

## REACTIONS OF TITANIUM(IV) PHENOXIDES WITH ACETOPHENONE AND BENZOPHENONE

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Reactions of titanium (IV) phenoxides with acetophenone and benzophenone in  $\text{CCl}_4$  are exothermic and result in the compounds of composition  $\text{TiCl}_{4-n}(\text{OPh})_n \cdot 2\text{L}$  (L = acetophenone or benzophenone,  $n = 1-4$ ). Based upon elemental analysis, conductance, cryoscopic and infrared spectral studies, an octahedral structure has been proposed for these compounds.

**Keywords:** Titanium Phenoxides; Acetophenone; Benzophenone

### INTRODUCTION

ACCEPTOR properties of metal phenoxides are low in contrast to those of their corresponding halides such as titanium(IV) chloride presumably because of the polymeric nature of these phenoxides (Bradley, 1960; and Clark, 1968) wherein the metal has already achieved its favoured coordination number. Among the few known adducts of titanium tetraphenoxides are those with pyridine, dioxane, aniline,  $\alpha$ -naphthylamine and acetone (Funk & Masthoff, 1956; and Yoshino *et al.*, 1961). The properties of these compounds have been extensively reviewed (Masthoff *et al.*, 1962). In our most recent publication (Malhotra *et al.*, 1981) we have reported a large number of adducts of  $\text{Ti}(\text{OPh})_4$ ,  $\text{TiCl}(\text{OPh})_3$ ,  $\text{TiCl}_2(\text{OPh})_2$  and  $\text{TiCl}_3(\text{OPh})$  with bases such as N-methylacetamide, N,N'-dimethylacetamide and dimethylformamide. In the present studies, we now report the reaction products of titanium (IV) phenoxides with acetophenone and benzophenone.

### EXPERIMENTAL

Titanium(IV) phenoxides of composition  $\text{Ti}(\text{OPh})_4$ ,  $\text{TiCl}(\text{OPh})_3$ ,  $\text{TiCl}_2(\text{OPh})_2$  and  $\text{TiCl}_3(\text{OPh})$  were prepared by the methods reported earlier (Malhotra *et al.*, 1981; and Luchinskii & Altman, 1935). Reactions of these phenoxides with acetophenone and benzophenone were carried out by suspending a known weight of the parent phenoxide (1 mol) in  $\text{CCl}_4$  to which was added a  $\text{CCl}_4$  solution of acetophenone or benzophenone (2 mols) The mixture was stirred for two hours and allowed to stand overnight when solid crystalline compounds separated out. In some cases, the components went into solutions and the compounds were

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isolated by the addition of petroleum ether. The products were filtered, washed with dry PhH to remove excess of base if any and finally dried under vacuum.

Titanium was estimated gravimetrically as  $TiO_2$  (Vogel, 1961). Molecular weights of some of the compounds were determined cryoscopically in  $PhNO_2$ . Infrared spectra were recorded on a Perkin Elmer 337 ( $4000-400cm^{-1}$ ) and 621 ( $600-2500cm^{-1}$ ) spectrophotometers in KBr plates.

## RESULTS AND DISCUSSION

Compounds of composition  $TiCl_{4-n}(OPh)_n \cdot 2L$  where L = acetophenone or benzophenone have been isolated in the present studies. In all cases, reaction has been found to be exothermic. Stoichiometric composition of these compounds has been established by elemental analysis given in Table I. Some of these compounds are extremely moisture sensitive and change their colours on exposure. It is evident from Table I

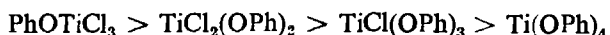
TABLE I

*Analytical and i.r. spectral data of the compounds of titanium(IV) phenoxides with acetophenone and benzophenone*

