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On the exciplex formation in the energy transfer from aromatic hydrocarbons to crystal violet

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Abstract

The interaction of a triphenyl methane (TPM) dye: crystal violet (CV) with the triplet state ($^3S^*$) of the aromatic molecules biphenyl, *p*-terphenyl or anthracene was studied by pulse radiolytic kinetic spectrophotometry. In each case, studies of time-resolved spectra and kinetics showed that an exciplex between sensitiser triplet and ground state of CV is formed as an intermediate before the former dissociates to give triplet state of CV, $[^3S^* + CV \underset{k_b}{\overset{k_f}{\rightleftharpoons}} {}^3(S..CV)^* \xrightarrow{k_3} S + {}^3CV^*]$. A detailed kinetic analysis has been carried out to evaluate various kinetic parameters. The equilibrium constant, K (k_f/k_b), was found to be 1.8×10^4 dm^3 mol^{-1}, 1.53×10^4 dm^3 mol^{-1} and 1.32×10^4 dm^3 mol^{-1} in the case of biphenyl, *p*-terphenyl and anthracene sensitiser triplet states, respectively.

Keywords: Exciplex; Energy transfer; Crystal violet; Aromatic hydrocarbons

1. Introduction

Molecular mechanisms wherein dyes participate are of direct relevance in the context of photodegradation of dyes applied on different substrates and evolving strategies for treatment of dye-containing effluents. Among the dyes having wide ranging popular usage, triphenyl methane (TPM) dyes are a prominent class. The TPM dyes also find interesting technological applications such as saturable absorbers for producing ultrashort laser pulses [1]. The photophysical and photochemical processes involving the TPM dyes have attracted considerable research interest and these have been recently reviewed [2]. Time-resolved studies concerning the free radical induced oxidative and reductive attack on some of the TPM dyes in aqueous medium have been recently reported from our laboratory [3,4]. Flash photolysis work on the photoreduction of some organic dyes including the TPM dye, crystal violet (CV), in acetonitrile solvent, has also been recently reported [5,6].

The reactivities of the excited states of the dye molecules would be limited by their life times and the efficiency of their energy disposal by the chemically unproductive internal conversion (IC) channel. The first excited singlet states (S_1) of the TPM dye molecules are, in general, marked by their very short life times (picoseconds) in low viscosity fluids [7]. Enhanced excited state lifetimes have been observed in the case of some TPM dye molecules bound to certain polyelectrolytes [8]. We have recently reported photoionization of CV, in aqueous solution excited by 248 nm, 10 ns laser pulses and postulated that higher excited states of longer life time could be involved in the observed formation of hydrated electron [9]. On the other hand, high viscosity matrices like polymers or fibres could facilitate the population of longer lived triplet states of dye molecules by better intersystem crossing (ISC) efficiency. In an early work, spectra obtained on illumination of CV in high viscosity glassy matrices have been attributed to the triplet state of the dye [10,11]. A process that would produce triplet states even in a low viscosity medium is the energy transfer from a higher energy triplet state of a sensitiser to the dye molecule. However, until recently, attention paid to the triplet states of the TPM dyes has been very limited. In our recent pulse radiolysis work, on the interaction of triplet states of benzene with CV, we have attributed the observed long lived transient absorption to the triplet state of CV ($^3CV^*$) and reported its absorption spectrum in the 360–450 nm region [12].

Recently, Naguib et al. have reported triplet sensitised photobleaching of crystal violet in acetonitrile solutions [13]. They have observed that, the quenching of $\pi\pi^*$ triplet states of anthracene and naphthalene by CV gives rise to absorbance build-up centered around 405 nm which is attributed to the

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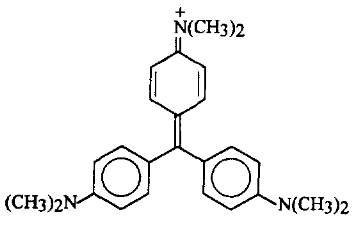
formation of $^3CV^*$ by energy transfer. In the case of interaction of a typical $n\pi^*$ triplet state (benzophenone) with CV, an additional reaction channel (~ 14%) forming benzophenone ketyl radical by H atom abstraction from the CV molecule has also been proposed. The assignment of 405 nm absorption peak to $^3CV^*$ is in agreement with the conclusions from our earlier work [12]. In view of the very low quantum yields [$\phi(-CV) \sim 10^{-5}$] for the net bleaching of CV, the $^3CV^*$ is considered to be 'unreactive' by Naguib et al [13]. However, in our previous as well as the present work, we have observed the decay of $^3CV^*$ in the millisecond time scale and attribute it to its reaction with the parent dye molecules, with a rate constant $\sim 4 \times 10^6$ dm^3 mol^{-1} s^{-1} [12].

Our present work deals with the time-resolved spectroscopic and kinetic details of the energy transfer from $\pi\pi^*$ triplet states of biphenyl ($^3Bip^*$) and related molecules (*p*-terphenyl and anthracene) to CV in benzene solutions. A characteristic feature of the energy transfer from the above molecules to the CV, in comparison with that from triplet benzene, is that a precursor state in the formation of $^3CV^*$ species can be clearly distinguished in each case.

