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Aqueous Chemistry of Bis(cyclopentadienyl)dihalotitanium(IV)

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Bis(cyclopentadienyl)dibromotitanium(IV) and bis(cyclopentadienyl)diiodotitanium(IV) have been prepared by the reaction of cyclopentadienylthallium(I) and the appropriate titanium tetrahalide. The aqueous chemistry of $(C_5H_5)_2TiX_2$ *has been reinvestigated. It has been found that compounds* $(C_5H_5)_2TiX_2$ *(X = F, Cl, Br, I) can be prepared in good yields by the action of haloacids on the bridged compounds* $[(C_5H_5)_2TiX']_2O$ *(X' = Cl, Br, I,* NO_3*). Other halogen exchange reactions involving* $(C_5H_5)_2TiX_2$ *have also been reported.*

Introduction

The reactions of bis(cyclopentadienyl)dihalotitanium(IV), $(C_5H_5)_2TiX_2$, have been studied by several workers. [1 - 4]. Wilkinson *et al.* [1] reported the formation of $(C_5H_5)_2Ti(OH)Br \cdot H_2O$ from the yellow aqueous solutions obtained by boiling $(C_5H_5)_2TiBr_2$ in water. Giddings [2] studied the hydrolysis of $(C_5H_5)_2TiCl_2$ on boiling in water and reported the reduction of $(C_5H_5)_2TiCl_2$ to $(C_5H_5)_2TiCl$ with zinc dust in acetone; the latter upon oxidation gave a bridged compound $[(C_5H_5)_2TiCl]_2O$. Samuel [3] reported the bridge compounds of the type $[(C_5H_5)_2TiX]_2O$ (X = Br, I, NO_3), the bridge Ti–O–Ti was established on the basis of an IR band at ~720 cm^{-1}. Kingston *et al.* [4] established the formation of the mixed halogen complexes of the type $(C_5H_5)_2MXX'$ (M = Ti(IV), Zr(IV), Hf(IV); X = Cl, X' = Br) in solution on the basis of proton magnetic resonance studies. Bhat *et al.* [5] prepared and investigated the xanthates of $(C_5H_5)_2Ti(IV)$ from aqueous solutions.

The present communication deals with a reinvestigation of the aqueous chemistry of $(C_5H_5)_2TiX_2$ (X = F, Cl, Br and I). The already known compounds $(C_5H_5)_2TiBr_2$ and $(C_5H_5)_2TiI_2$ have been prepared using cyclopentadienyl thallium(I) and the appropriate titanium tetrahalide. The preparation of $(C_5H_5)_2TiX_2$ (X = F, Cl, Br, I) by the reaction of haloacids (HX) with the bridge compounds $[(C_5H_5)_2TiX']_2O$ (X' = Cl, Br, I, NO_3) and $(C_5H_5)_2TiX_2$ respectively is also being reported.

Experimental

Reagents and General Techniques

Titanium tetrachloride (Travancore Titanium Products, India) was further purified by refluxing over copper turnings and the fraction boiling at 136 °C was collected. Titanium tetrabromide and titanium tetraiodide were prepared by methods reported in literature [6 - 8]. Cyclopentadienylthallium(I), $C_5H_5Tl(I)$ was prepared by the reaction of Tl_2SO_4 in aqueous KOH with cyclopentadiene [9].

Tetrahydrofuran (THF) (Riedel) was purified by refluxing over sodium metal for 24 hr and subsequently over $LiAlH_4$ for 4 hr. Infared spectra were recorded in the region 4000–700 cm^{-1} with a Perkin–Elmer Infracord Model 137 spectrophotometer.

Proton chemical shifts for the compounds $(C_5H_5)_2TiX_2$ were measured at ambient temperature with a Varian A-60A Spectrometer. The magnetic field sweep was calibrated with a standard sample of chloroform and tetramethysilane in carbon tetrachloride.

Preparation of $(C_5H_5)_2TiBr_2$

3.67 g of $TiBr_4$ (0.01 mol) and 5.38 g $(C_5H_5)Tl(I)$ (0.02 mol) in tetrahydrofuran (100 ml) were stirred at room temperature (30 °C) for 24 hr in a 250 ml flask fitted with a mercury seal. The resulting red coloured solution was filtered through a filtration unit fitted with a G-4 sintered glass frit. The THF in the filtrate was distilled off under reduced pressure (15 mm). The residue thus obtained was crystallised from chloroform to give the red coloured crystalline compound (yield 60%).

Preparation of $(C_5H_5)_2TiI_2$

This compound was prepared by the same procedure as that for $(C_5H_5)_2TiBr_2$ by the reaction of 2.75 g (0.005 mol) TiI_4 and 2.7 g (0.01 mol) $(C_5H_5)Tl$ (yield 70%, black crystals).

