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Excited states and electron transfer reactions of fullerenes

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ABSTRACT: Since the discovery of carbon clusters in the laser ablated graphite vapours, fullerenes C_{60} and C_{70} have provided a constant source of excitement for the experimental and theoretical scientists alike. Their brilliant colours in solutions and three dimensional aromaticity has fascinated the photochemists. Our group has recently characterised singlet and triplet states of fullerenes using complementary twin techniques of laser flash photolysis and electron pulse radiolysis. Singlet - singlet (S^*_1--->S^*_n) absorption spectra were studied in picosecond time domain and the rates of intersystem crossing were established. Triplet states were produced directly by photoexcitation in laser flash photolysis experiments and by energy transfer in pulse radiolysis. Triplet-triplet (T^*_1---->T^*_n) spectra were characterised and rate constants for various triplet decay channels were measured.

Fullerenes have low reduction potentials and form charge transfer (CT) complexes with good donors like aliphatic and aromatic amines. Exciting photochemical behaviour was observed on photoexcitation of the CT complexes which undergo ultrafast charge separation (CS) and charge recombination (CR) reactions. The dynamics of CS and CR reactions was studied in picosecond time scales in C_{60}-diphenylamine and C_{60}-triphenylamine systems. Using external heavy atom effect and solvent polarity variations, various steps in the CS and CR processes generating fullerene triplet on CR were elucidated.

Recent results of complexing fullerenes with suitable hydrophilic cage like γ-cyclodextrin (CD) making C_{60} water soluble will also be presented. Excited state behaviour of fullerene complex in CD cage would be discussed.

INTRODUCTION

The discovery of carbon clusters C_{60} and C_{70}, in the laser ablated graphite vapours (1,2) has provided an unending source of excitement for the theoretical and experimental scientists alike (3-4). Work on the separation and characterization of higher fullerenes like C_{76},C_{84},C_{96} etc is being persued vigorously (5). The brilliant colours of fullerenes in solutions and their three dimensional aromaticity has fascinated the photochemists. Both C_{60} and C_{70} show interesting photochemical behaviour in the solution phase. In our laboratory we have characterised the singlet and triplet states of these exciting molecules using the complementary techniques of laser flash photolysis,electron pulse radiolysis and time resolved fluorescence (6-14).

Both C_{60} and C_{70} have high electron affinity (2.4-2.6 eV) and low reduction potentials (-0.4 and -0.41 respectively) and form charge transfer complexes with suitable donor molecules like organic amines (15-17). Photoexcitation of these charge transfer complexes leads to an exciting sequence of charge separation and charge recombination processes (9,15). A new type of emissiom observed in the pulse radiolysis of C_{60} solutions of benzene containing CCl_4 is described.

Fullerenes can be complexed in the hydrophilic cages of γ-cyclodextrin and made water soluble (16,17). The photo and radiation chemical behaviour of this inclusion complex is studied in aqueous solutions (11,12,18,19). Radiolytically generated hydrated electron (e^-_{aq}) in the aqueous phase can react with C_{60} complexed in cyclodextrin cage to give anion of C_{60} (12). The work carried out in our laboratories in the above mentioned areas is reviwed in the present article.

MATERIALS AND METHODS

Synthesis, separation and purification methods for C_{60} and C_{70} have been described elsewhere (20). In some experiments fullerenes from SES Corp.USA were used after checking purity by spectroscopic methods. All solvents used were of spectroscopic grade. γ-Cyclodextrin (Sigma) was used as received. Nanosecond flash photolysis experiments were carried out on Laser Kinetic Spectrometer Model-K-347 (Applied Photophysics UK). Excitation sources were KrF and XeF excimer laser (Oxford Lasers,248nm,100mJ and 351nm, 50mJ respectively) and a nitrogen laser (Photon Technology Inc PL-2300, 337nm,1.5mJ,0.6ns). Picosecond flash photolysis experiments were carried out using higher harmonics (532,355 and 266nm) of Nd-YAG laser (Continuum USA model 501-C-10). Pump-probe spectrometer using continuum generated from the residual fundamental line and fibre optical dalay has been already described (6,7). Pulse radiolysis studies were carried out using 7 MeV, 50ns and 2μS pulses from an electron accelerator . The kinetic spectrometric arrangement for measuring transient optical absorptions has been described (10). Fluorescence measurements were carried using a time correlated single photon counting system (13,14).

RESULTS AND DISCUSSION

EXCITED STATE CHARACTERISTICS OF C_{60} and C_{70}: SINGLET STATES:

The solutions of C_{60} and C_{70} in an aromatic solvent like toluene show brilliant red and magenta colours respectively. The pump and probe transient absorption experiments by excitation of C_{60} using pico and subpicosecond laser pulses gave different life times for the singlet excited state e.g.33ps (21),660ps (22),1200ps (23) and 1400 ps (6,7).

