Journal of Photochemistry and Photobiology A: Chemistry 143 (2001) 17–21

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Interaction of triplet state of crystal violet with fullerene C_{60}

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Received 23 February 2001; received in revised form 8 May 2001; accepted 10 May 2001

Abstract

Interaction of fullerene C_{60} with triplet state of triphenyl methane dye crystal violet ($^3CV^{+*}$) has been studied by the pulse radiolysis technique. It is found that the $^3CV^{+*}$ is quenched by C_{60}. The resulting transient spectrum in the near IR region shows absorption peak at 1140 nm, which differs from that of anion radical of C_{60} and has been attributed to the exciplex between CV^+ and C_{60}. Addition of polar solvent does not seem to break this exciplex to give separated radical ions $CV^{\bullet 2+}$ and $C_{60}{}^{\bullet -}$. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fullerene C_{60}; Triphenyl methane dye; Pulse radiolysis

1. Introduction

Photoinduced electron transfer (PET) between fullerene C_{60} and suitable amine donors has been the subject of several studies [1–8]. The reduction potential of C_{60} (−0.33 V versus Ag/AgCl in benzonitrile) makes the fullerene a good electron acceptor [9]. A variety of interesting interactions between fullerenes and amine donors have been observed both in the electronic ground and excited state [6–8,13–17]. In the ground state, C_{60} forms weak charge transfer complexes with amines like dimethyl aniline (DMAN), diethyl aniline (DEAN), diphenyl amine (DPA), triphenyl amine (TPA), phthalocyanines, phenothiazine [5–8,13–18]. Electronically excited states, both S_1 and T_1, form exciplexes with the same amines, e.g. DMAN, DEAN in non-polar solvents like decalin, toluene, etc. [13,14,18]. In some cases, however, electron transfer reactions are seen resulting in complete charge separation [4]. In the case of complexes of C_{60} with DMAN and DEAN, it was found that a radical ion-pair state (RIPS) giving charge transfer emission is also formed [18]. Ito et al. have observed that the ET from the donor molecules to the triplet state of C_{60} would give the cation radical of the donor and the anion radical of C_{60}, i.e. ($C_{60}{}^{\bullet -}$) in a facile manner [4,5]. The $C_{60}{}^{\bullet -}$ radical anion has strong bands in the near infra red region of the spectrum at 1075,1038 and 988 nm [11,12].

Since the molecules in their electronically excited states can be better donors or acceptors, the electron transfer processes are more favoured when the reactants are in their excited state [19]. In our earlier work on the triplet state of the triphenyl methane (TPM) dye: crystal violet (CV^+), we reported that the triplet state of CV^+ ($^3CV^{+*}$) is quenched by C_{60} [20–22]. However, no triplet state of C_{60} could be observed by its absorption at 740 nm. In the present work, we take a closer look at the ET reaction between the $^3CV^{+*}$ and C_{60} molecule with the help of pulse radiolysis studies. Since crystal violet contains alkylamino groups attached to each of the three phenyl rings, it is interesting to know how its excited state interacts with the fullerene C_{60}. Recently, it is shown by Kitagawa et al. [23], that the radical $CV^\bullet$ obtained from reduction of CV^+ reacts with C_{60} to give ion-pair [CV^+ $C_{60}{}^{\bullet -}$] which can be crystallised and its properties can be studied. Our results are compared with this work.

2. Experimental

The TPM dye, crystal violet (chloride form, Sigma Chemicals), C_{60} (SES Corporation, purity >99.8%) were used as received. Solvents benzene and acetonitrile were of spectroscopic grade (spectrochem, Mumbai). Most of the experiments were done using 15% (v/v) acetonitrile as co-solvent with benzene for solubilizing the cationic dye CV^+. It is seen earlier for this solvent composition that the excited state processes would not be affected significantly as compared to those in benzene alone [20–22]. All the solutions were deoxygenated by purging with high purity N_2 (Indian Oxygen, Iolar Grade) for about 30 min. A solvent pretrap was used to minimise solvent loss and concentration changes during N_2 purging. Pulse radiolysis