$(C_5H_5)_2TiCl_2$ was prepared as reported in the literature [1], and recrystallised from thionyl chloride.

TABLE I. Melting Point[a] and Colour, Proton Chemical Shifts[b] (in $CDCl_3$) of $(C_5H_5)_2TiX_2$ and $[(C_5H_5)_2TiX]_2O$ (X = F, Cl, Br, I and NO_3).

Compound	Colour	M.p. (°C)	τ(ppm)
$(C_5H_5)_2TiF_2$	Yellow	260	3.57
$(C_5H_5)_2TiCl_2$	Red	289	3.43
$(C_5H_5)_2TiBr_2$	Dark Red	307–309	3.33
$(C_5H_5)_2TiI_2$	Black	316	3.17
$[(C_5H_5)_2TiF]_2O$	Light Yellow	220	–
$[(C_5H_5)_2TiCl]_2O$	Orange	230	–
$[(C_5H_5)_2TiBr]_2O$	Orange	210	–
$[(C_5H_5)_2TiI]_2O$	Yellow–Brown	200	–
$[(C_5H_5)_2TiNO_3]_2O$	Yellow–Orange	180	

[a] Except for $(C_5H_5)_2TiCl_2$ and $(C_5H_5)_2TiBr_2$, all compounds decompose at these temperatures. [b] The compounds $[(C_5H_5)_2TiX]_2O$ were insufficiently soluble for n.m.r. spectra.

Reactions of $(C_5H_5)_2TiX_2$ in Aqueous Solutions

Preparation of $[(C_5H_5)_2TiX]_2O$ (X = Br, I, NO_3)

These bridge compounds were prepared by adding an excess of the saturated solution of the sodium salt of appropriate anion to an aqueous solution of $(C_5H_5)_2TiCl_2$. The precipitates thus obtained were washed with water and dried at 150 °C.

Preparation of $(C_5H_5)_2TiX'_2$ from $[(C_5H_5)_2TiX]_2O$ and HX'

When the bridge complexes $[(C_5H_5)_2TiX]_2O$ (X = Cl, Br, I, NO_3) were treated with excess of the acid HX' (X' = F, Cl, Br, I) the compounds $(C_5H_5)_2TiX'_2$ were obtained. The products obtained were washed with alcoholic HX' and dried under vacuum. The yields were almost quantitative.

Preparation of $(C_5H_5)_2TiX'_2$ from $(C_5H_5)_2TiX_2$ and HX'

$(C_5H_5)_2TiX_2$ (X = F, Cl, Br, I) was refluxed with an excess of HX' for 15 minutes. The reaction mixture was allowed to cool and the precipitate of $(C_5H_5)_2TiX'_2$ (X' = F, Cl, Br, I) was filtered through G-4 filtration disc, and dried under vacuum. The yield was quantitative.

Preparation of $(C_5H_5)_2TiF_2$ from $(C_5H_5)_2TiCl_2$

$(C_5H_5)_2TiF_2$ was also prepared by adding an aqueous ammonium fluoride solution dropwise to an aqueous $(C_5H_5)_2TiCl_2$ solution. The yellow products so obtained was washed with water and dried under vacuum. The fluorine in $(C_5H_5)_2TiF_2$ is not exchanged in aqueous solution on treatment with NaX (X = Cl, Br, I, NO_3).

Preparation of $(C_5H_5)_2TiCl_2$ from $[(C_5H_5)_2TiX]_2O$ and thionyl chloride

The halogen of the bridge complex $[(C_5H_5)_2TiX]_2O$ (X = F, Cl, Br and I) is completely exchanged with chlorine using $SOCl_2$ to give $(C_5H_5)_2TiCl_2$.

Preparation of $[(C_5H_5)_2TiX]_2O$ from $(C_5H_5)_2TiX_2$ (X = Cl, Br, I)

The method adopted in this case was similar to the one by Giddings [2] for the preparation of $[(C_5H_5)_2TiCl]_2O$. $(C_5H_5)_2$ TiX_2 (X = Cl, Br, I)was refluxed with zinc metal in THF/acetone; it was reduced to $(C_5H_5)_2Ti(III)X$ which on aerial oxidation gave $[(C_5H_5)_2TiX]_2O$.

In each of the above cases, the products were identified by their m.p., IR and nmr spectra (in case of $(C_5H_5)_2TiX_2$; Tables I and II).

Discussion

The most common method reported for the preparation of $(C_5H_5)_2TiX_2$ is to react TiX_4 with NaC_5H_5 in the stoicheometric ratios. The preparation of $(C_5H_5)_2TiCl_2$ has also been reported [10] by the reaction of $TiCl_4$ and $(C_5H_5)Tl(I)$. We have prepared $(C_5H_5)_2$ TiX_2 (X = Br and I) in good yields by the reaction of (C_5H_5) Tl(I) and the appropriate titanium tetrahalide. The products have been characterized by their m.p., infrared and proton magnetic resonance spectra.

