

## 유기-티탄화학 (제 2 보). Dichlorodiacetatotitanium(IV)

### 여러 알콜과의 가용매반응

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한국과학기술연구소

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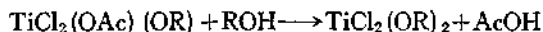
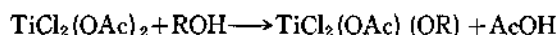
## Organotitanium Chemistry II. Solvolytic Reaction of Dichlorodiacetatotitanium(IV) with Various Alcohols

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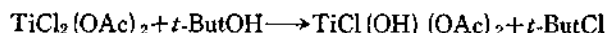
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**요 약.** 이클로리도비스아세테이트로 티탄(IV)은 알콜에 녹을때 화학반응을 일으킨다.  $TiCl_2(OAc)_2$ 의 이러한 가알콜분해 반응을 여러형태의 알콜에 대하여 반응용액의 핵자기 공명스펙트럼과 분리된 반응 생성물의 화학분석결과 등을 이용하여 완전히 구명하였다.  $TiCl_2(OAc)_2$ 와 1급 알콜과의 반응은 다음과 같은 2 단계의 리간드 치환반응이 정량적으로 일어남을 알았다.



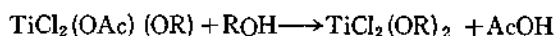
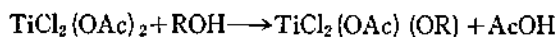
또한  $TiCl_2(OAc)_2$ 가 알콜에 녹을때 최초의 가용성 분자형태는  $TiCl_2(OAc)(OR)$ 임을 알수 있었다. 3급 알콜과의 가알콜분해 반응은 1급 알콜에와는 상당히 다름을 알수 있었다. 즉 3급 부칠알콜과  $TiCl_2(OAc)_2$ 의 몰비가 1:2이하인 경우에는 다음과 같은 치환 반응만 선택적으로 일어난다.



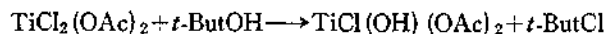
그러나 위의 몰비가 1:2이상이 되면 이러한 반응과 병행하여 1급 알콜과의 첫단계 반응과 똑같은 형의 치환 반응이 경쟁적으로 일어남을 발견하였다. 3급 알콜과의 반응이 1급 알콜과의 반응과 또 다른점은  $TiCl_2(OAc)_2$  중의 두개의 클로리도리간드 또는 두개의 아세테이트리간드 중 하나만이 3급부칠알콜의 OH 또는 *t*-ButO 기와 치환된다는 사실이다.

**Abstract.** Dichlorodiacetatotitanium(IV) dissolves in alcohols with chemical reaction. Such solvolytic reaction of  $TiCl_2(OAc)_2$  with various alcohols has been studied by means of solution NMR spectroscopy and chemical analysis of the isolated products. The reaction of  $TiCl_2(OAc)_2$  with primary alcohols has shown to be a quantitative two-step ligand substitution process as shown in the following:

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The molecular form initially soluble in organic solvents has been found to be the monosubstituted species  $\text{TiCl}_2(\text{OAc})(\text{OR})$ . Alcoholysis with *t*-butyl alcohol has shown remarkable differences. When the mole ratio of *t*-butyl alcohol to  $\text{TiCl}_2(\text{OAc})_2$  is less than 1/2, the following reaction is dominant.



However, at higher mole ratio another substitution process resembling the first step reaction with primary alcohols is competitively accompanied. The reaction with *t*-butyl alcohol also differs from that with primary alcohols in that only one either of the two chloro- or acetato-ligands in  $\text{TiCl}_2(\text{OAc})_2$  is subjected to substitution.

