

Electron-transfer and excited-state properties of radiolytically generated transients of acridine(1,8)dione dyes in an organic matrix

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Abstract

Pulse radiolysis technique has been employed to generate and investigate electron and energy transfer reactions involving acridine(1,8)dione dyes in hydrocarbons. The transient absorption spectra obtained on pulse radiolysis of N_2 -saturated solution in 1,2-dichloroethane are assigned to solute radical cation. The radical cations undergo charge transfer reaction with tetramethyl-*p*-phenylenediamine and triethyl amine. The transient absorption spectra in N_2 -saturated solution in benzene are assigned to triplet–triplet absorption. It was observed that biphenyl, *p*-terphenyl and benzophenone triplets undergo energy transfer to methyl and phenyl substituted acridine(1,8)dione dyes generating the triplets of the acceptor. With H substituted acridine(1,8)dione dye, benzophenone and chloranil triplets favor electron-transfer followed by H^+ transfer reaction forming benzophenone ketyl and chloranil semiquinone radicals respectively. © 2001 Published by Elsevier Science B.V.

Keywords: Acridine(1,8)dione; Laser dyes; Pulse radiolysis

1. Introduction

The acridine(1,8)dione dyes have gained importance in recent years due to their ability to act as efficient laser dyes with stimulated emission in the blue–green region. The lasing efficiency of these dyes is comparable to that of Coumarin-102 [1,2]. The bichromophoric structure of the dyes allows them to act as both an electron donor and acceptor [3–5]. The dyes are similar in structure to the 1,4-dihydropyridines and the biologically important β -dihyronicotinamide adenine dinucleotide (NADH) and its analogues, which are important coenzymes in biological systems [6]. The acridine(1,8)dione dyes have been shown to mimic NADH to a greater extent than the 1,4-dihydropyridines due to the tricyclic structure which is capable of protecting the enamine moiety [6]. The dyes have been used as photosensitizers in the polymerization of acrylates and methacrylates [7,8]. The electrochemical characteristics of acridine(1,8)dione dyes have been reported and the products formed by electrochemical and photochemical methods were observed to be the same [9]. One-electron oxidation and reduction of these dyes in aqueous solutions

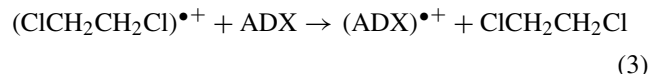
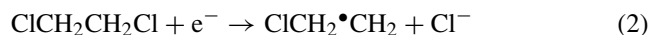
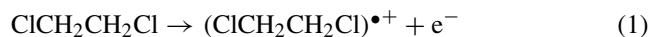
have been investigated in detail and the kinetic, spectral and redox properties are reported [5,10–13]. The photophysical studies have shown that acridine(1,8)dione dyes have high fluorescence quantum yield [14].

The photoinduced electron transfer reaction between the dyes and amines have been investigated [15]. The knowledge of spectral and kinetic properties of solute radical cation of these dyes is important to carry out redox reaction with other additives. The pulse radiolysis technique can be employed to monitor the absorption of solute radical cation and thus study the charge transfer process. Such studies are not reported in literature and with this objective, the present pulse radiolysis studies are carried out. The radiolysis of nonpolar substances such as aliphatic, alicyclic, and also halo-alkanes yields parent and free ions which can be easily used for the time-resolved study of electron transfer processes (reaction 1). The electrons produced during the radiolysis of 1,2-dichloroethane (DCE) are immediately scavenged by the solvent molecules by a dissociative electron capture process (reaction 2) thereby increasing the yield of matrix cations by preventing their geminate recombination. DCE has been employed as a solvent for the generation of solute radical cations due to its high ionization potential (11.1 eV) and formation of short-lived transient species with very little absorption at $\lambda > 300$ nm [16,17]. The ionization potential of acridine(1,8)dione dyes is in the range of 8–9 eV and therefore matrix cations can easily transfer positive charge to solute molecules (ADX) generating their radical cations

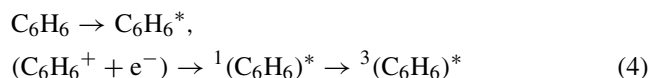
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(reaction 3).



