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Zirconium(IV) Fluorosulphates : Preparation and Characterization

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SUMMARY

$Zr(SO_3F)_4$, (A); $ZrO(SO_3F)_2$, (B); $Zr(O_2CCH_3)_2(SO_3F)_2$, (C); and $Zr(O_2CCH_3)_3SO_3F$, (D) have been prepared and characterized (elemental analysis, i.r. spectra and thermal analysis). The SO_3F groups are bidentate in (A) - (C) but have C_{3V} symmetry in D where all the three oxygen atoms of SO_3F group are coordinated in an equivalent manner. (A) - (D) are good Lewis acids and form coordination complexes with pyridine, triphenylphosphine oxide and 2,2'-bipyridyl. The thermal decomposition of the fluorosulphates is complex.

INTRODUCTION

ZrF_3SO_3F is the only zirconium(IV) fluorosulphate presently reported [1]. In continuation of our work on fluorosulphates [2-4], we now report the preparation and characterization of the novel zirconium(IV) fluorosulphates, $Zr(SO_3F)_4$, (A); $ZrO(SO_3F)_2$, (B); $Zr(O_2CCH_3)_2(SO_3F)_2$, (C); and $Zr(O_2CCH_3)_3SO_3F$, (D). Compounds C and D are to our knowledge the first examples of compounds having SO_3F and acetate groups in the same species. Some coordination complexes have also been prepared and characterized.

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EXPERIMENTAL

Materials

$Zr(O_2CCH_3)_4$ was prepared by the action of a 50:50 mixture (by volume) of acetic anhydride and acetic acid on hydrated $Zr(NO_3)_4$. Anhydrous $ZrOCl_2$ was obtained by dehydrating its octahydrate with thionyl chloride [5]. $Zr(O_2CCF_3)_4$ was prepared by anion exchange,i.e., reacting $Zr(O_2CCH_3)_4$ with trifluoroacetic acid at reflux temperature. Fluorosulphuric acid was prepared by the reaction of SO_3 with KHF_2 and purified as reported previously [6]. Pyridine, (Py) and solvents were purified as described in the literature [7]. 2-2' bipyridyl, (bipy), (B.D.H., A.R.), triphenylphosphine oxide, (TPPO), (E.Merck) and sulphuryl chloride (E.Merck) were used as such.

Tetra(fluorosulphato)zirconium(IV),(A)

Excess (5-6 fold) fluorosulphuric acid was distilled onto 3.04 gms (5.6 mmol) of $Zr(O_2CCF_3)_4$. The mixture was stirred magnetically for 10 hours at room temperature under nitrogen. The white solid formed was filtered under a positive pressure of nitrogen, washed repeatedly with fluorosulphuric acid followed by sulphuryl chloride and finally dried in 'vacuo'.

Bis(fluorosulphato)oxozirconium(IV),(B)

Excess (5-6 fold) fluorosulphuric acid was distilled onto 0.961 gms (5.4 mmol) of anhydrous $ZrOCl_2$. The mixture was refluxed under nitrogen till evolution of HCl ceased. The white solid formed was filtered, washed and dried as above.

Bis(acetato)bis(fluorosulphato)zirconium(IV),(C)

Freshly distilled fluorosulphuric acid (0.868 gms, 8.68 mmol) was added to the suspension of $Zr(O_2CCH_3)_4$ (1.419 g, 4.34 mmol) in 50 ml. sulphuryl chloride. The mixture was stirred for 5-6 hours at room temperature. The white solid formed was filtered, washed and dried as above.

Tris(acetato)(fluorosulphato)zirconium(IV),(D)

$Zr(O_2CCH_3)_3SO_3F$ was prepared as for C using HSO_3F (0.482 g., 4.82 mmol) and $Zr(O_2CCH_3)_4$ (1.576 g., 4.82 mmol). It was washed only with SO_2Cl_2 and dried in 'vacuo'.