Compound	Colour	Elemental Analysis				Molecular weight in $PhNO_2$	Molar (C = O) Shift conductance in $PhNO_2$ ( $ohm^{-1} cm^2$ )	Shift	
		% Foundcd (% calcd)							
		C	H	M	Cl	% Found (% calcd)			
Acetophenone (A)		79.96 (80.00)	6.62 (6.66)	—	—	—	—	1685	—
Ti(OPh) <sub>4</sub> ·2A	Brown	72.75 (72.72)	5.70 (5.45)	6.38 (7.27)	—	—	3.93	1600	85
TiCl(OPh) <sub>3</sub> ·2A	Brick red	67.83 (67.77)	5.20 (5.14)	7.48 (7.96)	5.32 (5.89)	589 (602)	2.73	1573	112
TiCl <sub>2</sub> (OPh) <sub>2</sub> ·2A	Very light brown	61.83 (61.65)	4.91 (4.77)	8.76 (8.80)	12.87 (13.02)	—	3.17	1555	130
TiCl <sub>3</sub> (OPh) <sub>2</sub> ·2A	Very light	54.05 (54.15)	4.22 (4.30)	9.28 (9.84)	21.90 (21.84)	481 (487)	2.09	1545	140
Benzophenone (B)		85.79 (85.73)	5.44 (5.49)	—	—	—	—	1665	—
Ti(OPh) <sub>4</sub> ·2B	Brown	76.67 (76.53)	5.21 (5.10)	6.34 (6.12)	—	—	4.01	1560	105
TiCl(OPh) <sub>3</sub> ·2B	Reddish brown	72.50 (72.67)	4.90 (4.81)	6.39 (6.60)	4.77 (4.48)	—	2.87	1505	160
TiCl <sub>2</sub> (OPh) <sub>2</sub> ·2B	Dirty white	68.09 (68.16)	4.61 (4.48)	7.11 (7.17)	10.48 (10.61)	648 (699)	3.25	1475	190
TiCl <sub>3</sub> (OPh) <sub>2</sub> ·2B	Light yellow	62.91 (62.79)	4.19 (4.08)	7.21 (7.85)	17.08 (17.41)	596 (611)	3.82	1460	205

that experimental values of hydrogen are generally higher than those calculated for 1 : 2 compounds. This is possibly due to the absorption of moisture and resulting hydrolysis during analysis. Similar observations have been made earlier also in case of compounds of niobium(V) and tantalum(V) (Feenan & Fowles, 1965). The compounds have no definite melting points but decompose before melting when heated in fine capillary tubes. They are sparingly soluble in dichloromethane and nitromethane but completely soluble in nitrobenzene. Molar conductances (millimolar solutions in  $\text{PhNO}_2$ ) are in the  $2\text{--}4\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  range which suggest that they are non-electrolytes. Molecular weight determinations of some of these compounds indicate that they are monomers.

The carbonyl stretching frequency of acetophenone and benzophenone is sufficiently lowered on compound formation (Table I) suggesting that carbonyl oxygen is the donor site (Cook, 1963). It is obvious from Table I that negative shift in the carbonyl stretching frequency is much larger in case of compounds of phenoxy-titanium(IV) trichloride than the compounds containing lesser or no chlorine atom which suggests that former is a much strong acceptor than the latter. Thus based on the magnitude of lowering in the carbonyl stretching frequency ( $\Delta\nu$ ), the following order of acceptor strength for titanium phenoxides may be proposed :



Similar orders of acceptor strength in case of metal halides (Malhotra & Sud, 1974) and metaphenoxides (Malhotra *et al.*, 1981), based on infrared spectral studies of their compounds with various ligands have been reported earlier.

Apart from the above observations, the carbonyl shift for the benzophenone complexes is somewhat greater than for acetophenone complexes which may be attributed to the more polarisable nature of the carbonyl group in the former (Cook, 1961). Similar observations have been made earlier also in the case of a number of metal halide complexes with the above ligands (Susz, 1959; and Paul & Chadha, 1969).

Furthermore, vibrational bands around  $460\text{--}480\text{cm}^{-1}$  region in the spectra of

parent phenoxides which were assigned to bridging  $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{Ti} \quad \text{Ti} \end{array}$  (Malhotra *et al.*, 1981) modes are completely missing in the spectra of the compounds. Instead, sharp bands in the region  $525\text{--}550\text{cm}^{-1}$  have been observed which may be assigned to terminal  $\nu(\text{Ti-O})$  stretching modes (Malhotra *et al.*, 1981; and Mikulski *et al.*, 1970), possibly resulting from the breakdown of phenoxy bridges present in the parent phenoxide, on complex formation followed by coordination of the ligand to the central metal which is also supported by cryoscopic studies (Table I). Similar observations have been made earlier also for antimony(V) alkoxides and for niobium(V) and tantalum(V) phenoxide adducts (Malhotra *et al.*, 1979; and Paul *et al.*, 1969, 1970). Furthermore, titanium-chlorine stretching vibrations have been observed in the range  $360\text{--}400\text{cm}^{-1}$  which may be assigned to terminal  $\nu(\text{Ti-Cl})$  and are in the same range as observed earlier in other compounds of titanium(IV) chloride adducts in octahedral environment (Malhotra & Chaudhry, 1974). No band that could be assigned to bridging



Ti—Ti modes has been observed in any of these compounds. Thus based on elemental analysis, conductance, cryoscopic and i.r. spectral studies, a possible octahedral structure may be proposed for the compounds of titanium(IV) phenoxides with acetophenone and benzophenone.

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