THERMAL DECOMPOSITION OF TETRAFERRICINIUM TRITIN(IV) BROMIDE HEXAHYDRATE [Fc$_4$Sn$_3$Br$_{16}$·6H$_2$O]

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Abstract

Thermal decomposition of Fc$_4$Sn$_3$Br$_{16}$·6H$_2$O was investigated by thermogravimetry. The decomposition products were characterized by U.V.-Visible spectroscopy, chemical analysis and X-ray diffraction. The TG curve of the complex showed three decomposition steps. In the first, a mixture of HBr and H$_2$O was evolved. A ferricinium tin bromide compound (Fc$_4$SnBr$_8$) was found to sublime in the second step, whereas a mixture of HBr and H$_2$O was given off in the third, leaving SnO$_2$ as the residue, The stoichiometry of the thermal decomposition of [Fc$_4$Sn$_3$Br$_{16}$·6H$_2$O] has been established and a possible mechanism for its decomposition is suggested.

Introduction

Since the discovery of ferrocene in 1951 [1], most of the research work in this field of organometallic chemistry has been directed to the synthesis of other metallocenes along with their derivatives, and to the elucidation of their structures and bondings [2]. Tin-based ferricinium salts have been proposed as anti-tumour drugs [3, 4]; also ferricinium salts, in general, have been reported to be better smoke suppressants in polymers than ferrocene [5]. In spite of this latter application, investigation of their thermal properties is sparse. The thermal decomposition of ferricinium oxo trichloroferrate(III), Fc$_2$[Fe$_2$OCl$_6$] was reported in 1986 [5] and we now report on the thermal decomposition of [Fc$_4$Sn$_3$Br$_{16}$·6H$_2$O].

Experimental

Preparation of Fc$_4$Sn$_3$Br$_{16}$·6H$_2$O

Solutions of ferrocene and SnBr$_4$ in the 1:1 molar ratio respectively were prepared in dichloroethane and mixed together to obtain blue crystals of [Fc$_4$Sn$_3$Br$_{16}$·6H$_2$O]. The compound was filtered off and dried under vacuum. The molecular formula was established by X-ray crystal structure analysis and was in agreement with the

elemental analysis ($C=19.95$, $H=1.82$, $O=3.64$, $Br=50.10$, $Fe=9.60$ and $Sn=14.88\%$ compared with the calculated values of $C=19.32$, $H=2.10$, $O=3.86$, $Br=51.41$, $Fe=0.98$ and $Sn=14.32\%$ respectively).

Instrumentation

Thermogravimetry was carried out using a Perkin-Elmer PC Series TGA7 thermobalance. Samples of mass approximately 10 mg were heated at $20°C$ min^{-1} in 2.5×5.00 mm platinum crucibles under a constant nitrogen flow (0.1 l min^{-1}). UV-Visible spectra were measured on a UV-Hitachi U-2000 spectrophotometer using 1 cm path length silica cells.

X-ray crystal structure and diffaction measurements were made on a Siemens P4 Diffractometer and XRD on a Siemens D5000/B02-147 instrument, respectively. X-ray crystal data were solved using SHELX-90 and refined by SHELXL-93 [6]. The elemental analysis (C, H, O) was carried out using a Fison EA 1108 instrument. Iron and tin were determined using a ICP Perkin-Elmer P1000 instrument and bromine by conductometric titration with standard sodium diethyldithiocarbamate solution.

Gaseous products and residue

The gaseous products and residue were obtained under the flow of dry nitrogen by heating the compound, [$Fc_4Sn_3Br_{16}·6H_2O$] in a porcelain boat placed inside a quartz tube using a tube furnace. The decomposition temperatures were inferred from the corresponding TG curves for the formation of the gaseous products and the residue.

Analysis

HBr was detected by passing the gaseous product through water under a flow of nitrogen. An acidic solution resulted containing bromide ions, detected by adding $AgNO_3$ solution [7]. A bluish-green sublimate collected on the cooler part of the silica tube which was outside the tube furnace on heating the starting material, [$Fc_4Sn_3Br_{16}·6H_2O$] at $210°C$ and was identified as Fc_4SnBr_8 by its characteristic U.V.-Visible spectrum [8].

