

유기티탄 화학(제 4 보),  $\text{TiCl}(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$  및  
 $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{C}_6\text{H}_5\text{OH}$  의 분자 및 전자구조

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Organotitanium Chemistry (IV). The Molecular and  
Electronic Structure of  $\text{TiCl}(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$   
and  $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{C}_6\text{H}_5\text{OH}$

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요 약.  $\text{TiCl}(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$  및  $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{C}_6\text{H}_5\text{OH}$  의 분자량 측정과 전자 흡수스펙트럼을 고찰함으로써 이들 두 유기-티탄 화합물들의 용액 상태에서의 분자 및 전자구조에 대하여 연구하였다.  $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{C}_6\text{H}_5\text{OH}$  는 고체상태에서는 이합체로 존재하지만 분자량 측정 결과 묽은 용액에서는 단위체로 완전해리되며  $\text{TiCl}(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$  도 8 mM 농도에서 해리를 시작함을 알수 있었다. 따라서 이들 두 착화합물은 묽은 용액에서 5 배위 착화합물로 존재하며 분자구조는 trigonalbipyramid 으로 생각된다.

두 화합물의 전자 흡수스펙트럼은 자외부쪽에 똑같은 진동구조를 갖는 벤젠고리 특유의 흡수밴드를 나타내며 가시부에서는  $\text{TiCl}(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$  의 경우 26.8 kK 에  $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{C}_6\text{H}_5\text{OH}$  는 29.6 kK 에 각각 흡수 밴드를 나타낸다. 이가시부 흡수밴드는 리간드에서 금속쪽으로 전하이전에 의한  ${}^1A_1'' \rightarrow {}^1E'$  or  ${}^1E''$  전이로 생각된다.

**Abstract.** The molecular and electronic structures of  $\text{TiCl}(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$  and  $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{C}_6\text{H}_5\text{OH}$  have been studied by employing cryoscopic and electronic spectroscopic methods. The cryoscopic data have shown that the dimeric tetraphenoxytitanium(IV) phenolate in solid undergoes complete dissociation into monomer in solution and also the chlorocomplex starts dissociation around the concentration of 8 m mole/l. Therefore, these two Ti-complexes are pentacoordinated in dilute solution and the local symmetry of the titanium ion in these complexes seems to be trigonalbipyramid.

The electronic spectra of  $\text{TiCl}(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$  and  $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{C}_6\text{H}_5\text{OH}$  each show two band systems, one vibration-structural band characteristic of the aromatic ring in the near UV and another visible band at 26.8 kK, 29.6 kK, respectively, which are assigned as a ligand to metal charge transfer band corresponding to  ${}^1A_1'' \rightarrow {}^1E'$  or  ${}^1E''$  transition.

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## Introduction

Preparations of tetraphenoxytitanium(IV) and halogenophenoxytitanium(IV) complexes were early described by several authors<sup>1-4</sup>. However, no study on their molecular and crystal structures has been reported until very recent years. According to the X-ray diffraction study by Svetich and Voge<sup>5</sup> the structure of tetraphenoxytitanium(IV) phenolate is a dimer bridged by two phenoxy-oxygen atoms so that the titanium atom is six-coordinated for a distorted octahedron, while Watenpaugh and Cauphan<sup>6</sup> have shown dichlorodiphenoxytitanium(IV) is also dimeric but each titanium is pentacoordinated.

A study on the electronic spectra of phenoxytitanium complexes<sup>7</sup> was recently reported but its interpretation was attempted simply assuming tetrahedral structure, since no definite evidence was available for their molecular structure at that time. In this paper we wish to present the results of our study on the molecular and electronic structures of  $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{C}_6\text{H}_5\text{OH}$  and  $\text{TiCl}(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$  employing cryoscopic and spectroscopic methods.

## Experimental

All the reactants and solvents used were dried or purified as described previously.<sup>8</sup> Chemical reactions and physical measurements of phenoxytitanium complexes were also performed in thoroughly dried state under inert atmosphere.

Tetraphenoxytitanium(IV) phenolate,  $\text{Ti}(\text{O}\phi)_4 \cdot \phi\text{OH}$ , was prepared from reaction of pure titanium tetraisopropoxide(K & K Lab. Inc.) and excess phenol. While the reacting mixture was heated, the resultant isopropyl alcohol was eliminated under vacuum. The product was subjected to recrystallization twice in a solvent pair of  $\text{CH}_2\text{Cl}_2$ -*n*-hexane and a reddish orange crystalline

compound was obtained.