Preparation of complexes

The complexes A.4Py, A.4TPPO, A.(bipy)$_2$, B.2Py, B.2TPPO, B.bipy, C.2Py, C.bipy, D.Py and D$_2$.bipy were prepared by stirring a suspension of A, B, C or D in an appropriate solvent (CCl_4 for pyridine complexes and benzene for others) with the ligand in the required stoichiometry for about 14 hours under N_2. The adducts formed were filtered under N_2, washed with solvent and finally dried in 'vacuo'. Complexes of the same stoichiometry were obtained even when the ligands used were in excess.

Analytical Methods and Instrumentation

Zirconium was determined as ZrO_2 gravimetrically after decomposing the complexes with concentrated nitric acid and igniting the residue. Sulphur and fluorine were determined as reported earlier [2,3]. Carbon, hydrogen and nitrogen were determined microanalytically. The analytical results are given in Table 1.

TABLE 1

Analytical Data

Compound	Found* (%)					
	Zr	S	F	C	H	N
A	18.4 (18.7)	26.9 (26.9)	15.9 (15.6)	-	-	-
B	29.4 (29.8)	21.2 (21.0)	12.7 (12.5)	-	-	-
C	22.6 (22.4)	16.1 (15.7)	9.0 (9.3)	12.4 (11.8)	1.4 (1.5)	-
D	24.8 (24.8)	8.9 (8.7)	5.4 (5.2)	20.2 (19.6)	2.3 (2.45)	-
A.4Py	10.9 (11.3)	16.1 (15.9)	9.6 (9.5)	30.6 (29.9)	2.6 (2.5)	7.3 (7.0)
B.2Py	20.2 (19.65)	14.1 (13.8)	8.0 (8.2)	26.7 (25.9)	2.3 (2.2)	6.3 (6.05)
C.2Py	16.4 (16.1)	11.6 (11.3)	6.5 (6.7)	30.5 (29.7)	2.6 (2.8)	5.0 (4.95)
D.Py	20.6 (20.4)	7.5 (7.2)	4.5 (4.3)	28.6 (29.6)	3.2 (3.1)	3.0 (3.1)
A.(bipy)$_2$	11.5 (11.4)	16.3 (16.0)	9.4 (9.5)	30.5 (30.0)	2.1 (2.0)	7.2 (7.0)
B.bipy	19.5 (19.7)	14.1 (13.9)	8.4 (8.2)	26.8 (26.0)	1.8 (1.7)	6.3 (6.1)
C.bipy	15.6 (16.2)	11.8 (11.4)	7.1 (6.8)	30.9 (29.8)	2.4 (2.5)	4.9 (5.0)
D$_2$.bipy	21.1 (20.45)	6.9 (7.2)	4.5 (4.3)	30.8 (29.7)	2.8 (2.9)	3.3 (3.1)
A.4TPPO	6.0 (5.7)	8.3 (8.0)	4.9 (4.75)	53.3 (54.0)	3.9 (3.8)	-
B.2TPPO	10.7 (10.6)	7.7 (7.4)	4.6 (4.4)	51.4 (50.2)	3.4 (3.5)	-

*Theoretical figures in parentheses.

The infrared spectra of the compounds were recorded as nujol or hexachlorobutadiene mulls between AgCl, NaCl and polythene plates using a Perkin-Elmer 621 spectrophotometer. Thermal analysis was carried out by means of a MOM/Budapest derivatograph (type : Paulik, Paulik and Erdey) at a heating rate of 5°C/minute. All manipulations were carried out in a dry box filled with dry nitrogen.

RESULTS AND DISCUSSION

Fluorosulphuric acid reacts with $Zr(O_2CCF_3)_4$ exothermally at room temperature to give A. The reaction temperature was maintained below 10°C. The reaction between fluorosulphuric acid and tetra(acetato)zorconium(IV) in 2:1 or 1:1 ratios at room temperature in SO_2Cl_2 yields C and D respectively. D was converted to C by reacting it with an appropriate amount of HSO_3F below 35°C. The reaction of $Zr(O_2CCH_3)_4$ with an excess of HSO_3F at room temperature also yields C. Compounds without definite stoichiometry were isolated, when $Zr(O_2CCH_3)_4$ and HSO_3F were refluxed. Anhydrous $ZrOCl_2$ reacts with fluorosulphuric acid on reflux to give $ZrO(SO_3F)_2$. All of these fluorosulphates are white hygroscopic solids insoluble in noncoordinating solvents and in HSO_3F.