### Introduction

The preparation of dichlorodiacetatotitanium (IV) was first reported in 1925<sup>1</sup> and repeated several times<sup>2-5</sup> including our previous work.<sup>6</sup> Although it has been cited as showing fire retardancy<sup>7</sup> and improving fuel combustion<sup>8</sup> when added as an additive, its fundamental chemical properties have been little known probably because of its insolubility in organic solvents and instability to moisture. During our previous study<sup>6</sup> it was found that  $\text{TiCl}_2(\text{OAc})_2$  dissolved in alcohol with chemical reaction. The purpose of this study is to investigate only the apparent nature of such solvolytic reaction with various alcohols (MeOH, EtOH, *n*-PrOH, *n*-OctOH) and *t*-ButOH) and the detailed mechanism or reaction rate will not be considered. In order to elucidate the nature of the reaction dichloromethane was employed, if necessary, as a reaction medium in which  $\text{TiCl}_2(\text{OAc})_2$  and alcohols were reacted, and its solution NMR spectra were measured. In some cases the reaction product was isolated and characterized.

### Experimental

Synthesis of  $\text{TiCl}_2(\text{OAc})_2$  and purification of

dichloromethane were achieved following our previous methods.<sup>6</sup> All alcohols used were reagent grade and dried by refluxing with calcium hydride, followed by fractional distillation. The whole procedure of NMR sampling was proceeded in a dry box using thoroughly dried glass equipments as was previously described.<sup>6</sup>

**Measurements of NMR Spectra.** Approximately 0.5g of dichlorodiacetatotitanium (IV) was accurately weighed in a tightly stoppered vial and suspended in dichloromethane (2ml). An accurate amount of alcohol corresponding to the predetermined mole ratio was added and then the mixture was shaken until dissolution was complete. The NMR spectra of this solution was recorded on a Varian Model HA-100D Spectrometer. If necessary, low temperature spectra were measured by varying the sample temperature in the range 30~ -67°C by means of a Varian Model V-6040 Variable Temperature Controller and liquid nitrogen.

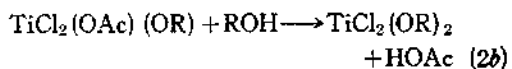
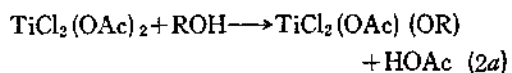
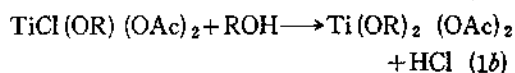
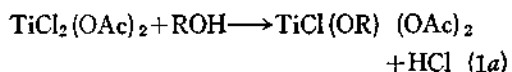
**Isolation of the Alcoholysis Products.** Ethanolysis product. —  $\text{TiCl}_2(\text{OAc})_2$  was dissolved in excess of ethanol and then all the volatile stuffs as well as the excess alcohol were evaporated by mild heating under dry nitrogen purge. The residual product was subjected to vacuum

drying at the ethanol boiling temperature in a drying pistol. A light yellow product soluble in organic solvents was obtained.

Butanolysis product. — $\text{TiCl}_2(\text{OAc})_2$  (10 m mole) was weighed into a two-necked flask and suspended in dichloromethane. An accurate amount of *t*-ButOH (5 m mole) was added dropwise to this suspension and then the reaction mixture was shaken until the reaction was completed. After the unreacted Ti-complex was filtered off, the filtrate was evaporated under reduced pressure at room temperature. A pale yellow product was yielded, which is insoluble in non-alcoholic solvents.

## Results and Discussion

(I) **Solvolytic Reaction with Ethanol and Other Primary Alcohols.** When dichlorodiacetatotitanium(IV) dissolves in excess alcohol, two different pattern of ligand substitution are possible depending on the lability of the leaving group as shown in the following:



The Ti-product of reaction (1b) or (2b) may undergo further substitution leading to the formation of tetrasubstituted complex  $\text{Ti}(\text{OR})_4$ , if the both ligands ( $\text{Cl}^-$  and  $\text{OAc}^-$ ) are more labile than the alkoxy group  $\text{RO}^-$ .

