



## **METAL DERIVATIVES OF ORGANO – PHOSPHOROUS COMPOUNDS: TITANIUM (IV) DERIVATIVES**

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### **ABSTRACT**

*Some new complexes of compositions have been isolated from the reaction of titanium (IV) chloride with dialkyl /diaryl phosphites in different molar ratios and under varying condition of temperature and solvent. The complexes have been characterized on the basis of elemental analysis infrared spectral data and magnetic susceptibility measurement. The lowering of the frequency in the spectra of complexes is a indicative of octahedral environment around the central of titanium metal ion and of the polymeric nature of complexes. All the complexes are expected to be octahedral.*

Some new complexes of compositions have been isolated from the reaction of titanium (IV) chloride with dialkyl /diaryl phosphites in different molar ratios and under varying condition of temperature and solvent. The complexes have been characterized on the basis of elemental analysis infrared spectral data and magnetic susceptibility measurement. The lowering of the frequency in the spectra of complexes is a indicative of octahedral environment around the central of titanium metal ion and of the polymeric nature of complexes. All the complexes are expected to be octahedral. Titanium (IV) chloride reacts with different donor molecules in varying ratios of up to 1: 4. Schwarzenbach<sup>1</sup> compared the stability of organophosphonic acid and carboxylic acid complexes and suggested that organophosphonic acid have been found to be forming more stable complexes in comparison to carboxylic acid.

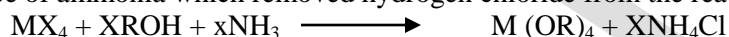
Attempts have been made to synthesize new class of organopolyphonic acids as chelating agents. KabaChnik et al.<sup>2</sup> synthesized ethylenediamine–N, N’-bis (isopropyl phosphonic) acid (EDBIP) and ethylene diamine–N, N’-bis (dimethyl methylene phosphonic) acid (EDBMMP) by condensation of ethylene diamine with acetone and dialkyl phosphites followed by the hydrolysis of the obtained ester. Bersworth<sup>3</sup>, Bank and Yerick<sup>4</sup> synthesized ethylene diamine–N, N, N’, N’-tetrakis (methylene phosphonic), acid (EDTMP) and 1, 2–cyclo–hexylenediamine–N, N’, N’-tetrakis (methylene phosphonic) acid by using the method suggested by Schwarzenback et al.<sup>5</sup> Moedritzer and Irani<sup>6</sup> reported that hydroxymethyl phosphonic acid is formed in a side reaction which interferes in the separation of pure aminophosphonic acid.

This method was used by Westuback et al.<sup>7</sup> and other researchers<sup>3-4</sup> in reactions with poly amines. Isbell and chambers<sup>8</sup> synthesized  $\alpha$ -amino-ethyl phosphonic acid by curtius reaction.  $\alpha$ -amino alkyl phosphonic acids were synthesized by Kabachnik et al<sup>9-10</sup> in reactions of dialkyl phosphates with ammonia and a carboxyl compound. The reactions of anhydrous titanium (IV) chloride with di-isopropyl methyl phosphonate were studied similar to reactions with anhydrous tin(IV) chloride and observed that isopropyl chloride and hydrogen chloride were evolved on heating the adduct<sup>11</sup>. TiCl<sub>4</sub>.DIMP. Lahe’s et al.<sup>12</sup> studied the structure containing two phosphonate

groups trans to each other. Similarly the reaction of titanium (III) chloride was carried out with diisopropyl methyl phosphonate (DIMP) at elevated temperature in benzene under reduced pressure. The complex tris (isopropyl methyl phosphonate) titanium (III) was obtained which was found in soluble in all common organic solvents. On the basis of IR spectral studies a hexa coordinated polymeric structure, has been suggested to the complex<sup>13</sup>.

## RESULT AND DISCUSSION

The reactions between titanium tetrachloride and dialkyl / diaryl phosphites were carried out in different molar ratios taking benzene as solvent. Some reactions were also carried out in absence of benzene solvent. Hydrogen chloride gas was evolved in the reactions. To avoid side reaction between evolved hydrogen chloride and dialkylphosphite, the reactions were carried out under reduced pressure (~20mm). The reaction between titanium tetrachloride with excess of dialkyl phosphite or in 1:4 molar ratio under refluxing at an oil bath temperature 110 – 120<sup>0</sup>C under reduced pressure (~20mm) yielded a product of the type Ti [OR(O) (OR) (R)]<sub>4</sub> in which all the four chlorine atoms of TiCl<sub>4</sub> was replaced. This result does not resemble with the results reported by Jennings et al<sup>14</sup> and Puri and Mehrotra<sup>17</sup> in their studies on the reactions of titanium tetrachloride with alcohols and β-diketones respectively where even in excess of ligands only two chlorine atoms from TiCl<sub>4</sub> could be replaced but the results obtained by all the resemble with the results obtained by Nelles<sup>15</sup>. Where all the four chlorine atoms were replaced by alkoxy group in presence of ammonia which removed hydrogen chloride from the reaction mixture.



