CHAPTER 4

PHOTOPHYSICAL AND ELECTRON TRANSFER STUDIES OF SELECTED PYRYLIUM DERIVATIVES IN THE PRESENCE OF β-CYCLODEXTRIN

4.1. Abstract

Photophysical properties of pyrylium salts 3-8 were studied in the absence and presence of β-cyclodextrin (β-CD). These studies include absorption spectra, fluorescence spectra, fluorescence quantum yields and fluorescence lifetimes. Our studies have shown that pyrylium salts 3 and 8 did not interact appreciably with β-CD, whereas, 3-7 formed stable inclusion complexes. In the case of 3-7, the association constants with β-CD were determined using the Benesi-Hildebrand treatment. Electron transfer to the singlet and triplet excited states of the encapsulated pyrylium salts were studied by fluorescence quenching and laser flash photolysis methods. The forward electron transfer rates in the presence of β-CD were slightly lower than those obtained in the absence of β-CD. The back electron transfer rates in the presence of β-CD were approximately 20 times lower. This is attributed to the enhanced binding of the pyranyl radicals to the β-CD cavity.

4.2. Introduction

A major disadvantage that arises in the use of pyrylium salts as PET sensitizers, is the formation of CT complexes between these salts and the donor molecules.\(^1\)\(^-\)\(^3\) In CT complexes, photoelectron transfer reaction is generally followed by extremely rapid back electron transfer. Hence formation of the
charge-separated state is suppressed. One way to circumvent this problem is to enforce a separation between the sensitizer and the donor by the use of suitable interfaces. One approach that has been used in the literature with some success, is the use of cyclodextrins (CDs) to selectively encapsulate one of the components. In this Chapter, we have made an attempt to encapsulate selected pyrylium salts in \( \beta \)-CD cavities and study their photophysical and electron transfer properties.

\( \beta \)-CD is a cyclic oligosaccharide made up of seven D-glucopyranose units linked by \( \alpha \)-(1,4) bonds (Figure 4.1).\(^{4-6}\) This molecule resembles a hollow truncated cone (torus) and has approximate \( C_7 \) symmetry. The primary hydroxyl groups are located on the narrower side of the torus and the secondary hydroxyl groups are on the broader side. \( \beta \)-CD has an internal diameter of approximately 6.5 Å and a height of 7.9 Å. The most remarkable property of CDs is their ability to form inclusion complexes with a variety of molecules. The inclusion process is analogous to the dynamic solubilization of molecules in micelles. A distinguishing feature of these host systems, however, is the existence of finite size cavities that lead to size and shape selectivity on the molecules they include. Photophysical studies of a large number of molecules have been carried out in the presence of CDs. These studies were generally aimed at probing the inner cavity of the CD and also to understand the inclusion process. Selected examples are listed in the reference section of this Chapter.\(^{7-27}\)
Few examples of PET reactions of guest molecules incorporated in CD cavities are reported in the literature.\textsuperscript{28-46} These studies suggest that CDs can play three different roles in PET reactions. (1) It solubilizes small amounts of organic substrates in water thereby making it possible to study PET of these
molecules in water, (2) it acts as a spacer and prevents CT formation and/or suppresses BET reactions and (3) it acts as a protecting cavity to stabilize the radicals from undergoing BET reactions. In most of the studies dealing with PET reactions of \( \text{C}_{60}-\text{CD} \) complexes in water, the role of CD is to solubilize the \( \text{C}_{60} \) in water.\(^{28-32}\) An elegant example of the use of CD as a spacer is provided by the viologen-linked phenothiazine 1 (Scheme 4.1).\(^{38,39}\) Irradiation of 1 did not lead to the formation of cation radicals. This was attributed to the exceedingly short lifetime of the cation radicals due to fast BET. Irradiation in the presence of \( \alpha \)- or \( \beta \)-CD gave transient signals corresponding to the radicals of 1. This is explained on the basis of structure 2 (supported by NMR studies) in which BET is expected to be slow. An example where CD acts as a protecting cavity is provided in the electron transfer quenching of zinc-\( \text{meso-tetra(N-propylsulphonato)pyrydiniumporphyrin} \) by anthraquinone-2-sulphonate encapsulated in \( \beta \)-CD.\(^{41}\) In this case, the photoreduced anthraquinone-2-sulphonate remains within the CD cavity and is protected from undergoing fast BET reaction. In general, use of CD as a spacer or a protecting cavity, results in reduced rates for PET reactions compared to that in homogeneous solutions.\(^{46}\) Compared to the forward reactions, the BET reactions are highly suppressed and this results in the formation of long-lived radical products.\(^{38}\)
In this Chapter we have attempted to encapsulate a few pyrylium salts in β-CD cavities. The structures of these molecules are given in Chart 4.1. In order to form an inclusion complex, the guest molecule should penetrate the cavity of β-CD, at least partially. In order to see whether the pyrylium salts can penetrate into the cavities, we have calculated the molecular dimensions of our substrates by AM1 methods and the values thus obtained are also indicated along with the structures in Chart 4.1.
Chart 4.1