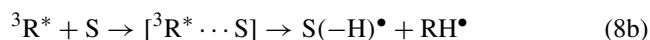
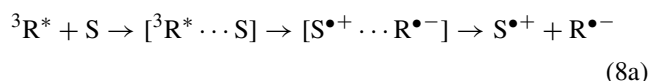
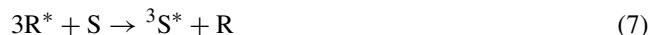
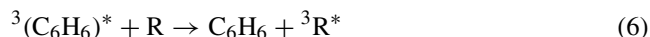
Due to extremely high mobility of ions in benzene, singlet and triplet excited states dominate. The excited triplet states are produced directly as well as via geminate ion recombination (reaction 4).



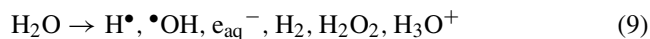
The radiolysis of benzene produces a triplet of very high energy (353 kJ mol^{-1}) in high yield [18,19]. The triplet state of benzene can transfer its energy to another solute having $E_T < 353 \text{ kJ mol}^{-1}$, thus generating the triplet of the latter. Pulse radiolysis of benzene showed absorption bands at 500 nm (singlet excimer) and 320 nm (biradical). In spite of short lifetime (3.4 ns) of benzene triplets, using a relatively high concentration of the solute (S) the benzene triplets can serve as a sensitizer for initiating the triplet–triplet energy transfer processes (reaction 5).



In presence of a second sensitizer (R) benzene triplet can also serve as sensitizer for generating solute triplets (reaction 6, 7) and subsequently initiating triplet induced electron (reaction 8a) and H^{\bullet} atom transfer (reaction 8b) processes. The pulse radiolysis technique can be conveniently used to study the triplet–triplet absorption and triplet sensitized energy and electron transfer process.



Radiolysis of aqueous solution leads to the formation of three highly reactive species (H^{\bullet} , $\bullet\text{OH}$, e_{aq}^-) in addition to the formation of less reactive or inert molecular products (H_2 , H_2O_2) [20].



The reaction of any one of these reactive species with a solute could be easily studied. While H^{\bullet} and e_{aq}^- are reducing in nature, $\bullet\text{OH}$ radicals can undergo a variety of reactions (addition, abstraction and electron transfer).

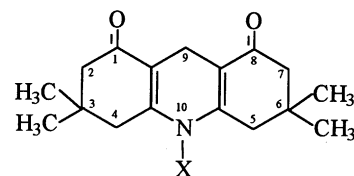
The radiolysis of a solute in a particular solvent can therefore be used to investigate any desired set of experiments and study the properties of different types of transient species generated on radiolysis. While the radiolysis in aqueous solutions has been investigated [9–13], the radiation chemical studies in organic solvents are not available in literature. With this objective, pulse radiolysis studies of acridine(1,8)dione dyes in organic solvents were carried out and are reported in this manuscript.

2. Experimental

Substituted 3,3,6,6-tetramethyl-2,4,5,7,9-decahydroacridine-1,8-dione (ADX) (Scheme 1) dyes were prepared following the procedure reported in the literature [9]. All other chemicals were of high purity and used without any further purification. Freshly prepared solutions were used in each experiment. The absorption spectra were recorded using a Hitachi 330 spectrophotometer. The fluorescence emission measurements were carried out with a Hitachi Model F-4010 spectrofluorimeter.

Pulse radiolysis experiments were carried out with high energy electron pulses (7 MeV, 50 ns) obtained from a linear electron accelerator whose details are given elsewhere [21,22]. The dose delivered per pulse was determined with aerated aqueous solution of KSCN ($1 \times 10^{-2} \text{ mol dm}^{-3}$) with $G\varepsilon = 21520 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ per 100 eV at 500 nm for the $(\text{SCN})_2^{\bullet-}$ species and it was close to 15 Gy per pulse ($1 \text{ Gy} = 1 \text{ J kg}^{-1}$) except for kinetic experiments which were carried out at a lower dose (10 Gy). The G denotes the number of species per 100 eV of absorbed energy ($G = 1$ corresponds to $0.1036 \mu\text{mol J}^{-1}$).