2. Experimental details

Crystal violet (structure given below) in its chloride form (Sigma Chemical) and biphenyl, *p*-terphenyl, anthracene (Fluka Puriss) were used as received. Benzene (Bz) and acetonitrile (ACN) solvents were of spectroscopic grade (Spectrochem, Bombay, India). All the solutions were carefully deoxygenated by flushing them with high purity N_2 gas (Iolar 99.9%) for about 30 min. A solvent pretrap was used during N_2 flushing so as to minimise solvent loss and concentration changes. In order to enhance the solubility of the cationic dye CV, 15% ACN (v/v) was added to the benzene solvent through out this work. It is assumed that at the concentration of ACN used, the excited state processes are not significantly affected as compared to those from benzene alone.



CV

Pulse radiolysis experiments were carried out using 50 ns electron pulses from a 7 MeV linear electron accelerator (Ray Technology, England). Detailed experimental set-up for the pulse radiolysis was as described earlier [14]. Solutions in 1 cm path-length suprasil cuvettes were irradiated at a radiation dose of 14–17 Gy per pulse as measured by an air saturated 0.05 mol dm^{-3} KCNS dosimeter, taking $G\varepsilon$ for $(CNS)_2^{\bullet -}$ as 21 522 dm^3 mol^{-1} cm^{-1} at 500 nm, G being defined as number of molecules formed per 100 eV energy absorbed and ε the molar extinction coefficient for $(CNS)_2^{\bullet -}$ at the wavelength monitored [15].

The transient optical absorption was monitored by a kinetic spectrophotometric arrangement using a 450 W pulsed Xenon lamp (Kratos) as analysing light source in conjunction with a 0.25 m monochromator (Kratos GM-252), photomultiplier (Hamamatsu R 955) and digital storage oscilloscope (L&T 4072). Suitable light filters were placed in the path of the analysing light to prevent UV photolysis of the solutions. Oscilloscope signals were transferred to a personal computer and analyses were performed using a kinetic analysis programme to obtain rate constants and lifetimes [16].

3. Results and discussion

Passage of ionizing radiation through liquid benzene offers a convenient source for generating solvent triplet states. The excited triplet species ($^3Bz^*$) are produced as the dominant reactive entities, directly as well as via geminate ion recombination in the primary processes of benzene radiolysis.

$$Bz \rightsquigarrow Bz^*, (Bz^+ + e^-) \rightarrow {}^1Bz^*, {}^3Bz^* \qquad (1)$$
$${}^1Bz^* \rightarrow {}^3Bz^*$$

Triplet molecules of interest can be then produced by energy transfer process from $^3Bz^*$ (triplet energy ~ 82 kcal mol^{-1}) to a chosen solute.

$$^3Bz^* \rightarrow Bz \qquad (2)$$

$$^3Bz^* + S \rightarrow Bz + {}^3S^* \qquad (3)$$

By the above approach, different aromatic solute triplets have been produced in the past several years for studying their spectroscopic characteristics and chemical interactions [17]. In the present work, S represents the molecules, biphenyl (Bip), *p*-terphenyl (Tp) and anthracene (An) whose triplet state is used for energy transfer. The sensitiser triplet transfers its energy to the chosen solute, CV in the present case, and the substrate triplet states are generated if the transfer is energetically favourable. Eq. (4) represents the overall formation of the triplet state of crystal violet ($^3CV^*$).

$$^3S^* + CV \rightarrow S + {}^3CV^* \qquad (4)$$

Benzene triplet can also transfer energy to the substrate, i.e., CV.

$$^3Bz^* + CV \rightarrow Bz + {}^3CV^* \qquad (5)$$

However, since lifetime of $^3Bz^*$ is very short (~ 4 ns), the energy transfer (Eq. (5)) process is inefficient even at the maximum concentration of the CV used. Hence, energy transfer via other aromatic molecules viz; Bip, Tp, An, whose triplet lifetimes are larger (e.g., $\tau_{^3Bip^*} \sim 20$ μs) were employed to generate better yields of $^3CV^*$. The relative concentrations of S and CV are uniformly adjusted such that $^3CV^*$ formation from $^3Bz^*$ itself, Eq. (5) is negligible.

3.1. Radiolysis of solutions containing biphenyl and CV

Fig. 1a shows the profile of the absorbance changes in the region 350–430 nm, at the end of 50 ns electron pulse applied to an oxygen-free 1.5×10^{-2} mol dm^{-3} biphenyl solution in Bz–ACN. The spectrum is similar to that of T–T absorption spectrum of ^{3}Bip* with λ_{max} at 360 nm [18].

However, the presence of CV ($1–3 \times 10^{-4}$ mol dm^{-3}) in the above solutions produced large changes in the resulting transient spectra, as well as the spectral decay characteristics. Fig. 1b and c shows the spectra recorded in the presence of 3×10^{-4} mol dm^{-3} CV at 1 μs and 8 μs, respectively, after the electron pulse. It may be mentioned that although CV exhibits strong UV–visible absorption spectrum, the spectral region 340–460 nm offers a window region where the absorption by ground state CV is small and can be neglected, i.e., transient absorption signals can be conveniently monitored even in the presence of CV.

