

유기티탄 화학(제 3 보). 사염화티탄과 피페리딘 및 디페닐아민과의 반응

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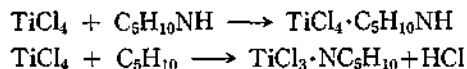
Organotitanium Chemistry(III). The Reactions of Titanium Tetrachloride with Piperidine and Diphenylamine

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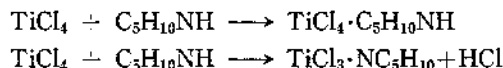
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요 약. 사염화티탄과 피페리딘 및 디페닐아민의 반응을 반응생성물들을 분리하여 규명함으로써 설명하였다. 사염화티탄과 피페리딘은 부가반응과 치환반응이 다음과 같이 동시에 일어남을 알 수 있었다.



부가반응은 비교적 빨리 일어나며 수분내에 반응이 완결되는데 비하여 치환반응은 매우 느리게 일어난다. 위의 두 반응생성물을 모두 분리하여 화학분석결과와 핵자기공명 및 적외선 스펙트럼을 고찰 함으로써 완전히 규명하였다. 이들 반응생성물에는 모두 피페리딘의 염화수소염이 공침됨을 알 수 있었다. 그러나 디페닐아민의 경우, 위의 반응과 아주 비슷하게 일어나지만 부가반응 생성물은 순수하게 얻을 수 있었다.

Abstract. The direct reactions of titanium tetrachloride with piperidine and diphenylamine in dichloromethane have been studied by examining the isolated reaction products. In the reaction with piperidine, titanium tetrachloride undergoes both addition and substitution reactions as in the following:



The addition reaction is relatively fast and completed in minutes whereas the substitution reaction is very slow. The both reaction products coprecipitated with piperidine hydrochloride formed during the substitution reaction were isolated and characterized. The reaction with diphenylamine resembles to the above reaction but the addition compound could be obtained in pure crystal form.

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Introduction

The reactions of titanium tetrachloride and aliphatic amines were extensively studied¹⁻⁶. In general, the reactions of $TiCl_4$ and amines afford both addition and substituted complexes depending on the type of the reacting amines⁵⁻⁷. According to Fowles, *et al.*⁶, titanium tetrachloride reacts with primary and secondary amines by solvolysis in which two chlorine atoms are replaced with primary amines whereas only one with secondary amines. On the other hand only addition compounds were claimed with tertiary and heterocyclic amines⁸. Actually a great deal of addition compounds of $TiCl_4$ with a variety of amines were reported⁶. However, few studies were reported on the direct reaction of $TiCl_4$ with piperidine and diphenylamine.

Although some substituted complexes of Ti-piperidine and Ti-diphenylamine were shown to be formed by indirect method using more reactive intermediates such as metal amides⁹⁻¹³, no evidence is available on the formation of such substituted complexes when $TiCl_4$ and piperidine or diphenylamine were directly reacted in solution. There is only one report by Dermer and Ferneli⁷ on the direct reaction, in which only addition compounds having the compositions close to $TiCl_4 \cdot HNC_5H_{10}$ and $TiCl_4 \cdot HN(C_6H_5)_2$ were obtained.

However, it has been found in our investigation that even during the direct reaction between $TiCl_4$ and piperidine or diphenylamine substitution reaction was always accompanied along with the addition reaction. In this paper we wish to report the details of such reactions and characterization of the isolated complexes.

Experimental

All reactions were performed under thoroughly dried nitrogen atmosphere using the same

reaction vessels as shown before¹⁴. Sampling for physical measurements was also carried out in inert atmosphere. Solvents and glass-ware used were all dried before use as previously described¹⁴.

Reagent grade titanium tetrachloride(Wako) was used without further purification. Piperidine was dried by refluxing over calcium hydride and then fractionally distilling. Diphenylamine was dissolved in anhydrous ethyl ether and dried over anhydrous sodium sulfate. After filtration diphenylamine was recovered by slow evaporation of the solvent.

The IR spectra of the isolated Ti-amine complexes were measured in nujol mull by means of the Beckmann Model 12 Infrared Spectrophotometer. The nuclear magnetic resonance spectra of the compounds in dichloromethane were recorded on a Varian Model HA-100D Spectrometer.