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1010-6030/01/$ – see front matter
PII: S1010-6030(01)00474-9

experiments were carried out using electron pulses from a 7 MeV electron accelerator. The details of the set-up have been described earlier [24–26]. Solutions in 1 cm path length suprasil cells were irradiated by 500 ns electron pulses at a radiation dose of ~40 Gy per pulse as measured by air saturated KCNS dosimeter, taking Ge for $CNS_2^{\bullet -}$ as 21,522 $dm^3\,mol^{-1}\,cm^{-1}$ at 500 nm [27]. The transient optical absorption was monitored by a kinetic spectrophotometric arrangement using a pulsed 450 W xenon lamp (Kratos) as an analysing light source. Two detection systems were used, i.e. a UV–VIS-monochromator (Kratos GM-252) and photomultiplier (Hamamatsu-R-928) in the region <800 nm and CVI CM-110 monochromator with NIR grating, a photodiode (Thorlabs Inc. PDA 55, bandwidth 10 MHz) for the region above 800 nm. Both the monochromators were suitably calibrated for the wavelength read out. The signals were read on a digital oscilloscope (100 MHz, L & T Gould Model 4072) and transferred to a PC for further kinetic and spectral analysis.

3. Results and discussion

Radiolysis was used as a source for producing triplet states benzene (Bz), which by energy transfer generate the triplet states of the substrate molecules (S) used for study.

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

$${}^1Bz^* \rightarrow {}^3Bz^* \qquad (2)$$

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

Since ${}^3Bz^*$ has a higher energy (E_T ~82 kcal/mol) than most of the molecules, energy transfer process is facile. By this approach triplet states of several molecules, including that of the TPM dye CV^+, have been generated and their properties have been characterised [22,28]. Cascade energy transfer processes have also been studied to obtain better yields of the solute of choice, e.g. biphenyl (Bip).

$${}^3Bz^* + Bip \rightarrow {}^3Bip^* + Bz \qquad (4)$$

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

In our attempts to study the quenching of ${}^3CV^{+*}$ (E_T = 39 kcal/mol) by energy transfer to fullerene C_{60} (E_T = 36 kcal/mol), it was seen that although the decay of ${}^3CV^{+*}$ is accelerated in the presence of C_{60}, the characteristic absorption peak due to ${}^3C_{60}{}^*$ at 740 nm does not grow. It was conjectured that an exciplex between C_{60} and CV^+ may have been formed similar to the exciplexes between CV^+ and aromatic molecules like biphenyl, terphenyl and anthracene or other amines mentioned above [20,21]. Hence, the present series of experiments was carried out to probe the reactions using the near infrared absorption of the products.

When solutions of CV^+ (1.6×10^{-3} mol dm^{-3}) were irradiated with 500 ns electron pulse, transient absorption due to the ${}^3CV^{+*}$ was seen at 420 nm. Mixtures of CV^+ and C_{60} absorb light in almost the entire wavelength region of 200–630 nm except a small window region around 430 nm, where the triplet state of CV^+ shows absorption. On progressive addition of C_{60}, to these solutions, it is seen that the 420 nm peak decreases and the initial rate of decay of the ${}^3CV^{+*}$ becomes faster. (Fig. 1, curves 1, 2, and 3). In the latter portion of the trace, the absorption decays slowly and is comparable to that of ${}^3CV^{+*}$ without C_{60}. Signature of the product formation from the interaction of ${}^3CV^{+*}$ with C_{60} was seen as a transient growth in the 1140 nm region. It is seen that the decay at 420 nm and the growth at 1140 nm well match. Fig. 2 shows the transient absorption spectrum recorded at 1 and 10 μs after the electron pulse in the visible and NIR region in a deaerated benzene–acetonitrile (15%v/v) solution containing CV^+ (1.6×10^{-3} mol dm^{-3}) and C_{60} (1×10^{-4} mol dm^{-3}). The spectra show an absorption peak at 420 nm due to ${}^3CV^{+*}$ and another broad absorption band having peak at 1140 nm with shoulder bands at 1098, 1052 and 1000 nm. Notable feature of the spectra is the absence of 740 nm absorption peak due to the ${}^3C_{60}{}^*$ [6,7], indicating the absence of a simple T–T energy transfer. Interestingly, the observed spectrum with peak at 1140 nm does not match with that of anion radical of C_{60}, i.e. $C_{60}{}^{\bullet -}$ at 1075, 1038 and 988 nm [2–4,10–13]. However, the shape of the spectrum shows some similarity with that of the anion radical. Triplet states of CV^+ were also generated through benzene–biphenyl route [22,28]. The solute concentrations in the solution were suitably adjusted so that

