PREFACE

Carbocations have been a fascinating subject of research since their discovery. Earlier it was thought that they occurred as transient and various transient carbocations have been characterized using modern time-resolved spectroscopic methods. It was later shown that stable carbocationic salts such as, xanthenyl, thioxanthenyl and suberenyl cations could be prepared using a variety of methods. The electron deficient nature of these species makes them useful as excited state electron acceptor in Photoinduced Electron Transfer process. Photoinduced Electron Transfer (PET) involves the transfer of an electron from a donor D to an acceptor A, following the absorption of photons. PET between two neutral molecules results in the formation of the radical cation of the donor (D$^{+}$) and the radical anion of the acceptor (A$^{-}$). Since these species are oppositely charged, they have a tendency to attract each other thereby leading to rapid back electron transfer (BET) resulting in the regeneration of the starting materials in their ground states. Thus, the efficiency of a PET reaction is controlled by the efficiency of the BET reaction. Over the years considerable amount of work has been done to circumvent or retard BET reactions and several strategies have been devised to achieve this goal. Use of ionic sensitizers for PET reactions is one such strategy results in the formation of neutral radical and a radical ion. Since species do not attract electrostatically each other, this will lead to a reduction in the rate of BET reactions. The work described in the thesis is related to the design of carbocation
senstitsizer and study of the photophysical and photochemical properties. The Chapter 1 of the thesis provides an overview of the photophysics and photochemistry of a few known carbocations.

Chapter 2 of the thesis presents the photophysical and electron transfer studies of trioxatriangulenium perchlorate \((1^{\Theta} \text{ClO}_4^{\Theta})\). This stable carbocation was first synthesized more than thirty years ago. However, its photochemistry was relatively unexplored until recently. Our studies using fluorescence quenching and laser flash photolysis techniques, have shown that the singlet and triplet excited states of \(1^{\Theta} \text{ClO}_4^{\Theta}\) can accept an electron from a variety of electron donors. The kinetic and mechanistic aspects of these PET reactions are examined in the light of electron transfer theories.

Chapter 3 of the thesis presents the photophysical and electron transfer studies of the azatriangulenium derivative \(13^{\Theta} \text{BF}_4^{\Theta}\). \(13^{\Theta} \text{BF}_4^{\Theta}\) is obtained from \(1^{\Theta} \text{ClO}_4^{\Theta}\) by replacing one of the oxygen atoms by a N-CH\(_3\) group. This leads to a substantial shift in the absorption and emission spectra. Our studies presented in Chapter 3 shows that \(13^{\Theta} \text{BF}_4^{\Theta}\) is also a good acceptor of electrons in the excited state. Fluorescence quenching rate constants for a series of donors followed the Rehm-Weller pattern. Laser flash photolysis of \(13^{\Theta} \text{BF}_4^{\Theta}\) in the presence of a donor leads to the formation of the radical cation of the donor and these studies have established electron transfer mechanism operating in this case.
In Chapter 4 of the thesis, a detailed account of the photochemistry of $6b\text{BF}_4^\ominus$ is presented. When $6b\text{BF}_4^\ominus$ was flash photolysed in the presence of a good electron donor, the radical cation of the donor was formed. On the other hand, flash photolysis in the presence of good electron acceptors resulted in the formation of the radical anion of the acceptor. Our studies have thus shown that $6b\text{BF}_4^\ominus$ can act both as an acceptor as well as a donor in PET reactions. These results were analyzed using Rehm-Weller theory in order to establish the electron transfer mechanism operating in these cases.

In Chapter 5 of the thesis the photophysical and electron transfer studies of the triazatriangulenium cation $4d\text{BF}_4^\ominus$ is presented. The fluorescence of $4d\text{BF}_4^\ominus$ was not quenched by aromatic hydrocarbons. When $4d\text{BF}_4^\ominus$ was flash photolysed in the presence of anthracene, triplet-triplet energy transfer took place leading to the formation of anthracene triplet. The fluorescence of $4d\text{BF}_4^\ominus$ was, however, quenched by several electron acceptors and the quenching rate constants could be fitted well by the Rehm-Weller equation. Thus, our studies reveal that the series of structurally related carbocations $1\text{ClO}_4^\ominus-4d\text{BF}_4^\ominus$, have considerable potential as PET sensitizers, but there role changes from an acceptor to that of a donor with increase in the number of nitrogen atoms in the molecule.

Note: The compound numbers given here correspond to those given under the respective Chapters.