In order to distinguish the above possibilities, ethanolysis product was isolated and characterized by chemical analysis and spectroscopic methods. Although the isolated compound has

not shown a definite composition, it presented decisive informations on the solvolysis pattern. By chemical analysis this product could be formulated to  $\text{TiCl}_x(\text{OH})_y(\text{OEt})_z$ , where  $x+y+z=4$ . The numerical values of  $x, y$  and  $z$  have been found to be variable depending on the ethanolysis condition, but important is that  $x$ -value is always between one and two, which certainly indicates that the alcoholysis reaction proceeded following the equation (2) instead of equation (1). In fact, free acetic acid resonances could be observed in the spectrum of  $\text{TiCl}_2(\text{OAc})_2$  in excess ethanol. The presence of chlorine in the isolated complex also excludes the possibility of tetrasubstitution beyond the reaction (2b). As a result, the lability of the ligands in Ti-complex must be increasing in the order  $\text{Cl}^- < \text{OEt}^- < \text{OAc}^-$ . The hydroxy group in the isolated complex seems to be originated from hydrolysis reaction of the Ti-product in reaction (2b). It has been proved by NMR spectrum of  $\text{TiCl}_2(\text{OAc})_2$  in excess ethanol that acetic acid formed in reaction (2) was subjected to slow esterification reaction with the excess alcohol. The water molecules thus formed may hydrolyze the product  $\text{TiCl}_2(\text{OEt})_2$ .

In order to examine more closely the solvolytic reaction illustrated by equation (2),  $\text{TiCl}_2(\text{OAc})_2$  was reacted with ethanol in an inert solvent ( $\text{CH}_2\text{Cl}_2$ ) by varying their mole ratio, and NMR spectra of the reacted solution were studied. When the mole ratio of ethanol to  $\text{TiCl}_2(\text{OAc})_2$  was less than one, the Ti-complex dissolved only in part where as its dissolution was complete at higher mole ratio. This fact implies that the molecular form soluble in dichloromethane is the monosubstituted product  $\text{TiCl}_2(\text{OAc})(\text{OEt})$  and also that ethanolysis-reaction is a clean-cut two step ligand substitution process represented by equations (2a) and (2b). Such a conclusion was further confirmed by NMR spectra of the reacted solutions shown.

in Fig. 1 and Table 1. No spectral difference is noticed between the solutions of  $TiCl_2(OAc)_2 + \frac{1}{2}EtOH$  and  $TiCl_2(OAc)_2 + EtOH$  (Fig. 1 a and b). This means that no chemical species other than  $TiCl_2(OAc)(OEt)$  and HOAc was produced in both of these solutions.

Increasing the mole ratio to 2 (Fig. 1c), the resonances generally all shifted to high field but no new resonance was observed. Since at room temperature fast exchange is expected between free and coordinated molecules both of entering and leaving groups, it could not be informed from such spectra whether the 2nd ligand substitution (Eqn. 2b) was completed or a part of free alcohol remained unreacted. When the mole ratio was further increased up to 4 at which a large excess of free alcohol must be present, a new chemical species, that is, ethyl ester  $CH_3COOC_2H_5$  has been found to be formed as is seen in the spectra Fig. 1d. The new singlet at 2.02 ppm and triplet centered at  $\sim 1.2$  ppm are methyl proton resonances of the carboxy and ethyl groups in  $CH_3COOC_2H_5$ , respectively. The methylene proton peak ( $CH_2COOCH_2CH_3$ ) is overlapped with the quartet at 4.1 ppm. On standing, the intensities of the new resonances were growing in parallel and

the esterification reaction between the released acetic acid and excess alcohol must be continu-