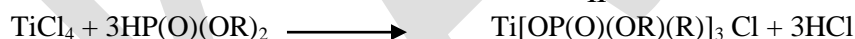
The reaction of titanium tetrachloride with dialkyl / diaryl phosphite may be represented as follows:



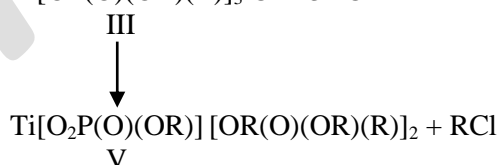
(R = ethyl, n-propyl, iso-propyl, n-butyl, diphenyl methyl)

Similar results have been reported by Peds et al<sup>16</sup> in the reactions studied between titanium tetrachloride and diphenyl phosphonate.

The reactions of titanium (IV) chloride with dialkyl / diaryl phosphites were also studied in 1:1, 1:2 and 1:3 molar ratios in benzene solvent medium under reflux condition and reduced pressure (~20mm) at an oil bath temperature 110-120<sup>0</sup>C. In the reaction one, two and three chlorine atoms from titanium tetrachloride were replaced. These reactions may be represented as follows:



In absence of benzene solvent.



The product (I-V) are violet or yellow solids. These are moisture sensitive and become sticky on exposure to moist air. They are insoluble in common organic solvents, hence are polymeric in nature. They do not melt at higher temperature(300<sup>0</sup>C).

The structure of the titanium derivatives of dialkyl/ diaryl phosphites have been characterized by infra-red spectral studies (Table-1). In IR-spectra of titanium (IV) derivatives of various dialkyl / diaryl phosphites absorption bands have been observed in IR-spectral region 1100-1060 cm<sup>-1</sup>. These have been assigned to phosphoryl group(P = O). The IR-absorption band due to free phosphoryl group (P=O) in dialkyl phosphites is observed in the region 1250-1220 cm<sup>-1</sup>. The observed shift (νP=O) to lower frequency in titanium (IV) complexes may be attributed to the coordination of the phosphoryl oxygen to the titanium atom of the neighbouring molecules<sup>7</sup>. Strong absorption bands in the range 1010-985 cm<sup>-1</sup> have been assigned to ν(P – O – C) absorption frequencies<sup>20</sup> of these complexes. In IT-spectra of titanium derivatives weak bands were observed at 2450-2425 cm<sup>-1</sup> which could be due to ν(P – H)

frequencies. These could be present due to partial hydrolysis of the products during mixing the sample with nujol for recording IR-spectra of the complexes.

The IR-absorption bands observed in far IR region  $595-370\text{ cm}^{-1}$  show characteristic absorption of (Ti – O – P) bonding in titanium derivatives<sup>5</sup>. The IR-absorption bands appearing in the far IR region  $415-370\text{ cm}^{-1}$  could be attributed to  $\nu(\text{Ti} - \text{Cl})$  frequencies 21 in complex is where chlorine atoms are partially replaced by ligand groups. The presence of an IR-absorption band at  $745-720\text{ cm}^{-1}$  has been attributed to  $\nu(\text{P} - \text{C})$  frequencies<sup>17</sup>.

The plausible mechanism of the formation of titanium derivatives of dialkyl / diaryl phosphite could be suggested in which two structures A and B are possible for these complexes.

## EXPERIMENTAL CHEMICALS

Titanium (IV) chloride (Fluka, AG) was used after analysis. Diethyl phosphite, Di-n-propyl phosphite, Di-is-propyl phosphite, Di-n-butyl. Phosphite (Both Fluka, AG) Di phenyl methyl phosphite (Aldrich, AG) were used after distillation under reduced pressure.

## ANALYSIS OF INSTRUMENTS

Estimations of Chlorine, Phosphorus was done grammatically by standard wet analysis. Infra-red spectra of compounds was scanned on Beckman IR-spectrophotometer, in nujol mull by taking care of atmospheric moisture. Magnetic susceptibility measurements were done on Gouy's balance taking copper sulphate as calibrant.

### Reactions between titanium (IV) chloride and diethyl phosphite in different molar ratios:

#### In benzene solvent

To a known amount of ice cooled titanium (IV) chloride in benzene was added calculated amount of respective diethyl phosphite and di-n-propyl phosphite in benzene under anhydrous conditions, Heat and hydrogen chloride were evolved in the reaction. After cooling the reaction mixture to room temperature it was refluxed under reduced pressure and at oil bath temperatures of  $110-120^{\circ}\text{C}$ . After 8-10 hrs of refluxing a yellowish orange product was formed which increased in amount on further refluxing till the completion of reaction. It took 30-40 hrs in each case. The excess of benzene was distilled off and its traces were removed in vacuo at  $80^{\circ}\text{C}$ . The product was washed with dry benzene and dried again in vacuo. White or yellowish white solid product was obtained. Analytical results have been reported in Table 1.