Results and discussion

A typical TG curve for the decomposition of $Fc_4Sn_3Br_{16}·6H_2O$ is presented in Fig. 1. The curve shows three stages of decomposition. The first stage shows a small mass loss of 2.33% due to decomposition between 49.6 and $81.0°C$. The second decomposition step shows a sudden loss of 60.60% between 164.9 and $249.6°C$. In the third stage, the curve indicates a slow loss of 24.95% between 257.2 and $490.8°C$. The total mass loss adds up to 87.89% giving a 12.11% mass of the residue. The X-ray crystallographic data gave the molecular formula of the
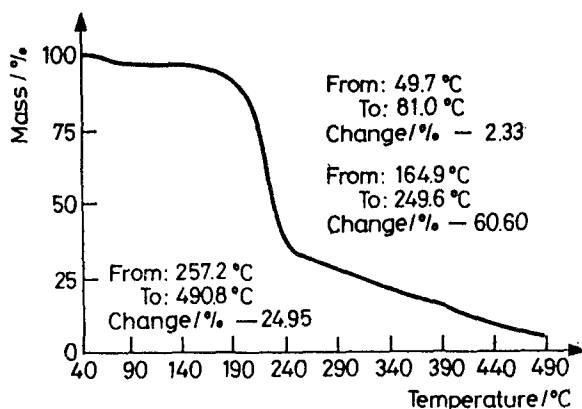
Fig. 1 TG curve for the thermal decomposition of $Fc_4Sn_3Br_{16} \cdot 6H_2O$

compound as $Fc_4Sn_3Br_{16} \cdot 6H_2O$ with a molar mass of 2486.62 [9]. On this basis, the molar masses of the species lost in the three stages of decomposition are 57.89, 1506.97 and 620.51, respectively. Table 1 shows these results and the possible gaseous species lost during the decomposition of $Fc_4Sn_3Br_{16} \cdot 6H_2O$.

The gaseous products were identified by various techniques mentioned in the experimental section and their molar masses calculated as outlined above. Based on the calculation similar to those for the gaseous products, the molar mass of the solid residue was predicted to be 301.13. The residue was analysed by the XRD method. The X-ray powder diffraction pattern of the residue gave 'd' values of 1.76 (m), 2.64 (s), 3.34 (s), 7.50 (m) and 6.74 (m) compared with the literature (ASTM) values of 1.77 (47), 2.46 (96), 3.35 (100), 7.50 (33) and 6.74 (32) listed for SnO_2. The molar mass of tin (IV) oxide is 150.69 but the molar mass predicted from the TG results is 301.13 which is almost twice as much indicating that two moles of SnO_2 are formed for every mole of $Fc_4Sn_3Br_{16} \cdot 6H_2O$ decomposed. The first decomposition reaction evolving a mixture of HBr and water is represented by Eq. (1). A predicted molar mass of 57.89 compares well with the actual molar mass of 58.45 for the loss of one mole of HBr and two moles of H_2O for two moles of $Fc_4Sn_3Br_{16} \cdot 6H_2O$.

Table 1 The predicted and found molar masses of the possible decomposition products in the thermal analysis of $[Fc_4Sn_3Br_{16} \cdot 6H_2O]$

| Decomp. step	$T_{range}/$ °C	Mass loss/ %	Molar mass predicted	Possible species	Molar mass actual
1	49.6– 81.0	2.33	57.89	$1/2HBr + H_2O$	58.45
2	164.9–249.6	60.60	1507.97	Fc_4SnBr_8	1502.04
3	257.2–490.8	24.95	620.51	$7.5HBr + H_2O$	624.81

$$2[Fc_4Sn_3Br_{16}\cdot6H_2O] \rightarrow Fc_8Sn_6(OH)Br_{31}\cdot9H_2O + HBr + 2H_2O \qquad (1)$$
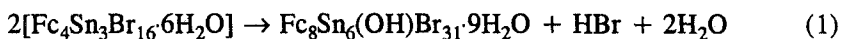
In the second stage of the reaction, the predicted molar mass of the evolved species was found to be 1507.97 compared with the molar mass of 1502.04 for the loss of one mole of (Fc_4SnBr_8) per mole of $[Fc_4Sn_3Br_{16}\cdot6H_2O]$ as expressed by Eq. (2).

$$Fc_8Sn_6(OH)Br_{31}\cdot9H_2O \rightarrow Sn_4(OH)Br_{15}\cdot9H_2O + 2Fc_4SnBr_8 \qquad (2)$$
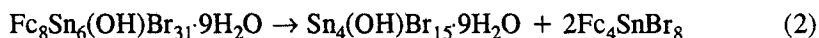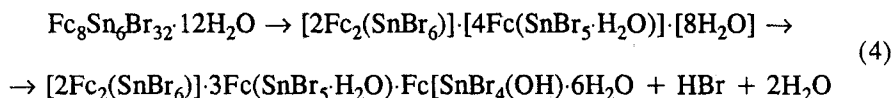
In the third mass loss the predicted molar mass of the species is 620.51 compared with the actual molar mass of 624.81 when a mixture of 15 moles of HBr and 2 moles of H_2O are lost for every 2 moles of $Fc_4Sn_3Br_{16}\cdot6H_2O$ as shown by Eq. (3).