3: R = CH₃
4: R = n-C₄H₉
5: R = n-C₈H₁₇

6

7

8
Photophysical studies of pyrylium salts incorporated in CDs have not been reported in the literature. We have observed that some of the pyrylium salts listed in Chart 4.1 can be incorporated into β-CD cavities. Complexation studies with CDs, however, have to be done in water, where pyrylium salts are reported to be unstable.\textsuperscript{47,48} Because of their instability in water, photophysical studies of pyrylium derivatives have rarely been attempted in water. Gird and Balaban observed that pyrylium salts are stable in buffer solutions in the pH range of 0.5-3.5 (citric acid-sodium phosphate or sodium acetate-hydrochloric acid buffers).\textsuperscript{49} They have studied the polarographic reduction of several pyrylium salts under these conditions. Cyclodextrins, on the other hand, are not very stable in aqueous acidic solutions.\textsuperscript{6} The glycosidic linkages in these molecules tend to hydrolyse at pH < 3.5. Hydrolysis is very slow at room temperature, but occurs at moderate rates above 60 °C. We have observed that both the pyrylium salts and β-CD are stable in a sodium acetate-hydrochloric acid buffer of pH 3.5 at room temperature for several days. Hence all the photophysical studies reported in this chapter were carried out in this buffer solution. Since photophysical studies of pyrylium salts in aqueous buffer solutions have not been reported earlier, these studies are also included in this Chapter.

4.3. Results and Discussion

4.3.1. Absorption spectra

Absorption spectra of 3 and 8 (2 x 10\textsuperscript{-5} M) in aqueous buffer solutions were unaffected by the addition of millimolar quantities of β-CD, indicating that these substrates have no interaction with β-CD. Absorption spectra of other derivatives, however, were slightly blue shifted in the presence of β-CD. Figure 4.2 shows the
absorption spectra of 4 (2 x 10^{-5} M) in the absence and presence of β-CD (2.5 x 10^{-3} M). Although the shift in the absorption maximum is very small, it can be taken as evidence for the association of 4 with β-CD. Similar results were obtained for 5-7.

![Absorption spectra of 5 in the absence (—) and presence (…) of β-CD.](image)

**Figure 4.2** Absorption spectra of 5 in the absence (—) and presence (…) of β-CD.

Changes in the absorption spectra can be used to estimate the association constants between the guests and β-CD. However, changes in the absorption spectra of 4-7 in the presence of β-CD were not large enough to allow for accurate analysis of the association processes. Hence no attempt was made to determine the association constants by using the absorption spectral changes.

### 4.3.2. Fluorescence properties

The fluorescence spectra of 3-8 in the aqueous buffer solutions were similar to those in acetonitrile. The fluorescence quantum yields were, however, lower in
buffer solutions. Addition of small amounts of \( \beta \)-CD did not lead to any change in the fluorescence spectra of 3 and 8. The fluorescence intensities and lifetimes of these compounds remained unaffected. The fact that the absorption and emission properties of these compounds are unaffected by \( \beta \)-CD, can be taken as conclusive evidence for the absence of inclusion complex formation in these two cases. Since 3 and 8 did not form inclusion complexes, these compounds were not used for other studies described in this Chapter.

Addition of small quantities of \( \beta \)-CD to solutions of 4-7 (4 \( \times \) \( 10^{-5} \) M), led to changes in their fluorescence properties. In these cases, the fluorescence quantum yields showed a 2-6 fold enhancement in the presence of \( \beta \)-CD. We have used these fluorescence enhancements to analyze the complex formation process and to determine the association constants in these cases.

Formation of complexes between the pyrylium salts 4-7 and \( \beta \)-CD can be analyzed quantitatively by considering the equilibrium given in equation (4.1).

\[
\text{PY} + \beta\text{-CD} \rightleftharpoons \text{PY}::\beta\text{-CD} \quad (4.1)
\]

In equation (4.1), ‘PY’ represents the pyrylium salts and ‘K’ the association constant. Equation (4.1) assumes that a 1:1 complex is formed between \( \beta \)-CD and the pyrylium salts. The association constant is then given by the equation (4.2).

\[
K = \frac{[\text{PY}::\beta\text{-CD}]}{[\text{PY}][\beta\text{-CD}]} \quad (4.2)
\]

The solute entry and exit rates into and out of CD cavities are usually of the order of \( 10^7 \) M\(^{-1}\) s\(^{-1}\) and \( 10^4 \) s\(^{-1}\), respectively.\(^{19}\) The rate constants of fluorescence decay for pyrylium salts are usually of the order of \( 10^9 \) s\(^{-1}\). Thus, there is very
little chance of any excited pyrylium molecule to enter or exit β-CD cavity during their lifetime. Therefore, we can safely assume that the enhancement of fluorescence intensity is entirely due to the presence of the ground state inclusion complex of pyrylium salt with β-CD. Fluorescence can occur from the associated and unassociated forms of the pyrylium salts. If α is the fraction of pyrylium salts associated, then the observed fluorescence (Φ_{obsd}) is given by equation (4.3).

