Triplet state characteristics of IR laser dyes: A pulse radiolysis study

M Rele, A K Singh, D K Palit & T Mukherjee*
Radiation Chemistry & Chemical Dynamics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
Email: mukherji@magnum.barc.ernet.in

Received 24 May 2004

The IR-dyes, having the absorption maximum in the range of 600 nm to 1100 nm, are expected to have very low triplet energy level. The triplet-triplet (T-T) absorption spectra and decay characteristics have been investigated for four IR laser dyes, namely, IR-140, IR-144, Q-Switch 1 and Q-Switch 5. Triplet state of these IR dyes are generated by electron pulse radiolysis in benzene-benzonitrile (BZ-BZN 80:20, % v/v) solvent mixture. Energy transfer from the pulse radiolytically generated anthracene triplet confirms the formation of triplet state of these IR dyes. Triplet state characteristics of these IR dyes have been measured. Using various triplet donors and acceptors, the triplet energy levels of these dyes have been estimated.

IPC Code: Int Cl7, G01N 21/00; G01J 3/00; C09B

Laser dyes are the active medium in pulsed and continuous wave dye lasers¹ as well as ultrafast shutters for Q-switching and passive modelocking². Great interest is generated in these dyes because of their broad absorption and fluorescence spectra. In addition, one can also choose from a large range of dyes for emission in any region of visible and IR spectral regions.

After photo-excitation, molecules from the S₁ state can also make a nonradiative relaxation to the triplet state through intersystem crossing. This transition process is detrimental to laser action for two reasons. Firstly, this process leads to a reduction of population of S₁ state. Secondly, the absorption spectrum of T₁-T₂ usually overlaps the emission spectrum of S₁-S₀, thus leading to a loss at the wavelength corresponding to the laser emission. As the triplet-singlet transition is spin forbidden, the lifetime of triplet state is long and hence triplet states are more reactive and may reduce the photo-stability of dye molecules. Thus, the efficiency as well as the photochemical stability of the dyes reduces due to the formation of the triplet state. It can bring down the lasing efficiency of these dyes and may prevent lasing. Hence, a study of the triplet state of dyes is therefore of great importance for the operation of dye lasers³.

Although several attempts have been made to characterize the triplet state properties of visible dyes, there is not sufficient information available on the spectral and kinetic properties of triplet state of IR dyes. Detailed knowledge of the triplet state is essential to judge their suitability in applications as laser dyes. The triplet state of these dyes cannot be studied by direct photo-excitation due to very low intersystem crossing yield and hence energy transfer technique has been used to study the triplet state of these dyes using pulse radiolysis techniques. In the present work, four IR dyes namely IR-140, IR-144, Q-Switch 1 and Q-Switch 5 have been studied. Among them, IR-140 and IR-144 are gain dyes (active medium), for which the lasing action has been achieved in 800-950 nm regions. QS-1 and QS-5 are non-emissive dyes and are frequently used in Q-switching or modelocking of Nd:YAG laser due to its high absorption cross section at 1064 nm. In the present study, an attempt has been made to characterize the triplet state of these dyes using pulse radiolysis technique and their photophysical characteristics are investigated.

Materials and Methods

Four IR laser dyes, namely IR-140, IR-144, Q-Switch 1 and Q-Switch 5, the structure of which are shown in Scheme 1, were obtained from Exciton Inc., USA and used without further purification. Triplet sensitizers such as anthracene and perylene were obtained from the Becker and Becker triplet quencher kit. The solvents were of spectroscopic grade and were used without further purification. The solutions were purged with oxygen-free N₂ in the pulse radiolysis cell using a BZ-BZN pre-trap and sealed with parafilm after purging.
The steady-state absorption spectra were recorded on a Shimadzu 160A UV-visible spectrophotometer. A detailed experimental set-up for the electron pulse radiolysis and the kinetic spectrophotometry has been described elsewhere. Sample solutions taken in a suprasil cuvette of 1 cm path length were irradiated by electron pulses of 50 ns duration from a 7 MeV linear electron accelerator (Forward Industries, England) at a radiation dose of 10–12 Gy per pulse. An aerated 5×10^{-2} mol dm^{-3} KSCN solution was used for dosimetry and (SCN)_2^- radical was monitored at 475 nm. The absorbed dose per pulse was calculated assuming Ge for (SCN)_2^- radical to be 2.6×10^{-4} m^2 J^{-1}. The transient absorption profiles were monitored by a kinetic spectrophotometric arrangement consisting of a 450 W pulsed xenon lamp in conjunction with a monochromator (CVI model 110) and photomultiplier tube (Hamamatsu R 928), connected to a digital oscilloscope (L&T Gould 4072). The data were transferred to an IBM PC where data analysis was carried out using indigenously developed programmes.