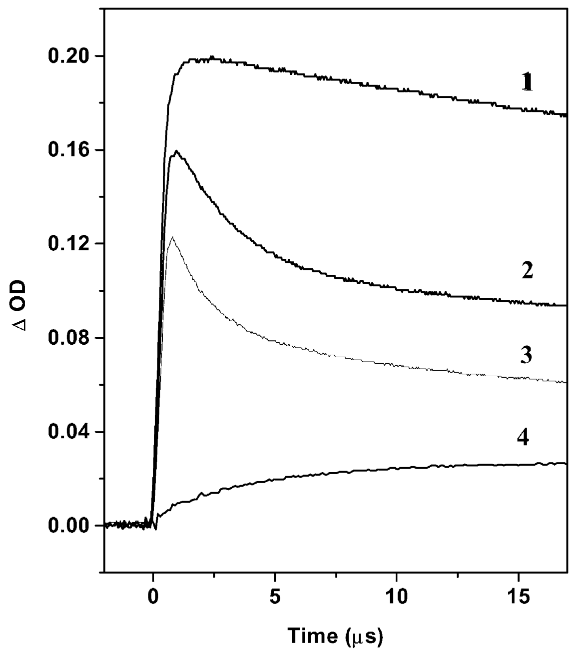


Fig. 1. Kinetic traces recorded at 420 nm in N_2 saturated benzene-acetonitrile solutions (15%) containing 1.6×10^{-3} mol dm^{-3} CV^+ and (1) none C_{60}, (2) 50×10^{-6} mol dm^{-3} C_{60}, (3) 100×10^{-6} mol dm^{-3} C_{60}. Trace 4 represents growth of transient absorption at 1140 nm in the solution containing 100×10^{-6} mol dm^{-3} C_{60}.

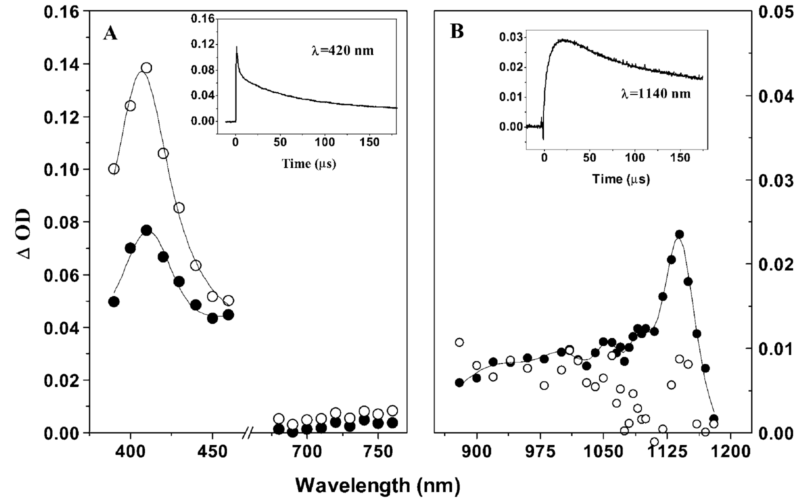


Fig. 2. Transient absorption spectra obtained in N_2 saturated benzene-acetonitrile (15%) containing 1.6×10^{-3} mol dm^{-3} CV^+ and 100×10^{-6} mol dm^{-3} C_{60} at 1 μs (○) and 10 μs (●) after the electron pulse. Inset of A shows the decay in this solution at 420 nm and inset of B shows decay at 1140 nm.

the triplet energy would cascade from benzene to biphenyl to CV^+ (Reactions 4, and 5). In this case, the longer triplet lifetime of biphenyl enhances the yield of $^3CV^{+*}$ [22]. The enhancements in the absorbency were readily seen as shown in Fig. 3. The kinetic growth profile recorded at 1140 nm in the above solution is given in the inset of Fig. 3 for comparison.