*Chemical anal.* (%): C, 69.4; H, 5.08; Ti, 9.35(Theory of  $\text{Ti}(\text{O}\phi)_4 \cdot \phi\text{OH}$ (%): C, 70.40; H, 5.10; Ti, 9.32).

Chlorotriphenoxytitanium(IV) phenolate,  $\text{TiCl}(\text{O}\phi)_3 \cdot \phi\text{OH}$ , was prepared by homogeneous solution reaction of  $\text{TiCl}_4$  and excess phenol in dichloromethane. Addition of *n*-hexane to the reaction mixture resulted in slow crystallization of a dark reddish brown complex, which was recrystallized twice in benzene-*n*-hexane pair. With a large excess of phenol under a more vigorous temperature condition(heating to boiling), the same product was yielded.

*Chemical anal.* (%): Ti, 10.58; Cl, 7.77; C, 61.3; H, 5.09 (Theory of  $\text{TiCl}(\text{O}\phi)_3 \cdot \phi\text{OH}$ (%): Ti, 10.49; Cl, 7.76; C, 63.05; H, 4.63).

The molecular weight of the titanium complexes in benzene(1~10mM)was determined cryoscopically using the specially built equipment as was described in detail in other paper<sup>9</sup>.

The UV-visible spectra of the Ti-complexes were measured in  $\text{CH}_2\text{Cl}_2$ -*n*-hexane solution or in benzene using Cary Model 14 Spectrophotometer and 1.0 cm standard quartz cell.

## Results and Discussion

The molecular weight of tetraphenoxytitanium(IV) and chlorotriphenoxytitanium(IV) phenolates has been determined in benzene at different concentrations and the results are shown in Fig. 1. The measured molecular weight(480) of tetraphenoxytitanium(IV) phenolate is shown to be almost constant in the range 1~10 mM and is close to the theoretical value(514.4) of the monomeric form. Such a result certainly indicates that the dimeric form of tetraphenoxytitanium(IV) phenolate in solid state completely dissociates into monomer in solution in the range at least below 10 mM.

On the other hand the cryoscopic data of chlo-

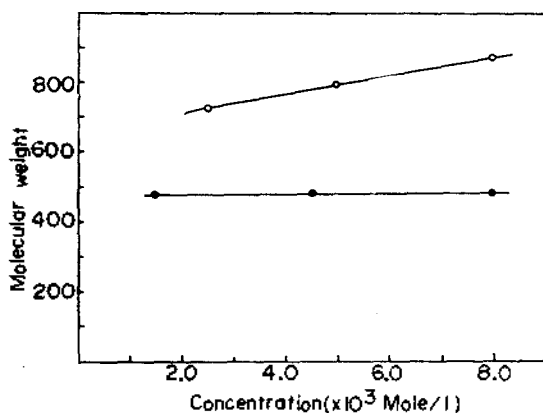


Fig. 1. Molecular weights of  $\text{Ti}(\text{O}\phi)_4 \cdot \phi\text{OH}$  (●●) and  $\text{TiCl}(\text{O}\phi)_3 \cdot \phi\text{OH}$  (○○).

rotriphenoxytitanium(IV) phenolate are concentration-dependent and the measured value (870) at 8 mM is found to be nearly the double of the expected molecular weight (456.8) of the monomer,  $\text{TiCl}(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$  and as such shows the dimeric nature of this chloro-complex at higher molar concentration. However, the gradually decreasing tendency at lower concentration suggests that molecular dissociation partly occurs and probably also a further dissociation into monomer may be reached in more dilute solution. Therefore, it seems that chlorotriphenoxytitanium(IV) phenolate exists also as dimeric form in solid state but dissociates into monomer in solution only less easily than the tetraphenoxy-complex.

The local symmetry of the titanium ion in the dimeric tetraphenoxytitanium(IV) phenolate was found to be octahedral as was mentioned earlier<sup>5</sup>. However, when this dimer dissociates in solution as the cryoscopic data show, its molecular symmetry must also be changed. The resultant pentacoordinate monomer must be either trigonal bipyramidal or tetragonal pyramidal, but in view of general nature of pentacoordinated Ti-complexes which are found to be the former in most cases,<sup>6,10</sup> the possibility of the tetragonal pyramidal form may be excluded.