\[ Φ_{obsd} = α Φ_{PY::CD} + (1- α) Φ^0_f \]  

where, \( Φ^0_f \) is the fluorescence quantum yield in the buffer solution in the absence of β-CD and \( Φ_{PY::CD} \) is the fluorescence quantum yield of the inclusion complex. The latter quantity cannot be measured accurately and hence graphical methods are used to determine the association constant. Equation (4.3) can be simplified to equation (4.4).^50,51

\[ \frac{1}{Φ^0_f - Φ_{obsd}} = \frac{1}{Φ^0_f - Φ_{PY::CD}} \quad + \quad K \frac{1}{Φ^0_f - Φ_{PY::CD}[β-CD]} \]  

According to equation (4.4), a plot of \( 1/(Φ^0_f - Φ_{obsd}) \) vs. \( 1/[β-CD] \) should be linear with slope = \( 1/K(Φ^0_f - Φ_{PY::CD}) \) and intercept = \( 1/(Φ^0_f - Φ_{PY::CD}) \). The association constant \( 'K' \) is then given by,

\[ K = \frac{\text{Intercept}}{\text{Slope}} \]  

In order to determine K, values of \( 1/(Φ^0_f - Φ_{obsd}) \) were plotted against \( 1/[β-CD] \) for pyrylium salts 4-7 (Figure 4.3). Straight lines were obtained in all cases, which indicated that the inclusion complexes formed have 1:1 stoichiometry. The K
values determined this way are given in Table 4.1. Note that the association constants obtained for 5 and 6 are very large.

Figure 4.3 Plots of $1/\Phi^0 - \Phi$ (obs) vs. $1/[\beta-CD]$ for the fluorescence yield enhancement of pyrylium salts (a) 4, (b) 5, (c) 6 and (d) 7.

Eventhough the pyrylium salts 4-7 formed complexes with $\beta$-CD, the nature of these complexes was not the same in all cases. This is evident from the fluorescence profiles of these derivatives in the presence of $\beta$-CD. Fluorescence profiles of 4 and 6 in the presence of $\beta$-CD were similar. The fluorescence enhancement of 6 is shown in Figure 4.4. In this case, the enhancement is associated with the appearance of fine structure, a blue shift of 26 nm for the emission maximum and a narrowing of the spectral bandwidth. The fluorescence spectrum in the presence of $\beta$-CD ($1 \times 10^{-3}$ M) is very similar to the spectrum of 6.
in dichloromethane solution. This clearly suggests that 6 is associated within the hydrophobic cavity of \( \beta \)-CD. An important feature in these cases is the presence of an isoemissive point, which suggests that only two forms of the fluorophore are present in the solution.

Figure 4.4 Effect of addition of \( \beta \)-CD on the fluorescence spectrum of 6. Inset shows a plot of fluorescence quantum yield vs. [\( \beta \)-CD].

The fluorescence enhancement of 5 in the presence of various concentrations of \( \beta \)-CD is shown in Figure 4.5. Here, even though the intensity showed a two-fold enhancement, the spectral shape was not altered very much. Also, the isoemissive point was not observed. The \( \lambda_{\text{max}} \) showed only a moderate blue shift of 15 nm. This indicated that the microenvironment of 5 is not the same as that experienced by 4 and 6.
Pyrylium salt 7 exhibited a different type of behaviour in the presence of β-CD. This is shown in Figure 4.6. In this case a 6-fold fluorescence enhancement was observed. Although the emission maximum showed a blue shift of 14 nm, the spectral shape remained unaltered. The insert in Figure 4.6 shows the fluorescence enhancement as a function of β-CD concentration. Note that the saturation behaviour is observed only at relatively large concentrations of β-CD in this case.
Fluorescence lifetimes (τᵢ) of 4-7 were measured in the absence and presence of β-CD. Figure 4.7 shows the fluorescence decay profiles of 5 in the absence and presence of β-CD. In the absence of β-CD, predominantly single exponential decays were obtained. We have fitted the fluorescence decay profiles in the presence of β-CD to single exponential functions. The fits were not very good (χ² ≤ 2) and the values we have obtained may have some error (vide infra). Nevertheless, we intend to use these values to extract useful information regarding the nature of the complex formed between these pyrylium salts and β-CD.
Duveneck et al. observed that the fluorescence decay of trans-stilbene in the presence of β-CD is double exponential. The two components of the decay were assigned to loose and tightly bound conformations of trans-stilbene within the β-CD cavity. It was shown later that the decay profiles of several anilinonaphthalene sulphonate (ANS) derivatives in the presence of β-CD could not be fitted to single or double exponential functions. \( \chi^2 \) values of 4-40 were reported in these cases. It was suggested that the decay functions could be best fitted by a distribution of fluorescence lifetimes. This suggested the presence of several slightly different conformations of the inclusion complexes in equilibrium, existing in the solution. The fact that we also did not observe good single
exponential decays, supported the presence of slightly different conformations for the pyrylium salt-β-CD complexes. However, the \( \chi^2 \) values we obtained were much better and hence fitting the decays to a single exponential may be justified.

