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THERMAL STUDIES OF SOME ARYLOXIDES OF TITANIUM(IV)

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Abstract

Thermal behaviour of aryloxides of titanium(IV) of composition $TiCl_n(OAr)_{4-n}$ (where $n = 0 \rightarrow 3$ and OAr= $OC_6H_4Bu^t$-4, OC_6H_4OMe-4 and OC_6H_2-Bu^t_2-2,6-Me-4) has been studied by DTA and TG analysis. Multiple decomposition steps have been indicated by thermal weight losses which are both exothermic and endothermic as shown by DTA curves. Based upon the total % loss in weight during entire decomposition titanium dioxide has been found to be the final residue in each case.

Keywords: aryloxides, titanium

Introduction

There has been significant recent-interest in the synthesis and reactivity of early transition metal complexes supported by sterically demanding aryloxide ligation with alkyl and aryl substituents at 2,4 and 6-positions [1, 2]. In particular, Rothwell, Chamberlain and their coworkers [3, 4] have reported several studies involving the large 2,6-di-*t*-butylphenol ligand capable of bringing about intramolecular C–H activation via cyclometallation of a *t*-butyl group of the phenoxide, but no work on thermal behaviour of such complexes has been carried out. Scrutiny of literature has revealed that only scattered references are available on such properties of metal alkoxides and aryloxides especially those of group (IV) elements [5]. During our studies on group (IV) metal aryloxide chemistry, we have reported the synthesis of fully substituted and chloroaryloxides of titanium(IV) [6–8]. Results of an investigation of the thermal behaviour of some of these titanium(IV) aryloxides are reported in this paper.

Experimental

Compounds of composition $TiCl_n(OAr)_{4-n}$ have been synthesised by reacting titanium(IV) chloride with different phenols in appropriate molar ratios under reflux as described earlier [6–8].

The DTA and TG curves were recorded on a DTG-40 (Simultaneous DTA-TG module Shimadzu Corporation) using Pt crucible and Pt/Pt-Rh thermocou-

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ple. The thermal investigations were carried out in air with the heating rate of 20 deg·min^{-1}.

Results and discussion

Thermal mode of decomposition of compound of composition $Ti(OC_6H_4Bu^t\text{-}4)_4$ shown as thermogravimetric curve in Fig. 1 reveals that there are two major stages in which it undergoes decomposition. The initial loss of about 5% has been attributed to the loss of moisture endothermally 96.9°C in DTA curves for $Ti(OC_6H_4Bu^t\text{-}4)_4$. A mass loss of 45.01% in the first step and 42.57% in the second step corresponds to the formation of $TiO(OC_6H_4Bu^t\text{-}4)_2$ and TiO_2 from $Ti(OC_6H_4Bu^t\text{-}4)_4$ with the loss of one molecule of diertbutyl diphenyl ether in each step which may be considered to have been removed as gaseous products like carbon dioxide, ethylene, acetylene, etc. The formation of such gaseous products during thermal decomposition is supported by earlier reports as well as the decomposition of alkali metal phenoxides [9, 10]. The exothermic peaks at 393.7 (sharp) and 480.7°C (broad) observed in its DTA curve have been attributed to the decompositions into di-t-butyl-diphenyl ether.

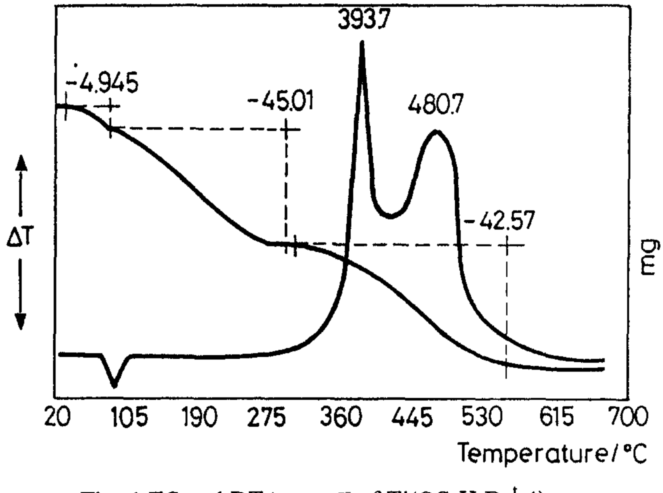

Fig. 1 TG and DTA curves of $Ti(OC_6H_4Bu^t\text{-}4)_4$

Similar trend of curve has been obtained in compound of composition $Ti(OC_6H_4OCH_3\text{-}4)_4$. The weight losses of 44.1% and 38.4% up to 250 and 500°C respectively are in good agreement with the proposed formulation of $TiO(OC_6H_4OCH_3\text{-}4)_2$ as an intermediate and TiO_2 as a final product. The two exotherms at 369.8 and 477.6°C correspond mainly to the loss of organic moiety as gaseous products.