Chemical analysis of carbon and hydrogen, chlorine and titanium were accomplished by the previous methods¹⁴.

Reaction between $TiCl_4$ and Piperidine. Titanium tetrachloride(10 m mole) in 20 ml of dichloromethane was added dropwise with stirring to piperidine(20 m mole) in the same solvent. The reaction proceeded exothermally producing a dense fume which was removed by flush with dry nitrogen. Formation of a yellow solid product(I) was completed in minutes and a green solution was resulted. The solid product(yield 10 % based on Ti) was immediately filtered off in vacuum and then washed with dichloromethane. The above reaction was repeated with a varied ratio of $TiCl_4$ and piperidine(1:4) and a greenish yellow solid(II) was obtained in this case when the product was filtered off 3~4 hours after the mixing. When the filtrate after the product(I) was slowly condensed under reduced pressure, white crystals(III) were isolated from

the green solution. After the white crystals were filtered off the solution was further condensed with heating and then a small amount of warm *n*-hexane was added. On slow cooling, platelet green crystals(IV) were formed.

Reaction between TiCl_4 and Diphenylamine.

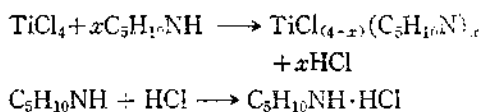
The reaction was carried out in the same way as in the above. Yellow needle-like crystals(V) were obtained when the reaction mixture was filtered off immediately after mixing the reactants, but the product appeared as green powder(VI) on standing for 3~4 hours. When the brick red filtrate was condensed under reduced pressure, a drak green solid product(VII) was isolated.

Results and Discussion

Reaction between TiCl_4 and Piperidine. The yellow product(I) obtained by immediate filtering after mixing the solutions of TiCl_4 and piperidine in dichloromethane was presumed to be the same as the yellow addition compound $\text{TiCl}_4 \cdot \text{C}_5\text{H}_{10}\text{NH}$ which was reported by Dermer and Fernelius.⁷ Since these authors claimed such addition compound prepared from carbon tetrachloride solution soley based upon the result of chemical analysis(Ti: Cl: $\text{C}_5\text{H}_{10}\text{NH}$ =1.0:3.95:1.13) and no other physical data are available, there is no way of comparison with the product(I). However, the chemical analysis data of this product (Ti, 10.5%; Cl, 40.0%; C, 27.0%; H, 5.4%) could hardly be fit to the formula not only of the addition compound but also of any other possible single species. Nevertheless, the mole ratio of the components calculated from the above experimental values (Ti: Cl: $\text{C}_5\text{H}_{10}\text{NH}$ =1.0:5.13:2.04) immediately suggests that the product(I) is probably an equimolar mixture of the addition compound $\text{TiCl}_4 \cdot \text{C}_5\text{H}_{10}\text{NH}$ and piperidine hydrochloride $\text{C}_5\text{H}_{10}\text{NH} \cdot \text{HCl}$. In fact, the hydrochloride was conti-

neously crystallized out following the precipitation of the mixed yellow product. The white crystalline compound(III) thus obtained was identified to be piperidine hydrochloride by chemical analysis (Found: Cl, 49.2%; H, 10.0%; Cl, 29.9%. Calc.: C, 49.2%; H, 9.95%; Cl, 29.2%) and confirmed by its NMR and infrared spectra.

The isolation of piperidine hydrochloride and evolution of the fuming gas which was found to be hydrogen chloride certainly indicate that besides the addition reaction also replacement of chlorine with the amine ligand occurred yielding the slightly soluble hydrochloride and a green solution as illustrated in the following:



where the value of *x* will be shown to be equal to one. When condensation of the resultant green solution was followed by addition of a small amount of *n*-hexane, green platelet crystals were formed. The result of the elemental analysis of this product(IV) (Ti, 16.1%; Cl, 42.0%; C, 29.4%; H, 5.6%) was not met with any formula of a single substituted species as given in *Table 1*, but fit to a mixture composition of 81% $\text{TiCl}_3 \cdot \text{NC}_5\text{H}_{10}$ and 19% $\text{C}_5\text{H}_{10}\text{NH} \cdot \text{HCl}$, which could be convinced from examination of its NMR and infrared spectra. In particular, the NMR spectrum of the green product(IV) represented together with those of free piperidine and its hydrochloride in *Fig. 1* gives a great deal of informations of its chemical composition and structure.