Infrared Spectra

The i.r. spectra of fluorosulphates (A - D) in the region 4000-200 cm^{-1} with their tentative assignments are tabulated in Table 2 . Bidentate fluorosulphate groups are postulated [8-11] in A, B and C based on the observation of three S - O stretching frequencies : [A : 1395, 1140 ($\nu_{as}SO$),

Table 2

IR Data

$Zr(SO_3F)_4$	$ZrO(SO_3F)_2$	$Zr(O_2CCH_3)_2(SO_3F)_2$	$Zr(O_2CCH_3)_3SO_3F$	$Zr(O_2CCH_3)_4$*	Assignments
		2934m	2925m 2980w	2930	CH sym. stretch.
		1620ms	1710s 1675w 1625m	1540	ν_{as}CO
		1480m	1400m	1455	ν_sCO
1395m 1140mb	1390s 1350m 1110mb	1340m 1135m	1220vs	-	ν_4(E)
1060s	1070mb	1065s	1115s	-	$\nu_1(A_1)$
-	-	1025mw	1020m	-	CH_3 rock.
-	965mw	-	-	-	M $\overset{\cdots}{-}$ O vibrations
-	-	990m	980m	945	C - C stretch.
835s	855s	820w	850m	-	$\nu_2(A_1)$
-	-	665w	660w	690 650	CO_2 sym.def.
650m 590m	620w 580m	- 575s	600m	-	ν_5(E)
550m	545m	525m	530ms	-	$\nu_3(A_1)$
440w 320w	440w 400w	455m 355w	430s	-	ν_6(E)
295s	290sb	-	295ms	-	M — O Lattice vibrations

*Ref.15

1060 (ν_sSO); B : 1390, 1110 (ν_{as}SO), 1070 (ν_sSO); C : 1340, 1135 (ν_{as}SO), 1065 (ν_sSO)]. The S-F and S-O bending frequencies are listed in TABLE 2 . A weak broad band centred around 965 cm^{-1} in B is attributed to zirconium-oxygen vibrations having a bond order between one and two [12,13]. An isolated $M=O$ group generally has a strong sharp band in the region of 900-1050 cm^{-1} [14]. The magnitude of $\Delta\nu$ (ν_{as}CO- ν_sCO) in C(140 cm^{-1}) indicates bidentate bridging acetate groups [15]. The peaks at 1710, 1675, 1625 and 1400 cm^{-1} (assigned to asymmetric and symmetric stretching carbonyl frequencies) in D indicate the presence of monodentate as well as bidentate acetate groups [15]. Two strong bands at 1220 and 1115 cm^{-1} in D are assigned to a fluorosulphate group having C_{3V} symmetry with the three oxygens of the fluorosulphato group coordinating to the zirconium equivalently [16,17].

On comparing the i.r. spectra of C and D with those of $Zr(SO_3F)_4$ and $Zr(O_2CCH_3)_4$, Table 2 , it is evident that C and D are not simple mixtures, but are definite novel fluorosulphate species.

The three S-O stretching frequencies ($\sim$1410, $\sim$1260 and $\sim$980 cm^{-1}) and a single value of S-F ($\sim$810 cm^{-1}) in A.4Py, A.4TPPO, A.(bipy)$_2$, C.2Py and C.bipy., indicate the presence of monodentate fluorosulphate groups [18], whereas bidentate fluorosulphate groups are indicated on the basis of ν_{S-O} frequencies ($\sim$1350, $\sim$1170 and $\sim$1110 cm^{-1}) in D.Py and D_2.bipy. The frequencies ($\sim$1400, $\sim$1370, $\sim$1150, $\sim$1080 and $\sim$ 990 cm^{-1}) of the S-O vibrations and two different values of S-F ($\sim$805 and $\sim$850 cm^{-1}) indicate monodentate as well as bidentate fluorosulphate groups in B.2Py, B.2TPPO and B.bipy.

