

Note

Carboxylato complexes of zirconium(IV). Part 5. The thermal decomposition of difluorobis(heptafluorobutyrate)zirconium(IV)

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Abstract

The thermal decomposition of $\text{ZrF}_2(\text{C}_3\text{F}_7\text{COO})_2$ has been studied by TG and macro-scale pyrolysis. The following products have been isolated and characterised: ZrOF_2 , $\text{ZrF}_3(\text{C}_3\text{F}_7\text{COO})$ and $(\text{C}_3\text{F}_7\text{CO})_2\text{O}$. The loss of ZrF_4 , C_3F_6 and CO_2 during the course of thermal decomposition is also postulated.

INTRODUCTION

A number of carboxylato complexes of zirconium(IV) have been prepared, both from the oxide chloride and the tetrachloride, and their properties studied [1–5]. However, only a few polyfluorinated carboxylated derivatives have been synthesised, of which the trifluoroacetates, the trifluoroacetate chlorides and the heptafluorobutyrate show particularly interesting decomposition behaviour [6–8]. These three groups of compounds, upon pyrolysis, form a thermally stable zirconium oxide fluoride, the stoichiometry of which depends upon the ratio of zirconium to perfluorocarboxylato groups in the parent compound. The various oxide fluorides finally decompose with loss of zirconium tetrafluoride and the formation of zirconium dioxide.

In view of the current interest in new routes for the synthesis of zirconium tetrafluoride and the recently published synthesis of difluorobis(heptafluorocarboxylato)zirconium(IV), it was decided to investigate the thermal decomposition of the latter compound [9].

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EXPERIMENTAL

Infrared spectra were measured with a Pye Unicam 1025 or Perkin-Elmer 297 spectrometer. Samples were prepared as Nujol or hexachlorobutadiene mulls. NMR spectra were measured using a Perkin-Elmer R32 spectrometer.

Thermogravimetric analysis was carried out using a Mettler TA 3000 instrument at a heating rate of $10^{\circ}\text{C min}^{-1}$.

Zirconium was determined by a back titration technique using EDTA and Zn^{2+} solution. Other elemental analysis was carried out by Butterworths Microanalytical Consultancy Ltd.

Difluorobis(heptafluorocarboxylato)zirconium(IV) was prepared as previously described and its identity confirmed by elemental and infrared spectroscopic analysis [9].

Thermal gravimetric analysis of $\text{ZrF}_2(\text{C}_3\text{F}_7\text{COO})_2$

TG analysis was carried out in both air and argon. The two thermograms showed very little difference, the one in air being illustrated in Fig. 1.

Macro-scale pyrolysis

The pyrolysis was carried out using a pyrex glass tube which was equipped with glass joints and stopcocks to allow a flow of nitrogen

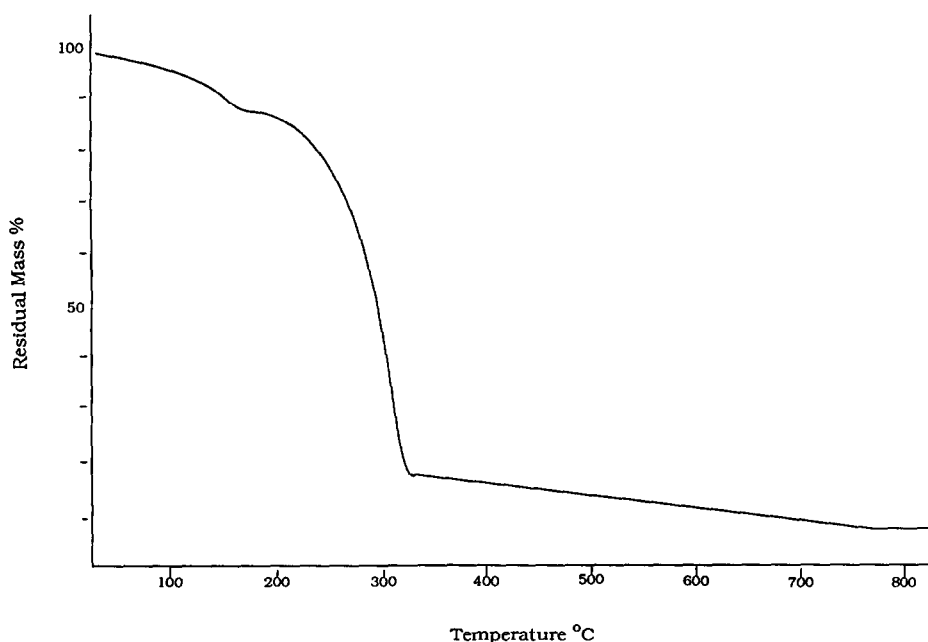


Fig. 1. Thermogram of $\text{ZrF}_2(\text{C}_3\text{F}_7\text{COO})_2$ in air.

