

CARBOXYLATO COMPLEXES OF ZIRCONIUM(IV)

Part 3. The Thermal Decomposition of Trifluoroacetatozirconium Chlorides and the Formation of Zirconium Tetrafluoride

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The preparation and thermal decomposition of several trifluoroacetatozirconium chlorides is described. A mechanism for the thermal decomposition is proposed and the formation of zirconium tetrafluoride discussed in terms of composition of the parent compound.

A number of carboxylato complexes of zirconium(IV) have been prepared and studied [1–7]. Of these the trifluoroacetates and the heptafluorobutyrate show particularly interesting thermal decomposition behaviour [4, 7]. Both groups of compounds 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 to zirconium tetrafluoride it was decided to study a group of zirconium trifluoroacetates where the zirconium to trifluoroacetato ratio is varied, to see if there is a correlation between this ratio and the formation of zirconium tetrafluoride.

Experimental

Infrared spectra were measured using Perkin–Elmer Instruments 297 and 521; samples were prepared as nujol and hexachlorobutadiene mulls.

Elemental analysis was carried out by Butterworths Microanalytical Consultancy Ltd. Zirconium was determined as zirconium dioxide via the tetramandellate [8]. Thermogravimetric analysis was carried out using a Stanton–Redcroft TG750

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at a heating rate of 10 deg min^{-1} in air and differential thermal analysis with a DuPont DTA 900 using the same heating rate in air.

Deuterated zirconium oxide chloride was prepared as previously described [6].

The preparation of trifluoroacetato derivatives of zirconium

A series of compounds having different zirconium to trifluoroacetato ratios were prepared. The following procedure is typical:

Zirconium oxide chloride hexahydrate (6.83 g, 24 mmol) was dissolved in deionized water, trifluoroacetic acid added (5.48 g, 48 mmol) and the solution refluxed for 2.5 hours. Water and any unreacted trifluoroacetic acid was removed either by rotary evaporation under reduced pressure or by freeze drying, to yield a white product.

The reaction conditions are summarised in Table 1 together with analytical data and proposed empirical formulae. The products were further characterised by infrared spectroscopy, the data for which is presented in Table 2.

The thermal analysis results are given in Table 3 which includes also the proposed molecular losses at each stage. These results are also shown graphically in Figures 1 and 2, clearly illustrating the existence of a relatively thermally stable product over the approximate temperature range 600–1000 K. The differential thermal analysis results are given in graphical form in Figures 3 and 4.

The preparation of a deuterated trifluoroacetatozirconium chloride [ZrCl(TFA)-d]

Zirconium oxide chloride heptadeuterate (2.79 g, 8.61 mmol) was dissolved in deuterium oxide (20 cm^3), trifluoroacetic acid-d (1.90 g, 16.5 mmol) added, and the mixture refluxed under nitrogen for 2.5 hours. The deuterium oxide and any unreacted trifluoroacetic acid-d was removed by distillation, and the residue dried in vacuo over silica gel to leave a white product ZrCl(TFA)-d (2.36 g). Infrared spectroscopic data is presented in Table 2 and analytical data in Table 1. A saturated solution of ZrCl(TFA)-d in deuterium oxide gave the Raman absorption bands listed in Table 2.

Discussion

The reaction of zirconium oxide chloride with aqueous trifluoroacetic acid gives rise to a series of products, all of which contain residual chloride ion. The ratio of zirconium to trifluoroacetato groups in the products varies from 1 : 0.75 to 1 : 1.15. This ratio does not appear to vary in any systematic way with reactant ratios or acidity of the reaction medium (see Table 1).