**Table 1 Preparation and Analysis of Titanium (IV) Chloride Derivatives with diethyl phosphite and di-n-propyl phosphite**

Sl. No.	TiCl <sub>4</sub>	Reactants	Compound	Colour	Ratio	C	H	P	Cl
1	1.92	1.38	Ti [OP(O)(OC <sub>2</sub> H <sub>5</sub> )(C <sub>2</sub> H <sub>5</sub> )]Cl <sub>3</sub>	yellow orange solid	1:1	8.12	3.40	10.56	36.29
2	1.92	2.78	Ti [OP(O)(OC <sub>2</sub> H <sub>5</sub> )(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	brown violet solid	1:2	24.30	5.06	15.70	17.97
3	1.92	4.14	Ti [OP(O)(OC <sub>2</sub> H <sub>5</sub> )(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ]Cl	Yellow violet solid	1:3	29.01	6.04	18.73	7.05
4	1.92	5.52	Ti [OP(O)(OC <sub>2</sub> H <sub>5</sub> )(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	yellow violet solid	1:4	32.11	6.69	20.73	-
5	1.92	1.66	Ti [OP(O)(OC <sub>3</sub> H <sub>7</sub> )(C <sub>3</sub> H <sub>7</sub> )]Cl <sub>3</sub>	yellow brown solid	1:1	18.68	4.35	9.64	33.13
6	1.92	3.32	Ti [OP(O)(OC <sub>3</sub> H <sub>7</sub> )(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	violet solid	1:2	31.93	3.10	13.75	15.74
7	1.92	4.98	Ti [OP(O)(OC <sub>3</sub> H <sub>7</sub> )(C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> ]Cl	violet solid	1:3	54.44	7.24	16.02	6.12
8	1.92	6.64	Ti [OP(O)(OC <sub>3</sub> H <sub>7</sub> )(C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> ]	violet solid	1:4	41.02	7.98	17.66	-

## WITHOUT SOLVENT

To a known amount of titanium (IV) chloride was added calculated amount of dialkyl / triethyl phosphite dropwise in dry conditions by keeping the flask in ice. The reaction is exothermic so heat and hydrogen chloride evolved very fastly. The reaction mixture was heated at an oil bath temperatures of 50-60°C and 110-125°C and reduced pressure. The reaction was very fast in beginning. After 3-4 hrs of heating the reaction mixture turned to a solid form. It was heated upto 10-15 hrs till the reaction was over. In the end the product was washed with benzene and dried in vacuo at 80°C. White or yellowish solid obtained as a product. The analytical results have been shown in Table 2.

**Table 2 Infra-Red spectra of diethyl phosphite and di-n-propyl phosphite of titanium IV**

Sl. No.	Complex Compound	$\nu(\text{P}-\text{O}-\text{C})$ $\text{cm}^{-1}$	$\nu(\text{P}=\text{O})$ $\text{cm}^{-1}$	$\nu(\text{P}-\text{C})$ $\text{cm}^{-1}$	$\nu(\text{P}-\text{H})$ $\text{cm}^{-1}$	$\nu(\text{Ti}-\text{O}-\text{P})$ $\text{cm}^{-1}$	$\nu(\text{Ti}-\text{Cl})$ $\text{cm}^{-1}$
1	Ti [OP(O)(OC <sub>2</sub> H <sub>5</sub> )(C <sub>2</sub> H <sub>5</sub> )]Cl <sub>3</sub>	1010	1090	730	2430	595-580	415, 400
2	Ti [OP(O)(OC <sub>2</sub> H <sub>5</sub> )(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	1005	1080	725	2440	295-570	420, 375
3	Ti [OP(O)(OC <sub>2</sub> H <sub>5</sub> )(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ]Cl	1000	1080	724	2430	590-570	360
4	Ti [OP(O)(OC <sub>2</sub> H <sub>5</sub> )(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ]	1000	1090	722	2440	590-580	-
5	Ti [OP(O)(OC <sub>3</sub> H <sub>7</sub> )(C <sub>3</sub> H <sub>7</sub> )]Cl <sub>3</sub>	990	1080	730	2445	595-570	420
6	Ti [OP(O)(OC <sub>3</sub> H <sub>7</sub> )(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	990	1080	724	2430	590-570	415
7	Ti [OP(O)(OC <sub>3</sub> H <sub>7</sub> )(C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> ]Cl	995	1070	730	2420	595-575	400
8	Ti [OP(O)(OC <sub>3</sub> H <sub>7</sub> )(C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> ]	985	1075	725	2430	590	-

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