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PREPARATION OF OXIDE FLUORIDES AND OXOFLUOROMETALLATES OF TRANSITION METALS BY THERMAL DECOMPOSITION OF FLUOROPEROXO SPECIES

J.K. GHOSH and G.V. JERE*

Department of Chemistry, Indian Institute of Technology, New Delhi - 110 016, (India)

SUMMARY

Thermal decomposition of fluoroperoxo species of transition metals provides a new and convenient route for the preparation of oxide fluorides and oxofluorometallates. This method neatly generates *in situ* an oxide ion in a lattice.

INTRODUCTION

Fluoroperoxo complexes attracted our attention because, on modifying the pH conditions, a number of fluoroperoxo metallates can be prepared with varying ratios of fluoride and peroxide [1-5]. The solid fluoroperoxo complexes thus prepared have been subjected to thermal and photodecomposition studies [6-9] for thermal characterisation, kinetic data and mechanistic information. They undergo clean decomposition leading to the formation of oxide fluorides and oxofluorometallates.

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This communication reports a convenient and versatile method for the preparation of oxide fluorides and oxofluorometallates of transition elements via their respective fluoroperoxo species.

EXPERIMENTAL

The fluoroperoxometallates were prepared by the literature methods reported earlier [1-5, 10]. All the complexes were analysed for their constituents by standard methods. Fluoride was estimated using an ion-selective electrode (Orion 94-09). The compounds were further confirmed by IR and Raman spectroscopy

X-ray powder data, etc. IR spectra were recorded on Unicam SP-1200 IR spectrophotometer, Raman spectra were obtained on Jobin Yvon HG-25, Ramanor spectrometer using He-Ne laser source for excitation. X-ray diffraction studies were conducted on Phillips-1130, X-ray generator using CuK_{α} radiation. The thermograms were recorded on a STA-781 (Stanton-Redcroft, U.K.), simultaneous thermal analyzer in static air atmosphere with a heating rate of 10°C/min. The thermograms of some representative solids are given in Figures 1-3.

Several oxide fluorides and oxofluorometallates have been prepared for the first time by heating the corresponding fluoroperoxo metallates in a muffle furnace at the temperatures corresponding to the flat plateau in the thermograms. This data has been summarised in Tables 1 and 2.

