

INTRODUCTION

Chemists have long been familiar with the formation of intensely coloured molecular complexes when certain aromatic hydrocarbon, amines as phenols are mixed with a large class of aromatic nitro-compounds, quinones or halogens and like⁽¹⁾. Pfeiffer, who was the first to classify these complexes, suggested the utilization of secondary valencies for their formation. The brightly coloured crystalline picrates of alkyl benzenes and of condensed ring aromatic hydrocarbons are striking examples of these complexes. It may not be possible to isolate solid complexes in many cases. However, when solutions of the two reagents are mixed, with marked change in colour clearly indicates the formation of a complex.

Various aspects of such complex formation are best described on the basis of the charge-transfer model of Mulliken⁽²⁾. The main spectral feature accompanying complex formation in most systems is the broad intense absorption band in the visible or ultra-violet region due to an electronic transition such as the excitation of an electron in an individual molecule by a quantum of radiation which may be associated with intra-

molecular rearrangement of the electron cloud. Similarly in the complex formed by the association of two molecular or ionic species, the excitation of an electron by a photon can involve a charge rearrangement in the complex. This rearrangement according to the Mulliken theory⁽³⁾, involves a transfer of an electron or part of it from one component of the complex to the other.

Mulliken's charge-transfer theory of electron donor-acceptor complexes has provided a unified basis to understand various types of inter- and intramolecular interactions including hydrogen bonding. E.g. the red colour of the ferric ion thiocyanate complex (where $\text{Fe}^{3+} = \text{A}$, and $\text{CNS}^- = \text{D}$), and the green colour produced when solutions of pyrene (D) and tetracyanoethylene (A) are mixed. Absorption bands of this type are known as charge transfer bands, since they involve electronic transitions from filled orbitals on the donor to vacant orbitals on the acceptor.

Theory of charge transfer complexes:

Absorption spectra of alkali halides presented earlier show how the energies of optical excitation are governed by the electron affinities of the halogen