The appearance of a weak band at ~1235 cm^{-1} and upward shift of bands at 1578, 601 and 403 cm^{-1} to ~1605, ~640 and ~430 cm^{-1} in pyridine complexes indicates the coordination of pyridine to zirconium [19]. A peak which is not present in free bipyridyl, but has been found in several chelated complexes [20], appears at ca. 1325 cm^{-1} and a peak at 990 cm^{-1} is intensified and shifts to ca. 1015 cm^{-1} in its adducts with A, B and C. On chelation, the 402 cm^{-1} band of bipyridyl shifts to ca. 415 cm^{-1} [21]. A peak at ~1320 cm^{-1} found in several chelates of bipyridyl is not observed in D_2.bipy. However, the ring vibration bands of the free base at 1580, 1558, 1540, 1522 cm^{-1} shift to 1610, 1585, 1565 and 1550 cm^{-1} in D_2.bipy. Lowering of $\nu_{P=O}$ (1190 cm^{-1}) in free base to ca. 1120 cm^{-1} in the complexes indicates that coordination occurs through oxygen in case of the triphenylphosphine oxide complexes [22].

It is difficult to make very meaningful assignments for acetate groups in case of complexes of C and D with pyridine and bipyridyl, as pyridine and bipyridyl complexes have a number of strong bands in the region 1425-1630 cm^{-1}.

Thermal analysis

TG and DTG curves recorded in the presence of air show the thermal decomposition of A - D as a process consisting of several steps (Fig.1). DTG minima have been projected onto the TG curves to get various inflexion points.

The probable modes of decomposition resulting from these curves are given in scheme I. The number on the arrow heads indicates the observed percentage weight loss for that step with the theoretical values in parentheses. The