Changes in the decay of ^{3}Bip* caused by CV, are shown in Fig. 2, at two different wavelengths in the window region. The fast formation and slow decay of ^{3}Bip* can be seen in Fig. 2a. The decay profiles, monitored at 360 and 440 nm, respectively, in the presence of CV are given in Fig. 2b and c. The two wavelengths respectively correspond to the maximum and relatively small absorptions in the spectrum of ^{3}Bip* shown in Fig. 1a. It is clear that at both the wavelengths, a fast decay is seen up to 4–6 μs which is followed by a much slower decay. The long lived absorption beyond ~6 μs is found to decay in the time scale of hundred microseconds. Furthermore, the spectrum and the decay of the transient obtained with a delay of 8 μs after the electron pulse is in very good agreement with the properties of ^{3}CV* as reported recently in our studies of CV in Bz–ACN [12]. Therefore, we attribute the spectrum shown in Fig. 1c to the spectrum ^{3}CV*. The slow decay behaviour of ^{3}CV* formed according to Eq. (4) monitored at 440 nm (i.e., in the absence of biphenyl) is shown in Fig. 2d for comparison.

The observed changes in the decay of ^{3}Bip* have to be understood in terms of the interaction of ^{3}Bip* with CV. The development of time-resolved spectra in Fig. 1b and c show that energy transfer from ^{3}Bip* to CV proceeds via an intermediate which decays in <6 μs to give the ^{3}CV*.

In solutions containing 1.5×10^{-2} mol dm^{-3} Bip and varying concentration of CV between $5–50 \times 10^{-5}$ mol dm^{-3}, the kinetics of the faster decay was followed at 360 nm. At all the [CV], the decay conformed to a first-order kinetics. However, the values of the first-order rate constant, k_{obs} did not increase linearly with [CV], as would be typical of a clean pseudo first-order process. After an initial rise with increasing [CV], the k_{obs} was found to rise more slowly, with indications of levelling off at higher [CV]. The plot of k_{obs} against CV concentration is shown in Fig. 3. Clearly again, the above kinetic behaviour is not in accordance with simple quenching of ^{3}Bip* by CV, as in Eq. (4). However, the behaviour could be understood by postulating excited state equilibria as in Eqs. (6a) and (6b).

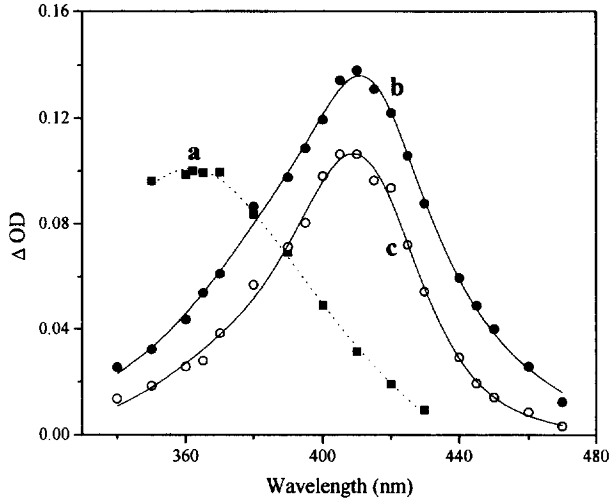


Fig. 1. Transient absorption spectra obtained in deoxygenated benzene–acetonitrile (15% v/v) solution containing biphenyl and CV. (a) Absorption spectrum obtained at the end of pulse in solution containing 1.5×10^{-2} mol dm^{-3} biphenyl alone; and (b) and (c) are the transient absorption spectra recorded at 1 μs and 8 μs, respectively in solutions containing 1.5×10^{-2} mol dm^{-3} biphenyl and 3×10^{-4} mol dm^{-3} CV. Dose per pulse = 15.8 Gy.

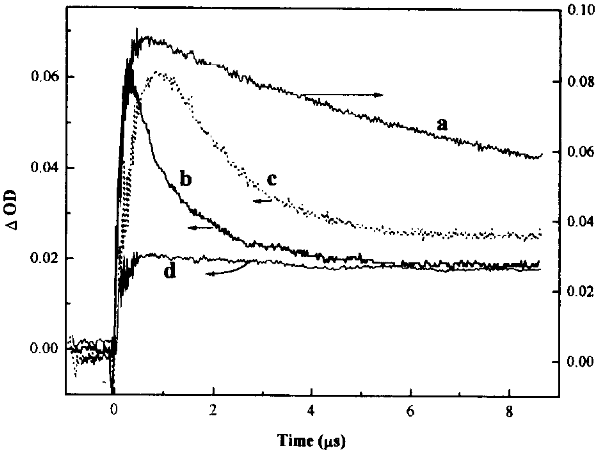


Fig. 2. Kinetic traces of transient absorptions at different wavelengths in deoxygenated benzene–acetonitrile (15% v/v) solution containing biphenyl and CV. (a) and (b) respectively show the decay traces recorded at 360 nm in solutions containing 1.5×10^{-2} mol dm^{-3} biphenyl in the absence and presence of 3×10^{-4} mol dm^{-3} CV. (c) and (d) respectively show the decay traces recorded at 440 nm in solutions containing 3×10^{-4} mol dm^{-3} CV in the presence and absence of 1.5×10^{-2} mol dm^{-3} biphenyl.