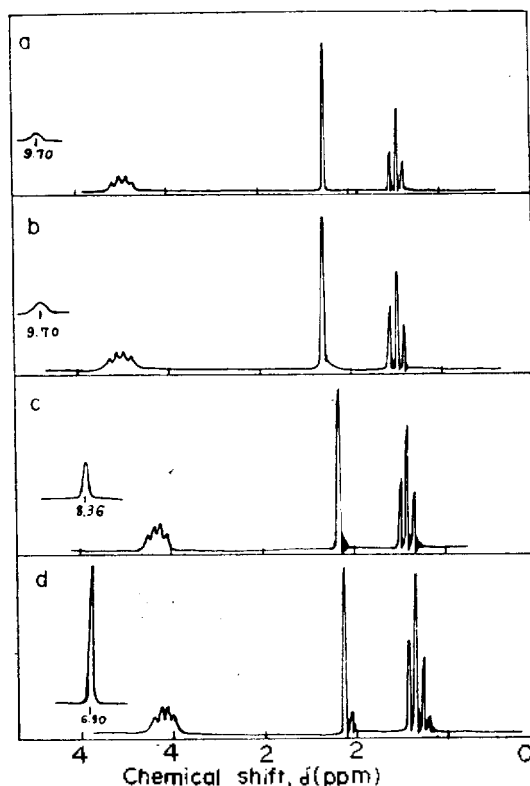


Fig. 1. NMR spectra of  $TiCl_2(OAc)_2 + EtOH$  in  $CH_2Cl_2$  solvent at different mole ratios: a; 1:0.5, b; 1:1, c; 1:2, d; 1:4

Table 1. Chemical shifts of the chemical species in  $TiCl_2(OAc)_2 + EtOH$  solution\*

Ratio $TiCl_2(OAc)_2:EtOH$	Temp °C	Chemical shift, (ppm vs. TMS)				Species
		$CH_3-CH_2-O-$	$CH_3-CH_2-O$	$CH_3COO-$	$-OH + -COOH$	
1 : 0.5	30	1.48	4.53	2.26	9.70	
1 : 1	30	1.48	4.53	2.26	9.70	
1 : 2	30	1.38	4.34	2.14	8.36	
	-67	1.42	$\sim 4.3$	2.20	$\sim 11$	
1 : 4	30	1.32	4.10	2.10	6.90	
	-67	$\sim 1.2$	$\sim 4.1$	2.02	—	Ester
		1.32	$\sim 4.3$	—	—	Cordinated
		1.26	4.13	2.12	—	Ester
		1.28	3.82	2.16	9.18	Free

\*Measured in dichloromethane solvent.

ously proceeding. Such esterification reaction was confirmed by simulated experiment. The resultant water molecules would hydrolyze Ti-product  $\text{TiCl}_2(\text{OEt})_2$  to form hydroxy compound as was already described for the isolated complex. In this connection, the singlet at 6.90ppm in Fig. 1d will be commented. This resonance represents the average field<sup>9</sup> of the three components, that is,  $-\text{COOH}$  of the liberated acetic acid,  $-\text{OH}$  of excess alcohol and proton originated from water produced by esterification.

It was above-mentioned that the 2nd ligand substitution reaction (2b) could not be envisioned from the room temperature spectra. Therefore, low temperature NMR spectra have been measured for the reaction mixtures of  $\text{TiCl}_2(\text{OAc})_2 + 2\text{EtOH}$  and  $\text{TiCl}_2(\text{OAc})_2 + 4\text{EtOH}$  and their temperature dependence is listed in Table I. As is seen in the low temperature spectra of the latter shown in Fig. 2, a fantastic resolution was attained for the methyl ( $\text{CH}_3\text{CH}_2\text{O}-$ ) and methylene ( $\text{CH}_2\text{CH}_2\text{O}-$ ) proton resonances at  $-67^\circ\text{C}$  (Fig. 2d). In particular, the methylene proton resonance centered at 4.10 ppm in the room temperature spectrum (Fig. 2a) is clearly resolved at  $-67^\circ\text{C}$  into three components which could be all identified. The quartet at 3.18 ppm corresponds to the  $\alpha$ -proton resonance of free alcohol and its up-field shift is probably caused by the change in degree of hydrogen bonding among the alcohol molecules. The other quartet at 4.13 ppm has been experimentally confirmed to be methylene proton resonance of ethyl acetate ( $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$ ) and its temperature independence is in concord with its nonassociative properties. Now the broad and decoupled resonance around 4.3 ppm must be attributed to the ethoxy group coordinated to the metal. Integrated area ratio of these three components represents the mole ratio of the different species present in the reacted solution,