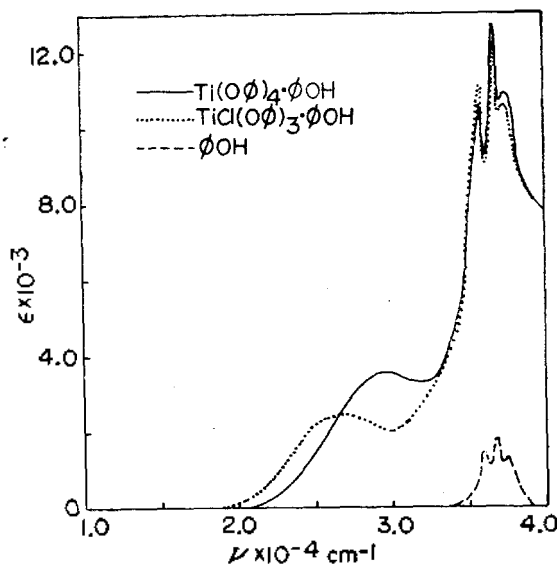


Fig. 2. Electronic spectra of Ti-complexes in  $\text{CH}_2\text{Cl}_2$ -hexane.

Now the electronic spectra of the Ti-complexes may be examined. Their electronic spectral data are given in Fig. 2 and in Table 1 together with the data of free phenol. The two Ti-phenolates show a very similar spectral pattern in which there are two band systems, one with vibrational structure and the other structureless, whereas the free phenol shows only one structural band characteristic of its parent ring. The spectral similarity of the two Ti-complexes confirms as expected the resemblance of the two compounds in molecular and electronic structures.

Although the intensity of the structural bands of the Ti-complexes appears much higher than that of the free phenol system, their band structure and positions are all identical. Furthermore, if the band intensity of the Ti-complexes is divided by the number of aromatic rings involved in each molecule and is corrected for the tailing by the adjacent visible bands, there is no remarkable enhancement of band intensity from the value of free phenol. Therefore, the electronic transition associated with this band system has probably the same origin as that of the free phenol band which

Table 1. UV-visible spectral data.

Compound	$\nu_{\max}$ (cm <sup>-1</sup> )	$\epsilon_{\max}$	Assignment
Ti(OO) <sub>4</sub> ·OOH	29,600	3,550	${}^1A_2 \rightarrow {}^1E'$ or ${}^1E''$
	35,970	10,700	${}^1A \rightarrow {}^1L_b$
	36,830	12,800	
	37,670	11,000	
TiCl(OO) <sub>3</sub> ·OOH	26,800	2,500	${}^1A_1 \rightarrow {}^1E'$ or ${}^1E''$
	35,970	11,200	${}^1A \rightarrow {}^1L_b$
	36,830	12,200	
	37,670	10,600	
OOH	35,970	1,500	${}^1A \rightarrow {}^1L_b$
	36,830	1,780	
	37,670	1,260	

is well known to be a secondary band  ${}^1A \rightarrow {}^1L_b$  ( ${}^1A_{1g} \rightarrow {}^1B_{2u}$ ) localized in the aromatic ring.<sup>11</sup> The fact that the vibrational structure is still retained in this system and there is no noticeable change of the absorption energy implies that the electronic structure of the phenol aromatic ring is not significantly affected by coordinating through oxygen atom to the metal.

More important is the structureless visible bands of tetraphenoxo- and chlorotriphenoxytitanium (IV) phenolates located at 29,600 and 26,800cm<sup>-1</sup> respectively. These broad bands are missing in free phenol, and consequently must be associated with Ti-phenol coordination band. The aromatic rings may be disregarded from consideration of Ti-O bonding, since their electrons are highly localized and not affected by the coordination. Thus only the local symmetry around the metal atom discussed earlier may be considered. The local symmetry of titanium ion in both phenolates is approximately octahedral in solid or in concentrated solution, and the molecular orbitals for the local TiL<sub>6</sub>(L=O or Cl) may be represented following the general scheme of MX<sub>6</sub> type<sup>12</sup> as shown in Fig. 3. However, it has already been mentioned above that in the spectroscopic concentration ( $\sim 0.1mM$ ) the Ti-complexes undergo complete

dissociation into monomer and the local symmetry changes from octahedral(*O<sub>h</sub>*) to trigonal bipyramidal form(*D<sub>3h</sub>*). In order to interpret the spectra based on the molecular orbital scheme, only the relevant orbitals concerning the transition may be modified according to symmetry change of the appropriate orbitals. The molecular orbitals highest occupied and lowest empty modified according to *D<sub>3h</sub>* point group are shown in Fig. 4.

