NVESTIGATIONS ON TRANSITION METAL COMPOUNDS

I. SOLID STATE DECOMPOSITION STUDIES OF FLUOROPEROXO AND TETRAPEROXO COMPLEXES

AND

II. PREPARATIVE AND PHYSICO CHEMICAL STUDIES ON SOME SELENATO SPECIES

BY

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CERTIFICATE

This is to certify that the thesis entitled, "Investigations on Transition Metal Compounds, I. Solid State Decomposition Studies of Fluoroperoxo and Tetraperoxo Complexes, and II. Preparative and Physicochemical Studies on Some Selenato Species", being submitted by Mr. M.K. Gupta to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bona fide research work carried out by him.

Mr. M.K. Gupta 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.

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ABSTRACT

A survey of the literature on peroxo complexes of transition metals shows, that apart from the work from this laboratory on some fluoroperoxo complexes, the kinetic aspects of isothermal and photochemical decomposition of these solids remained uninvestigated. The encouraging results obtained on fluoroperoxo zirconates, niobates and tantalate prompted the author to continue this work with other fluoroperoxo compounds on an elementwise basis. In addition to this the solid tetraperoxo species are being subjected to kinetic studies for the first time. In view of all these the scope of this work is restricted to, (a) examining the feasibility of the systems for kinetic investigations, (b) summarizing the salient features of kinetic findings including the evaluation of kinetic parameters and (c) proposing a probable mechanism of peroxide decomposition in these solids.

Work is also in progress in this laboratory on the preparative and physicochemical studies of peroxo complexes of transition elements. Literature survey shows no mention of peroxo-selenato complexes. Two new peroxo selenato complexes of titanium(IV) have been isolated and subjected to some physico-chemical studies. The nature of selenate vibrations has been examined in these solids as well as with yttrium and some rare-earth selenate hydrates.

This thesis consists of seven chapters divided into two sections.

<u>Section I:</u> <u>Solid state decomposition studies</u>

The following systems have been studied,

(a) Fluoroperoxo complexes, $K_3Ti(O_2)F_5$ and $K_2VO(O_2)_2F$,

and (b) Tetraperoxo complexes, $K_3Nb(O_2)_4$ and $K_3Ta(O_2)_4$.

The first chapter introduces the topics of thermal and photochemical decompositions, covering the experimental techniques, kinetic models and rate equations. A literature survey is presented and the scope of the present work defined.

The second chapter describes the experimental details. The methods of preparation and analysis of these compounds are given. The vacuum apparatus and the experimental procedures used for the study of the decomposition reactions are also given.

The third chapter describes the isothermal decomposition of two fluoroperoxo complexes, $K_3Ti(O_2)F_5$ and $K_2VO(O_2)_2F$. The results show that these solids are amenable for kinetic studies. The shapes of the α-time plots for $K_3Ti(O_2)F_5$ show a very short initial induction and acceleratory region; otherwise the decomposition is predominantly deceleratory in nature. The initial stage of the decomposition, may be described by the unimolecular decay law, whereas the later stage fits into the contracting volume equation. The activation energies of these two processes are 54 and 48 kJ mol^{-1} respectively.

The second solid $K_2VO(O_2)_2F$ shows a typical sigmoidal α-time curve with a short induction period, followed by an acceleratory region, and then a deceleratory one. The initial portion of the curve obeys the Avrami Erofe'ev equation (n=2), and the later portion obeys the contracting volume equation. The activation energies of these two processes are 108 kJ mol^{-1} and 53 kJ mol^{-1} respectively. A summary of the salient findings of isothermal decomposition studies on fluoroperoxo complexes of transition elements is given.

Chapter four describes the isothermal decomposition studies of tetraperoxo species for the first time. The two solids $K_3Nb(O_2)_4$ and $K_3Ta(O_2)_4$ undergo neat thermal decomposition and are amenable for kinetic studies. These solids show predominantly deceleratory nature of decomposition and obey the unimolecular deçay law over most of the temperature range studied. The activation energies are 126.53 kJ mol^{-1} and 95.86 kJ mol^{-1} respectively. The factors responsible for facile nucleation are the small particle size of the crystallites, plus the strain imposed by the four peroxide rings around the metal atom. The present study shows that the tetraperoxo complexes also hold good promise for solid state decomposition studies.

Chapter five presents the results of the photochemical decomposition studies on the above four solids. It is seen from the experimental results that the fluoroperoxo, as well as tetraperoxo complexes in solid state undergo neat photolysis when irradiated with uv light and show almost similar kinetic behaviour. The pressure time data are parabolic in nature indicating the deceleratory nature of photolysis. The rate of photolysis is linearly dependent on the intensity of irradiation showing that it involves a monoexcitation process. This may be visualized as below:

$$O_2^{2-} \xrightarrow{h\nu} (O_2^{2-})^*$$

$$O_2^{2-} + (O_2^{2-})^* \longrightarrow O_2 + 2O^{2-}$$

The fluoroperoxo and tetraperoxo complexes (typical coordination compounds) serve as near ideal systems for understanding the kinetic behaviour and the reactivity of solid coordination compounds.

Section II: Preparative and physico-chemical studies on some selenato species

Chapter six describes the synthesis of two peroxo-selenato complexes of titanium(IV). These have been synthesised for the first time starting from freshly precipitated titanium hydroxide, selenic acid and hydrogen peroxide under controlled pH conditions. The solid isolated at pH 0.5 has the composition $M_2[Ti(O_2)(SeO_4)_2]3H_2O$, (where M = K^+, Rb^+, Cs^+ and NH_4^+), whereas the solid obtained at pH 1.5 has the composition $M_2[TiO(O_2)SeO_4]3H_2O$, where (M = K^+, NH_4^+).

Both solids show characteristic infrared bands of the peroxo group i.e. ν_{O-O} 850 and selenato groups. In addition the solids obtained at pH 1.5 shows the presence of $(Ti = O)^{2+}$ moiety in it.

Chapter seven incorporates the results of i.r. and laser Raman studies of yttrium and some rare-earth selenate hydrates. This was necessitated to examine the nature of selenate vibrations. It is of interest to note that solid state effects - 'static and dynamic', are seen clearly for selenate vibrations. A vibrational spectroscopic study of the thermal decomposition of the above selenate hydrates has also been given.

Note: Most of the results presented in this thesis have been published. Please refer P. 133.

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