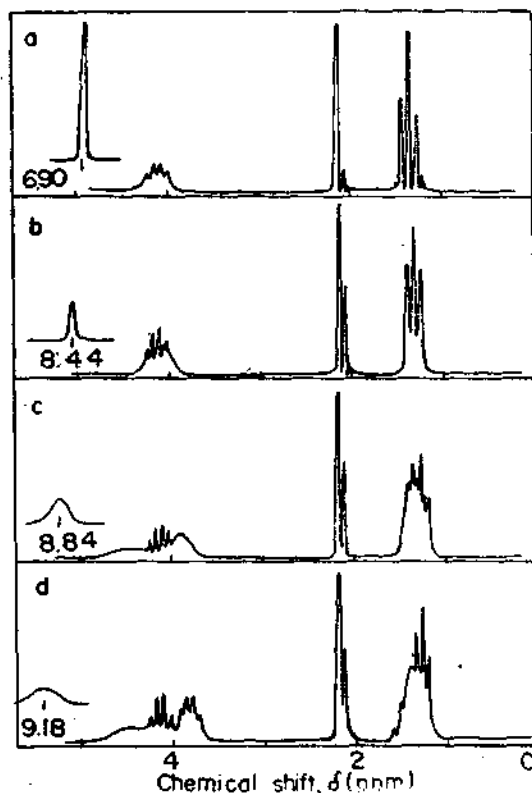


Fig. 2. NMR spectra of  $\text{TiCl}_2(\text{OAc})_2 + 4\text{EtOH}$  in  $\text{CH}_2\text{Cl}_2$  solvent at various temperatures: a;  $30^\circ\text{C}$ , b;  $-28^\circ\text{C}$ , c;  $-48^\circ\text{C}$ , d;  $-67^\circ\text{C}$

but its attempt was not successful. Instead, when  $\text{TiCl}_2(\text{OAc})_2 + 2\text{EtOH}$  solution in which no esterification was detected was cooled down to  $-67^\circ\text{C}$ , only the broad resonance at 4.3 ppm was observed and the other two quartets completely disappeared. Such a result proves that the 2nd ligand substitution reaction (2b) has also been quantitatively completed. In conclusion, the reaction of dichlorodiacetatotitanium (IV) and ethanol is a clean-cut two-step ligand substitution process which are quantitatively proceeded and the molecular form soluble in non-alcoholic solvents is a monosubstituted species  $\text{TiCl}_2(\text{OAc})(\text{OEt})$ . When ethanol was replaced with other primary alcohols such as methanol, *n*-propanol or *n*-octanol, the

alcoholysis reaction in dichloromethane proceeded exactly in the same way. However, the reaction rate seems to decrease with increasing carbon number  $\text{MeOH} > \text{EtOH} > n\text{-PrOH} > n\text{-OctOH}$ .

### (II) Solvolytic Reaction with *t*-Butyl Alcohol.

The solvolytic reaction of  $\text{TiCl}_2(\text{OAc})_2$  with *t*-butyl alcohol has been studied in the same way as with primary alcohols.  $\text{TiCl}_2(\text{OAc})_2$  was reacted with *t*-butyl alcohol in dichloromethane by varying their mole ratio and the NMR spectra of the reacted solution were examined. Their room temperature spectra are shown in Fig. 3 and Table 2.