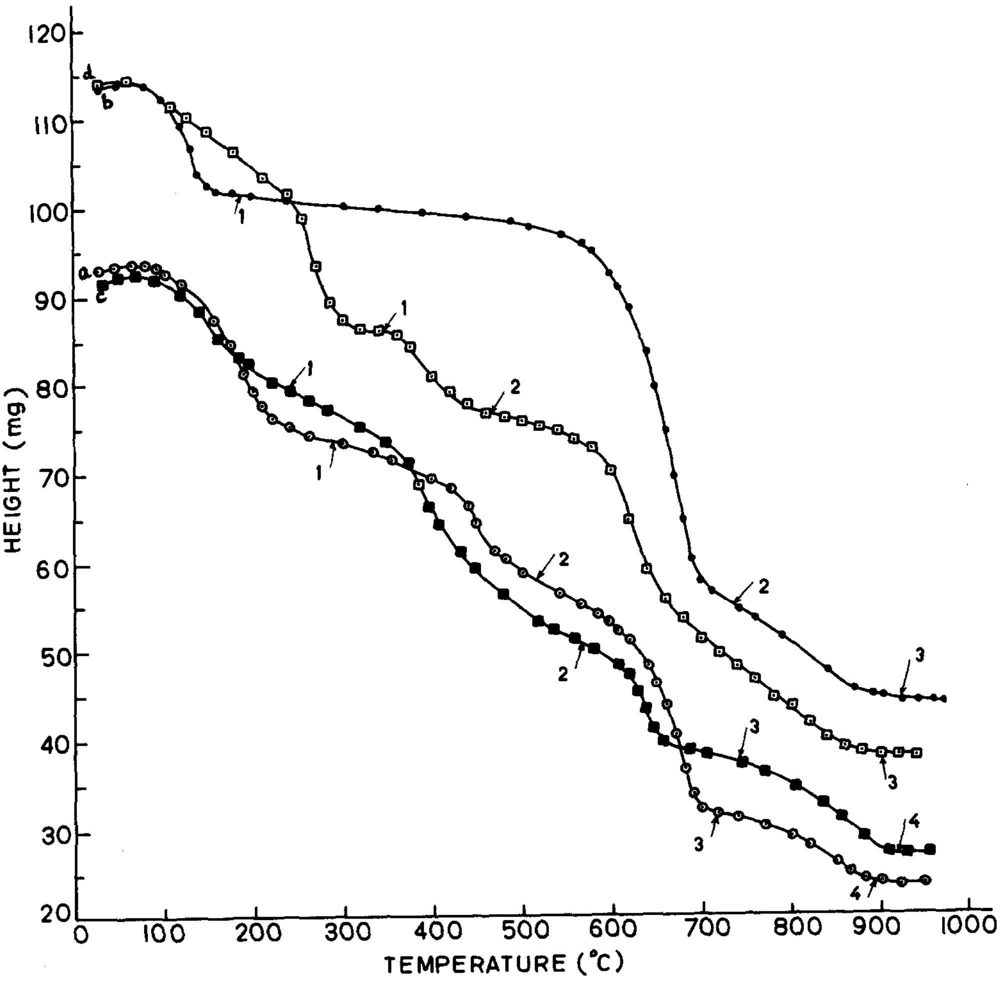
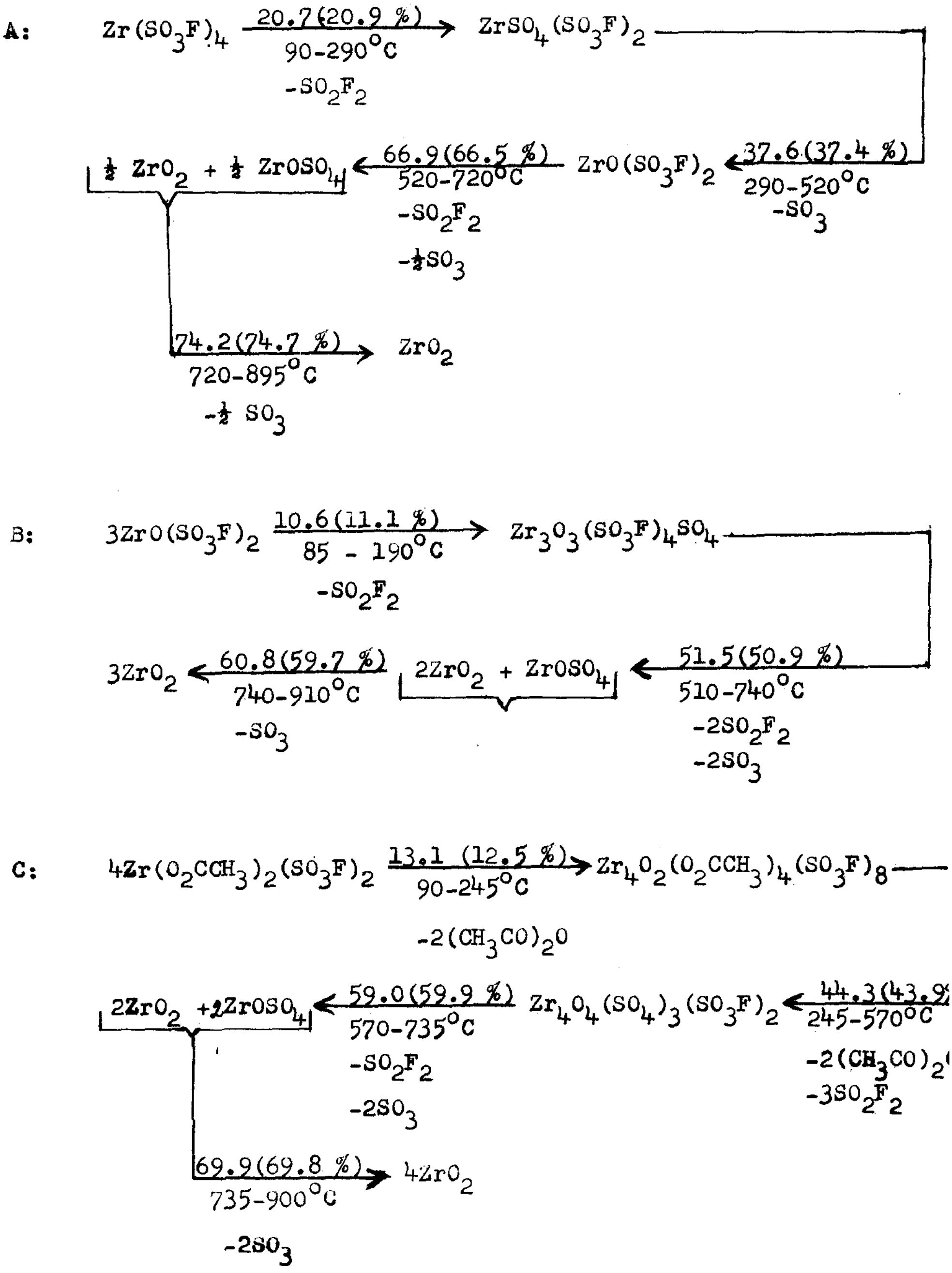
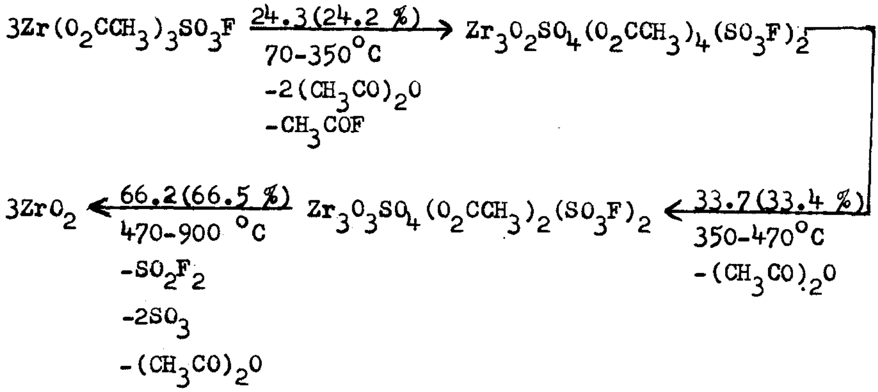