TABLE 1

Pyrolysis results

Mass of $\text{ZrF}_2(\text{C}_3\text{F}_7\text{COO})_4$ (g)	Mass of sublimate (g)	Mass of condensate (g)	Mass of residue (g)
1.55	0.057 (4.9%)	^a	0.232
3.612	0.524 (14.5%)	^a	0.709
2.512	0.715 (28.5%)	0.234	0.439
5.015	1.320 (26.3%)	0.613	1.139

^a Not collected.

through the tube during the course of a reaction. The exit to the tube was fitted with a separate U-tube which could be cooled in a suitable freezing mixture. Approximately half of the tube was heated using a conventional tube furnace. The sample to be pyrolysed was contained in a silica boat and placed in the centre of the heated zone.

In a typical pyrolysis experiment, a sample of $\text{ZrF}_2(\text{C}_3\text{F}_7\text{COO})_2$ (1.155 g, 2.08×10^{-3} moles) was placed in the silica boat and heated to 400°C in a flow of nitrogen ($30 \text{ cm}^3 \text{ min}^{-1}$). At $\approx 120^\circ\text{C}$, a clear condensate collected in the cooled U-tube and at $\approx 290^\circ\text{C}$, a white sublimate was observed on the cooler part of the tube; no attempt was made to trap any gaseous products. After cooling, the silica boat was found to contain an off-white residue.

The results from this and three other pyrolyses are given in Table 1.

The sublimate was shown to contain 25.5% Zr and 12.5% carbon; $\text{ZrF}_3(\text{C}_3\text{F}_7\text{COO})$ requires Zr, 25.2% and C, 13.3%. Butterworths Laboratories were unable to obtain consistent results for the fluorine content of this compound. Infrared spectroscopy showed the following bands: 1660 (s, sp), 1442 (m, sp), 1425 (m, sp), 1270 (w, sp), 1210 (s, sp), 1110 (w, sp), 1075 (w, sp), 960 (w, sp), 930 (w, sp), 705 (m, sp) cm^{-1} .

The condensate was shown, by Ir and NMR spectroscopy, to be a mixture of heptafluorobutyric anhydride and heptafluorobutyric acid, the latter probably arising during handling procedures.

The residue was shown to contain 62.3% zirconium; ZrOF_2 requires 62.8% Zr. The infrared spectrum showed no bands which could be attributed to heptafluorocarboxylato groups.

DISCUSSION

Thermogravimetric analysis of $\text{ZrF}_2(\text{C}_3\text{F}_7\text{COO})_2$ shows five regions of mass loss: A ($25\text{--}120^\circ\text{C}$), 5% gradual mass loss; B ($120\text{--}170^\circ\text{C}$), 7% more rapid mass loss; C ($170\text{--}270^\circ\text{C}$), 18% slow but accelerating mass loss; D ($270\text{--}330^\circ\text{C}$), 52% rapid mass loss; E ($330\text{--}800^\circ\text{C}$), 9% slow mass loss; Residue, 9%.

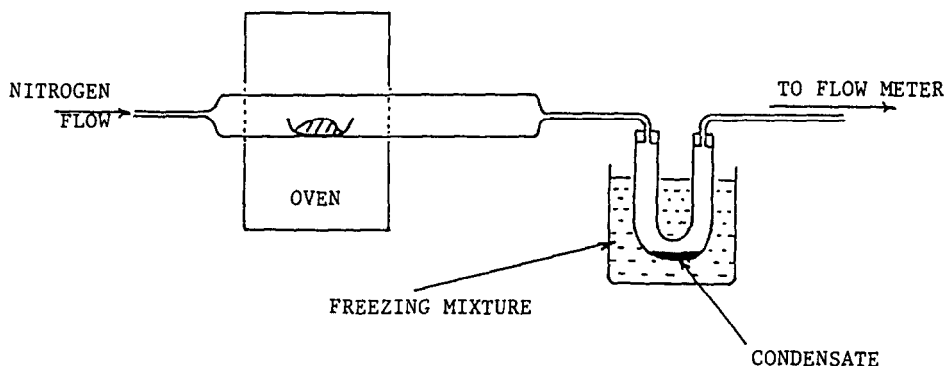


Fig. 2. Apparatus used for the macro-scale pyrolysis.