$$^3\text{Bip}^* + \text{CV} \rightleftharpoons {}^3(\text{Bip..CV})^* \qquad (6a)$$

$$\text{Bip} + {}^3\text{CV}^* \rightleftharpoons {}^3(\text{Bip..CV})^* \qquad (6b)$$

In order to distinguish between Eqs. (6a) and (6b), kinetic analyses of the absorption decay at 360 nm were carried out by keeping the [CV] constant at 3×10^{-4} mol dm^{-3} and varying the [Bip] from 5×10^{-3} to 4×10^{-2} mol dm^{-3}. The values of k_{obs} did not show significant dependence on [Bip],

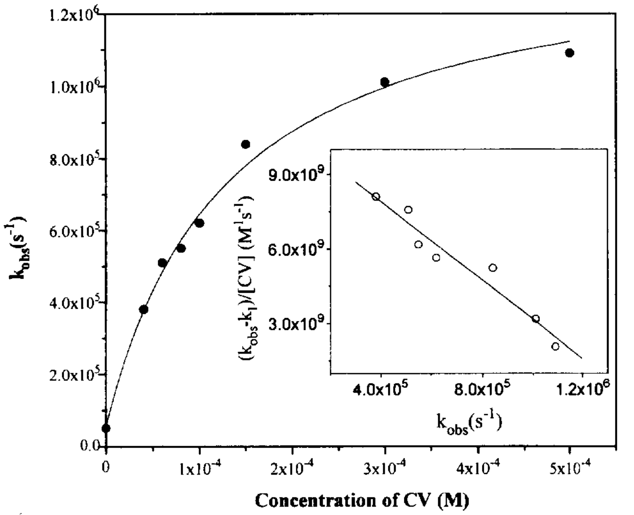


Fig. 3. Decay of biphenyl triplet (k_{obs}) obtained at 360 nm in deoxygenated solution containing 1.5×10^{-2} mol dm^{-3} biphenyl with varying concentrations of CV (●). The solid line represents the calculated curve generated according to Eq. (14). Inset shows the linear plot obtained as per Eq. (15).

confirming that the complex formation takes place between ^{3}Bip* and the ground state CV molecules as represented in Eq. (6a). By separate ground state absorption measurements we have verified that under the experimental conditions employed by us, there was no ground-state complex formation either between biphenyl and CV or between benzene and CV.

Systematic studies on triplet exciplex formation between aromatic ketones and alkyl amines have been reported in a recent series of communications in Refs. [19–22]. Following the exciplex formation equilibrium, electron transfer and H atom transfer reactions have also been studied. The presence of substituted amino groups in the TPM dye might be a factor in facilitating the formation of exciplex with aromatic compounds having $\pi\pi^*$ excited states, as in the case of crystal violet and biphenyl.

The triplet exciplex formed according to Eq. (6a) might decay by electron transfer and energy transfer processes as follows:

$$^3(\mathrm{Bip..CV})^* \rightarrow \mathrm{Bip}^{\cdot+} + \mathrm{CV}^{\cdot} \quad (7a)$$

$$\rightarrow \mathrm{Bip}^{\cdot-} + \mathrm{CV}^{\cdot+} \quad (7b)$$

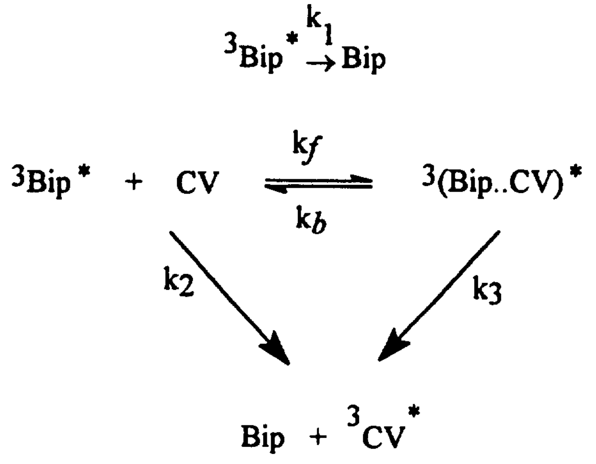
$$\rightarrow \mathrm{Bip} + {}^3\mathrm{CV}^* \quad (7c)$$