Since the different groups used different wavelengths for excitation, the variation in the lifetimes could be due to the excitation of different excited states of C_{60}. Hence C_{60} solutions in toluene,benzene and hexane were photolysed using three higher harmonics of Nd-YAG laser namely 532,355 and 266nm, thus exciting three different electronic levels of C_{60}. The lifetimes of the singlet states were obtained following the growth of the C_{60} triplet at 740nm. We find that the singlet lifetimes do not vary by changing the wavelength of excitation. This indicates that the observed variation in the the singlet state lifetimes is related to the nature of sample separation and purification process employed. Our values of the singlet state lifetimes are very close to the fluorescence lifetime of 1.15ns (24). Nadtochenko et al (25) recently reported a value of 830 ps which is somewhat lower than this value.

Similarly for the singlet state lifetime of C_{70} a value of 450+50 ps was obtained by us by excitation at 532 nm. This value is smaller than 770 ps obtained by Tanigaki et al (22) but higher than 115 ps reported by Wasielewski et al (21). A fluorescence lifetime of 640 ps has been measured for C_{70} (24).

The intersystem crossing (ISC) rates are high and almost unity for both the fullerenes. The fluorescence from C_{60} is extremely weak while that of C_{70} is weak in solution phase (24,26).

TRIPLET STATE: The triplet state of the fullerene was generated by both radiolytic and photolytic means. Photoexcitation of the fullerene gives singlet excited state (C_n^{*1}) which on ISC gives the triplet (C_n^{*3}) excited state (Process 1 and 2)

$$C_n \longrightarrow C_n^{*1} \qquad 1)$$

$$C_n^{*1} \longrightarrow C_n^{*3} \qquad 2)$$

C_n stands for either C_{60} or C_{70}. The triplet-triplet absorption spectrum (T-T) with λ_{max} at 745nm can be conveniently monitored to study the triplet of C_{60}. The molar extinction coeficient of for the triplet was evaluated to be 15,000 $dm^3\ mol^{-1}\ cm^{-1}$ in toluene solutions of C_{60} at 745nm. The same state can be generated using the technique of pulse radiolysis by energy transfer from other suitable triplet states e.g. benzene, biphenyl etc. The radiolysis of benzene generates benzene triplets in copious amounts which in turn transfer their energy to give C_{60}^{*3} by reactions 3 and 4.

$$C_6H_6\ . \rightsquigarrow C_6H_6^{*3} \qquad 3)$$

$$C_6H_6^{*3} + C_{60} \longrightarrow C_6H_6 + C_{60}^{*3} \qquad 4)$$

Since benzene triplet states are short lived (τ=40ns) the energy transfer is not efficient and the yields are poor. To obtain better yields solute with longer triplet lifetime like biphenyl has to be used (Reactions 5 and 6).

$$C_6H_6^{*3} + \text{biphenyl} \dashrightarrow C_6H_6 + \text{biphenyl}^{*3} \qquad 5)$$

$$\text{Biphenyl}^{*3} + C_{60} \dashrightarrow \text{Biphenyl} + C_{60}^{*3} \qquad 6)$$

At suitable concentrations of biphenyl ($>10^{-2}$ mol dm^{-3}) almost all the benzene triplets are converted to biphenyl triplets which in turn transfer energy and generate C_{60} triplets. The triplet decay constants are found to be $2.1X10^4$ s^{-1} for C_{60} and for C_{70} respectively. For the self quenching ($C_{60}^{*3}+C_{60}$) and T-T annihilation processes the rate constants of $2X10^8$ and $2.3X10^9$ dm^3 mol^{-1} s^{-1} respectively, were obtained.

PHOTOCHEMISTRY OF CT COMPLEXES

Amines have low ionization potentials and C_n have good electron affinity and oxidation potentials. Hence, C_n and amines form good donor acceptor pairs for ground state CT complex formation. Complexes of C_{60} with diphenylamine (DPA), triphenylamine (TPA), triethyl amine (TEA) and DABCO are weak and have low equilibrium constants (~1 mol dm^{-3}). Photoexcitation of these complexes in their CT band by 532nm (8,9) excitation results in charge separation (CS) (Reaction 7).

$$\underset{\text{CT Complex}}{C_{60}^{\delta-} \,..\, Am^{\delta+}} \dashrightarrow \underset{\text{Singlet Ion Pair}}{{}^1[\, C_{60}^- \,..\, Am^+ \,]} \qquad 7)$$