In an independent experiment, a sample of $\text{ZrF}_2(\text{C}_3\text{F}_7\text{COO})_2$ was heated to 800°C . The residue was shown by X-ray powder analysis to be zirconium dioxide.

The residue of 9% from TG may be safely assumed to be zirconium dioxide and is equivalent to a 6.7% zirconium value. This does not correspond with the measured zirconium content (16.4%) of the starting material and clearly indicates that a zirconium-containing compound is evolved during the course of the thermolysis. The high-temperature loss of 9% (E above) may be attributed to ZrF_4 arising from the decomposition of a zirconium oxide fluoride (see below). This pattern of thermal breakdown is consistent with similar behaviour observed for other perfluorocarboxylate derivatives of zirconium [7]. The loss of zirconium fluoride only accounts for a 4.9% loss of zirconium during thermolysis. Therefore the mass losses below 330°C must also involve zirconium loss by virtue of another volatile zirconium compound(s). This cannot be attributed to ZrF_4 because the temperature is well below that of the sublimation temperature of this compound [10]. A macro-scale thermolysis was therefore carried out in order to isolate and characterise those intermediate products.

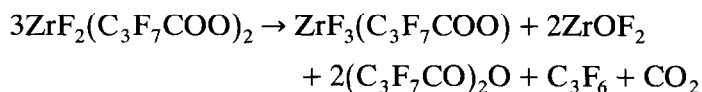
Macro-scale pyrolysis of $\text{ZrF}_2(\text{C}_3\text{F}_7\text{COO})$ in nitrogen atmosphere up to a temperature of 400°C using the apparatus illustrated in Fig. 2 gave three isolateable products. A summary of the results obtained is given in Table 1. These results are not very quantitatively consistent; this may be attributed to the known hydrolytic instability of this compound and to pick-up of atmospheric moisture during transfer to the pyrolysis equipment.

At $\approx 120^\circ\text{C}$, a colourless condensate collected in the cold trap and was shown to be a mixture of heptafluorobutyric anhydride and heptafluorobutyric acid, the latter probably arising by hydrolysis during handling. The temperature at which this product is evolved correlates well with part B of the thermogram given in Fig. 1. As the pyrolysis temperature was increased, a white sublimate collected on the cooler parts of the tube when

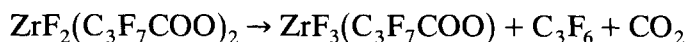
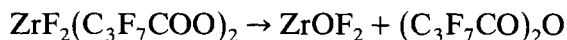
the furnace temperature reached $\approx 300^\circ\text{C}$. This temperature is in agreement with that observed at the onset of section D of the thermogram where a substantial, rapid mass loss was observed. The infrared spectrum of this compound showed (inter alia) an absorption band at 1660 cm^{-1} , typical of ν_{asym} of a coordinated carboxylate group, as compared with a value of 1620 cm^{-1} for a similar band in the starting material. Bands typical of C–F stretches were also observed. This evidence, coupled with the zirconium and carbon analysis, suggests that the sublimate may be formulated as $\text{ZrF}_3(\text{C}_3\text{F}_7\text{COO})$. No attempt was made to collect the gases which were evolved during the course of this pyrolysis. From the known thermal behaviour of metal heptafluorobutyrate, it is most likely that these would be carbon dioxide and hexafluoropropene arising from some decarboxylation [11].

The residue remaining after the completion of the pyrolysis was shown by zirconium analysis and lack of any evidence for carboxylate groups, to be the zirconium oxide fluoride ZrOF_2 . This confirms the nature of the product observed at the commencement of section E of the thermogram. In addition, ZrOF_2 is known to decompose thermally to ZrF_4 and ZrO_2 [12].

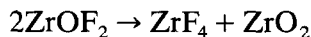
The thermal decomposition of $\text{ZrF}_2(\text{C}_3\text{F}_7\text{COO})_2$ is clearly a complex process but to a first approximation may be represented by the following equation at temperatures below $\approx 350^\circ\text{C}$



This may be broken down into the following simpler steps, some of which may occur concurrently



and at higher temperatures



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