The fluorescence maxima, quantum yields and lifetimes of pyrylium salts 4-7 in the absence and presence of β-CD are presented in Table 4.1 along with the equilibrium association constants for complex formation.

Table 4.1 Fluorescence maxima (\( \lambda_{\text{max}} \)), quantum yields (\( \Phi_f \)), lifetimes (\( \tau_f \)) and association constants (K) for pyrylium salts 4-7 in the presence of β-CD. Values given in parenthesis are those in the absence of β-CD.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}}(\text{em}), ) nm</th>
<th>( \Phi_f )</th>
<th>( \tau_f, ) ns</th>
<th>K, M(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>410 (436)</td>
<td>0.072 (0.040)</td>
<td>1.4 (1.5)</td>
<td>4070</td>
</tr>
<tr>
<td>5</td>
<td>421 (436)</td>
<td>0.11 (0.063)</td>
<td>1.6 (2.0)</td>
<td>15000</td>
</tr>
<tr>
<td>6</td>
<td>410 (436)</td>
<td>0.11 (0.078)</td>
<td>1.8 (2.0)</td>
<td>18400</td>
</tr>
<tr>
<td>7</td>
<td>496 (510)</td>
<td>0.11 (0.025)</td>
<td>0.8 (0.2)</td>
<td>2700</td>
</tr>
</tbody>
</table>

An inspection of the table reveals that the association constants vary over a wide range. This clearly suggests that the inclusion complexes do not have the same structure in all cases. In the following section, an attempt is made to draw some conclusions regarding the structure of these inclusion complexes based on the results we obtained.
It is generally accepted that, the binding forces involved in the complex formation are: (1) hydrophobic interactions between the hydrophobic moiety of the guest molecules and the β-CD cavity; (2) release of high-energy water molecules from the cavity in the complex formation process; (3) hydrogen bonding between the functional groups of the guest molecules and hydroxyl groups of β-CD and (4) release of strain energy in the ring frame of cyclodextrin. The latter two aspects are not important in the present case. Regardless of what kind of stabilizing forces are involved, the geometric capability and the polarity of the guest molecules, the medium and the temperature are the most important factors that determine the stability of the inclusion complex. It is suggested that geometric, rather than the chemical, factors are decisive in determining whether the guest molecule can form an inclusion complex with β-CD. If the guest is too small, it will easily pass in and out of the cavity with little or no binding at all. Complex formation with guest molecules significantly larger than the cavity may also be possible, but the complex is formed in such a way that only certain groups or side chains penetrate into the cavity. The stability of the inclusion complexes is generally proportional to the hydrophobic character of the guest molecule. Highly hydrophilic molecules complex very weakly or not at all.

The β-CD cavity has a diameter of 6.0-6.5 Å. An inspection of Chart 4.1 will show that, except for 8, all other pyrylium salts studied have widths smaller than 6.5 Å. Thus, if molecular size is the only criteria, pyrylium derivatives 3-7 should be able to complex with β-CD. Our studies have shown that 3 do not form inclusion complex with β-CD. This indicates that complex formation in these cases is determined by other factors as well. Because of the positive charge present
in the molecule, the pyrylium salts are polar and somewhat hydrophilic in nature. Encapsulation of these salts will be possible only if the pyrylium ring is substituted with hydrophobic moieties. Since 3 does not undergo encapsulation in β-CD, we can safely assume that presence of a phenyl or p-toluyl group at the 4-position of the pyrylium ring does not enhance the hydrophobicity of the molecule to the extent required for complex formation. When the 2-, 4- and 6-positions are substituted by phenyl groups as in 8, the molecule becomes larger than the cavity and inclusion do not take place in this case because of geometric constrains (see Chart 4.1). The fact that 4 -7 form inclusion complexes with β-CD, suggests that the 4-aryl groups present in these molecules make them sufficiently hydrophobic for inclusion in the cavity. If the association constant can be taken as directly proportional to the hydrophobicity of these groups, the order of hydrophobicity will be t-butyl > n-octyl > n-butyl > phenyl >> methyl.