In our previous work on aqueous solutions of CV we have characterised the above CV$^{\cdot}$ and CV$^{\cdot+}$ transients arising from CV (Eqs. (7a) and (7b)) [3,4,9]. The CV$^{\cdot}$ radical (λ_{max} at 380 nm) decayed by a second-order process with a dimerisation rate constant ~ 10^8 dm^3 mol^{-1} s^{-1}. However, in the present system, the decay of the slower component (> 8 μs), monitored at 410 nm as well as 440 nm, was found to follow a first-order kinetics. Assuming that the mode of the radical decay would not alter with the change of solvent from water to benzene, electron transfer formation of CV$^{\cdot}$ according to reaction (Eq. (7a)) appears to be unlikely. Further, Gould et al. have reported the absorption spectrum of the biphenyl radical cation, Bip$^{\cdot+}$ with λ_{max} at 670 nm and ε_{max} ~ 1.5×10^3 dm^3 mol^{-1} cm^{-1} in acetonitrile [23]. However, no significant transient absorption was detected in our work in the 670 nm region, where solutions under study have no ground-state absorptions. Considering Eq. (7b), it is known that both CV$^{\cdot+}$ and Bip$^{\cdot-}$ have absorptions at ~650 nm [4,9,24]. But as stated above we did not observe any absorptions in this region. Hence Eq. (7b) can also be ruled out. These results led us to the conclusion that energy transfer process, according to Eq. (7c) would be an important channel for the exciplex decay with the concomitant formation of the ^{3}CV*. The various kinetic processes subsequent to ^{3}Bip* formation and leading up to the ^{3}CV* build-up, can be represented by Scheme 1.

At 1.5×10^{-2} mol dm^{-3} Bip, the formation of ^{3}Bip* by energy transfer from ^{3}Bz* according to Eq. (3) would be completed in ~ 10^{-7} s (rate constant ~ 10^{10} dm^3 mol^{-1} s^{-1}) [17]. In the time-resolved spectra, Fig. 1b represents all the species present at 1 μs, according to Scheme 1. However, the absorbance growth and decay profile at 440 nm (Fig. 2a) where ^{3}Bip* absorption would be small, indicates that the formation of the exciplex is complete by 1 μs after the electron pulse. Therefore, it is reasonable to assign the spectrum in Fig. 1b essentially to the triplet exciplex species ^{3}(Bip..CV)*.

3.2. Kinetic analysis of the decay curves

Scheme 1 is kinetically similar to that involving the interaction between excited triplet state of Chloroindium (III) tetraphenyl porphyrin and methyl viologen (MV^{2+}), studied by Hoshino et al. in methanolic solutions [19]. The experimental values for k_1 and the variation of k_{obs} with [CV] could be utilised for estimating the values of the equilibrium constant, K (k_f/k_b), and other parameters, with certain reasonable assumptions, as given below.



Scheme 1.

Under the equilibrium condition and assuming that establishment of equilibrium is faster than the rates of other decay channels [25], K can be given by

$$K=\frac{k_{\mathrm{f}}}{k_{\mathrm{b}}}=\frac{[\mathrm{Ex}]}{[\mathrm{B}][\mathrm{CV}]} \tag{8}$$

where [Ex] and [B] are the concentration of the triplet exciplex and biphenyl triplet, respectively. At all the concentrations of CV employed for studying the kinetics, the ^{3}CV* decay was found to be slow enough that it could be neglected in comparison with the faster decay of the triplet exciplex. At any time t, the 360 nm absorbance along the decay curves (as represented by Fig. 2b) would be the sum of the absorbance due to the ^{3}Bip* (A_{B}), the exciplex (A_{Ex}) and ^{3}CV* ($A_{^3\mathrm{CV}^*}$).

$$A=A_{\mathrm{B}}+A_{\mathrm{Ex}}+A_{^3\mathrm{CV}^*}$$

However, our kinetic analysis programme was such that the rates of absorbance build up due to ^{3}CV* formation were taken into account and subtracted from the apparent decay curves for estimating the k_{obs} values. Therefore, for the further kinetic evaluation of the k_{obs} vs. [CV] plots (see Fig. 3), A is given by Eq. (9)

$$A=A_{\mathrm{B}}+A_{\mathrm{Ex}}=\varepsilon_{\mathrm{B}}[\mathrm{B}]+\varepsilon_{\mathrm{Ex}}[\mathrm{Ex}] \tag{9}$$

where ε_{B} and $\varepsilon_{\mathrm{Ex}}$ are the molar extinction coefficients of biphenyl triplet and triplet exciplex, respectively at 360 nm.

$$\frac{\mathrm{d}A}{\mathrm{d}t}=\varepsilon_{\mathrm{B}}\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}+\varepsilon_{\mathrm{Ex}}\frac{\mathrm{d}[\mathrm{Ex}]}{\mathrm{d}t} \tag{10}$$

From Scheme 1,

$$\frac{-\mathrm{d}[\mathrm{B}]}{\mathrm{d}t}=(k_{\mathrm{f}}+k_2)[\mathrm{B}][\mathrm{CV}]+k_1[\mathrm{B}]-k_{\mathrm{b}}[\mathrm{Ex}]$$

$$\frac{-\mathrm{d}[\mathrm{Ex}]}{\mathrm{d}t}=(k_{\mathrm{b}}+k_3)[\mathrm{Ex}]-k_{\mathrm{f}}[\mathrm{B}][\mathrm{CV}].$$