These observations suggest that the electron transfer reaction

$$^3CV^{+*} + C_{60} \rightarrow CV^{\bullet 2+} + C_{60}{}^{\bullet -} \quad (6)$$

does not take place in the present system. The reaction of the reduced radical of CV^+ with C_{60} proceeds by ET mechanism (Reaction 7) as shown by Kitagawa et al. [23] and the resulting products have been isolated as micro-crystals in the form of an ion-pair.

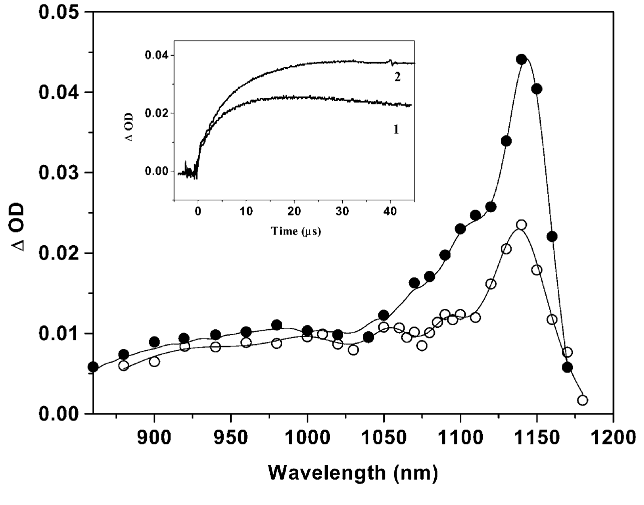


Fig. 3. Transient absorption spectra recorded in N_2 saturated benzene-acetonitrile (15%) solutions containing A (○): 1.6×10^{-3} mol dm^{-3} CV^+ and 100×10^{-6} mol dm^{-3} of C_{60} and B (●) 20×10^{-3} mol dm^{-3} biphenyl, 1×10^{-3} mol dm^{-3} CV^+ and 50×10^{-6} mol dm^{-3} C_{60}. The absorption values are taken at the maximum growth (10 μs). Inset: kinetic traces recorded at 1140 nm in the above solutions A (1) and solution B (2).

$$CV^{\bullet} + C_{60} \rightarrow CV^+ + C_{60}{}^{\bullet -} \quad (7)$$

To identify the nature of the transient absorbing at 1140 nm we have carried out experiments at varying polarity of the solvent by varying the ACN concentration from 10 to 45% (v/v). Under such conditions, if the absorption is due to an ion-pair, the same should increase with increase in polarity of the medium as its yield increase. On the other hand, if the absorption is due an exciplex, it should dissociate to give ion-pair. It is seen that with changing the solvent polarity the overall spectrum in the NIR region does not change significantly, however, the decay rates are affected. Fig. 4 shows the decay of the OD at 1140 and 1075 nm as a function of ACN concentration. It is seen that the decay of the transient absorption becomes faster at 1140 nm, indicating that the transient dissociates at higher polarity. From these observations the species absorbing at 1140 nm could be attributed to the formation of exciplex between CV and C_{60}.

$$^3CV^{+*} + C_{60} \rightarrow [CV^+ \cdots C_{60}]^* \quad (8)$$

The curves (1) and (2) for the growth of absorbency given in the inset of Fig. 3 confirmed to first-order kinetics with the pseudo first rate constant k_{pseudo} as 2.2×10^5, and 1.2×10^5 s^{-1}, respectively. From this the bimolecular rate constant for the Reaction 8 is evaluated as $\sim 2.0 \times 10^9$ dm^3 mol^{-1} s^{-1}.