The fluorescence profiles of 4-7 in the presence of β-CD prompted us to make certain assumptions regarding the structures of the inclusion complexes in these cases. Considering the molecular dimensions, the pyrylium derivatives can enter the cavity only along its long axis, through the wider secondary hydroxyl entrance. In the case of 6, the very high association constant suggests that the molecule is tightly bound within the cavity and the exit rate is low. Since the length of the molecule is only slightly larger than the height of the cavity, 6 is not exposed very much to the aqueous environment. Observation of an isoemissive point suggests the presence of only one conformation for the inclusion complex. Similarly, the inclusion complex of 4 also has only one conformation. The low association constant in this case is most probably due to a faster exit rate of 4 from
the cavity. In the other two cases, we did not observe isoemissive points. This is most probably due to the presence of slightly different conformations of the inclusion complexes in these cases. In the case of 5, high value of $K$ suggests tightly bound complex. Since the length of the molecule is much larger than the cavity height, some part of the molecule has to project outside the cavity. Because of the hydrophilicity and positive charge, we expect the pyrylium ring to stick out of the cavity. Thus, we believe that the $n$-octyl group is coiled inside the cavity and the pyrylium chromophore is mostly exposed to the aqueous environment in the most stable conformation of the inclusion complex. This is supported by the fact that the emission maximum is blue shifted by only 15 nm. Presence of different conformations can be attributed to the flexibility of the long alkyl chain.

In the case of 7, one of the aryl rings has to project outside the cavity. Because of this, the hydrophobic stabilization of the complex is low and this results in low association rates. It is difficult to predict the most stable conformation in this case. We believe that the molecule is moving up and down the cavity and the observed fluorescence is the average from several conformational isomers in equilibrium.

The lifetime measurements also suggest that pyrylium salts 4-7 are included within the CD cavity. Compounds 4-6 show a marginal decrease in $\tau_f$ and 7 shows an increase in $\tau_f$ upon complexation. This is consistent with the results we obtained earlier. Note that, $\tau_f$ values for 5 and 6 are larger in polar solvents due to the formation of TICT states (Chapter 2). For these compounds we expect the lifetimes to decrease in less polar media. In the case of 7, the 4-biphenyl group shortens fluorescence lifetime in polar media due to facile intramolecular electron transfer quenching of the excited state (Chapter 3). Since the CD cavity is less
polar, electron transfer quenching is reduced for molecules encapsulated within the cavity and results in enhanced lifetime. Also, note that the fluorescence enhancement (6-fold) observed in this case is larger. This is also attributed to the reduced rates of intramolecular electron transfer quenching within the CD cavity.

4.3.3. Laser flash photolysis studies

Laser flash photolysis of 4-6 in aqueous buffer solutions led to the formation of transients which exhibit bleaching below 400 nm and absorption above 400 nm. These transients were quenched by oxygen and hence we assign them to the triplets of the substrates. Oxygen quenching rate constants obtained in aqueous media were similar to those reported in other solvents.\textsuperscript{52,53} Since the bleaching maxima coincided with the absorption maxima of these compounds, we have estimated the extinction coefficients of the T-T absorptions using the singlet depletion method. The triplet quantum yields ($\Phi_T$) were then determined using relative actinometry (see Chapter 2 for details). $\Phi_T$ values thus obtained were very low compared to those in acetonitrile solutions. For all these compounds, the T-T absorption maxima were red shifted by $\approx 20$ nm. Triplet lifetimes, however, were larger in the buffer solutions (5-8 $\mu$s). The triplets decayed to the ground states and residual absorptions assignable to product formation were not observed in any of these cases. Pyrylium salt 7 did not give good transients under these conditions.

Laser flash photolysis experiments of 4-6 were also carried out in the presence of $\beta$-CD. Relatively high concentrations of $\beta$-CD were employed in these experiments in order to ensure complete complexation of the pyrylium salts. Laser flash photolysis of $\beta$-CD-encapsulated 4-6 also led to the formation of transients, assignable to the triplets of these substrates. A representative example is given in
Figure 4.8. The extinction coefficients and quantum yields of the triplets were determined in the presence of $\beta$-CD. Table 4.2 summarizes the absorption maxima, extinction coefficients, quantum yields and oxygen quenching rate constants for 4-6 in the absence and presence of $\beta$-CD in aqueous buffer solution.

![Transient absorption spectra of 4 in the absence (O) and presence (Δ) of $\beta$-CD. Inset shows the decay profile at 460 nm in the absence of $\beta$-CD.](image)

An inspection of Table 4.2 shows that inclusion within $\beta$-CD did not have any major effect on the triplet state properties of these molecules. T-T absorption maxima remained unaffected in all cases. Except in the case of 4, $\Phi_T$ and $\varepsilon_T$ values also remained unaffected. The triplet lifetimes of all the derivatives, however, were lowered in the presence of $\beta$-CD. The lifetimes in the presence of $\beta$-CD were similar to those observed in organic solvents. Rates
of quenching of the triplets by oxygen were reduced in the presence of β-CD. This is due to the fact that the pyrylium salts incorporated in the CD cavities are less accessible to quenching by oxygen.