Substituting the above equations in Eq. (10), we obtain

$$\begin{aligned}\frac{-\mathrm{d}A}{\mathrm{d}t}&=\{k_1\varepsilon_{\mathrm{B}}+k_{\mathrm{f}}(\varepsilon_{\mathrm{B}}-\varepsilon_{\mathrm{Ex}})[\mathrm{CV}]+k_2\varepsilon_{\mathrm{B}}[\mathrm{CV}]\}[\mathrm{B}]\\&\quad+\{(k_3+k_{\mathrm{b}})\varepsilon_{\mathrm{Ex}}-k_{\mathrm{b}}\varepsilon_{\mathrm{B}}\}[\mathrm{Ex}]\end{aligned} \tag{11}$$

By using Eqs. (8) and (9), a first-order rate equation can be obtained as

$$\frac{-\mathrm{d}A}{\mathrm{d}t}=k_{\mathrm{obs}}A \tag{12}$$

where

$$k_{\mathrm{obs}}=\frac{k_1\varepsilon_{\mathrm{B}}+\{k_{\mathrm{f}}(\varepsilon_{\mathrm{B}}-\varepsilon_{\mathrm{Ex}})+k_2\varepsilon_{\mathrm{B}}+K[(k_3+k_{\mathrm{b}})\varepsilon_{\mathrm{Ex}}-k_{\mathrm{b}}\varepsilon_{\mathrm{B}}]\}[\mathrm{CV}]}{\varepsilon_{\mathrm{B}}+\varepsilon_{\mathrm{Ex}}K[\mathrm{CV}]} \tag{13}$$

Eq. (13) can be rearranged to get

$$k_{\mathrm{obs}}=\frac{k_1+\left\{k_f\left(1-\dfrac{\varepsilon_{\mathrm{Ex}}}{\varepsilon_{\mathrm{B}}}\right)+k_2+K\left[(k_3+k_{\mathrm{b}})\dfrac{\varepsilon_{\mathrm{Ex}}}{\varepsilon_{\mathrm{B}}}-k_{\mathrm{b}}\right]\right\}[\mathrm{CV}]}{1+\dfrac{\varepsilon_{\mathrm{Ex}}}{\varepsilon_{\mathrm{B}}}K[\mathrm{CV}]} \tag{14}$$

Values of ε_{B} are known to be solvent-dependent, being 27 100 and 42 000 dm^3 mol^{-1} cm^{-1} in benzene and cyclohexane, respectively [26]. However, in solutions without added CV, we found that the end of pulse absorbances due to ^{3}Bip* did not change significantly between neat Bz and Bz–ACN solvents. Since the actual ε_{B} value could be somewhat uncertain in the Bz–ACN mixture, we have used the ratio $\varepsilon_{\mathrm{Ex}}/\varepsilon_{\mathrm{B}}$ with reasonable assumption that at 3×10^{-4} mol dm^{-3} [CV], essentially all the ^{3}Bip* would react with [CV], the ratio $\varepsilon_{\mathrm{Ex}}/\varepsilon_{\mathrm{B}}$ at 360 nm was obtained as 0.44 from absorption spectra shown in Fig. 1a and b. Thus Eq. (14) is rearranged as

$$\begin{aligned}\frac{k_{\mathrm{obs}}-k_1}{[\mathrm{CV}]}&=0.56k_{\mathrm{f}}+k_2+K[0.44(k_3+k_{\mathrm{b}})-k_{\mathrm{b}}]\\&\quad-0.44Kk_{\mathrm{obs}}\end{aligned} \tag{15}$$

We estimated the value of k_1 for the self-decay of ^{3}Bip*, in the absence of added CV, from the absorbance decay at 360 nm and obtained $k_1=5.2\times10^4$ s^{-1}. A plot of $(k_{\mathrm{obs}}-k_1)/$[CV] vs. k_{obs} is shown in the inset of Fig. 3. From the slope of the linear plot, K, the equilibrium constant for the above reaction, is obtained as 1.8×10^4 dm^3 mol^{-1}. The value of the intercept for the plot is 1.1×10^{10} dm^3 mol^{-1} s^{-1}. The solid line in Fig. 3 shows the curve generated by substituting the value of slope and intercept in Eq. (14). As can be seen from the figure the agreement between the observed and calculated curves for the proposed exciplex mechanism is quite satisfactory.

The full growth of the exciplex in microsecond time scales at the micromolar concentrations of CV shows that the forward reaction between ^{3}Bip* and CV is fast enough to be considered as diffusion limited. Thus, taking $k_{\mathrm{f}}=10^{10}$ dm^3 mol^{-1} s^{-1}, k_{b} is estimated to be 5.5×10^5 s^{-1}. By substituting these values in the parameters for the intercept of the plot in the inset of Fig. 3, the limiting values for k_2 and k_3 have been estimated as $k_2<1.1\times10^{10}$ dm^3 mol^{-1} s^{-1} and $k_3<1.4\times10^6$ s^{-1}.