The proton resonance of piperidine hydrochloride(*Fig. 1b*) appears expectedly at lower fields with better resolution compared with those of free piperidine(*Fig. 1a*) probably because of protonation of the amine nitrogen. The dramatic

Table 1. Theoretical compositions of substituted complexes.

Compound	Ti(%)	Cl(%)	C(%)	H(%)
$C_5H_{11}NH \cdot HCl$	0	29.2	49.2	9.95
$TiCl_3 \cdot NC_5H_{10}$	20.1	44.6	25.2	4.23
$TiCl_2 \cdot (NC_5H_{10})_2$	17.2	25.4	43.1	7.23
$TiCl \cdot (NC_5H_{10})_3$	14.3	10.6	53.7	8.94
81% $TiCl_3 \cdot NC_5H_{10} +$ 19% $C_5H_{10}NH \cdot HCl$	16.1	41.7	29.5	5.3

downfield shift of the N—H proton resonance of free piperidine ($\delta=2.22$ ppm, multiplet) to 9.5 ppm with broad band width must be ascribed to the formation of ammonium ion $>NH_2^+$ by protonation. It seems also worthwhile to point out that the α -proton resonance of the hydrochloride appearing as a clear quintet centered at 3.08 ppm is another evidence of the protonation. Now the spectrum of the green product(IV) may be examined.

It is clearly seen in Fig. 1c that there are two species of piperidine different in chemical environment. Although the β - and γ -proton resonances of the two piperidine species are not separated from each other, their α -proton peaks appear at different fields far apart, which means that in particular the nitrogen environments of the piperidine species are remarkably different. The unresolved multiplet at 3.36 ppm which appears as a quintet at high sensitivity is probably originated from the α -protons of piperidine hydrochloride coprecipitated with the major green compound which is represented by the triplet at 4.78 ppm. Such a remarkable down-field shift of the α -proton resonance of piperidine is a strong evidence that the amine nitrogen is coordinated to metal, that is, titanium. The clear triplet appearance of this α -proton peak implying no proton available at the nitrogen atom further confirms the nitrogen to metal coordination.

The infrared spectra of piperidine and the rel-

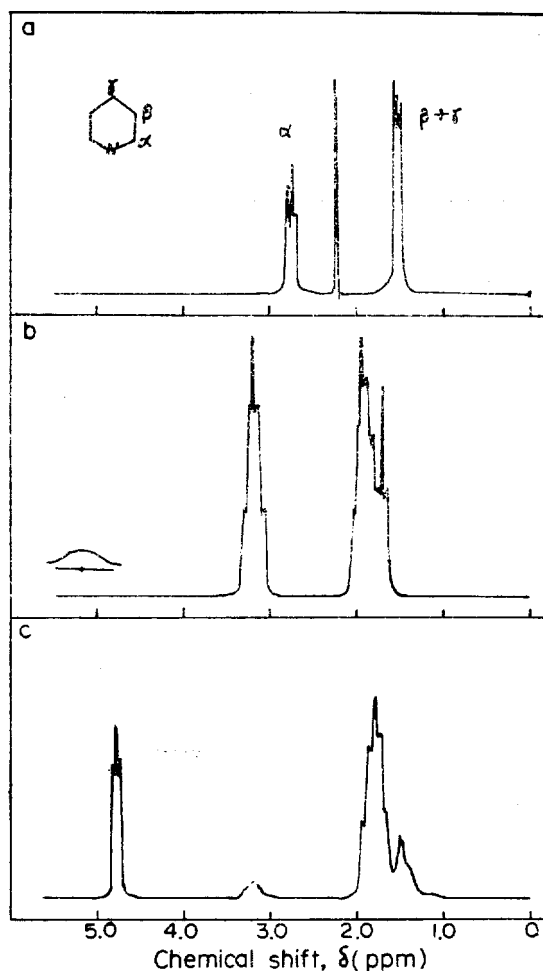


Fig. 1. The NMR spectra of free piperidine(a), piperidine hydrochloride(b) and the green compound(IV) (c) in dichloromethane.

