begin{matrix} H \\ Cl \end{matrix} \right\rangle SiR_3 \right] \longrightarrow \underset{\displaystyle TiCl_3 + 1/2H_2}{\overset{}{HTiCl_3}\downarrow} + R_3SiCl \qquad (2)$$

In these experiments, the volatile fraction consisting of titanochloroform and the recovered titanium tetrachloride was obtained in a dry-ice-acetone trap by vacuum distillation of the products at room temperature. In most cases the fraction liberates hydrogen by alcoholic potash which was measured by volume. One typical example, the analysis of the condensate obtained from the reaction of titanium

Tabl I. Reaction of commercial titanium hydride TiH with titanium tetrachloride

TiH g.	$TiCl_4$ g.	Reaction		Product g.	Analysis$^{\text{a, b)}}$				IR absorpn. of H-Ti$^{\text{c, d)}}$ cm^{-1}
		Temp. °C	Time hr.		Ti^{III}	Ti^{f}	$H(OH^-)$	Cl^{f}, %	
5	19	210$^{\text{e)}}$ (5 atm.)	2.5	Brown liq. 5.5					1590$^{\text{f)}}$m
				Purple sol. 7.0	9.01	12.5	0.068 0.014$^{\text{f}}$	24.0	1590 m (1635 s)$^{\text{g)}}$
3.0	31	135	7	Yellow liq. 30.2		25.4	0.044$^{\text{f}}$	74.5	
				Purple sol. 3.1	2.63	6.14	0.044 0.035$^{\text{f}}$	11.7	

a) Analysis was performed by the soluble part in 1 N H_2SO_4.
b) Ti: Total titanium, f: about the filtrate
c) In Nujol
d) The starting material TiH has an IR absorption at 1635 cm^{-1} (vw).
e) In 100 cc. autoclave
f) Partially hydrolyzed
g) About the benzene extract of the solid (in benzene)

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[1] The name was used in J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. VII, Longmans, Green and Co., Ltd., London (1927), p. 80.

[2] D. Cooper and H. L. Finkbeiner, *Chem. & Eng. News*, 39, No. 37, p. 60 (1961).

[3] I. Shiihara, W. Kawai and T. Ichihashi, International Symposium on Macromolecular Chemistry, Montreal, August, 1961.

tetrachloride and triphenylsilane as a benzene solution showed; Ti(total) 4.54, Cl 12.8, H(OH^- active) 0.029, Si 0.10%, and thus Cl/Ti=3.82, H/Ti=0.37. The amount of hydrogen does exist twice as much as that of the amount required from the silicon content, even if the all silicon was assumed to compose silane. This fact affords one evidence that some part of the hydrogen is originated from the volatile H-Ti containing compounds, i. e. titanochloroform in this case.

Moreover, this condensate showed a characteristic infrared absorption at 1610 cm^{-1} (m). It is plausible to consider the absorption is due to H-Ti bond stretching vibration, because the product obtained from the other route by reacting commercial titanium hydride TiH and titanium tetrachloride as Eq. 3 showed the same absorption at about 1600 cm^{-1}. These data are given in Table I.

$$TiH + 3TiCl_4 \rightarrow HTiCl_3 + 3TiCl_3 \qquad (3)$$

The H-Ti bond was also observed in the solid phase of titanium trichloride. Analytical value and infrared data (in Nujol) of some examples are: Titanium trichloride originated from $TiCl_4 + Et_3SiH$, Ti^{III} 24.8, Ti 28.7, Cl 64.6, H(OH^- active) 0.092, Si 0.70%, H-Ti absorption, at 1595 cm^{-1} (w); from $TiCl_4 + (MeHSiO)_n$, Ti^{III} 10.1, Ti 14.8, H(OH^-) (about the acid extract) 0.038%, H-Ti absorption, at 1602 cm^{-1} (vs); from $TiCl_4$+Al (in benzene)[4], Ti^{III}/Ti> 95%, H-Ti absorption, at 1605 cm^{-1} (m).

This compound in high concentration is unstable liquid, and the blackening, precipitation and then gelation occurred after a few days. The studies on the isolation of titanochloroform and the catalytic action are now undertaken.

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[4] Esso Reserch and Engineering Co., Brit. Pat.857181, Dec. 29, 1960.