3.3. Other π–π triplet sensitisers*

We have explored the possibility of exciplex formation between other $\pi\pi^*$ triplet sensitisers and CV, by taking *p*-terphenyl and anthracene, respectively, in place of biphenyl. It was interesting to observe that in both the cases, the profiles of absorbance growth and decay as well as time-resolved spectra were quite indicative of the exciplex formations preceding the growth of ^{3}CV*, very similar to the case of biphenyl triplet state as the sensitiser.

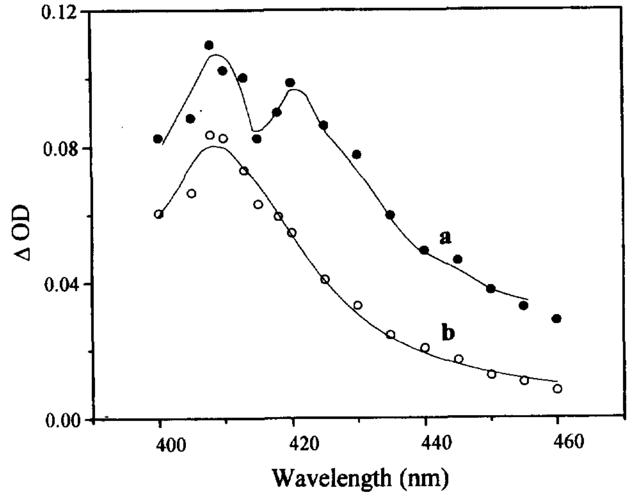


Fig. 4. (a) and (b) are the transient absorption spectra recorded in deoxygenated solutions containing 1.5×10^{-2} mol dm^{-3} p-terphenyl and 3×10^{-4} mol dm^{-3} CV at 1 μs and 8 μs after the electron pulse respectively. Dose per pulse = 15.8 Gy.

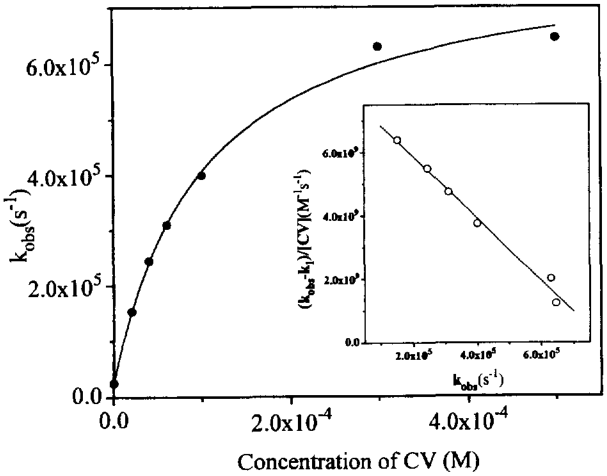


Fig. 5. Decay of p-terphenyl triplet (k_{obs}) obtained at 440 nm in deoxygenated solution containing 1.5×10^{-2} mol dm^{-3} p-terphenyl with varying concentrations of CV (●). The solid line represents the calculated curve generated according to Eq. (14). Inset shows the linear plot obtained as per Eq. (15).

The time-resolved spectra recorded at 1 μs and 8 μs, respectively in the solutions containing p-terphenyl (1.5×10^{-2} mol dm^{-3}) and CV (3×10^{-4} mol dm^{-3}) are given in Fig. 4. The inset of the figure shows the faster absorbance decay, near the λ_{max} of ^{3}Tp* ($\lambda_{max}=460$ nm [26]) and the build-up of the longer lived ^{3}CV*. The spectra in Fig. 4a and b could be attributed to the exciplex species ^{3}(Tp..CV)* and ^{3}CV*, respectively. In the Tp–CV system, we did not observe any signal due to either p-terphenyl cation or CV cation at 640 nm. Thus, it appears that any intramolecular electron transfer process within the exciplex is absent and Scheme 1 properly represents the consequence of the interaction between ^{3}Tp* and CV. The results from the runs conducted for obtaining the kinetic parameters are given in Fig. 5. The rate constant k_1 for the decay of ^{3}Tp* without CV, was estimated as 7.8×10^4 s^{-1} by monitoring at 440 nm. On treating the data by Eqs. (9)–(15), the values of $K=1.53\times10^4$ dm^3 mol^{-1}, $k_2<6.5\times10^9$ dm^3 mol^{-1} s^{-1} and $k_3<9.2\times10^5$ s^{-1} have been obtained.

Figs. 6 and 7 show the results obtained by replacing biphenyl or p-terphenyl with anthracene. By similar arguments as in the case of the former two sensitisers, it becomes clear that Scheme 1 represents the exciplex formation and subsequent reaction channels in the anthracene–CV system as well. Thus, Fig. 6a and b corresponds to the spectrum of ^{3}(An..CV)* and ^{3}CV*, respectively. It may be noted that owing to considerable ground-state absorption by anthracene, spectra could not be recorded below 390 nm. By treating the data as in the previous cases and using $k_1=2.5\times10^4$ s^{-1}, we

