SOLID STATE THERMAL AND PHOTOCHEMICAL DECOMPOSITION STUDIES ON FLUOROPEROXO AND TETRAPEROXO COMPLEXES OF TRANSITION ELEMENTS

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By

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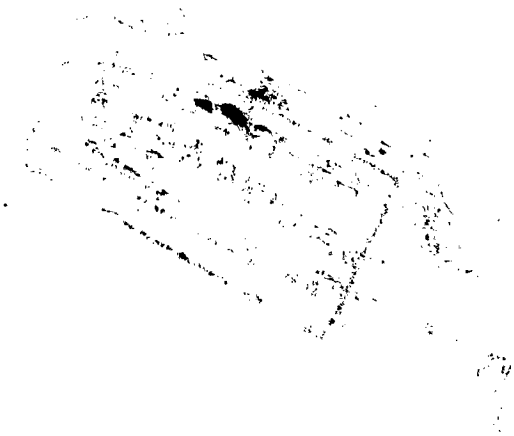

Dedicated

to

My Parents

C E R T I F I C A T E

This is to certify that the thesis entitled, "Solid State Thermal and Photochemical Decomposition Studies on Fluoroperoxo and Tetraperoxo Complexes of Transition Elements", being submitted by Mr. Jayanta Kumar Ghosh to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him.

Mr. Jayanta Kumar Ghosh has worked under my guidance and supervision and has fulfilled the requirements for the submission of his thesis.

The results contained in this thesis have **not** been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

3.8.87

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ABSTRACT

Work is going on in this laboratory on various aspects of peroxide chemistry of transition elements in solid state. The encouraging results obtained on the kinetic aspects of solid state decompositions of some fluoroperoxo and tetraperoxo complexes of transition elements, prompted the author to extend this work on related solids to understand their kinetic features in a generalized way. Further, the fluoroperoxo compounds hold good promise as the source material for the synthesis of oxide fluorides and oxofluoro-metallates of transition elements by thermal decomposition method. Hence the decomposition studies have been carried out with twin objectives in mind.

(A) To understand the kinetic features of thermal and photochemical decompositions.

(B) To establish a new and convenient route for the preparation of oxidefluorides and oxofluorometallates of transition elements by the thermal decomposition of fluoroperoxo complexes.

The thesis is divided into six chapters.

Chapter I gives introduction to the solid state isothermal, non-isothermal (TG-study) and photochemical decomposition aspects with experimental techniques, various rate equations, kinetic models and other related topics. A literature survey of the preparative methods of oxidefluorides

and oxofluorometallates of transition elements is also given. The scope of the present study has been indicated.

Chapter II incorporates the kinetics of isothermal decomposition of solids, $K_2[V_2O_3(O_2)_2F_2]$, $K_3[Ta(O_2)_2F_4]$ and $K_4[Ti(O_2)_4]2H_2O$, using an accumulatory system. The methods of preparation of the above solids and other experimental details have been described.

Ths shapes of the 'α'-time plots for two solids, $K_2[V_2O_3(O_2)_2F_2]$ and $K_3[Ta(O_2)_2F_4]$ are sigmoidal in nature. The kinetics obey the Avrami-Erofeev equation (n = 2) for the initial stage of the decomposition. The contracting volume equation fits well for the deceleratory region. The obedience of Avrami-Erofee'v equation with n = 2, implies that the solids undergo decomposition by random nucleation followed by two dimensional growth of the nuclei. The activation energies are 164.8 and 105.4 kJ mol^{-1} for $K_2[V_2O_3(O_2)_2F_2]$; 85.2 and 76.6 kJ mol^{-1} for $K_3[Ta(O_2)_2F_4]$.

The shapes of the α-time plots for the third solid, $K_4[Ti(O_2)_4]2H_2O$, are deceleratory in nature. The kinetic obedience to the unimolecular edecay law is observed for the initial stage of the decomposition. The contracting volume equation fits well for the latter part of the decomposition. Instantaneous nucleation has been attributed to two factors, namely the loss of lattice water preceeding the peroxide decomposition, thereby generating defects and also the strain

imposed by four rings and the consequent kinetic obedience to the unimolecular decay law. The activation energies are 61.9 and 44 kJ mol^{-1}.

It is seen that the activation energies of the surface processes are greater than that of the reactions in the bulk of the solid.