**Table 4.2** Absorption maxima, extinction coefficients, quantum yields and oxygen quenching rate constants for 4-6 in the presence of β-CD. The values given in parenthesis are those in the absence of β-CD.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}(T)$, nm</th>
<th>$\varepsilon_T$, M$^{-1}$ cm$^{-1}$</th>
<th>$\Phi_T$,</th>
<th>$\tau_T$, $\mu$s</th>
<th>$k_{q[O_2]}$, M$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>460 (460)</td>
<td>2.3 x 10$^4$ (1.4 x 10$^4$)</td>
<td>0.077 (0.12)</td>
<td>1.3 (5.6)</td>
<td>2.7 x 10$^8$ (5.0 x 10$^8$)</td>
</tr>
<tr>
<td>5</td>
<td>460 (460)</td>
<td>3.0 x 10$^4$ (2.2 x 10$^4$)</td>
<td>0.06 (0.07)</td>
<td>3.8 (8.3)</td>
<td>1.98 x 10$^8$ (2.7 x 10$^8$)</td>
</tr>
<tr>
<td>6</td>
<td>460 (460)</td>
<td>2.8 x 10$^4$ (3.5 x 10$^4$)</td>
<td>0.067 (0.07)</td>
<td>3.2 (7.6)</td>
<td>2.8 x 10$^8$ (4.3 x 10$^8$)</td>
</tr>
</tbody>
</table>

**4.3.4. Electron transfer studies**

In order to study the electron transfer reactions of pyrylium salts in aqueous media in the presence of β-CD, water-soluble quenchers are required. Also the quencher should not displace the pyrylium salts from the cyclodextrin cavities. If this happens, quenching will occur in the aqueous solution and β-CD will have no influence on the quenching process. Lin and Schuster recently observed that sodium-2-naphthalene sulphonate (2-NS) quenched the fluorescence of several 2,6-di-tert-butyl-4-arylpyrylium derivatives in organic solvents such as acetonitrile and dimethyl carbonate by electron transfer mechanism. They could not determine the oxidation potential of this molecule.
directly. From a plot of the oxidation potentials of substituted naphthalenes against the Hammet $\sigma$ constants of the substituents, they have estimated $E_{ox} = 1.7 \text{ V vs. SCE}$ for this compound. Using this value for $E_{ox}$, we have calculated the free energy ($\Delta G_{el}^S$) of electron transfer from this molecule to the singlet and triplet excited states of 4-7. $\Delta G_{el}^S$ values thus obtained were negative for all compounds, indicating that these reactions are thermodynamically favourable.

In order to see whether this quencher molecule has any interaction with $\beta$-CD, we have carried out absorption and emission measurements of 2-NS in the presence of $\beta$-CD. The absorption and fluorescence spectra of 2-NS remained unaffected in the presence of $\beta$-CD, suggesting that this molecule did not undergo inclusion complex formation and prefer to remain in the aqueous phase. Thus we can safely conclude that this molecule will not be able to displace the pyrylium salts from the $\beta$-CD cavities. Hence, we have used this water-soluble quencher to study the electron transfer reactions of 4-7 in aqueous media in the presence and absence of $\beta$-CD.

**Fluorescence quenching:** Fluorescence of 4-7 were quenched by 2-NS in the absence and presence of $\beta$-CD. The quenching was analyzed by Stern-Volmer kinetics in the usual manner. Stern-Volmer plots obtained for 5-7 in the absence and presence of $\beta$-CD are shown in Figure 4.9. The quenching rate constants determined from these plots are presented in Table 4.3, along with $\Delta G$ values calculated using the Weller equation.
Figure 4.9 Stern-Volmer plots for the fluorescence quenching by 2-NS in the (O) absence and (Δ) presence of β-CD for (a) 5, (b) 6, and (c) 7.