Table I Reaction conditions and analytical data

Product	Molar Zr: TFA	Reaction time, h	Reaction temp., °C	Molarity CF ₃ COOH	Product analysis			Proposed formula			Required analysis, %		
					Zr	Cl	H	Zr	Cl	H	Zr	Cl	H
ZrC(TFA)-1	1:2	2.6	100	1.52 ^a	33.70	8.17	9.19	2.09	[Zr _{1,6} (TFA) _{1,6} (OH) _{3,8} (H ₂ O) ₄]Cl ₁₀	33.62	8.17	8.85	1.07
ZrC(TFA)-2	1:2	3.0	100	0.26	35.26	7.81	7.80	1.84	[Zr _{1,6} (TFA) _{1,3} (OH) _{4,2} (H ₂ O) ₂]Cl ₉	36.50	7.98	7.81	1.16
ZrC(TFA)-3	1:2	2.1	95	1.77	30.40	10.87	6.35	2.53	[Zr _{1,6} (TFA) ₆ (OH) _{1,3} (H ₂ O) _{1,6}]Cl ₈ ·6H ₂ O	30.48	11.85	6.02	2.62
ZrC(TFA)-4	1:5	2.0	100	3.55	30.20	8.69	7.55	2.11	[Zr ₈ (TFA) ₈ (OH) ₈ (H ₂ O) _{1,2}]Cl ₆ ·4H ₂ O	29.89	8.71	7.87	2.07
ZrC(TFA)-5	1:5.4	2.5	102	3.69	26.44	7.79	8.52	1.97	[Zr ₄ (TFA) ₃ (OH) ₈ (H ₂ O) ₆]Cl ₃ ·5H ₂ O	26.62	7.76	8.76	2.21
ZrC(TFA)-6	1:10	2.0	115	5.01	26.57	6.76	10.21	1.67	[Zr ₆ (TFA) ₆ (OH) _{1,1} (H ₂ O) ₉]Cl ₄ ·3H ₂ O	25.94	6.72	10.25	1.68
ZrC(TFA)-d	1:2	2.5		0.78	31.17	11.78	5.04	—					

Table 2 Infrared Raman spectroscopic data cm^{-1}

ZrCl(TFA)-1 & -2	ZrCl(TFA)-3		ZrCl(TFA)-6	ZrCl(TFA)-d		Assign- ments
	IR	Raman		IR	Raman	
3400-3100 s, b	3400-3100 s, b		3650 m, sh 3400-3100 m, b	3400-3100 m 2500-2260 s, b		bridging OH str. OD str.
1660 s	1660 sh	1693 s	1670 s	1660 s		CO ₂ asym. str.
1480 m, sp	1620 s 1480 m, sp		1640 s 1479 s 1480 s, sp	1480 w	1480 w	H—OH bend CO ₂ sym. str.
			1436 m	1440 w	1440 w	CO ₂ sym. str.
1205 s	1205 s	1238 w	1190 s	1200 s	1204 s	CF ₃ asym. str.
		1216 w				CF ₃ asym. str.
1160 s	1160 s		1155 s	1160 s	1145 s	CF ₃ asym. str.
					1099 s	
			960 w	1025 w 960 w		
855 m, sh	855 m, sh	854 s	850 m, sp	855 w, sp	857 m	CF ₃ sym. str. ⁷
790 m, sh	790 m, sh	796 s	785 s, sp	780 w, sp	797 w	C—C str., C—CF str.
730 m, sh	730 m, sh	732 w	720 s, sp	725 m	736 w	C—CO ₂ in plane bend ⁷
660 m; sh 650 s	660 m, sh 650 s			650 m		Zr—O str. Zr—O str.
		612 m			609 w	
520 m	520 m	551 w, b	565 w	540 m	554 w	C—F bending mode ⁷
			520 m			
470 m	470 m	477 w, b	470 m	460 m	474 w	Zr—O str.
		400 w, b				
375 w	375 w		380 m	360 w	372 w	
			360 w			
310 w	310 w			310 w		