The kinetic characteristics of the decomposition of fluoroperoxo species so far studied are summarized (Please refer page 74). The following features are noted. The solids can be grouped into two categories, those contain water of hydration and those without it. They all suitable for kinetic studies. However, those without water molecules could also be subjected to 'TG' study in order to improve our understanding of their kinetic feature. This forms the subject of investigation of the following chapter.

Chapter III presents the results of kinetic features of 'TG' study at linearly rising temperatures and also at constant temperature in static air atmosphere, for the following representative solids,

$K_3[Nb(O_2)_4]$, $K_3[Ta(O_2)_4]$, $K_2[VO(O_2)_2F]$, $K_2[V_2O_3(O_2)_2F_2]$ and $K_3[Nb(O_2)_2F_4]$

The methods of preparation of the above solids and other experimental details have also been described. In order to

obtain reliable kinetic parameters from the rising temperature method (TG study), three different heating rates are employed, taking care of the particle size (250 mμ) and a small mass (~ 7 mg) of the solid for 'TG' study.

The shapes of the α-time plots in the isothermal 'TG' study for the two tetraperoxo complexes, $K_3[Nb(O_2)_4]$ and $K_3[Ta(O_2)_4]$ are predominantly deceleratory in nature. The reactions obey the unimolecular decay law over a long period of time, on the other hand shapes of the α-time plots in the isothermal 'TG' study for the three fluoroperoxo complexes, $K_2[VO(O_2)_2F]$, $K_2[V_2O_3(O_2)_2F_2]$ and $K_3[Nb(O_2)_2F_4]$ are sigmoidal in nature. The kinetics obey the Avrami-Erofeev equation (n = 2) for the initial stage of the decomposition. The contracting volume equation fits well for the deceleratory region.

Close agreement is seen in the kinetic parameters obtained with three heating rates in the non-isothermal 'TG' study for the above five solids, showing internal consistency, however, the kinetic parameters obtained from the dynamic 'TG' are larger than those from the isothermal 'TG' method. This may be due to kinetic compensation effect or decomposition mechanism (n = 2).

Interestingly the peroxo complexes undergo neat photochemical decomposition under the influence of UV light.

The kinetic features of photochemical decomposition of selected solids are presented in Chapter IV.

Chapter IV deals with the results of photochemical decomposition of solids $K_4[Ti(O_2)_4]H_2O$, $K_3[Ta(O_2)_2F_4]$ and $K_2[V_2O_3(O_2)_2F_2]$ studied under vacuum as a function of intensity and temperature. Experimental details and diffuse reflectance spectra of these compounds are presented. All the three solids show similar kinetic behaviour in this case. They undergo neat photolysis with the evolution of oxygen. No water is evolved. The pressure of the evolved oxygen at different time intervals shows a parabolic trend i.e. p vs. t plots are linear and the photolysis is deceleratory. The rate of photolysis is linearly dependent on the intensity of irradiation showing that the decomposition involves a monoexcitation process. There is no back reaction, no change in the colour of the complexes and no dark reaction. A probable mechanism of decomposition is proposed.

The peroxo complexes investigated so far serve as excellent systems for studying the kinetic behaviour and the reactivity of solid coordination compounds.

Chapter V incorporates preparation of oxidefluorides and oxofluorometallates by thermal decomposition of fluoroperoxo complexes of transition elements and some physico-chemical studies on them.

In the present study, fifteen solids have been subjected to chemical analysis (Fluoride by an ion-selective electrode, Orion 94-09), IR, Raman, X-ray diffraction studies and thermal characterization by TG & DTA (STA-781, STANTON-REDCROFT, UK).

Some of the above solids are stable from ambient to about 900°C. They are crystalline in nature and unit cell dimensions of some oxofluorometallates have also been worked out. These solids may possess interesting electrical, optical and magnetic properties and find use as solid state materials.

The thermal decomposition of ammonium salts of solid fluoroperoxo compounds leads to the formation of oxidefluorides and those of other cations to oxofluorometallates. This method neatly generates "in situ" an oxide ion (by the peroxo group decomposition) into a lattice.

The salient findings of the present investigations are summarised briefly in (Chapter VI) the last chapter of the present thesis.

Most of the experimental findings incorporated in the thesis have been published in professional international Journals like Thermochimica Acta, Journal of Photochemistry and Journal of Fluorine Chemistry.

A C K N O W L E D G E M E N T S

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C O N T E N T S