Table 4.3 Quenching rate constants \( k_q^S \) and \( \Delta G_{el}^S \) values for the fluorescence quenching of 5-7 in the presence and absence (values in parenthesis) of β-CD.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( k_q^S, \text{M}^{-1} \text{s}^{-1} )</th>
<th>( \Delta G_{el}^S, \text{kcal M}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>( 1.36 \times 10^{10} )</td>
<td>-21.2</td>
</tr>
<tr>
<td></td>
<td>(2.08 \times 10^{10})</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( 1.11 \times 10^{10} )</td>
<td>-21.2</td>
</tr>
<tr>
<td></td>
<td>(2.46 \times 10^{10})</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>( 1.93 \times 10^{11} )</td>
<td>-15.0</td>
</tr>
<tr>
<td></td>
<td>(3.17 \times 10^{11})</td>
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</tbody>
</table>
An examination of the quenching rate constants presented in Table 4.3 reveals that pyrylium salts exhibit different types of quenching behaviour. In the absence of β-CD, quenching rates were in the (2-2.5) \( \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \) range for 5 and 6. Lin and Schuster observed \( k_q^S \) value of \( 2.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \) for the quenching of 2,6-di-tert-butyl-4-phenylpyrylium perchlorate by naphthalene sulphonate in acetonitrile solution. Although, this value is close to the diffusion limited rate constant, it is higher than that observed (1.4 \( \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \)) for quenching of the same salt by naphthalene. The higher value obtained in the case of NS was attributed to Coulombic attraction, which will affect the relative motion of the ions when they are close together. In the case of 7, \( k_q^S \) was ten times larger. Large \( k_q^S \) values are generally attributed to static quenching. We believe that the positively charged 7 and negatively charged 2-NS associate in the ground state and lead to static quenching of the excited state. For all the substrates, quenching rates were lower in the presence of β-CD. When a fluorophore is residing inside and a quencher is present outside the β-CD cavity, a reduction in the quenching rate is expected. In these cases, the donor and acceptor are separated by a distance equal to the thickness of the wall of β-CD (7 Å). The distance is smaller if the approach of the quencher is through the opening of the cavity. Electron transfer occurs at a distance in these cases. Since the rate of electron transfer depends exponentially on distance, \( k_q \) values are reduced. In the case of 7, although \( k_q^S \) is lowered in the presence of β-CD, the observed value is still larger than the diffusion limited value. This suggests that static quenching is observed even in the presence of β-CD indicating that β-CD is not very effective in partitioning the reactants in this case. We attribute this to the low association constant of 7 and β-CD.
Triplet quenching experiments: Attempts were made to quench the triplets of 4-6 by 2-NS in the absence and presence of β-CD. The quencher concentrations employed in these cases were in the range (1-4) x 10^-4 M. Less than 10% of the singlets of 4-7 were quenched under these conditions. The quenching rate constants were determined by plotting the observed pseudo-first-order rate constants against the quencher concentration as described in Chapter 2. The quenching rate constants obtained in the absence of β-CD were in the range (3.5-5) x 10^9 M^-1 s^-1 (Table 4.4). Slightly lower values were obtained in the presence of β-CD and, as in the case of singlet quenching, this is attributed to the spatial separation of the donor and acceptor.

Table 4.4 Quenching rate constants ($k_{q,T}$) and free energy change ($\Delta G_{el,T}$) for electron transfer from the triplet excited states of compounds 4-6 in the presence and absence (values in parenthesis) of β-CD.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_{q,T}$, M^-1 s^-1</th>
<th>$\Delta G_{el,T}$, kcal M^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2.2 x 10^9</td>
<td>-7.4</td>
</tr>
<tr>
<td></td>
<td>(3.6 x 10^9)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.0 x 10^9</td>
<td>-7.4</td>
</tr>
<tr>
<td></td>
<td>(3.8 x 10^9)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.7 x 10^9</td>
<td>-7.4</td>
</tr>
<tr>
<td></td>
<td>(4.9 x 10^9)</td>
<td></td>
</tr>
</tbody>
</table>

Transient absorption spectra: Lin and Schuster studied the quenching of several pyrylium salts by 2-NS. Laser flash photolysis in these cases led to the formation of transients which were assigned to pyranyl radicals ($\lambda_{max} = 430-480$ nm) and 2-
NS radical cation ($\lambda_{\text{max}} = 600-700$ nm). Based on these results they have suggested that quenching in these cases occurred by electron transfer from 2-NS to the pyrylium salts. In order to see whether electron transfer occurred in our systems, we have recorded the transient absorption spectra of 4-7 in presence of 2-NS. A representative example is given in Figure 4.10.

![Figure 4.10](image)

**Figure 4.10** Transient absorption spectra of 6 in the presence of 0.01 M 2-NS, (O) $\beta$-CD = 0 mM and (Δ) $\beta$-CD = 2.5 mM.

The transient absorption spectrum showed a maximum at 420-440 nm and small absorptions in the 600-700 nm region. The 440 nm absorption was assigned to the pyranyl radical based on literature reports and our own earlier results, and the long wavelength absorption was assigned to 2-NS radical cation. Thus it is clear that quenching of the singlets and triplets of 4-7 by 2-NS occurs by an electron transfer mechanism. Transient absorption spectra of the above systems in the presence of
$\beta$-CD were also similar (Figure 4.10). This confirmed that electron transfer occurs even when the pyrylium salt is encapsulated within $\beta$-CD and quencher is present in the aqueous phase.

The most important results of these studies is the substantial reduction of the BET rates in the presence of $\beta$-CD. We have observed that the lifetimes of the radicals were enhanced approximately 20 times in the presence of $\beta$-CD. This is shown in the kinetic traces in Figure 4.11, which shows the decay of the 440 nm species in the absence and presence of $\beta$-CD.

![Figure 4.11 Kinetic traces in the (a) absence and (b) presence of $\beta$-CD for 6 / 2-NS system.](image)

In the absence of $\beta$-CD, the transients decayed in about 20 $\mu$s time. The small residual absorption in this case is attributed to product formation. In the presence of $\beta$-CD, decay of the radical species is not complete even at 150 $\mu$s. Residual absorptions attributable to product formation is absent in this case. This clearly indicated that the radicals are protected within the $\beta$-CD cavity for relatively long
periods. Reduced rates of BET in these cases can be attributed to two factors: (1) the spatial separation of the donor and acceptor achieved by encapsulation and (2) increased hydrophobicity of the radicals compared to the cationic pyrylium salts.