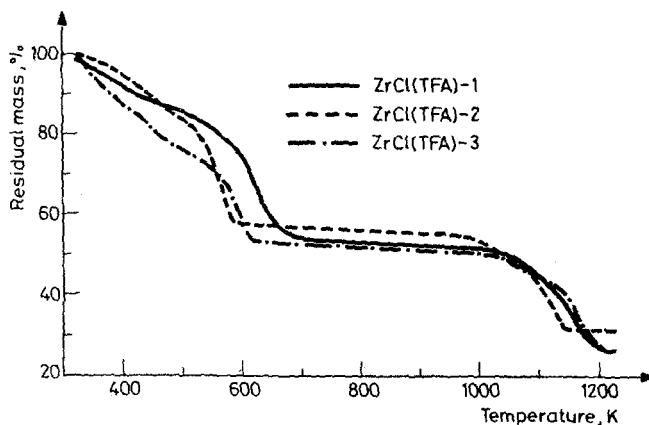


Fig. 1 TG trace of ZrCl(TFA)-1, -2 and -3 in air

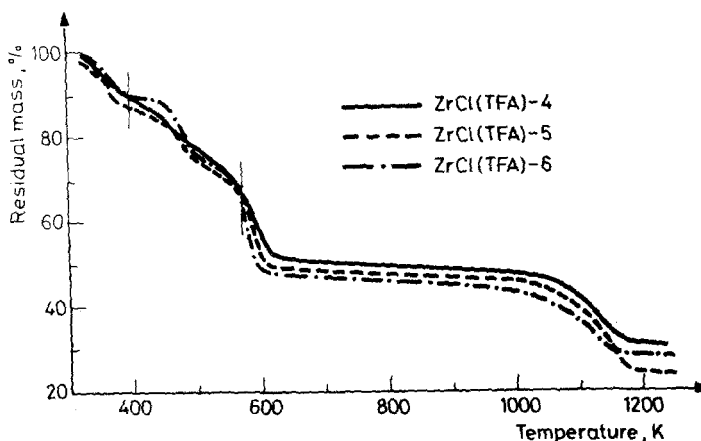


Fig. 2 TG trace of ZrCl(TFA)-4, -5 and -6 in air

In aqueous solution zirconium oxide chloride exists as the cyclic tetramer $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ with a tendency to ionise to give species such as $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{14}(\text{OH})_2]^{6+}$ (where (OH)' represents terminal OH groups) formed by ionisation of a coordinated water [9]. Ultracentrifugation and electromigration studies have shown that up to acid concentrations of 2 mol dm^{-3} the cyclic tetramer is the dominant species and that depolymerisation is not extensive until acidities of $3\text{--}5 \text{ mol dm}^{-3}$ are reached [9]. Thus in the present work it may be expected that all products except ZrCl(TFA)-6 are formed by trifluoroacetato substitution on the cyclic tetramer $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ with retention of the tetrameric structure.

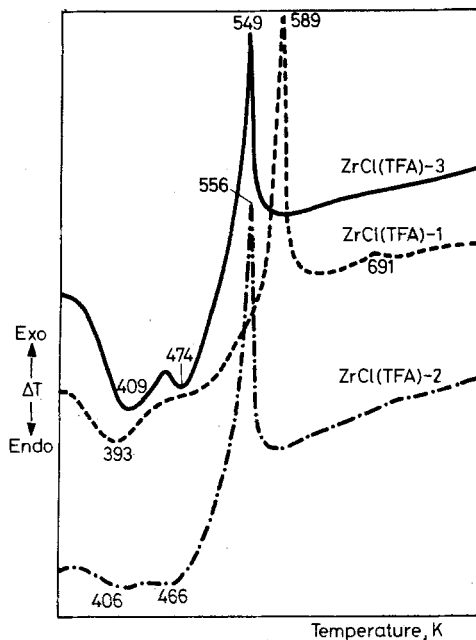
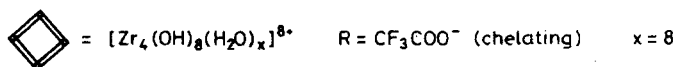
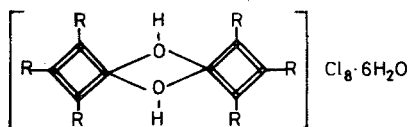