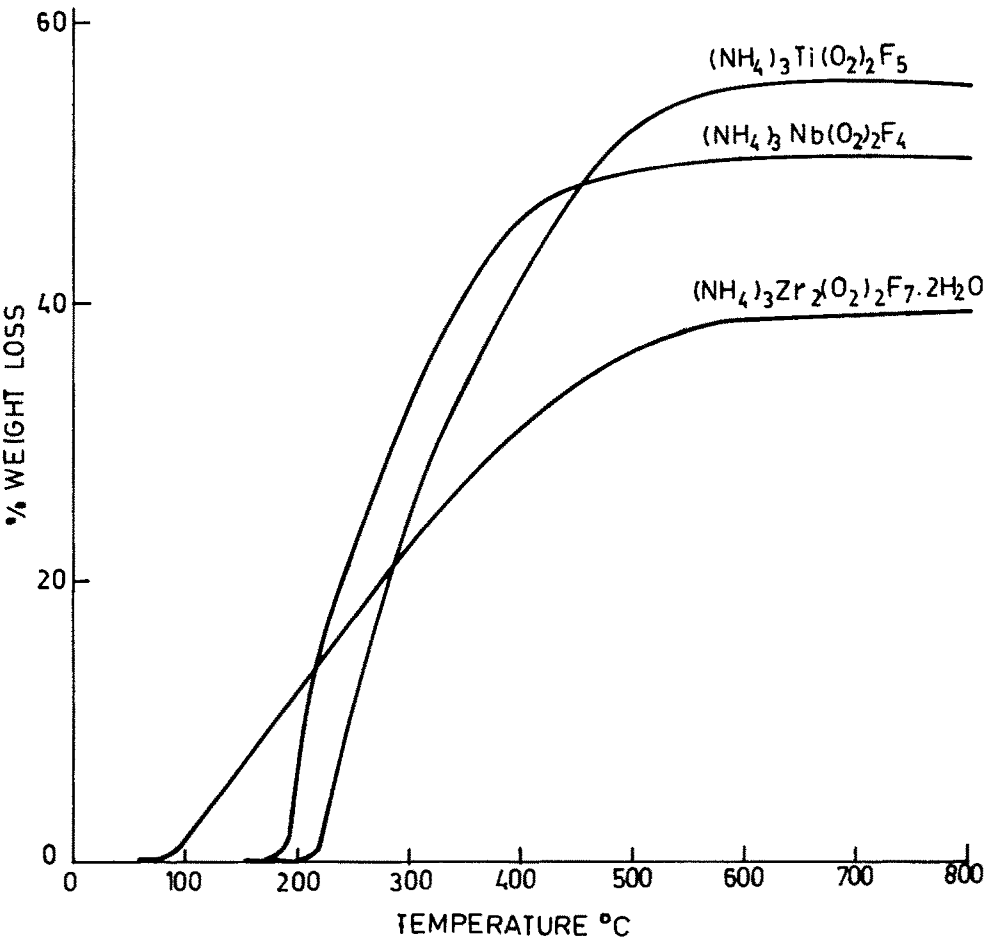

Fig. 1. Thermograms of representative solids.

RESULTS AND DISCUSSION

The results of the present investigation are discussed by citing the representative examples, $(NH_4)_3Ti(O_2)F_5$, $K_3Zr_2(O_2)_2F_7.2H_2O$ and $K_2VO(O_2)_2F$. It is seen from thermograms that during the thermal decomposition, a flat plateau ensues indicating the formation of stable oxide fluoride and oxofluorometallates according to the equations on p. 675.

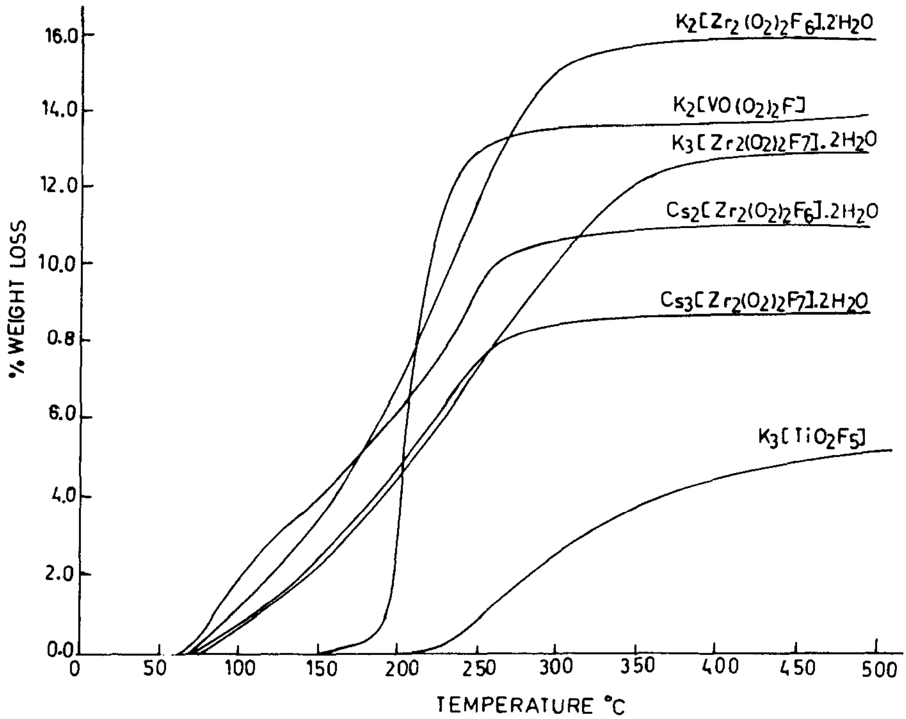

Fig. 2. Thermograms of representative solids.

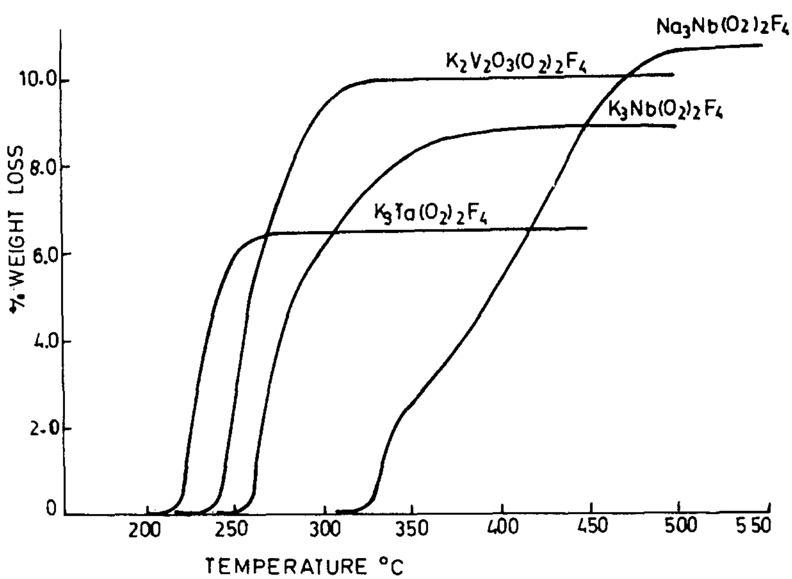

Fig. 3. Thermograms of representative solids.