Fig. 1 THERMAL DECOMPOSITION OF COMPOUNDS A, B, C & D


A:
Zr(SO3F)4
20.7(20.9 %)
90-290°C
-SO2F2
ZrSO4(SO3F)2
37.6(37.4 %)
290-520°C
-SO3
ZrO(SO3F)2
66.9(66.5 %)
520-720°C
-SO2F2
-½SO3
½ ZrO2 + ½ ZrOSO4
74.2(74.7 %)
720-895°C
-½ SO3
ZrO2
B:
3ZrO(SO3F)2
10.6(11.1 %)
85 - 190°C
-SO2F2
Zr3O3(SO3F)4SO4
51.5(50.9 %)
510-740°C
-2SO2F2
-2SO3
2ZrO2 + ZrOSO4
60.8(59.7 %)
740-910°C
-SO3
3ZrO2
C:
4Zr(O2CCH3)2(SO3F)2
13.1 (12.5 %)
90-245°C
-2(CH3CO)2O
Zr4O2(O2CCH3)4(SO3F)8
44.3(43.9
245-570°C
-2(CH3CO)2
-3SO2F2
Zr4O4(SO4)3(SO3F)2
59.0(59.9 %)
570-735°C
-SO2F2
-2SO3
2ZrO2 +2ZrOSO4
69.9(69.8 %)
735-900°C
-2SO3
4ZrO2

SCHEME 1

D:



$$3Zr(O_2CCH_3)_3SO_3F \xrightarrow[\substack{70\text{-}350^\circ C\\ -2(CH_3CO)_2O\\ -CH_3COF}]{24.3(24.2\ \%)} Zr_3O_2SO_4(O_2CCH_3)_4(SO_3F)_2 \xrightarrow[\substack{350\text{-}470^\circ C\\ -(CH_3CO)_2O}]{33.7(33.4\ \%)} Zr_3O_3SO_4(O_2CCH_3)_2(SO_3F)_2 \xrightarrow[\substack{470\text{-}900\ ^\circ C\\ -SO_2F_2\\ -2SO_3\\ -(CH_3CO)_2O}]{66.2(66.5\ \%)} 3ZrO_2$$

denominator shows the probable molecules eliminated and the temperature range in which the decomposition takes place.