ated complexes shown in Fig. 2 are also in accord with the NMR data. It is seen in Fig. 2c and d that the infrared spectrum of the green

product(IV) includes all the characteristic bands exhibited by piperidine hydrochloride. Among the additional bands originated from the green-component the band at 630 cm^{-1} not observed in any other spectra should be noticed. The Ti—N stretching mode¹⁵ is generally cited as appearing

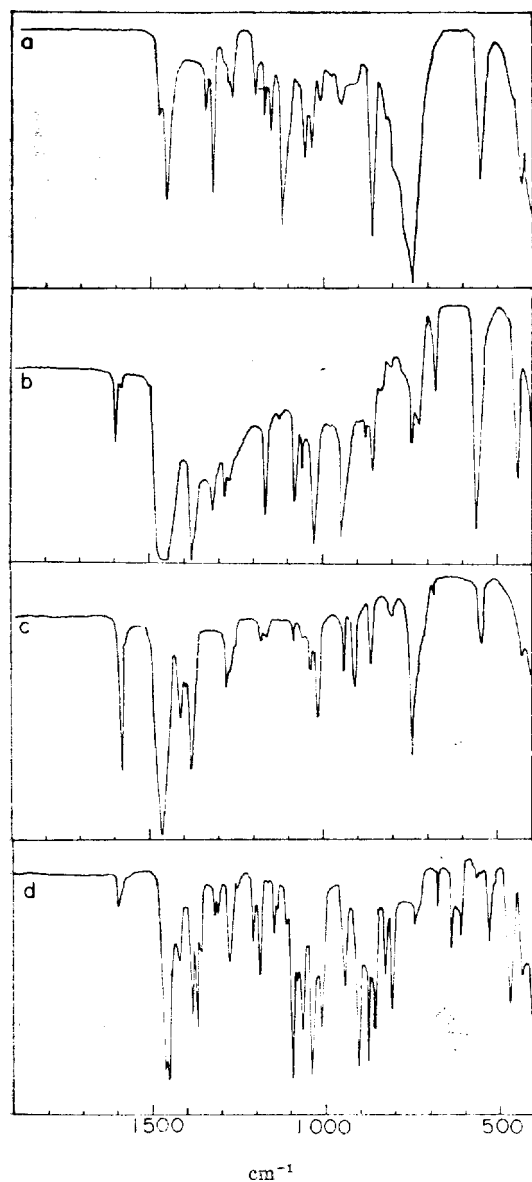
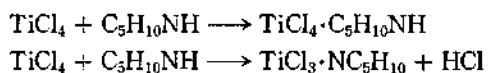


Fig. 2. The IR spectra of free piperidine(a), piperidine hydrochloride(b), the yellow product (I) (c) and the green product(IV) (d) in nujol mull.

in the range $600\sim 650\text{ cm}^{-1}$ and as such the band at 630 cm^{-1} indicates Ti—N bond formation by ligand substitution of titanium tetrachloride with piperidine. Therefore, it may be concluded that the green product(IV) is a crystal mixture composed of the green complex $\text{TiCl}_3 \cdot \text{NC}_5\text{H}_{10}$ and a small amount of the white piperidine hydrochloride. A few attempts to purify the green compound by recrystallization was not successful because of its partial decomposition during redissolution in the solvent.

In conclusion, when titanium tetrachloride and piperidine are directly reacted in solution, both the addition and substitution reactions occur simultaneously as in the following:



The addition reaction proceeds very rapidly and is completed in minutes while the substitution reaction takes place slowly yielding hydrogen chloride which is consumed to form piperidine hydrochloride slightly soluble in dichloromethane.

Finally, the greenish yellow product(II) should be commented. The results of chemical analysis of this product were not consistent depending of the reaction conditions and it seems probably a mixture of the addition compound, piperidine hydrochloride and the green substituted complex.

Reaction between TiCl_4 and Diphenylamine.