When the mole ratio of *t*-butyl alcohol to  $\text{TiCl}_2(\text{OAc})_2$  was 1:2, a part of the solid Ti-complex remained undissolved similarly to the case of reaction with primary alcohols. However, its solution spectra presented in Fig. 3a revealed quite a different result from the expected. The resonance at 1.62 ppm has been proved to be originated from *t*-butyl chloride instead of coordinated *t*-butoxy group. Such a result suggests that the chloride ligand in  $\text{TiCl}_2(\text{OAc})_2$  is substituted with hydroxy group of the alcohol, that is,

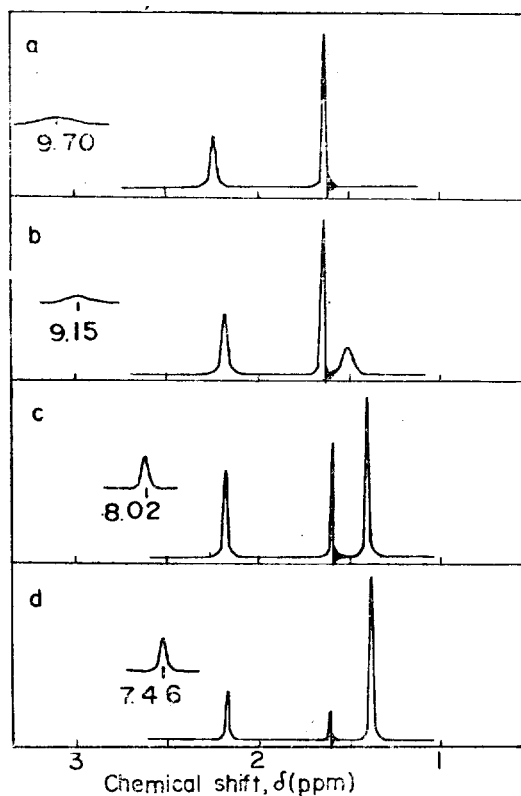
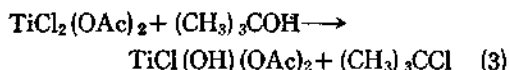


Fig. 3. NMR spectra of  $\text{TiCl}_2(\text{OAc})_2 + t\text{-BuOH}$  in  $\text{CH}_2\text{Cl}_2$  solvent at different mole ratios: a; 1:0.5, b; 1:1, c; 1:2, d; 1:4

Table 2. Chemical shifts of the chemical species in  $\text{TiCl}_2(\text{OAc})_2 + t\text{-BuOH}$  solution\*

Ratio $\text{TiCl}_2(\text{OAc})_2 : t\text{-BuOH}$	Temp. °C	Chemical shift. (ppm vs. TMS)			Species
		$(\text{CH}_3)_3\text{C}-$	$\text{CH}_3\text{CO}$	$-\text{OH} + -\text{COOH}$	
1 : 0.5	30	1.62	2.24	~9.7	
	-67	1.63	2.24	—	
1 : 1	30	1.50	2.18	9.16	Chloride
		1.62	—	—	
1 : 2	30	1.40	2.17	8.02	Chloride
		1.62	—	—	
	-67	1.38	2.19	~9.8	Free
		1.50	2.24	—	Coordinate
1 : 4	30	1.64	—	—	Chloride
		1.37	2.14	7.49	
		1.61	—	—	Chloride

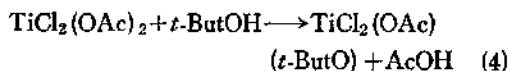
\*Measured in dichloromethane solvent.



This process contrasts to the reaction (2a) in which acetato-ligand is substituted with alkoxy group. Such an unusual substitution seems to be related to the greater basicity of *t*-butyl alcohol. The Ti-product of the reaction (3) could be isolated by evaporating *t*-butyl chloride along with the solvent, and its composition has been confirmed by its IR spectra and chemical analysis (Found: Ti, 23.7%; Cl, 13.5%; Calc: Ti, 22.0%; Cl, 16.2 %).

