STUDIES ON FLUOROPEROXO AND OXOFLUORO COMPLEXES OF NIOBIUM AND TANTALUM

LATHA SURENDRA

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CERTIFICATE

This is to certify that the thesis entitled "Studies on Fluoroperoxo and Oxofluoro Complexes of Niobium and Tantalum", being submitted by Mrs. Latha Surendra (neé Vijayaraghavan) 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 her.

Mrs. Latha Surendra has worked under my guidance and supervision and has fulfilled the requirements for the submission of her 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.

(G.V. Jere)
Professor,
Department of Chemistry,
I.I.T., Delhi,
New Delhi 110016

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ABSTRACT

A survey of the literature on fluoroperoxo complexes of transition metals showed that apart from the work from this laboratory on fluoroperoxo zirconates, no work has been done on the kinetics of thermal and photochemical decomposition of these solids. Another aspect that was noticed, was that no detailed study has been made of the vibrational spectra of these complexes. The reports of the vibrational spectra that do exist, are incomplete and assignment of bands partial. This thesis presents work on fluoroperoxo niobates(V) and tantalate(V), covering both these aspects. It is divided into two sections.

Section One: Solid state decomposition studies

The study of the kinetics of decomposition of potassium pentafluoroperoxo niobate(V), $K_2Nb(O_2)F_5.H_2O$, potassium tetrafluorodiperoxo niobate(V), $K_3Nb(O_2)_2F_4$ and potassium pentafluoroperoxo tantalate(V), $K_2Ta(O_2)F_5.H_2O$, is given in this section.

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 analyses 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 the three fluoroperoxo complexes, $K_2Nb(O_2)F_5.H_2O$, $K_2Ta(O_2)F_5.H_2O$ and $K_3Nb(O_2)_2F_4$. The results show that the α -time curves for the first two solids are similar and follow a deceleratory path throughout. No induction or acceleratory periods were observed. The initial stages of the decomposition of both these solids is described by the unimolecular decay law and the activation energies for this process are 146 kJ mol^{-1} and 120 kJ mol^{-1} for $K_2Nb(O_2)F_5.H_2O$ and $K_2Ta(O_2)F_5.H_2O$ respectively. The later part of the reaction follows a contracting volume equation with activation energies , 63 kJ mol^{-1} and 90 kJ mol^{-1} for the niobate and the tantalate respectively. It is seen that the activation energy of the surface process is greater than that of the reaction in the bulk of the solid.

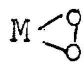
The third solid $K_3Nb(O_2)_2F_4$ shows a typical sigmoidal o -time curve with a short induction period, an acceleratory region following the Avrami-Erofe'ev equation (n = 2) and a deceleratory region that is described by the contracting volume equation. This shows that there is random nucleation followed by two-dimensional growth. The activation energies are 163 kJ mol^{-1} and 120 kJ mol^{-1}, for the acceleratory and the deceleratory processes respectively. Grinding of the solid $K_3Nb(O_2)_2F_4$ affects its kinetic behaviour. The o -time curves become deceleratory and follow the unimolecular decay law initially and the contracting volume equation subsequently. This demonstrates the topochemical nature of the decomposition.

The last chapter of this section describes the photochemical decomposition of the three fluoroperoxo complexes. 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 $\sqrt{t}$ 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.

It is seen that these solid fluoroperoxo metallates form near-ideal systems for the study of the thermal and photochemical decomposition reaction kinetics.

<u>Section Two</u>: <u>Vibrational spectra and normal coordinate analyses</u>

This section consists of the study of the vibrational spectra of some fluoroperoxo and oxofluoro metallates. The topic of vibrational spectroscopy is introduced in the first chapter. Vibrational assignments by empirical correlations and by the method of normal coordinate analysis (NCA) is discussed. The method of NCA is described and the use of constrained force fields discussed. A survey of literature on the vibrational spectra of oxofluoro and fluoroperoxo metallates is presented, covering the reported force constant data.

The second chapter in this section, describes the NCA of $K_2Nb(O_2)F_5$ and $K_2Ta(O_2)F_5$. A modified Urey-Bradley force field was used in the NCA , with force constants transferred from similar molecules. The vibrations of the  ring have been treated using reduced internal coordinates to eliminate the ring redundancies. The results show that the M—O and M—F vibrations are coupled. The O—O vibration is however distinct in the region 900 cm^{-1} to 850 cm^{-1}. The M—F vibrations fall in the region 650 cm^{-1} to 500 cm^{-1} and the deformation modes below 350 cm^{-1}. The force field used is reasonable and gives a good frequency fit. The values of the force constants for the niobate and the tantalate are comparable.

The vibrational spectra of $K_3Nb(O_2)_2F_4$ is also described in this chapter. NCA on this system has not been done since its structure is not known. The bands are assigned by comparison with the spectra of $K_2Nb(O_2)F_5$.

The last chapter in this section describes the vibrational spectra of oxofluoro metallates. The vibrational spectra of the compounds Rb_2NbOF_5 and Cs_2TaOF_5 , reported by Pausewang have been used for their NCA in a modified Urey-Bradley force field. The force constants transferred from similar molecules give a good frequency fit and the assignments are similar to those made for other such molecules. The vibrations are all localised and no coupling is observed.

Oxofluoro niobates, tantalate, vanadate and zirconates were obtained by the thermal decomposition of the corresponding fluoroperoxo metallates. The ir and laser Raman spectra of these were recorded and the bands assigned by comparison with other oxofluoro metallates. The thermolysed products were found to be polymeric in nature with both M═O and M–O–M type of bonds generated by the decomposition.

An appendix to the thesis describes the synthesis and some physicochemical properties of a new potassium oxofluoroperoxo vanadate(V).

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