# Reactions of Titanium Trichloride with Amines

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As a study of the roles of the amines in the polyolefin catalysts,[1-5] the reactions of titanium trichloride ($\alpha$- type) with various amines have been investigated.

Some reactions of titanium trichloride with amines have previously been studied by several authors. Trimethylamine reacts with titanium trichloride to give a 1 : 2 adduct, $TiCl_3 \cdot 2NMe_3$.[6] On the other hand, Fowles *et al.* have reported that triethylamine does not react with titanium trichloride under reflux.[6] However, Boor *et al.* reported a polyolefin catalyst consisting of titanium trichloride and triethylamine, and suggested some interaction between the above catalyst components.[5] In general, aromatic amines react easily to form additive complexes; pyridine, for instance, gives the 1 : 3 complex $TiCl_3 \cdot 3Py$.[6] Recently, the formation of the 1 : 1 complex $TiCl_3 \cdot Py$ has been reported by Garrasi and Danielli[7].

In the present work, the reactivities of titanium trichloride with various amines are studied, and the reactions of two typical amines, *i. e.*, triethylamine and pyridine, are further investigated.

**Reactivities of Amines toward Titanium Trichloride.** The reactivities of titanium trichloride with various amines were investigated at room temperature. Although trimethylamine as well as quinoline and pyridine reacted with titanium trichloride rapidly, triethylamine, like *N*, *N*-diethylaniline and *N*, *N*-dimethylaniline, did not cause any appreciable reaction at room temperature. The reactivities of the amines seem to be affected predominantly by their steric hindrances. The nucleophillic attack of the lone pair of the amine on titanium trichloride, which is covered almost entirely with negatively-charged chlorine ions, may be hindered by the bulky alkyl groups bound to the nitrogen atom.

**Reaction of Titanium Trichloride with Triethylamine.** Triethylamine did not cause any appreciable reaction with titanium trichloride under mild conditions, as was observed by Fowles *et al.*[6] However, a reaction did take place when the mixture was heated at 150°C without a solvent. As the reaction proceeded the titanium trichloride changed in color from violet to black. The product was insoluble in *n*-hexane. The results of the

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TABLE 1. REACTION OF TITANIUM TRICHLORIDE WITH TRIETHYLAMINE
Temperature : 150°C

| Reaction condition | | | | Appearence | Solid product | | | | | Postulated formula |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Analysis* | | | | | |
| $TiCl_3$ g | $Et_3N$ cc | Time hr | Yield g | | Ti, % | Cl, % | N, % | C, % | H, % | |
| 7.0 | 150 | 24 | 10.0 | Black powder | 21.08 (1.00) | 45.39 (2.92) | 4.13 (0.67) | 22.86 (Et=2.17) | 5.49 | $TiCl_3(Et_3N)_{0.67}$ |
| 7.0 | 150 | 48 | 10.0 | Black powder | 20.75 (1.00) | 44.93 (2.93) | 4.10 (0.68) | 22.45 (Et=2.16) | 5.39 | $TiCl_3(Et_3N)_{0.68}$ |

* Values in parentheses show atomic or molar ratios.

reaction and the analysis of the solid products are shown in Table 1. The compositions of the solid products are represented by $TiCl_3 \cdot (NEt_3)_n$, where $n$ is 0.6—0.7. When hydrolyzed, the products gave nearly theoretical amounts of triethylamine. The IR spectra of the products were identical to each other and were closely related to that of triethylamine. These results show that the products are simple adducts of triethylamine with titanium trichloride. The coordination number, $n$, did not increase further when the reaction was continued for a long time. The X-ray diffraction patterns of the products did not show any lines characteristic of $\alpha$-titanium trichloride, indicating the absence of unreacted titanium trichloride. Accordingly, it may be supposed that the products are mixtures of the 1 : 1 complex $TiCl_3 \cdot NEt_3$ and the 1 : 2 complex $NEt_3 \cdot 2TiCl_3$.

**Reaction of Titanium Trichloride with Pyridine.** The reaction was carried out at 60°C in *n*-hexane over a wide range of reactant ratios. Results of the chemical analysis, the X-ray powder-diffraction patterns, and the IR spectra of the solid products indicated that only the $TiCl_3 \cdot 3Py$ complex was formed, as has been reported by Fowles;[6] such complexes as the previously-claimed $TiCl_3 \cdot Py$[7] or $TiCl_3 \cdot 2Py$ could not be obtained under the present conditions.

## Experimental

**Materials.** A commercially available titanium trichloride (Stauffer Chem. Corp., HR Grade, $\alpha$- type) was used after evacuation at room temperature.

**Analysis.** X-Ray powder-diffractometry was accomplished under a nitrogen atmosphere with a Shimadzu diffractometer, GX-1, by the use of a scintillation counter and Cu$K\alpha$ radiation. The IR spectrum was obtained according to the Nujol method. Triethylamine coordinated with titanium trichloride was isolated and was determined as the hydrochloric salt after the hydrolysis of the complex.

**Reactions of Titanium Trichloride with Amines.** *Triethylamine.* The reaction was carried out at 150°C in a sealed ampoule. The experimental conditions are given in Table 1.

*Pyridine.* Into a suspension of 5 g of titanium trichloride in 50 cc of *n*-hexane, pyridine diluted with 50 cc of *n*-hexane was added at room temperature under a nitrogen atmosphere. The reaction was then also carried out at 60°C in a simlar manner, and the solid product was treated as before.

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