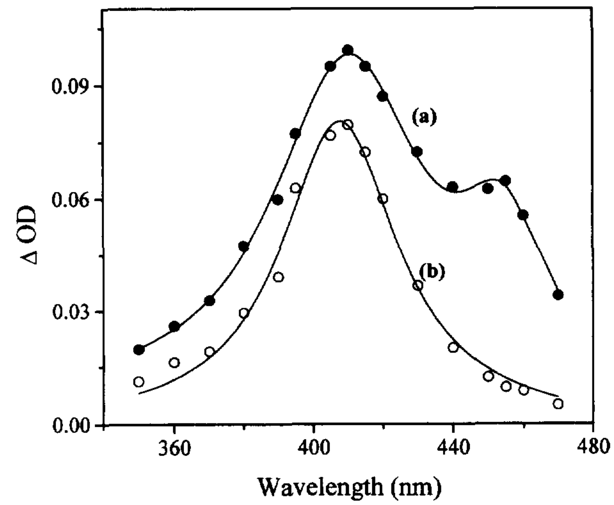


Fig. 6. (a) and (b) are the transient absorption spectra recorded in deoxygenated solutions containing 1.5×10^{-2} mol dm^{-3} anthracene and 3×10^{-4} mol dm^{-3} CV at 1 μs and 8 μs after the electron pulse, respectively. Dose per pulse = 15.8 Gy.

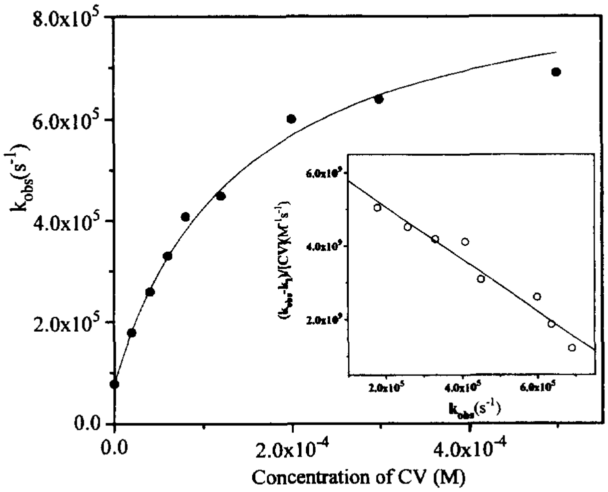


Fig. 7. Decay of p-terphenyl triplet (k_{obs}) obtained at 430 nm in deoxygenated solution containing 1.5×10^{-2} mol dm^{-3} anthracene with varying concentrations of CV (●). The solid line represents the calculated curve generated according to Eq. (14). Inset shows the linear plot obtained as per Eq. (15).

obtained the following values: $K = 1.32 \times 10^4$ dm^3 mol^{-1}, $k_2 < 7.85 \times 10^9$ dm^3 mol^{-1} s^{-1}, $k_3 < 7.98 \times 10^5$ s^{-1}.

Some experiments were done using fullerene C_{60} as an acceptor ($E_T = 36$ kcal mol^{-1}) of triplet energy from CV ($E_T = 39$ kcal mol^{-1}). Concentrations of C_{60} and CV are adjusted so that energy should cascade from $^3Bz^*$ to $^3CV^*$ to $^3C_{60}^*$ (equivalent to Eqs. (3) and (4)). No formation of $^3C_{60}^*$ absorption with λ_{max} at 740 nm was seen. Instead, the decay of the transient absorption at 410 nm (due to $^3CV^*$) became much faster followed by a slow one as mentioned in the case of other polyphenyl sensitiser triplets. It is tempting to think that an exciplex species, similar to that observed in the studies described above may be formed involving $^3CV^*$ and C_{60}, i.e., $^3(CV..C_{60})^*$. However, when the slow decaying component was followed up to 2 ms, we could not observe any signal that could be attributed to species like $CV^{\cdot+}$ and $C_{60}^{\cdot-}$ or $CV^{\cdot-}$ · and $C_{60}^{\cdot+}$ or even $^3C_{60}^*$ [27]. It appeared that should exciplex get formed, it would decay to form the separated ground-state molecules, i.e., $^3(CV..C_{60})^* \rightarrow CV + C_{60}$. Alternately, an incomplete energy transfer from $^3CV^*$ to C_{60} at the concentrations used and lower ε value of $^3C_{60}^*$ could be responsible for the apparent lack of adequate signals. These aspects are being looked into in detail.

4. Conclusions

By employing pulse radiolysis technique, the formation of triplet state of a triphenyl methane dye, crystal violet, is investigated using energy transfer from triplets of typical polyaromatic molecules (e.g., biphenyl, *p*-terphenyl, anthracene) which in turn are formed from the triplets of solvent benzene. The spectral and kinetic behaviour in the decay of the sensitiser triplets in the presence of CV can be explained on the basis of formation of an intermediate triplet exciplex between the sensitiser triplet state and CV,

$$\left({}^3S^* + CV \underset{k_b}{\overset{k_f}{\rightleftharpoons}} {}^3(S..CV)^* \right),$$

in addition to direct energy transfer. The exciplex then decays forming triplet state of CV. Detailed kinetic analysis for the above reaction scheme has been worked out and the equilibrium constant for the exciplex formation and other kinetic parameters involved in the proposed scheme have been estimated.

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