

## REACTION OF TITANIUM(IV) CHLORIDE WITH THE ETHYL ESTERS OF SOME $\beta$ -DIKETO ACIDS

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**Abstract**—The preparation and characterization of some titanium dichloro complexes of the ethyl esters of some  $\beta$ -diketo acids are reported. The compounds have been characterized by their elemental analysis, molecular weight determination, i.r. spectra and magnetic susceptibility.

### INTRODUCTION

THE REACTION between titanium tetrahalides or titanium alkoxides and  $\beta$ -diketo compounds has been studied by many authors.

$\beta$ -Diketones react with titanium alkoxides and halides to form complexes of this type:  $Ti(\beta\text{-diketone})_2X_2$  [1–12, 14–17]. All evidence showed that these compounds have a cis octahedral structure [8, 9, 11, 12, 15, 16, 18, 19], are monomeric [6, 7, 9, 11, 12, 16, 20] and nonelectrolytes [9, 11, 12, 16, 17]. Similarly to the  $\beta$ -diketones,  $\beta$ -keto esters react with titanium alkoxides giving chelated compounds [20–23]. When the reaction proceeds in a molar ratio 2:1, the titanium atom in the resulting compounds is hexa-coordinated [20].

In the presented work, which represents a part of our investigations concerning the reactions of keto compounds with titanium tetrachloride and titanium alkoxides, we report the reaction between titanium tetrachloride and the ethyl esters of some  $\beta$ -diketo acids.

The reaction between titanium tetrachloride and the ethyl esters of  $\beta$ -diketo acids was carried out in benzene in a molar ratio 1:2. Under the conditions described, a reaction between titanium tetrachloride and the ethyl esters of: benzoyl pyruvic acid, 4-bromobenzoyl pyruvic acid, 4-chlorobenzoyl pyruvic acid, 1-naphthoyl pyruvic acid, 2-furoyl pyruvic acid and 2-fluorenyl pyruvic acid, was attempted. In all cases coloured crystalline products were obtained. Molecular weight measurements indicate that the products obtained are monomeric. From the results of elemental analysis and molecular weight determination, the reaction is considered to proceed according to the following equation:

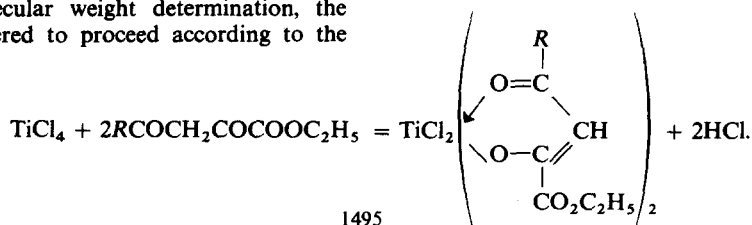


Table 1. Infrared frequencies ( $cm^{-1}$ ) of titanium complexes  $TiCl_2(RCOCHCOCOOC_2H_5)_2$

R	$\nu C \cdots O$ and $\nu C \cdots C$	$\nu Ti-O$	$\nu Ti-Cl$
	1590–1520	430	380–360 (388)*
2. 4-Bromophenyl-	1580–1500	450	395–375 (386)
3. 4-Chlorophenyl-	1580–1510	450	390–375 (389)
4. 1-Naphthyl-	1530–1495	420	375–360 (382)
5. 2-Furyl-	1575–1505	420	385–360 (389)
6. 2-Fluorenyl-	1580–1500	440	380–360 (380)

\*The values in the brackets are obtained from dichloro-methane solutions.

This conclusion is in agreement with earlier investigations [2, 5, 7, 9, 11, 12, 16, 23] concerning the reaction of titanium tetrachloride or alkoxy titanates with  $\beta$ -diketones and  $\beta$ -ketoesters in a molar ratio 1:2.

In order to determine the structure of these compounds of empirical formula  $TiCl_2(RCOCHCOCOOC_2H_5)_2$  the i.r. spectra were recorded (see Table 1). The i.r. spectra of these titanium complexes were compared with the spectra of dihalo-bis( $\beta$ -diketonato)titanium(IV) complexes and also with corresponding complexes of other metals and are generally similar. They all show the absorption bands characteristic for the chelating structure of the acetyl-acetonate ligand [11, 12, 18, 24–28]. In each case the carbonyl stretch frequency for the ligand is replaced by a metal chelated carbonyl absorption at lower fre-

quency, excepting the absorption due to the carboxyl group. The carbonyl absorptions of the enol tautomer of the chelating agents occur in the 1650–1550  $\text{cm}^{-1}$  region as a strong very broad band, whereas the chelate carbonyl absorptions of the complexes occur at 1600–1500, also as a very strong broad multiple band.