As the polarity of the medium increases the exciplex becomes unstable and breaks. Some exciplexes of C_{60} are already known [14,15,18]. Since the life time of the transient is long (>10 μs), the proposed exciplex would have a spin multiplicity of three (i.e. triplet) and it might undergo decomposition by following channels:

$$[CV^+ + C_{60}]^* \rightarrow CV^+ + C_{60} \text{ (dissociation)} \quad (9)$$

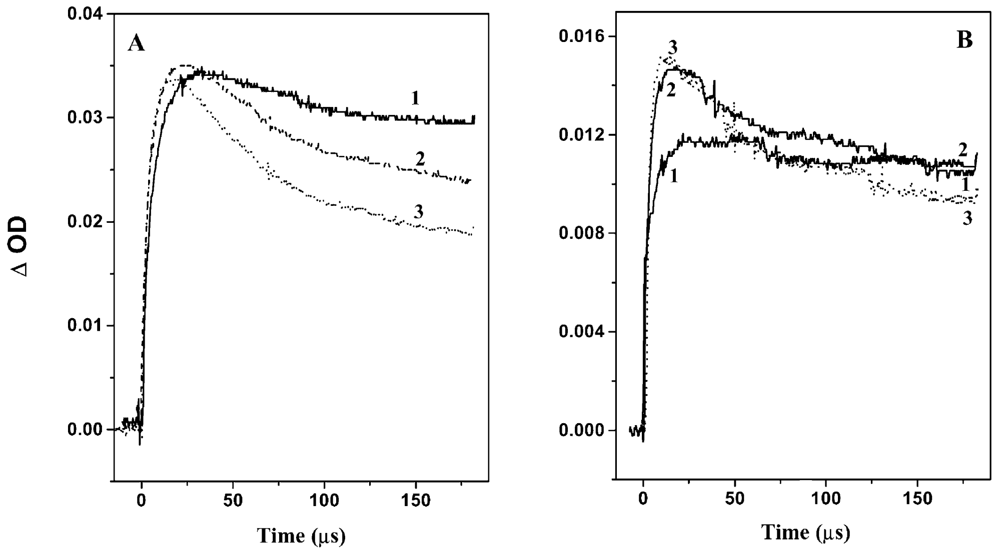


Fig. 4. Kinetic traces showing the decay of the transient A at 1140 nm and B at 1075 nm with varying concentrations of acetonitrile (v/v): (1) 10%; (2) 20%; (3) 45%.

$$[CV^+ + C_{60}]^* \rightarrow CV^+ + C_{60} + h\nu \text{ (phosphorescence)} \quad (10)$$

$$[CV^+ + C_{60}]^* \rightarrow CV^{\bullet 2+} + C_{60}^{\bullet -} \text{ (ion separation)} \quad (11)$$

Since the exciplex is likely to have a triplet character, the emission should be phosphorescence. However, attempts to monitor emission were not successful, probably as the excited states of both CV^+ and C_{60} are poor emitters.

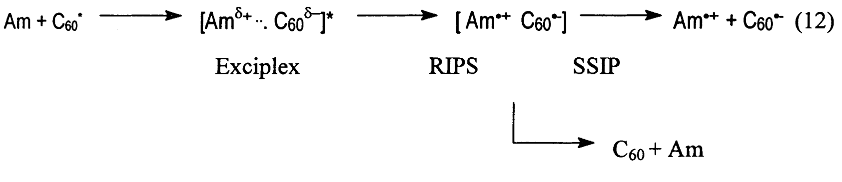
Usually, as the polarity increases, contribution to the ion separation process increases and hence the concentration of the anion radical should increase. This was not very apparent from the results. Fig. 4B is indicative of such change. Another possibility is that the exciplex has much higher absorptivity than that of the anion radical. In such a case, the dissociation of the exciplex gives the radical ion but the process is reflected as a decrease of absorption with time as seen in Fig. 4B. It was not possible to evaluate the molar absorbency of the exciplex due to uncertainties in the T–T energy transfer efficiencies. However, careful observations ~1075, 1038 and 988 nm did not support the formation of $C_{60}^{\bullet -}$ from the decay of 1140 nm absorptions, in the higher polarity matrix. Therefore, in our opinion such ion separation process represented by Eq. (11) does not occur significantly.