The decomposition starts at <u>ca</u>. 90°C in A, B and C but at 70°C in D. In all the four cases, the weight and analysis of the final residue corresponds to the formation of ZrO_2. In B (curve b), the percentage weight loss is only 3.4 % from 200-500°C. To understand this step, compound B was heated separately at 130°C (maximum loss in weight) under vacuum (10^{-3} torr) and the residue and volatiles were examined separately. SO_2F_2 was found as the volatile species and analysis (Calc. for $Zr_3O_3(SO_3F)_4SO_4$: Zr, 33.6; S, 19.7; F, 9.35; Found : Zr, 33.1; S, 19.8; F, 9.0 %) and i.r. of the residue indicate an empirical formula $Zr_3O_3(SO_3F)_4SO_4$. This intermediate was stable up to about 500°C. The nature of the volatiles evolved in A and C (scheme I) was confirmed from their i.r. spectra. Volatiles from D show CH_3COF and $(CH_3CO)_2O$ and from i.r., the residue contains fluorosulphate and acetate groups (step 1). The formation of a mixture of ZrO_2 and $ZrOSO_4$ has been observed in A, B and C prior to the formation of the end product ZrO_2. This step is not observed in D, where the intermediate $Zr_3O_3SO_4(CH_3COO)_2(SO_3F)_2$ decomposes in a single step to give ZrO_2.

REFERENCES

1 E. Hayek, J. Puschmann and A. Czaloun, Monatsh., <u>85</u> (1954), 359.

2 R.C.Paul, S. Singh and R.D.Verma, J. Fluorine Chem., <u>16</u> (1980), 153.

3 R.C.Paul, R.D.Sharma, S. Singh and R.D.Verma, J. Inorg.Nucl. Chem., in press.

4 R.C.Paul, S. Singh, R.D.Sharma, R.C.Kumar and R.D.Verma, Ind. J. Chem., <u>17A</u> (1979), 273.

5 R.C.Paul, S.L.Chadha and S.K. Vasisht, J. less common Metals, <u>16</u> (1968), 288-

6 J.Barr, R.J. Gillespie and R.C.Thompson, Inorg. Chem., <u>3</u> (1964), 1149.

7 J.A. Riddick and W.B.Bunger, Techniques of Chemistry,Vol.II, 3rd Edition, Wiley-Interscience, 1970.

8 D.W.A. Sharp and J. Thorley, J. Chem. Soc., (1963), 3557.

9 F.H. Allen, J.A. Lerbscher and J. Trotter, J.Chem.Soc.,(A), (1971), 2507.

10 A. Storr, P.A. Yeats and F. Aubke, Can. J. Chem., <u>50</u> (1972), 452.

11 P.A. Yeats, J.R. Sams and F. Aubke, Inorg. Chem., <u>11</u> (1972), 2634.

12 J.Selbin, Angew. Chem. Int. Ed. Engl., <u>5</u> (1966), 712.

13 K. Dehnicke and J. Weidlein, Angew. Chem. Int. Ed. Engl. <u>5</u> (1966), 1041.

14 C.G.Barraclough, J.Lewis and R.S.Nyholm, J. Chem. Soc., (1959), 3552.

15 N.W.Alcock, V.M. Tracy and T.C.Waddington, J.Chem.Soc., Dalton, (1976), 2243.

16 C.S.Alleyne, K.O. Sullivan Mailer and R.C.Thompson, Can. J. Chem., 52 (1974), 336.

17 J.Goubeau and J.B.Milne, Can. J.Chem., 45 (1967), 2322.

18 H.A.Carter, S.P.L. Jones and F.Aubke, Inorg. Chem., 9 (1970), 2485.

19 N.S.Gill, R.H. Nuttall, D.E.Scaife and D.W.A. Sharp, J. Inorg. Nucl. Chem., 18 (1961), 79.

20 S.P.Sinha, Spectrochim Acta, 20 (1964), 879.

21 L. Doretti, S. Sitran, P. Zanella and G. Faraglia, Inorg. Nucl. Chem. Letters, 9 (1973), 7.

22 J.P.Clark, V.M. Langford and G.J. Wilkins, J. Chem. Soc. (A), (1967), 792.