$$Sn_4(OH)Br_{15}\cdot9H_2O \rightarrow 4SnO_2 + 15HBr + 2H_2O \qquad (3)$$
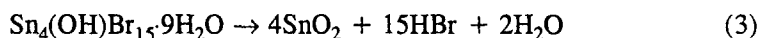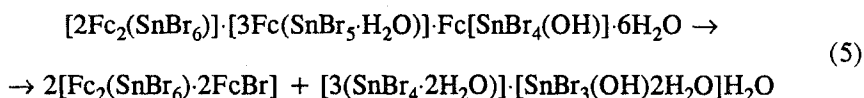
A possible mechanism may be suggested for the decomposition of $Fc_4Sn_3Br_{16}\cdot6H_2O$ based on the structure as derived from the unique unit cell packing of the crystal [9]. According to this structure, the unit cell is a dimerised form of the molecular structure i.e., $[Fc_4Sn_3Br_{16}\cdot6H_2O]_2$, or $Fc_8Sn_6Br_{32}\cdot12H_2O$ and consists of:

(a) two moles of $Fc_2(SnBr_6)$ containing symmetrical units $[SnBr_6]$.
(b) four moles of $Fc(SnBr_5\cdot H_2O)$ containing unsymmetrical units $[SnBr_5\cdot H_2O]$.
(c) eight moles of H_2O present as water of crystallisation.

Because the TG results are consistent with the loss of a mixture of $(HBr+2H_2O)$, it may be assumed that the first mass loss consists of reactions involving dehydration of two moles of water and hydrolysis of one mole of the unsymmetrical species as indicated by Eq. (4).

$$Fc_8Sn_6Br_{32}\cdot12H_2O \rightarrow [2Fc_2(SnBr_6)]\cdot[4Fc(SnBr_5\cdot H_2O)]\cdot[8H_2O] \rightarrow$$
$$\rightarrow [2Fc_2(SnBr_6)]\cdot3Fc(SnBr_5\cdot H_2O)\cdot Fc[SnBr_4(OH)\cdot6H_2O + HBr + 2H_2O \qquad (4)$$

It is necessary to suggest the rearrangement of the solid product at the end of the first mass loss to account for the sublimation of two moles of $[Fc_2(SnBr_6)\cdot2FcBr]$ as observed in the present study. The rearrangement is shown below along with the sublimation as observed in the second mass loss.

$$[2Fc_2(SnBr_6)]\cdot[3Fc(SnBr_5\cdot H_2O)]\cdot Fc[SnBr_4(OH)]\cdot6H_2O \rightarrow$$
$$\rightarrow 2[Fc_2(SnBr_6)\cdot2FcBr] + [3(SnBr_4\cdot2H_2O)]\cdot[SnBr_3(OH)2H_2O]H_2O \qquad (5)$$

For stability reasons, it is assumed that tin (IV) in these species is 6 coordinate. The sublimed species $[Fc_2(SnBr_6)\cdot2FcBr]$ is formed when $Fc_2(SnBr_6)$ attracts three FcBr moities from $Fc(SnBr_5\cdot H_2O)$ and one from $FcSnBr_4(OH)$. When these species lose FcBr, they are stabilised by attracting water of crystallisation in order to attain octahedral geometry. In $[SnBr_3(OH)2H_2O]H_2O$ species, tin (IV) may extend its co-

ordination to seven and have the water molecule inside the coordination sphere. However, the third mass loss is consistent with the formation of solid SnO_2 evolving a mixture of HBr and H_2O as indicated in the reaction:

$$3(SnBr_4 \cdot 2H_2O) \cdot [SnBr_3(OH)2H_2O]H_2O \rightarrow 4SnO_2 + 15HBr + 2H_2O \qquad (6)$$
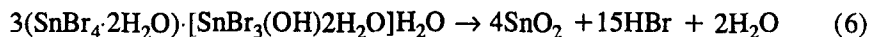
Though the mechanism for the decomposition of $Fc_4Sn_3Br_{16} \cdot 6H_2O$ is speculative, it does agree with the thermogravimetric results discussed above.

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