When titanium tetrachloride was reacted with diphenylamine in solution the reaction proceeded somewhat similar to the reaction with piperidine. However, contrary to the case of piperidine no diphenylamine hydrochloride was separated in pure form during the reaction process. The addition was completed also very rapidly yielding a yellow crystalline product(V) but the replacement reaction with diphenylamine pro-

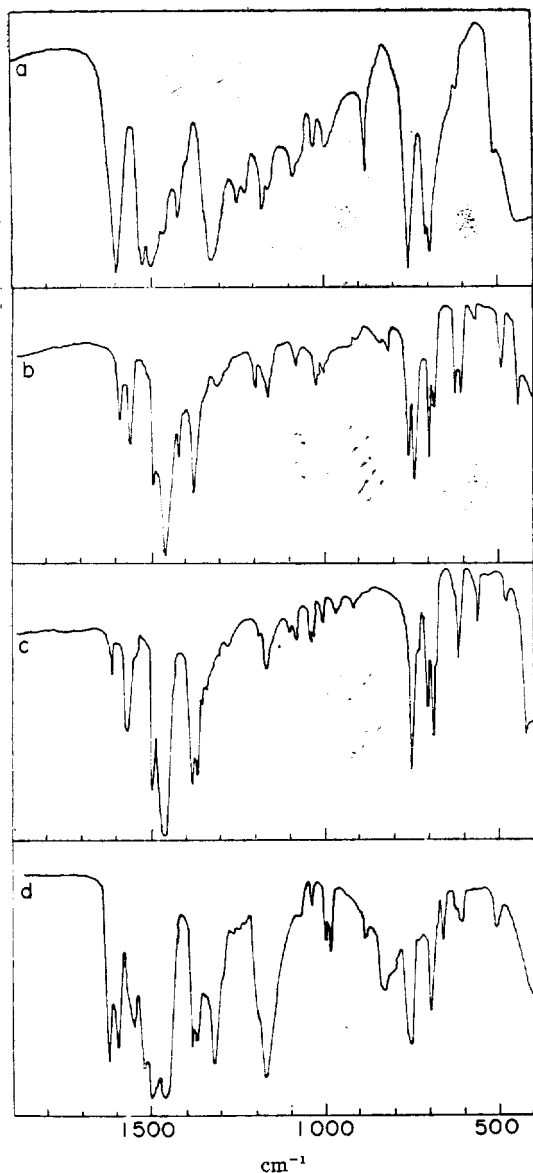


Fig. 3.-The IR spectra of free diphenylamine(a), its hydrochloride(b), the yellow compound V (c) and the green product (VII)(d) in nujol mull.

ceeded much slower than with pi peridine. The analysis of this addition compound(V) obtained by immediate filtering after mixing has been found to be a pure equimolar adduct $\text{TiCl}_4 \cdot (\text{C}_6\text{H}_5)_2\text{NH}$ (found (%): Ti, 12.0; Cl, 38.0. Calc. (%): Ti, 13.3; Cl, 39.5).

The isolation of such a relatively pure addition

compound could be achieved probably because the substitution rate was so slow that the coprecipitation by the resulting diphenylamine hydrochloride was not significant. On the other hand, the product(VI) was not consistent in its composition depending on the reaction conditions and must be a complicated mixture of more than two compounds. However, the dark green product(VII) resembling in appearance the reported^{12,13} monosubstituted species $\text{TiCl}_3 \cdot \text{N}(\text{C}_6\text{H}_5)_2$ could be identified to be a binary mixture of the color component $\text{TiCl}_3 \cdot \text{N}(\text{C}_6\text{H}_5)_2$ and diphenylamine hydrochloride.

The infrared spectra of diphenylamine and the related complexes given in Fig. 3 support such a conclusion. The spectrum of the product (VII) in Fig. 3d shows evidently the inclusion of the hydrochloride(Fig. 3b). In fact, its analytical data(Ti, 11.3 %; Cl, 30.0 %) could be fit to the composition of a binary mixture of 67 % $\text{TiCl}_3 \cdot \text{N}(\text{C}_6\text{H}_5)_2$ and 33 % $(\text{C}_6\text{H}_5)_2\text{NH} \cdot \text{HCl}$ (Theory: Ti, 11.3 %; Cl, 29.2 %). It was also difficult to purify the substituted complex by recrystallization since the mixed product was only slightly soluble in organic solvents.

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