Since all ligand orbitals are filled and the metal orbitals are empty, the lowest energy band would arise from one electron transition from ( $a_2' + 2e''$ ) to  $e''$ , that is,  $(a_2' + 2e'')^{10}e''^0 \rightarrow (a_2' + 2e'')^9e''^1$ . Such a transition corresponds to a state transition  ${}^1A_1'' \rightarrow {}^1E'$  or  ${}^1E''$ , which is allowed. Therefore, the visible bands of the Ti-complexes may be assigned to a ligand to metal charge transfer(L→M) corresponding to  ${}^1A_1'' \rightarrow {}^1E'$  or  ${}^1E''$  transition.

The molar extinction coefficients of the visible bands at 29,600( $\epsilon=3,500$ ) and 26,800cm<sup>-1</sup>( $\epsilon=2,500$ ) in the Ti-complexes are relatively low compared with that of fully allowed organic  $\pi \rightarrow \pi^*$  transitions ( $\epsilon > 10,000$ ). However, in many cases of inorganic or organometallic complexes the oscillator strength of allowed bands appears smaller. For example, in ruthenium and osmium halides<sup>13,14</sup> the molar extinction coefficients of

the  $\pi \rightarrow t_{2g}$  bands resembling the  $L \rightarrow M$  transition in the Ti-complexes are in the range of  $\epsilon = 1000 \sim 8000$ .

Finally, the difference in the spectra of the two Ti-complexes may be commented. The  $L \rightarrow M$  charge transfer band of chlorotriphenoxytitanium (IV) phenolate appears at slightly lower energy than the tetraphenoxo complex. The reason seems to be due to the lower electronegativity of chlorine

atom than that of oxygen. Although the chlorine ligand is not distinguished from the other phenolic oxygen atoms as far as Ti-local symmetry is concerned, its less electronegativity may induce more easily the  $L \rightarrow M$  charge transfer transition.

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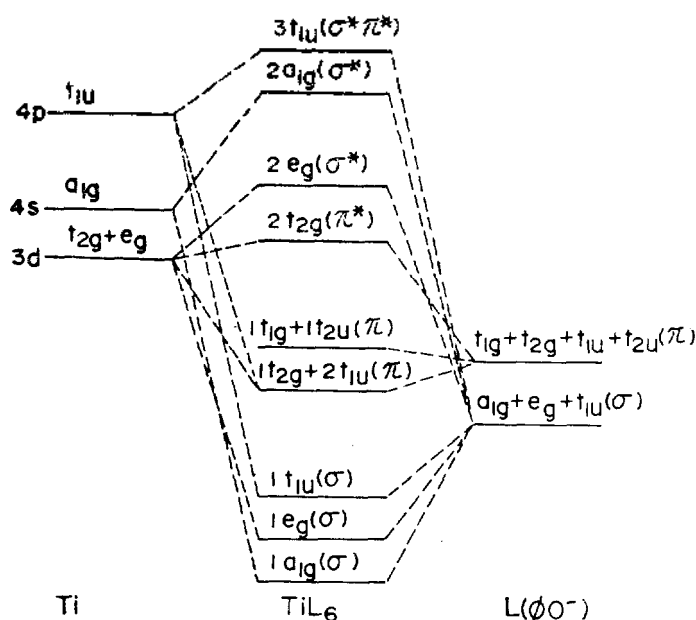


Fig. 3. The molecular orbital scheme of octahedral  $TiL_6$ .

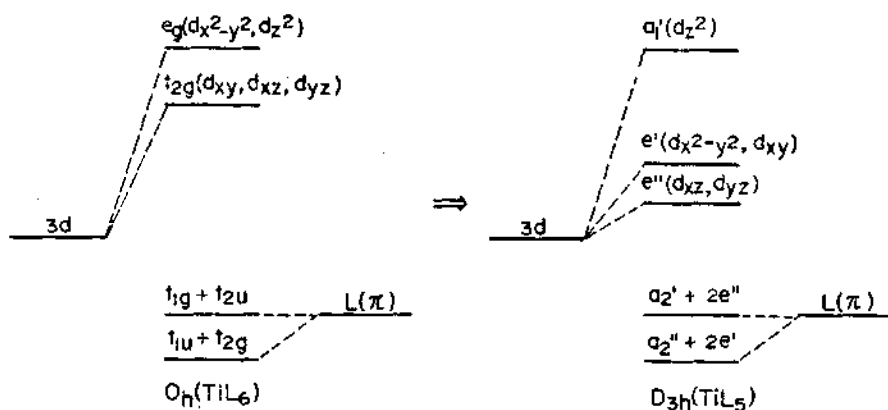


Fig. 4. Correlation of important energy levels of octahedral  $TiL_6$  and trigonal-bipyramidal  $TiL_5$ .

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