Results and Discussion

Figure 1A shows the optical absorption spectrum of IR-140 and IR-144 dyes in benzene. The spectra exhibit a broad absorption band in the region 500-900 nm. The absorption spectra of IR-144 has absorption maximum at 750 nm and shoulder at 550 nm, while the absorption spectrum of IR-140 is red shifted in comparison with that of IR-144 and exhibits maximum absorption at 800 nm and two shoulders at 575 and 710 nm. These two dyes are reported to have strong emission in the 800-950 nm regions. Figure 1B shows the absorption spectrum of two saturable absorber laser dyes QS-1 and QS-5 in benzene. The absorption spectrum of QS-1 shows three absorption bands at 500, 950 and 1064 nm, while the absorption spectrum of QS-5 exhibits a broad absorption band in the region of 800-1100 nm having maximum absorption at 980 nm. These two dyes are non-emissive and widely used as saturable absorber in Nd-YAG laser due to its high absorption coefficient at 1064 nm.

Pulse radiolysis is an excellent technique for selective creation of the excited triplet states of organic molecules using triplet-triplet energy transfer method in aromatic solvents such as benzene. However, in the pulse radiolysis of benzene, formation of singlet and triplet excited states are the major processes. The radiolysis of benzene produces the benzene triplet (^3BZ) of very high energy (353 kJ mol^{-1}) in high yield. ^3BZ can transfer its energy to another solute having E_r < 353 kJ mol^{-1}, thus generating the triplet state of the latter. Hence, in the pulse radiolysis of benzene containing a relatively higher concentration (~10^{-3} mol dm^{-3}) of scavenger species, the ^3BZ can serve as a sensitizer for initiating the triplet-triplet energy transfer process. The low intersystem crossing efficiency for the conversion of the singlet to the triplet state of the solute molecule does not pose any limitation to the
production of the triplet state. Also, the triplet production process being selective, conclusive evidence for the assignment of the photolytically generated transient species to the triplet state can be obtained from the pulse radiolysis studies of the solutes in deaerated solutions of benzene.

The primary processes in the radiolysis of benzene are dominated by the formation of excited benzene molecules directly as well as by geminate ion recombination. The higher excited states are expected to cascade to the lowest triplet state of benzene by fast internal conversion (IC) and intersystem crossing (ISC) process.

The processes in radiolysis of benzene can be represented as follows:

\[ \text{Bz} \rightarrow \text{Bz}^* \quad \text{Bz}^* + e^- \rightarrow \text{Bz}^* , \text{Bz}^* \rightarrow \text{Bz}^* \quad \text{Bz}^* \rightarrow \text{Bz}^* \quad \text{(1)} \]

The electron cation pair undergoes geminate neutralization to give excited states. Thus, benzene radiolysis is a good source of generating excited states, especially triplets, with a \( G(\text{Bz}) \approx 4.2 \).

The chemical and the physico-chemical interactions of solutes at low concentrations (< 0.1 mol dm\(^{-3}\)) in irradiated benzene are generally interpreted in terms of their encounter with lowest triplet state of benzene (\( ^3\text{Bz} \)). In this work, benzonitrile is chosen as a co-solvent based on their poor reactivity with \( e^- \) or triplet states and this enhances the solubility of IR dyes. Using standards, such as benzophenone and benzil, we have observed that the triplet state could be generated exclusively by electron pulse radiolysis technique in benzene-benzonitrile (80/20 % v/v) mixture, and no other species, such as, radical anion or ketyl radical are produced. Thus, we assume that this does not significantly affect/alter the primary species formation in benzene radiolysis. From the triplet benzene, energy transfer as shown in reaction 2 generates triplet state of solute.

\[ ^1\text{Bz}^* + S \rightarrow ^3\text{Bz} + ^3S^* \quad \text{(2)} \]