Based upon above observations the following general scheme of decomposition may be represented as:

$$Ti(OAr)_4 \rightarrow TiO(OAr)_2 + ArOAr$$

$$TiO(OAr)_2 \rightarrow TiO_2 + ArOAr$$

$$(OAr = OC_6H_4Bu^t\text{-}4 \text{ and } OC_6H_4OCH_3\text{-}4)$$

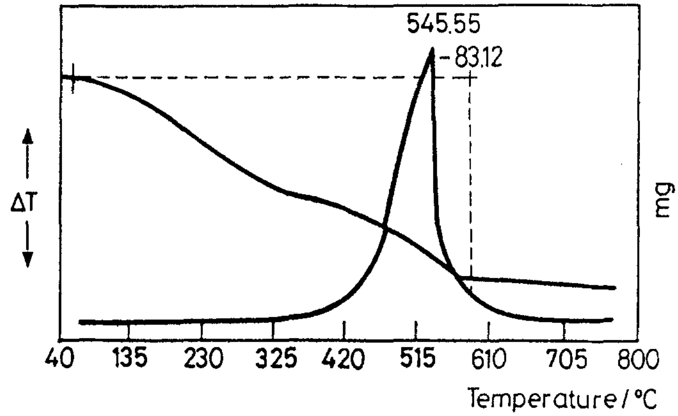

Fig. 2 TG and DTA curves $Ti(OC_6H_2Bu^t_2\text{–}2,6\text{–}Me\text{–}4)4$

The decomposition of $Ti(OC_6H_2Bu^t_2\text{-}2, 6\text{-}Me\text{-}4)_4$, (Fig. 2) however does not parallel with that of $Ti(OC_6H_4Bu^t\text{-}4)_4$ and $Ti(OC_6H_4OCH_3\text{-}4)_4$ as there was a continuous loss of 88.12% without any break in the curve. The one step decomposition of compound indicates the formation of TiO_2 as the ultimate product without involving the formation of any intermediate of type $TiO(OC_6H_2Bu^t_2\text{-}2, 6\text{-}Me\text{-}4)_2$ as follows:

$$Ti(OC_6H_2Bu^t\text{-}2,6\text{-}Me\text{-}4)_4 \rightarrow TiO_2 + 2O(C_6H_2Bu^t\text{-}2,6\text{-}Me\text{-}4)_2$$

The process of decomposition in entirely exothermic indicated by the appearance of only one exothermic peak at 545.5°C compared to two peaks in case of other tetraaryloxides of titanium(IV).

Interestingly, the trend of decomposition of monochloro-, dichloro- and trichloro-aryloxides of titanium(IV) of composition $TiCl(OAr)_3$, $TiCl_2(OAr)_2$ and $TiCl_3(OAr)$ are comparable to that of $Ti(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_4$. A continuous loss of weight of 78 to 82% in the temperature range of about 40–570°C without showing any break in the curve exactly corresponds to the formation of TiO_2 as the final residue as:

$$TiCl_n(OAr)_{4-n} \rightarrow TiO_2 + n ArCl + \text{Organic matter}$$

One step decomposition of chloroaryloxides of titanium(IV) is further confirmed by the appearance of a single sharp exothermic peak in DTA curves of these compounds. However, in case of compound of composition $TiCl_3(OC_6H_4OCH_3\text{-}4)$ (Fig. 3) two exothermic peaks have been observed at 330.5 and 420.4°C in the DTA curve.

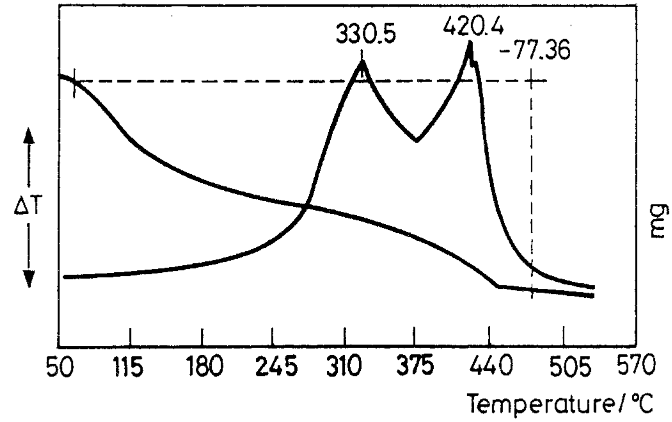

Fig. 3 TG and DTA curves $TiCl_3(OC_6H_4OMe\text{-}4)$

Based upon these experimental observations on chloro-aryloxides of titanium(IV), it may be concluded that these compounds are fairly stable and titanium-chlorine bond is comparatively weaker than titanium-oxygen as evidenced by the retention of titanium oxygen bond even on strong heating, forming TiO_2 as the final residue.

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