TABLE 1

Summary of Data on Fluoroperoxo and Oxofluorometallates

Transition element	Fluoroperoxo metallates	Temperature where flat plateau ensues (°C)	% Weight loss on heating		Oxofluorometallates formed
			Calc.	Obs.	
Titanium	$K_3Ti(O_2)F_5$	450	5.2	5.1	K_3TiOF_5
Zirconium	$K_3Zr_2(O_2)_2F_7{\cdot}2H_2O$	375	12.6	12.7	$K_3Zr_2O_2F_7$
	$K_2Zr_2(O_2)_2F_6{\cdot}2H_2O$	325	14.4	15.8	$K_2Zr_2O_2F_6$
	$Cs_3Zr_2(O_2)_2F_7{\cdot}2H_2O$	300	8.6	8.8	$Cs_3Zr_2O_2F_7$
	$Cs_2Zr_2(O_2)_2F_6{\cdot}2H_2O$	275	10.6	10.9	$Cs_2ZrO_2F_6$
Vanadium	$K_2VO(O_2)_2F$	275	13.3	13.5	K_2VO_3F
	$K_2V_2O_3(O_2)_2F_2$	325	9.7	9.9	$K_2V_2O_5F_2$
Niobium	$K_2Nb(O_2)F_5{\cdot}H_2O$	300	10.8	11.3	K_2NbOF_5
	$K_3Nb(O_2)_2F_4$	400	9.1	8.8	$K_3NbO_2F_4$
	$Na_3Nb(O_2)_2F_4$	490	10.5	10.6	$Na_3NbO_2F_4$
Tantalum	$K_2Ta(O_2)F_5{\cdot}H_2O$	300	8.5	8.9	K_2TaOF_5
	$K_3Ta(O_2)_2F_4$	275	7.3	6.5	$K_3TaO_2F_4$

TABLE 2

Summary of Data on Fluoroperoxo and Oxide Fluorides

Ammonium fluoroperoxo metallates	Temperature where flat plateau ensues (°C)	% Weight loss on heating		Oxide fluorides formed
		Calc.	Obs.	
$(NH_4)_3Ti(O_2)F_5$	640	55.5	56	$TiOF_2$
$(NH_4)_3Zr_2(O_2)_2F_7\cdot 2H_2O$	600	38.0	39	$ZrOF_2$
$(NH_4)_3Nb(O_2)_2F_4$	610	49.9	51	NbO_2F

$$(NH_4)_3Ti(O_2).F_5 \xrightarrow{640°C} TiOF_2 + \frac{3(NH_4F)}{3NH_3+3HF} + \frac{1}{2} O_2 \quad (1)$$

$$K_3Zr_2(O_2)_2F_7.2H_2O \xrightarrow{375°C} K_3Zr_2O_2F_7 + O_2 + 2H_2O \quad (2)$$

$$K_2VO(O_2)_2F \xrightarrow{275°C} K_2VO_3F + O_2 \quad (3)$$

The thermal decomposition of ammonium salts of solid fluoroperoxo compounds leads to the formation of oxide fluorides and those of other cations to oxofluorometallates. Similar features are noted with other fluoroperoxo compounds and their decomposition products, i.e., oxide fluorides and oxofluorometallates (Tables 1 and 2). Some are stable from ambient temperature to about 900°C and some show phase transitions (DTA). They are crystalline in nature and may possess interesting electrical, optical, and magnetic properties and find use as solid state materials.

The preparation of oxide fluorides and oxofluorometallates by the thermal decomposition of fluoroperoxo metallates is a convenient route since it does not require strong fluorinating agents unlike in the case of conventional methods [11]. It produces an oxide ion in situ and the product formation is reproducible. This confirms the observation that thermal decomposition serves a good preparative method for solid state materials [12].

The study on fluoroperoxo species of transition metals is very limited. A lot needs to be done in this area on an element-wise basis.

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