However, since the lifetime of \( ^3\text{Bz} \) is very short (~ 4 ns), to make the energy transfer (reaction 2) process efficient, one has to use the high concentration of solute. Alternatively, to get better yield of \( ^3S \), is to use of an intermediate triplet sensitizer, having higher \( E_T \) than that of solute and large lifetime. The relative concentrations of \( S \) and intermediate are adjusted such that \( ^3S \) formation from \( ^1\text{Bz} \) is negligible.

\[ ^1\text{Bz}^* + D \rightarrow ^3\text{Bz} + ^3D^* \quad \text{(3)} \]

\[ ^3D^* + S \rightarrow ^3D + ^3S^* \quad \text{(4)} \]

Following the interaction of 50 ns electron pulse with solution of IR-140 in benzene-benzonitrile (80/20, % v/v) solvent, a fast growth of the transient absorption with a maximum at 540 nm region is observed. Figure 2A shows the transient optical absorption spectrum of 1×10\(^{-4}\) mol dm\(^{-3}\) IR-140 solution. Despite strong and broad absorption of IR-140 in the IR region, the 400-600 nm region offered a convenient window to monitor the transient changes. The transient absorption is quenched in aerated solution showing that the species is reactive towards oxygen. This observation suggests that the transient is triplet of IR-140. The triplet-triplet absorption spectrum of IR-144 is shown in Fig. 2B. It exhibits maximum absorption at 515 nm with two shoulders at 440 and 590 nm. The triplet absorption spectra of other two dyes (QS-1 and QS-5) are shown in Fig. 3. We observe three absorption bands of triplet state at 400, 550 and
The temporal profile of the decay of the triplet state of these IR dyes is sensitive to the concentration of dye used. Hence, it is expected that in addition to normal first order decay of the triplet to the ground state, quenching of the triplet state by ground state dye is also contributing to the decay of triplet state and these processes are represented by following reactions.

\[ \text{Dye} (T_1) \xrightarrow{k_T} \text{Dye} (S_0) \quad \ldots \quad (5) \]

\[ \text{Dye} (T_1) + \text{Dye} \xrightarrow{k_{T-S}} 2 \text{Dye} (S_0) \quad \ldots \quad (6) \]

The self quenching rate constant \((k_{T-S})\) for the radiolytically generated triplet dye is determined by monitoring its decay at maximum absorption for the triplet state for various concentrations of dye \(0.39 - 1 \times 10^4\) mol dm\(^{-3}\) at same radiation dose \(^5\). Figure 4 shows such decay of the triplet state of IR-140 dye. The lifetime of the triplet is increased when the concentration of the dye is reduced. The pseudo first order rate constant thus obtained is plotted against the concentration of dye (inset of Fig. 4), the self quenching rate constants \((k_{T-S})\) thus determined from the slope of the linear fit is \(1.3 \times 10^6\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\). The value of the rate constant obtained by extrapolation of the linear fit to zero concentration of dye is measured to be \(3.1 \times 10^3\) s\(^{-1}\), which provides the value of \(k_T\), the triplet decay rate. The inverse of this provides the actual lifetime \((\tau = 320\ \mu s)\) of triplet state of IR-140 in the absence of self-quenching reaction. The triplet lifetime for other three dyes are determined in similar manner and are shown in Table 1.

The energy transfer process from anthracene triplet \((E_T = 177\) kJ mol\(^{-1}\)) to triplet state of IR dyes has also been studied. The anthracene triplet is generated on pulse radiolysis of de-aerated solution of anthracene \((1 \times 10^2\) mole dm\(^{-3}\)) and various concentrations of dye. Under these conditions, the anthracene triplet, initially produced, transfers its energy to the dye, leading to the formation of the triplet state of the dye. The decay
of the triplet state of anthracene is monitored as a function of dye concentration. The pseudo first order decay ($k_{obs}$) of anthracene triplet became faster with increase in dye concentration, indicating energy transfer from the triplet anthracene to the triplet state of the dye. The energy transfer rate is determined from the plot of $k_{obs}$ vs dye concentration and the value is calculated to be $5.1 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ for IR-140. The energy transfer rate from triplet anthracene to other three dyes are shown in Table I. The energy transfer rate has been seen to be diffusion limited.

