

STUDIES OF IMIDO DERIVATIVES OF TITANIUM (IV)

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ABSTRACT. Imido derivatives of the type $(i\text{-PrO})_{4-n}\text{Ti}(\text{NHOCR})_n$ where $n = 1, 2, 3, 4$ and $R = \text{CH}_3, \text{C}_6\text{H}_5$ and $\text{C}_5\text{H}_4\text{N}$ have been prepared by the reaction of titanium (IV) isopropoxide with acetamide, benzamide and nicotinamide in different stoichiometric ratios in anhydrous benzene. The derivatives were found to be stable upto 300°C and were characterised by elemental analysis and IR spectra.

INTRODUCTION

A variety of organometallic compounds have been prepared using metal alkoxides as starting materials [1,2]. Also many organo derivatives of titanium (IV) alkoxides are known [3-5]. The protonation behaviour, hydrogen bonding and Lewis acid complexation have been studied. The complexes of the alkyl halides and alkoxides of tin (IV) with amides have been reported [6-8]. This has promoted interest to study the reactions of titanium (IV) isopropoxide with three amides.

EXPERIMENTAL

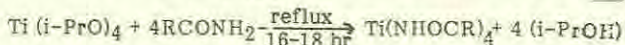
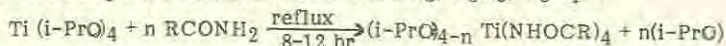
Anhydrous conditions were maintained throughout the preparations. Benzene and isopropanol were dried before use. Benzamide and nicotinamide were recrystallised from ethanol and dried under vacuum. Infrared spectra were recorded in KBr pellet. The results of the elemental analysis of the compounds synthesised showed a good agreement with the calculated values.

Titanium isopropoxide was prepared [9] and distilled at $77\text{-}80^\circ\text{C}$, its infrared spectra gave absorption bands as reported [10]. The derivatives were prepared by mixing titanium isopropoxide and the corresponding amide in the molar ratio of 1:1, 1:2, 1:3 and 1:4 in dry benzene and refluxing for 10 hr, the liberated isopropanol collected as benzene-isopropanol azeotrope at 72°C and the excess benzene removed by fractionation at 80°C . The solid product was washed with ethanol and dried at room temperature under reduced pressure. The derivatives were found to be insoluble in acetone, benzene, chloroform, ether, methanol, acetonitrile, carbontetrachloride and petroleum ether. Titanium was estimated gravimetrically as titanium dioxide and nitrogen determined by Kjeldahl method [11]. Isopropanol in the azeotrope was also estimated [16].

RESULTS AND DISCUSSION

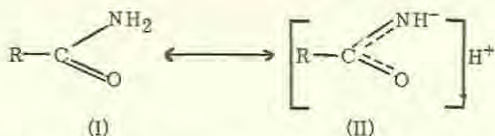
On refluxing titanium (IV) isopropoxide with acetamide benzamide and nicotinamide in the molar ratio of 1:1, 1:2, 1:3 and 1:4 the mixed imido-alkoxy derivatives like $(i\text{-PrO})_3\text{Ti}(\text{NHOCR})$, $(i\text{-PrO})_2\text{Ti}(\text{NHOCR})_2$, $(i\text{-PrO})\text{Ti}(\text{NHOCR})_3$

and $\text{Ti}(\text{NHOCR})_4$ were obtained where R is CH_3 , C_6H_5 , $\text{C}_5\text{H}_4\text{N}$.

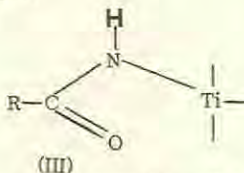


$n = 1, 2, 3$ and $\text{R} = (\text{CH}_3, \text{C}_6\text{H}_5, \text{C}_5\text{H}_4\text{N})$

The progress of the reactions was determined by estimating the isopropanol in a binary azeotrope collected at regular intervals. Derivatives were solid, of different colours and hydrolysable in air hence could not be recrystallised due to absence of inert atmosphere. Their insolubility in many organic solvents suggest the polymeric nature [2] which may be due to intermolecular bridging of isopropoxy groups and/or inter/intramolecular hydrogen bonding or NH groups. However Bradley [2] has suggested the insolubility of metal alkoxides due to the presence of bridging alkoxy groups. Many workers have shown that the metal halide complexes with amides generally show metal bonded through oxygen of carbonyl groups [6-8]. It has further been supported by many workers that in complexes of nicotinamide with some divalent metal ions [13] and in derivatives of tributyl tin alkoxides with certain amides, the metal atoms are bonded through the nitrogen of amides [14,15] which has been confirmed by synthetic and infrared studies of tin (IV) isopropoxide and amide derivatives, that titanium atom is bonded strongly with nitrogen as reverse reaction does not take place even on long refluxing. Amides generally show two resonance structures, shown below.



Richards and Thompson have shown that all amides show strong band in $1600-1700 \text{ cm}^{-1}$ due to C - O stretching vibrations (16,17). On comparing spectra of free imides and imido derivatives no change is observed which eliminates structure (II). Hence the imido derivatives (III) are formed from structure (I) through deprotonation [16,18].



As reported by Richards and Thompson [16,17] free primary amides show strong bands at 3372 cm^{-1} and 3180 cm^{-1} due to antisymmetric and symmetric stretching vibrations of N-H group respectively. But the imido derivatives show weak absorption bands in the region $3360-3370 \text{ cm}^{-1}$ and $3165-3167 \text{ cm}^{-1}$ which can similarly be due to antisymmetric and symmetric N-H vibrations respectively. The presence of weak band indicate the deprotonation of NH_2 group due to the formation of imido derivatives. The observed lowering in the stretching frequency of N-H vibrations ($2-12 \text{ cm}^{-1}$ and $13-15 \text{ cm}^{-1}$ in antisymmetric and symmetric (N-H) vibrations respectively) may be due to hydrogen bonding, and also the insoluble nature of the derivatives may in part be due to the hydrogen bonding as has been suggested by Nakamoto and others [12,18].

Strong to medium intensity bands observed in these derivatives in the region of 1020-1025 and 1120-1135 cm^{-1} can be assigned to the bridging and terminal isopropoxy group vibrations respectively [16,19-22]. The bridging isopropoxy group indicated in the IR spectra of these derivatives also support their polymeric nature. However in complexes of nicotinamide it is difficult to assign bands in the region 1000-1025 cm^{-1} exclusively to the bridging isopropoxy group as in this region ring vibrations of the pyridine also occur [23]. Three bands observed in the region 612-400 cm^{-1} in the derivatives of acetamide and benzamide and two bands observed in the region 620-390 cm^{-1} in the nicotinamide derivative can tentatively be assigned to Ti-N and or Ti-O stretching vibrations [19,21,22,24].

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