The presence of a strong band at 1735–1730  $\text{cm}^{-1}$  in the infrared spectra of the titanium complexes as well as the parent chelating agents which is attributed to the carbonyl group of the carboxyl group, suggests that this group is not coordinated.

The presence of a band of variable intensity, in the region 450–420  $\text{cm}^{-1}$ , in the infrared spectra of the titanium complexes can be assigned to a Ti–O stretching frequency. This is in agreement with the findings of Nakamoto and co-workers [26, 29, 30] and also of other authors [18, 25, 28, 31–35] who demonstrated that the nearly pure M–O stretching band occurs in the region 500–400  $\text{cm}^{-1}$ .

Below 400  $\text{cm}^{-1}$ , which is the region of the titanium chlorine stretching frequencies [10, 12, 36–43], the spectra of the solid complexes (Nujol mull and KBr pellets) show a strong peak at about 380  $\text{cm}^{-1}$ . That this band is due to a Ti–Cl stretching vibration is confirmed also by the absence of the same band in the infrared spectra of the hydrolysis products of the corresponding dichlorotitanium complexes. The hydrolysis products will be reported in due course. In each case this peak is broad and resolved or with a shoulder at a lower frequency (at ca. 360  $\text{cm}^{-1}$ ). In dichloromethane solutions, the complexes exhibit in the same region, a very intense, practically unresolved band. On the basis of these observations alone it is not possible to establish a *cis* or *trans* configuration for these compounds. The value of the frequency (about 380  $\text{cm}^{-1}$ ) suggests that the complexes are six-coordinated [11, 12, 36–44].

The complexes were found to be diamagnetic, as expected for  $3d^0$  system.

#### EXPERIMENTAL

The i.r. spectra were run as KBr pellets, in Nujol and in dichloromethane solution on a Perkin–Elmer Model 521 i.r. Spectrophotometer.

The room temperature magnetic susceptibility measurements were carried out with solid specimens by the Faraday method using A.R.  $\text{HgCo}(\text{CNS})_4$  as a calibrant.

Molecular weights were determined in benzene solution

( $6 \times 10^{-3}$  M) at 45°C using a Dampfdruck–Osmometer KNAUER. The instrument was calibrated with benzil.

Melting points are uncorrected.

Special care was taken to exclude moisture from the apparatus during the experiments.

Titanium tetrachloride was freshly distilled immediately before use. The chelating agents used were analytically pure reagents.

Titanium was estimated as dioxide by dissolving the compounds in water, precipitating as hydroxide and igniting.

Chlorine was estimated in the filtrate as silver chloride.

#### GENERAL METHOD OF SYNTHESIS OF THE COMPLEXES

To a solution of 0.004 mole of the corresponding ethyl ester of  $\beta$ -diketoacids in 10 ml dry benzene a solution of 0.002 mole of titanium tetrachloride in 10 ml dry benzene was added. The mixture turned orange or dark red in colour. The reaction mixture was refluxed for 4 hr to remove HCl and then kept overnight during which time an orange or dark red coloured precipitate was obtained. The supernatant liquid was decanted and the precipitate washed several times with dry benzene and dried under reduced pressure at 60°C. All complexes were obtained in quantitative yield. The results of elemental analysis, molecular weight measurements and their properties are summarized in Table 2.

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Table 2. Data of titanium complexes  $\text{TiCl}_2(\text{RCOCHCOCOOC}_2\text{H}_5)_2$

R	Color	M.P. (°C)	C %	Analysis found (calc.)			Mol. wt. found (calc.)
				H %	Ti %	Cl %	
1. Phenyl-	red cryst.	130 (dec)	51.40 (51.79)	3.63 (3.99)	8.61 (8.60)	12.59 (12.74)	554 (556)
2. 4-Bromophenyl-	orange cryst.	157 (dec)	40.50 (40.28)	2.73 (2.82)	6.46 (6.70)	9.59 (9.77)	735 (715)
3. 4-Chlorophenyl-	red cryst.	155 (dec)	46.30 (46.01)	3.01 (3.22)	7.58 (7.65)	11.50 (11.33)	646 (626)
4. 1-Naphthyl-	brown cryst.	216 (dec)	58.70 (58.44)	3.48 (3.98)	7.60 (7.29)	10.98 (10.79)	673 (657)
5. 2-Furyl-	red-brown cryst.	114 (dec)	44.78 (44.69)	3.71 (3.38)	9.26 (8.92)	13.00 (13.30)	552 (536)
6. 2-Fluorenyl-	brown cryst.	180 (dec)	61.98 (62.21)	3.91 (4.12)	6.25 (6.53)	9.23 (9.67)	757 (733)

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