We have used the well-documented technique of Bensasson and Land$^9$ to determine the extinction coefficient of T-T absorption of IR laser dyes. In these experiments, anthracene is used as intermediate (donor) due to its more intense and shorter wavelength T-T absorption at 430 nm. The de-areated solution of anthracene ($10^{-2}$ mol dm$^{-3}$) both with and without the presence of IR dyes ($1 \times 10^{-4}$ mol dm$^{-3}$) are subjected to pulse radiolysis at identical radiation dose. Under these conditions, the initial yield of anthracene triplet produced as a consequence of energy transfer from triplet benzene will be identical with and without IR dyes. The correspondence between the decay time of anthracene triplet and formation time of IR-140 triplet clearly shows that the energy transfer from the former produces the latter (Fig. 5).

In such a system, the competing processes involving the donor and acceptor molecules are

\[ ^3D^* \rightarrow D \]
\[ ^3D^* \rightarrow ^3S^* + D \]

When $[S] >> [D^*]$, the decay of the triplet state of donor molecule can be represented as (under pseudo first order condition)

\[ k_3 = k_1 + k_2 [S] \]

For identical electron pulse radiolysis dose, the absorbance of the donor triplet in absence of solute (acceptor) molecule, $OD_{\delta^*,0}$ and the absorbance $OD_{\delta^*}$ due to acceptor in combined system are related by

\[ \frac{1}{OD_{\delta^*}} = \frac{\varepsilon_{\delta^*}}{\varepsilon_{\delta^*}} \frac{1}{OD_{\delta^*,0}} \left( 1 + \frac{k_1}{k_2[S]} \right) \]

where $\varepsilon_{\delta^*}$ and $\varepsilon_{\delta^*}$ are the extinction coefficients of the donor and acceptor (solute) at corresponding wavelength with no overlapping absorption of these two triplet states. These relations are used to calculate the extinction coefficients at the wavelength of maximum absorption of triplet state of IR dyes and have been shown in Table 1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>IR-140</th>
<th>IR-144</th>
<th>QS-1</th>
<th>QS-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption maximum (nm)</td>
<td>540</td>
<td>520</td>
<td>400, 550, 710</td>
<td>410, 560, 710</td>
</tr>
<tr>
<td>Energy transfer rate from anthracene (× 10$^9$ dm$^3$ mol$^{-1}$ cm$^{-1}$)</td>
<td>5.1</td>
<td>2.4</td>
<td>4.6</td>
<td>4.3</td>
</tr>
<tr>
<td>Molar extinction coefficient (× 10$^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$) (540 nm)</td>
<td>2.4</td>
<td>1.3</td>
<td>1.1</td>
<td>1.38</td>
</tr>
<tr>
<td>Triplet self quenching constant, $k_{T, S}$ (× 10$^9$ dm$^3$ mol$^{-1}$ s$^{-1}$)</td>
<td>1.3</td>
<td>7.6</td>
<td>0.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Triplet lifetime (µs)</td>
<td>322</td>
<td>77</td>
<td>100</td>
<td>188</td>
</tr>
</tbody>
</table>

Table I—Triplet characteristics of IR laser dyes
These IR dyes are expected to have very low triplet energy level. The fact that triplet state of these dye are produced from energy transfer from anthracene triplet ($E_T = 177$ kJ mol$^{-1}$) and quenched by the oxygen ($E_T = 90$ kJ mol$^{-1}$). We have also observed the energy transfer from triplet state of perylene ($E_T = 148$ kJ mol$^{-1}$) to the triplet state of these dyes. This shows that energy level of the triplet state of these dyes falls in the range of 90-148 kJ mol$^{-1}$. However, we could not determine the triplet energy level within closer limits due to unavailability of triplet donors in this range.

**Conclusion**

The triplet states of IR laser dyes have been produced through the energy transfer technique using electron pulse radiolysis technique in benzene-benzonitrile (80/20, % v/v). Spectral as well as kinetic parameters of the triplet state of these dyes have been measured. Triplet-triplet absorption spectrum, extinction coefficient, triplet state lifetime and self quenching rate constants have been evaluated for all the four IR dyes. The rate of triplet-triplet energy transfer from anthracene to the IR dyes has been seen to be diffusion-controlled process. The energy level of these IR laser dyes is estimated to be in the range of 90 kJ mol$^{-1}$ to 148 kJ mol$^{-1}$ using various triplet donors. These results on the triplet state of these IR dyes are useful for their operation in laser system.

**References**