Fig. 3 DTA trace of ZrCl(TFA)-1, -2 and -3 in air

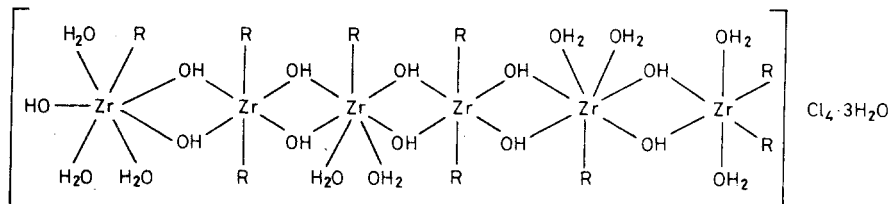
Examination of the infrared spectra of the products shows that none of them contains free trifluoroacetic acid. But in all cases bands at $\sim 1660\text{ cm}^{-1}$ and 1480 cm^{-1} are observed, and assigned to the COO asym and COO sym stretching frequencies respectively. These values are very similar to those reported by Hughes for the compound $\text{Zr}(\text{CF}_3\text{COO})_4$ and are therefore assigned to a bidentate trifluoroacetato group [10].

The empirical formulae determined for this group of complexes may be tentatively represented structurally as substituted tetramers linked by double hydroxo bridges. Taking $\text{ZrCl}(\text{TFA})\text{-3}$ as a typical example we have:



Similar polymeric species have been suggested previously for oxalato complexes [11].

In the case of the product $ZrCl(TFA)-6$ no satisfactory structure can be drawn involving linked substituted tetramers. Indeed, under the conditions of acidity used in the preparation, the tetrameric structure would be expected to breakdown. An open chain structure may be envisaged where the distribution of trifluoroacetato groups is random.



Thermal decomposition

Examination of the data in Table 3 and Figures 1 and 2 enables the following generalisation to be made:

- Step 1** Between 45 and 52% of the volatile products are evolved at temperatures up to 660 K (387°) giving rise to a relatively stable intermediate.
- Step 2** The slow decomposition of this relatively thermally stable intermediate over a wide temperature range to yield a zirconium oxide fluoride.
- Step 3** The final stage, a relatively rapid mass loss to leave zirconium dioxide.

Examination of the TG profiles shows that Step 1 exhibits two or more regions of different slope, and therefore indicates at least two overlapping decomposition modes over this temperature range. The early part of the reaction is thought to

Table 3 Zirconium tetrafluoride yields

Compound	Ratio of			Mole % ZrF_4		Wt %, ZrF_4
	Zr	CF_3COO	Cl	per mole Zr	per mole F	
$ZrCl(TFA)-1$	1	1	0.63	44	58	26
$ZrCl(TFA)-2$	1	0.81	0.56	31	51	23
$ZrCl(TFA)-3$	1	0.75	1	38	67	23
$ZrCl(TFA)-4$	1	1	0.75	25	33	13
$ZrCl(TFA)-5$	1	1.25	0.75	38	40	16
$ZrCl(TFA)-6$	1	1.50	0.67	17	15	14
$Zr(TFA)-1^4$	1	2.5	0	25	13	12

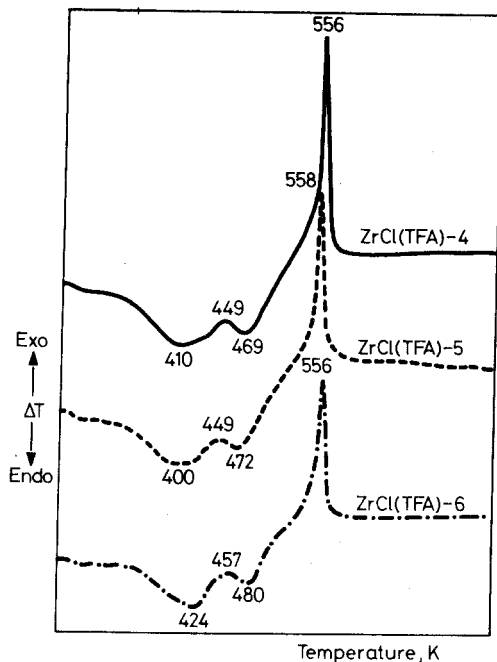
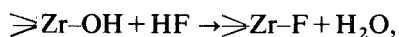
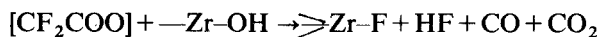
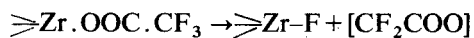