In a recent report, Mirzoian and Kaifer studied the binding abilities of viologen derivatives and their one and two electron reduction products with β-CD using cyclic voltammetry. They have observed that the dicationic viologens have no affinity towards cyclodextrins. The two electron reduction products (neutral form) formed extremely stable inclusion complexes with association constants in the range $10^3$-$10^4$ M$^{-1}$. The radical cations (single electron reduction products) exhibited intermediate binding affinities ($K \approx 10^2$ M$^{-1}$). Enhanced binding of the radical cations and neutral forms is due to their hydrophobicity. This study clearly established that the radicals are more hydrophobic compared to the cations. Pyrylium salts also present a similar case. Based on the study of Mirzoian and Kaifer, we propose that the neutral pyranyl radicals will be more hydrophobic compared to the cationic pyrylium salts. Thus, compared to the pyrylium salts, the binding constants of the radicals with β-CD will be higher.

Based on our fluorescence studies we have suggested that in the pyrylium salt-β-CD inclusion complex, the pyrylium ring is partly exposed to the aqueous environment. Upon electron transfer from 2-NS, the charge on the pyrylium ring is neutralized. The radical formed is more hydrophobic and will have better binding affinity with β-CD. Thus, the pyranyl radical formed may move towards the interior of the cavity and the 2-NS radical cation formed may move away from the β-CD. This would lead to an effective separation of the products of PET reactions.
and can account for the approximately 20 times enhancement of the radical lifetime in the presence of β-CD.

In this Chapter, we have described the photophysical and electron transfer properties of selected pyrylium derivatives in aqueous solutions in the absence and presence of β-CD. Our studies showed that pyrylium salts with proper size and hydrophobic groups can be encapsulated into the β-CD cavities. For those pyrylium salts, which form inclusion complexes, the fluorescence enhancements were measured and used in the calculation of the binding constants. We have shown that encapsulated pyrylium salts can undergo electron transfer reactions. The radicals obtained in these cases were long-lived compared to those in the absence of β-CD. Our results suggest that β-CD can be employed in suitable cases to control BET reactions to some extent.

4.4. Experimental

Measurements: All melting points are uncorrected and were determined on a Büchi Model 530 melting point apparatus. IR spectra were recorded on a Perkin Elmer Model 882 IR spectrometer. 1H NMR spectra were recorded on a JEOL EX-90 spectrometer. The absorption spectra were recorded on a Shimadzu UV-2100 or a GBC double beam UV-VIS spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluorolog F 112X spectrofluorimeter with a right-angle geometry using 4 x 10⁻⁶ M solutions. Fluorescence lifetimes were determined using Edinburgh Instruments FL900CD single photon counting system. Laser flash photolysis experiments were carried out by employing an Applied Photophysics Model LKS-20 Laser Kinetic Spectrometer using GCR-12 Series
Quanta Ray Nd:YAG laser. The analyzing and laser beams were fixed at right angles to each other. The laser energy was 60 mJ at 355 nm.

Materials: Synthesis of 4 is described below. Compound 8 was prepared according to a reported procedure.\textsuperscript{56} Syntheses of other pyrylium derivatives are described in earlier chapters of this thesis. \(\beta\)-CD purchased from Aldrich was used as received. 2-NS was prepared according to a reported procedure\textsuperscript{57} and was recrystallized before use.

Synthesis of 2,6-dimethyl-4-(\(p\)-\(n\)-butylphenyl)pyrylium perchlorate (4)

4-(\(n\)-Butylphenyl)magnesium bromide was prepared through the reaction of 1-(4-bromophenyl)butane (20 mM) and magnesium (20 mM) in dry THF (20 mL). This reagent was added to a suspension of 2,6-dimethyl-4-pyrone (20 mM) in dry THF (50 mL) at 0 °C. The solution was allowed to warm up to room temperature and stirred for 30 minutes. Ice cold solution of 10\% perchloric acid (100 mL) was added and the precipitated pyrylium salt (4) was collected by filtration. The salt thus obtained was dissolved in dichloromethane and reprecipitated by adding ether. This process was repeated several times to give 2.1 g (31\%) of a pure product, mp 120-121 °C; IR (\(\nu_{\text{max}}\)): 3094, 2935, 2861, 1647, 1095 cm\(^{-1}\); \(^1\)H NMR (90 MHz, CDCl\(_3\)), \(\delta\) 0.9 - 1.6 (m, 9 H), 2.9 (s, 6 H), 7.3 - 8.2 (m, 6 H); Anal. Calcd for C\(_{17}\)H\(_{21}\)O\(_5\)Cl: C, 59.98; H, 6.22. Found: C, 59.71; H 6.35.

All experiments were carried out in aqueous buffer solutions of pH 3.5. Double distilled water was used for preparing solutions. Solutions for flash photolysis experiments were deaerated with argon for 15 minutes, prior to the experiments.
4.5. References


