This thesis deals with the electron spin resonance studies on the oxidation products of some
vanadyl porphyrins and supporting cyclic voltammetric studies on these systems. It consists of six chapters.

Chapter I consists of a review on the esr and other structural studies on the oxidation products
of TiO, VO, Cr, Mn, Fe, Cu and Ni porphyrins. The material presented in this chapter gives an overall
picture about the structural aspects of the oxidation products of transition metal porphyrins. Oxidation
products of Mn and Fe porphyrins are considered to be active intermediates in the biological reactions
catalysed by enzymes like catalase, peroxidase etc. This review also provides a backdrop for the esr studies
on the oxidation products of vanadyl porphyrins presented in the later chapters of this thesis.

The details of the experimental procedures adopted in the present work are described in Chapter II.

In Chapter III, the esr studies of the one-electron oxidation products of vanadyl octaethyl-
porphyrin at liquid nitrogen temperature are presented. The radical cation has been found to exist as a dimeric
species in triplet state. From the triplet state -esr
spectrum the distance between the two vanadium atoms in the dimer has been obtained.

Cyclic voltammetric studies on zinc, Cu and vanadyl complexes of proto- and mesoporphyrins are presented in Chapter IV. Evidence for the existence of dimers in solution has been obtained in the case of Zn, and VO protoporphyrins. The oxidation potentials for the monomeric and dimeric forms of VO mesoporphyrin have been obtained.

In Chapter V detailed esr studies on the oxidation products of vanadyl protoporphyrin-IX dimethyl-ester and mesoporphyrin IX dimethylester are presented. ESR spectra of the samples at room temperature and liquid nitrogen temperature and at about 10K are presented. Wherever possible, computer simulations of the esr spectra have been included. Monomeric radical cations (S = 1) and dimeric radical cations (S = \frac{3}{2}) have been identified in solution at room temperature. Different types of dimeric species have been shown to exist at low temperatures. A monomeric radical cation has also been identified at 10K. The results presented in this chapter are amply supported by the cyclic voltammetric studies discussed in Chapter III.
The results of cyclic voltammetric studies on some metal complexes of tetrabromo tetraphenyl porphyrin (Cu, Ni, VO and Zn) are discussed in Chapter VI. Wherever possible, the oxidation products were characterised by esr and optical spectroscopy.

The oxidation products of transition metal porphyrins offer challenging structural problems to the chemist and a study of these systems is important to understand the redox reactions occurring in biological system. In this thesis an attempt has been made to identify the products obtained on oxidation of vanadyl porphyrins which are the simplest systems among the transition metal porphyrins.