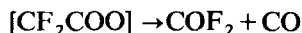
Fig. 4 DTA trace of ZrCl(TFA)-4, -5 and -6 in air

involve loss of water followed by loss of HCl and CF_3COOH and/or its decomposition products. The two stage loss of water is confirmed by the two endotherms which are observed in the DTA studies of these compounds. This is then followed by further decomposition of trifluoroacetato ligands with the formation of Zr-F bonds. The large exotherm observed by DTA at 549–558 K is consistent with this decomposition of the trifluoroacetato ligand. The thermal decomposition of other metal trifluoroacetates also results in decarboxylation and the formation of a metal fluoride[12]. In no case is the end of Step 1 consistent with the complete loss of all the trifluoroacetato ligands. Thus the intermediate formed at or about 660 K (387°) contains some trifluoroacetato ligands.

A possible breakdown scheme in this temperature region is:



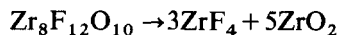
possibly also accompanied by some decomposition as follows,



It is quite clear from the results in Table 3 that more than one fluorine per trifluoroacetate group eventually becomes bonded to zirconium, and the above scheme goes some way towards explaining this observation.

In step 2 further decomposition of residual trifluoroacetate groups takes place with the formation of zirconium to fluorine bonds and the eventual formation of a zirconium oxide fluoride. The stoichiometry of the oxide fluoride depends on the ratio of zirconium to trifluoroacetate ligands in the parent complex. Zirconium oxide fluorides of various stoichiometries e.g. $\text{Zr}_4\text{O}_5\text{F}_6$, $\text{Zr}_7\text{O}_9\text{F}_{10}$, $\text{Zr}_{10}\text{O}_{13}\text{F}_{14}$ have been reported previously [13]. This ability for zirconium oxide fluorides to exist in such a wide variety of stoichiometries may be due to the similar size of the O^{2-} and F^- ion (140 and 136 pm respectively) allowing random packing in the zirconium lattice, limited only by electrical neutrality.

The third and final step in the thermal decomposition is breakdown of the zirconium oxide fluoride to zirconium dioxide and zirconium tetrafluoride e.g.



The final mass of zirconium dioxide, as determined by TG analysis, when compared with the zirconium content of the starting compound clearly demonstrates a loss of zirconium during thermal decomposition. The only conceivable compound which can bring about this mass loss is zirconium tetrafluoride which would be lost in the last stage of thermal decomposition since it sublimes above 600° .

Table 3 shows the theoretically possible zirconium tetrafluoride yields (based on TG analysis) for the products studied during this work, together with that for a trifluoroacetate derivative.

The best yields of zirconium tetrafluoride, per mole of zirconium, are obtained with low trifluoroacetate to zirconium ratios, i.e. at or below 1.25:1.0. Above this value the yield falls off considerably. However, from a consideration of the wt % yields the compound $\text{ZrCl}(\text{TFA})\text{-1}$ gives a far better yield of zirconium tetrafluoride than $\text{ZrCl}(\text{TFA})\text{-4}$ despite them having the same zirconium to trifluoroacetate ratio. In the case of $\text{ZrCl}(\text{TFA})\text{-1}$ and $\text{ZrCl}(\text{TFA})\text{-3}$ the conversion of carboxylate fluorine to zirconium tetrafluoride is high, 58 and 67% respectively lending further support to the proposed breakdown mechanism postulated above. The presence of some chloride ion in the molecule appears to favour the formation of zirconium tetrafluoride although specific trends are not obvious from the above data.

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Zusammenfassung — Es wurde die thermische Zersetzung und die Darstellung einiger Trifluoroacetatozirkoniumchloride beschrieben. Für die Zersetzungsreaktion wurde ein Mechanismus vorgeschlagen und die Bildung von Zirkoniumtetrachlorid unter den Gesichtspunkten der Zersetzung der Mutterverbindung erläutert.

Резюме — Описано получение и термическое разложение некоторых трифторацетатоцирконий хлоридов. Предложен механизм их термического разложения, а образование тетрафторида циркония обсуждено на основе состава родственного соединения.