Recently it was found [18] that the exciplex between C_{60} and DMAN and DEAN reorganises to give another state called RIPS. The latter can revert back radiatively or non-radiatively to the respective ground state molecules or undergo ion-separation to give solvent separated ions (Reaction 12) where, 'Am' is the amine donor and SSIP is the solvent separated ion pair. Usually the ground state charge transfer complexes on photoexcitation give the RIP state while the interaction between the excited state of donor/acceptor or acceptor/donor yields the exciplex. Using this model in the present case it can be proposed that on increasing the solvent polarity i.e. addition of acetonitrile, the exciplex $[CV^{\delta +} \cdots C_{60}{}^{\delta -}]^*$ undergoes further charge transfer to give the RIP state. The absorption spectra of both the exciplex and the RIPS seem to be similar. The faster decay of absorption of absorption at higher polarity can be attributed to the recombination in the RIPS to give ground state CV^+ and C_{60} as shown in Reaction 12. It was not possible to increase the polarity further due to the solubility restrictions and without affecting the radiolytic processes drastically.

Another possibility is that as complete charge separation is not achieved on increasing the solvent polarity, the exciplex itself may be unstable and reverts back to the ground states of the reactants (Eq. (13))

$$[Am^{\delta +} \cdots C_{60}{}^{\delta -}]^* \rightarrow Am + C_{60} \quad (13)$$

Another interesting observation is the lack of exciplex formation when C_{60} is excited. In this case the energetic considerations seem to play an important role, with E_T for CV^+ is higher than that for C_{60}. Hence, with energetic triplet of CV^+ the exciplex is formed while less energetic C_{60} triplet does not seem to give the exciplex.



$$Am + C_{60}^* \longrightarrow \underset{\text{Exciplex}}{[Am^{\delta +} \cdots C_{60}{}^{\delta -}]^*} \longrightarrow \underset{\text{RIPS}}{[Am^{\bullet +}\, C_{60}^{\bullet -}]} \longrightarrow \underset{\text{SSIP}}{Am^{\bullet +} + C_{60}^{\bullet -}} \quad (12)$$
$$[Am^{\bullet +}\, C_{60}^{\bullet -}] \longrightarrow C_{60} + Am$$

(12)

In the reaction between the CV^+ and C_{60}, as reported by Kitagawa et al. [23], the charge transfer is complete and ion pair so formed (SSIP) is between a stable molecule CV^+ and long lived anion radical $C_{60}{}^{\bullet -}$, stable for hours as a radical ionic salt. In our case, the reaction between excited molecule CV^{+*} and C_{60} seems to give exciplex which at higher polarities forms a radical ion pair (RIP). Since, in the RIP, the cationic species $CV^{\bullet 2+}$ is a radical ion, the ion pair is unstable and the back electron transfer is faster.

4. Conclusions

Reaction of $^3CV^{+*}$ with fullerene C_{60} has been studied by pulse radiolysis. Although $^3CV^{+*}$ is quenched by C_{60}, as seen by reduction in the 420 nm absorption, the triplet state of the latter is not formed. Transient spectrum in the infrared region shows new absorption peak at 1140 nm with shoulders at 1098, 1052 and 1000 nm which do not match with the radical anion of C_{60}, i.e. $C_{60}{}^{\bullet -}$. It is proposed that the new absorption peaks are due to the exciplex between CV^+ and C_{60}. On increasing polarity of the medium, the 1140 nm peak decays faster, probably to give RIP ($CV^{\bullet 2+} \cdots C_{60}{}^{\bullet -}$) but complete charge separation to give $CV^{\bullet 2+}$ + and $C_{60}{}^{\bullet -}$ is not observed. Neither the exciplex nor the separated ion pair was observed when C_{60} was excited.

Acknowledgements

The authors wish to thank Mr. V. N. Rao for help in pulse radiolysis measurements with IR photodiode. Thanks are due to Dr. J.P. Mittal, Director, Chemistry and Isotope Group, BARC, for his interest in this work and encouragement.

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