SOLID STATE THERMAL AND PHOTOCHEMICAL DECOMPOSITION STUDIES ON FLUOROPEROXOZIRCONATES

BY

S. M. KAUSHIK

THESIS SUBMITTED TO
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
FOR THE AWARD OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
DECEMBER 1979

CERTIFICATE

This is to certify that thesis entitled "Solid State Thermal and Photochemical Decomposition Studies on Fluoroperoxozirconates", being submitted by Mr. S.M. Kaushik 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. S.M. Kaushik 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.

(G.V. Jere)
Associate Professor,
Department of Chemistry,
I.I.T. Delhi,
New Delhi 110029

ACKNOWLEDGEMENTS

I am deeply indebted to Dr. G.V. Jere, Associate Professor, Chemistry Department, Indian Institute of Technology, Delhi, for his thorough and searching supervision, constant encouragement, critical review and taking care of my interests and welfare.

I express my profound thanks to Professors R.D. Dua, J.C. Ahluwalia and R.P. Gandhi for providing the necessary research facilities.

I am deeply grateful to Professors A.K. Galwey, G.G.T. Guarini, B. Claudel, E.A. Secco and I.I. Vol'nov for their critical comments and encouragement for the furtherance of this work. My thanks are due to Dr. H. Sautereau for recording the luminescence spectra of these solids.

I express my profound thanks to Dr. C.R. Jagga whose long experience in the field of solid state decomposition reactions has been of immense help. I am grateful to Dr. G.N.Rao for the valuable discussions and kind suggestions.

I acknowledge the cooperation received from all the members of the supporting staff of the Chemistry Department. I am also thankful to Mr. S.L. Aneja for his painstaking typing of the manuscript and Mr. N.L. Arora for the neat tracings.

The financial help from I.I.T. Delhi is gratefully acknowledged.

Lastly, I thank all my friends and colleagues who shared my sorrows and joys throughout the course of my work.

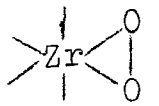
December 24, 1979

S.M. Kaushik
Chemistry Department,
I.I.T. Delhi.

ABSTRACT

It is noticed from the review article of Galwey and other literature that kinetic studies, on thermal and photochemical decompositions of solid peroxo compounds of transition elements are lacking. Also, as yet, a well founded mechanism of liberation of oxygen from solid peroxy compounds has not been worked out. The kinetic study though not sufficient in itself is the first important step in this direction, and provides most secure foundation for mechanistic interpretation. The present thesis, which embodies the results of solid state thermal and photochemical decomposition studies on fluoroperoxozirconates of alkali metals, is the first attempt on solid peroxo compounds of transition elements. Therefore, the scope of the present work is restricted to, (a) examine the feasibility of the system 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.

The kinetics of isothermal decomposition of two sets of fluoroperoxozirconates of alkali metals, $M_3Zr_2(O_2)_2F_7.XH_2O$ and $M_2Zr_2(O_2)_2F_6.2H_2O$ (M = K, Rb, Cs), have been studied under vacuum, with a constant volume system, at different temperatures. It is of interest to note that there is close similarity in the kinetic behaviour of all these solids. The α-time plots show the absence of induction and acceleratory regions. The maximum rate of decomposition is obtained at the onset of reaction and further course is deceleratory

throughout. The initial stage of decomposition fits into the unimolecular decay law, while the later stage obeys the contracting volume kinetics. The activation energy values, computed from Arrhenius plots, are unusually low, but comparable amongst themselves. In the case of present solids, the triangularly linked bidentate peroxo group  , constitutes, a highly strained ring system. The factors accountable for facile (instantaneous) nucleation are the dehydration step before the onset of peroxide decomposition with contribution from the strained metal-peroxide ring system.

The photochemical decomposition of these solids, under a high pressure ultraviolet lamp, have been studied as a function of intensity and temperature. Once again, the kinetic behaviour of all these solids is found to be similar in nature. Although the molecular formulations of these compounds are big, the only photoexcitable species in them is the peroxo group, which on photolysis gives out oxygen. The pressure-time data obey the parabolic rate equation, which describes a diffusion controlled process. The rate of photolysis is a linear function of intensity indicating a mono-excitation process. This may be visualized as below:

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

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

CONTENTS