In the event that the alcohol concentration is slightly increased from the ratio of 1:2, a new broad peak begins to grow and its area becomes equal to that of the *t*-butyl chloride peak at equimolar ratio (Fig. 3b). Further increasing the mole ratio, the new resonance becomes sharper with up-field shift as is seen in Fig. 3c and d. It should also be noted that the more the alcohol concentration is raised, the more increased its relative area. Such experimental results indicate that the new resonance ( $\delta=1.37$  ppm in Fig. 3d) is ascribed at least partly to the free *t*-butyl alcohol and probably also to the coordinated *t*-butoxy group. Actually, when low temperature spectra of  $\text{TiCl}_2(\text{OAc})_2 + 2$  *t*-ButOH reaction solution were measured, our expectation has been proved to be true. The singlet at 1.40 ppm in its room temperature spectrum (Fig. 4a) is split into two components at lower temperatures as shown in Fig. 4b, c and d. The higher field component turned out to be the resonance by free *t*-butyl alcohol and the broader resonance at 1.50 ppm in Fig. 4d must be contributed from the coordinated *t*-butoxy group. It should be pointed out here that the broader component and the resonance at 1.50 ppm in the room temperature spectrum of equimolar solution (Fig. 3b) were attributed to the same chemical species, that is,

coordinated *t*-butoxy group. This fact indicates that at higher mole ratio than 1/2 another ligand substitution resembling the reaction (2a) is competitively accompanied along with the reaction (3).



In this case, unlike the reaction with primary alcohols, only one acetato-ligand is substituted with alkoxy group (*t*-ButO<sup>-</sup>) even in the presence of excess alcohol. It is seen in Fig. 3 that the methyl proton resonance of acetato-ligand at 2.17 ppm is separated into two components at  $-67^\circ\text{C}$ , the broader shoulder being the resonance by the coordinated acetato-ligand. In conclusion, when the mole ratio of *t*-butyl

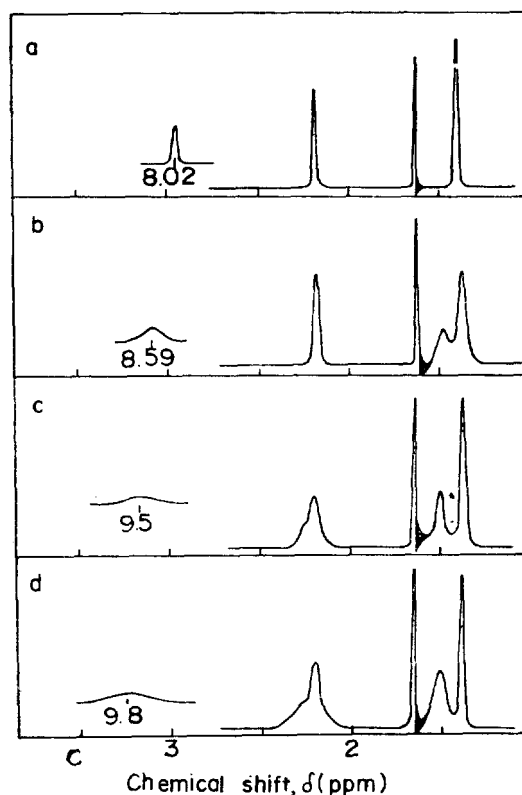


Fig. 4. NMR spectra of  $\text{TiCl}_2(\text{OAc})_2 + 2$  *t*-ButOH in  $\text{CH}_2\text{Cl}_2$  solvent at various temperatures: a;  $30^\circ\text{C}$ , b;  $-28^\circ\text{C}$ , c;  $-48^\circ\text{C}$ , d,  $-67^\circ\text{C}$

alcohol to  $\text{TiCl}_2(\text{OAc})_2$  is less than 1:2, the reaction (3) is dominant, but another substitution process (4) is competitively followed at higher mole ratio. The solvolytic reaction of  $\text{TiCl}_2(\text{OAc})_2$  with *t*-butyl alcohol also remarkably differs in that only one either of chloro- or acetato-ligand in the Ti-complex is substituted whereas the two acetato-ligand are all substituted in the reaction with primary alcohols.

#### Acknowledgment

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