In non polar solvent like benzene, the ion pair undergoes fast charge recombination (CR) which can result in 1) ground state of the CT complex or 2) singlet or triplet states of the individual donor or acceptor molecules. The CR in the case of TPA-C_{60} pair was found to result in good triplet yield of C_{60} while in the case of CR in DPA-C_{60} and TEA-C_{60} complexes, poor fullerene triplet yields were seen. Such a behaviour was attributed to the possibility of proton donation by DPA and TEA to C_{60} which isabsent in TPA. The ion pair formed in reaction 7 is a singlet ion pair and its ISC to triplet ion pair competes with the proton transfer route which is fast for DPA and TEA systems (Reactions 8,9)

$$^1[\, C_{60}^- \,..\, Am^+] \dashrightarrow {}^3[C^- \,..Am^+] \qquad 8)$$

$$\dashrightarrow C_{60}H + Am\,(-H) \qquad 9)$$

$$^3[C_{60}^- \,..Am^+] \dashrightarrow Am + C_{60}^{*3} \qquad 10)$$

Hence, for DPA and TEA reaction 9 dominates over reaction 8 and hence triplet yields are small. In the case of TPA the proton transfer route does not exist, ISC dominates and triplet yields are high. To prove these points external heavy atom effect was studied on the C_{60}-DPA system. In neat bromobenzene,and 20% iodobenzene in benzene it was found that the ISC rates increase and C_{60} triplet yields improve. Similarly, using deuterated DPA it was seen that C_{60} triplet yields improve since the H^+ transfer from DPA-d is slower than DPA-h. In the case of TEA -C_{60} pair it was found that the proton transfer was very fast (9).

Since TPA has no transferable proton, ISC dominates. To prove this point solvent polarity effects were carried out so as to increase the escape probability and reduce the fraction of the ions from recombining. Hence, C_{60} triplet yield was studied as a function of solvent dielectric constant (D) in the photoexcited TPA-C_{60} system. It was found that as the D increases from 2 to 24,the triplet yields reduce drastically from 0.9 to 0.3. The variation of the separated ion yield ϕ (estimated from DPA cation absorption) follows a semilogarithemic relationship with D given by Masuhara et al (Eqn 11)

$$\log(1/\phi) = a + b/D \qquad 11$$

where a and b are constants. The fitting of the data with eqn 11 confirms Onsager's ion recombination model extended by Mozumder (27).

FLUORESCENCE STUDIES ON THE CT COMPLEXES

C_{70} molecule in solutions is more fluorescent than C_{60} (26,28). Dimethylaniline (DMAN) and diethylaniline (DEAN) are known to form weak CT complexes with C_{60} (K ~0.1-0.3 $dm^3\ mol^{-1}$) but not with C_{70}. Addition of these amines changes the absorption spectrum of C_{60} much more than that of C_{70}. Interesting fluorescence behaviour was observed for C_{70}-amine system in methylcyclohexane (MCH), hexane (HX) and benzene. In benzene solutions of C_{70}, progressive addition of DMAN or DEAN quenched the C_{70} fluorescence at 700nm but no new peak appeared. Interestingly,C_{60} and C_{70} also form weak CT complex with benzene with K~ 0.2 $dm^3\ mol^{-1}$. In MCH or HX solutions of C_{70}, the addition of DMAN or DEAN quenched the fluorescence at 700nm and an additional peak appeared at 730nm and was attributed to the exciplex between C_{70} and the amine studied. The fluorescence lifetime of C_{70} was measured to be 650 ps which decreases on the addition of the amines (13,14).

NEW EMISSION OBSERVED IN PULSE RADIOLYSIS EXPERIMENTS: An interesting observation was made (29) in the pulse radiolysis studies on C_{60} ($1X10^{-4}\ dm^3\ mol^{-1}$) solutions of benzene containing CCl_4 ($3.4\ X10^{-3}\ dm^3\ mol^{-1}$). These studies were carried out to confirm the transient absorption of C_{60} cation at 640nm as seen by Hou et al (30) formed by electron transfer from C_{60} triplet to CCl_4 with exciplex as probable intermediate. An absorption peak at 740nm was seen 200ns after the 50ns electron pulse (analysing light booster on,no filter before the sample cell), which reduces and becomes negative (emission) >30μS (Fig 1). Simultaneously another absorption peak appears at 380nm in the same time scale. A peak at 640nm was seen but its origin could not be confirmed. With the booster on, when the optical cut off filters before the sample cell was changed from 450 nm to 515nm (Fig 2A,2B) the emission signal decreased. With 650nm filter only transient absorption signal is seen (Fig 2C). Similar observation was made when the booster was off Fig 2D). This clearly indicates that the analysing light is strong enough to excite the transient produced to a highly emissive state. Two probable transients are 1) exciplex between C_{60} and CCl_4 and 2) radical adduct between C_{60} and CCl_3, the latter being formed by the electron scavanging (Reaction 12)

$$e_s^- + CCl_4 \text{--------->} CCl_3^{\cdot} + Cl^- \qquad 12)$$

The adduct probably has a good absorption in 450-550nm range excitation of which produces the highly emissive species.