Our studies have shown that the proton magnetic resonance spectra can be used as a sensitive tool for identification of $(C_5H_5)_2TiX_2$ since the proton chemical shifts for the halogen derivatives (X = F, Cl, Br and I) are sufficiently separated. On the other hand, the infrared spectra in the range 4000–700 cm^{-1} for these compounds are nearly identical (see Table II) so that they cannot be used satisfactorily for distinguishing them.

Attempts at preparing $(C_5H_5)_2TiBr_2$ and $(C_5H_5)_2TiI_2$ by the method described by Wilkinson *et al.* [1], *viz.*, by refluxing $(C_5H_5)_2TiCl_2$ and KBr for $(C_5H_5)_2TiBr_2$, and $(C_5H_5)_2TiBr_2$ and KI for $(C_5H_5)_2TiI_2$ were unsuccessful. In both cases the products isolated were a mixture of the unconverted reactant $(C_5H_5)_2TiX_2$ and the product $(C_5H_5)_2TiX'_2$, in almost compatible amounts. This was clearly indicated by the two signals due to cyclopentadienyl moiety corresponding to the two compounds. Even on refluxing for as long as 48 hr (*cf.* 30 min in ref. 1), the complete halogen exchange was not observed.

Addition of saturated aqueous solutions of NaBr, NaI and $NaNO_3$ separately to aqueous $(C_5H_5)_2TiCl_2$ solution results in the immediate precipitation of compounds which have been identified as $[(C_5H_5)_2TiX]_2O$ (X = Br, I, NO_3), similar to $[(C_5H_5)_2TiCl]_2$-

TABLE II. Infrared Bands of $(C_5H_5)_2TiX_2$ and $[(C_5H_5)_2TiX]_2O$.[a]

1. $(C_5H_5)_2TiF_2$:	3140(m), 1440(s), 1385(w), 1130 (vw), 1015(s), 955(vw), 928(vw), 870(s), 820(vs).
2. $(C_5H_5)_2TiCl_2$:	3140(m), 1440(s), 1365(m), 1130(w), 1015(s), 955(vw), 925(vw), 865(s), 815(vs).
3. $(C_5H_5)_2TiBr_2$:	3140(m), 1440(s), 1360(w), 1130(w), 1015(s), 950(vw), 928(vw), 865(s), 820(vs).
4. $(C_5H_5)_2TiI_2$:	3140(m), 1440(s), 1365(w), 1130(vw), 1015(s), 955(sh), 928(sh), 860(s), 815(vs).
5. $[(C_5H_5)_2TiF]_2O$:	3140(w), 1630(w), 1440(s), 1360(w), 1130(w), 1060(w), 1015(s), 860(sh), 820(s), 715(vs).
6. $[(C_5H_5)_2TiCl]_2O$:	3150(w), 1630(w), 1440(s), 1365(w), 1130(w), 1065(w), 1015(s), 870(sh), 815(s), 715(vs).
7. $[(C_5H_5)_2TiBr]_2O$:	3140(m), 1610(m), 1440(s), 1350(w), 1125(vw), 1060(vw), 1015(s), 860(sh), 825(vs), 730(vs).
8. $[(C_5H_5)_2TiI]_2O$:	3110(m), 1610(m), 1440(s), 1355(w), 1130(w), 1065(w), 1010(s), 860(sh), 825(vs), 730(vs).
9. $[(C_5H_5)_2TiNO_3]_2O$:	3140(m), 1630(m), 1380(s), 1290(m), 1125(sh), 1070(vw), 1015(s), 840(sh), 825(vs), 730(vs).

[a] vw = very weak, w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

O. These bridge compounds were also prepared by the method of Giddings [2].

We have observed that the bridge compounds undergo complete halogen exchange on treatment with the appropriate halo acid.

$$[(C_5H_5)_2TiX]_2O \xrightarrow{HX'} (C_5H_5)_2TiX'_2$$

where X = Cl, Br, I, NO_3; X′ = anion other than X. Similarly, reaction of $[(C_5H_5)_2TiX]_2O$ with HX (X = Cl, Br, I) gives $(C_5H_5)_2TiX_2$.

Though we have evidence for the formation of intermediate species of the type $(C_5H_5)_2TiXX'$ in solution, we have not isolated any of these in the solid state. Attempts will, however, be made in our future studies to isolate these compounds.

Preparation of $(C_5H_5)_2TiX_2$ by the above reactions involving halogen exchange is significant, in that the method is quick, less expensive, and the yields are almost quantitative.

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