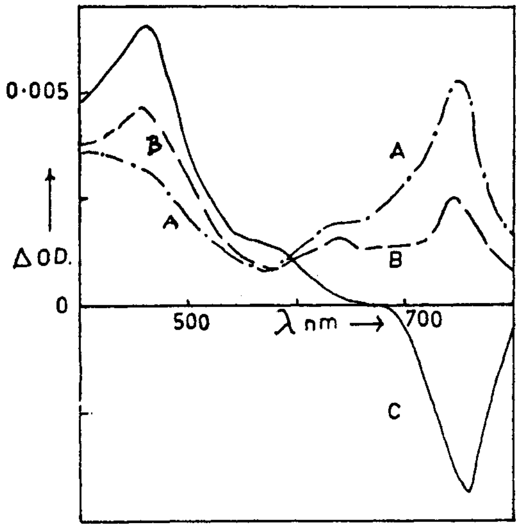

FIGURE I

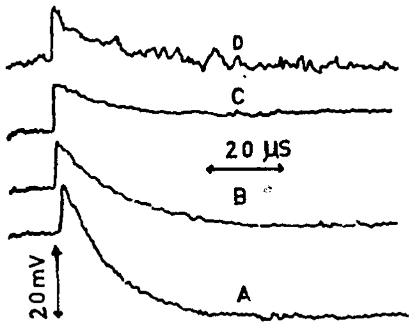

FIGURE II

Figure I: Transient spectra obtained on irradiation of C_{60} ($1X10^{-4}$ mol dm^{-3}) in benzene containing CCl_4 ($3.4X10^{-3}$mol dm^{-3}) **A:** 200ns **B:** 1μS C:30μS after 50ns electron pulse.

Figure II: Decay of transient absorption at 750nm **A:** booster on, 450nm filter **B:**booster on,515nm filter **C:** booster on,650nm filter **D:**Booster off.

STUDIES ON THE COMPLEXES WITH γ CYCLODEXTRIN

γ-Cyclodextrin is a well known host molecule with a cage diameter of ~ 0.6nm which is the right size of cavity to accomodate a guest molecule like C_{60} (18,19). The $CD:C_{60}$ inclusion complexes were prepared earlier and electrochemical and photochemical investigations have been carried out on it (31-32). The complex made by precipitation from methanolic solution was found to be a host guest inclusion complex with a molecular ratio of 2:1 $CD:C_{60}$. It was characterised using optical absorption spectra,X-ray diffraction and thermogravimetry (11-12). The complex was found to be very strong with equilibrium constant of $2.6X10^7 dm^6 mol^{-2}$. On complexation the solubility of the fullerene in water was increased to ~ $1.0\ X10^{-4}$mol dm^{-3}. From the flash photolysis studies in picosecond time scales it was found that the ISC rates are lowered in the complexed C_{60} as compared to the toluene solutions ($6X10^8$ s^{-1} as against $7.2X10^8$ s^{-1}). The molar extinction coefficient for the triplet state at 745nm is reduced from 15,000 (in toluene) to 4350 dm^3 mol^{-1} cm^{-1} and the triplet yield is reduced to 0.53 on complexation. CD-C_{60}-CD complex was found to form other weak complexes with organic amines like TEA,DABCO etc.

The CD-C_{60} complex was dissolved in aqueous solutions ($1X10^{-4}$mol dm^{-3},pH 8), flushed with N_2 and irradiated with 50ns electron pulses. The hydrated electron generated enters the CD cage, reacts with C_{60} and the anion of C_{60} is produced with transient optical absorption at 960 and 1080nm (Reaction 13)

$$e^-_{aq} + CD\text{-}C_{60} \longrightarrow CD\text{-}C_{60}^- \qquad 13)$$

The rate constant for the e_{aq} decay at 720nm was estimated to be $1.8X10^{10}$ dm^3 mol^{-1} s^{-1}

The study on aqueous solutions of C_{60} might prove useful from the point of view of photodynamic therapy and inhibiting the activity of some HIV enzymes. The photochemical investigations on fullerenes and their CT complexes are useful to their use as nonlinear optical materials.

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