The transient species formed from pulse radiolysis were monitored using a 450 W pulsed xenon arc lamp, a monochromator (Kratos, GM-252), and a Hamamatsu R-955 photomultiplier as the detector. The photomultiplier output was digitized with a 100 MHz storage oscilloscope (L&T) interfaced to a computer for kinetic analysis [23]. The rate constant values were taken from that kinetic analysis for which very good correlation was obtained between



$\text{X} = \text{H}$; ADH

CH_3 ; ADMe

C_6H_5 ; ADPh

Scheme 1.

the experimental and calculated results. The bimolecular rate constant was determined from the linear regression plot of k_{obs} versus solute concentration for at least three experiments and the variation was within $\pm 10\%$. The ground state optical absorption spectra of these acridine(1,8)dione dyes in hydrocarbons showed absorption maxima in 360–380 nm with very little absorption at $\lambda > 410$ nm. Therefore, pulse radiolysis studies do not require any correction for ground state absorption in 410–700 nm region.

3. Results and discussion

3.1. Formation of radical cations

Pulse radiolysis of N_2 -saturated solution of ADH ($2 \times 10^{-3} \text{ mol dm}^{-3}$) in DCE showed the formation of transient absorption band at 420 nm with a broad band in 520–580 nm region (Fig. 1a). The entire spectrum decayed by first-order kinetics with $k = 1.2 \times 10^5 \text{ s}^{-1}$ (inset of Fig. 1, Table 1). This spectrum should be due to the formation of ADH radical cation as solvent radical cations do not absorb in this region (Fig. 1d). Similar studies have been carried out with other dyes and the spectral (Fig. 1) and kinetic parameters are shown in Table 1. The decay kinetics remained same in presence of air, thus supporting the assignment of the transient species to solute radical cation.

The confirmative evidence for the formation of solute radical cation could be obtained on charge transfer to a standard solute whose solute radical cation is well characterized. *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) is a well known reductant with absorption bands at 335, 565 and 610 nm. The charge transfer from solute radical cation to TMPD was monitored at 610 nm as other absorption bands are not suitable in the present case. The transient absorption

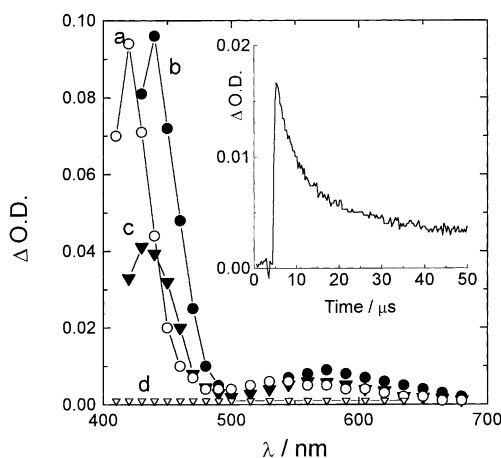


Fig. 1. Transient optical absorption spectra obtained on pulse radiolysis of N_2 -saturated solution of acridine(1,8)dione dyes in DCE. (a) ADH; (b) ADMe; (c) ADPh and (d) neat DCE, dose = 40 Gy per pulse. Inset shows absorption–time profile at 420 nm for the decay of radical cation of ADH, dose = 15 Gy per pulse.

Table 1
Kinetic and spectral parameters of radical cations of acridine(1,8)dione dyes

ADX	λ_{max} (nm)	Decay, k (s^{-1})
X = H	420, 520–580	1.2×10^5
X = Me	440, 540–600	3.7×10^4
X = Ph	430, 530–610	6.7×10^4

band, formed on pulse radiolysis of N_2 -saturated solution of ADH ($2 \times 10^{-3} \text{ mol dm}^{-3}$, $\lambda = 420 \text{ nm}$) in DCE (Fig. 2a) was observed to decay faster in presence of low concentration of TMPD ($3 \times 10^{-5} \text{ mol dm}^{-3}$) (Fig. 2b). Under these conditions, $(\text{DCE})^{\bullet+}$ would not be able to transfer its charge to TMPD directly, and $(\text{ADH})^{\bullet+}$ formed via reaction (3) would transfer its charge to TMPD (reaction 10).



The bimolecular rate constant for reaction (10), determined from the decay at 420 nm, was $4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Simultaneously, the absorption was observed to grow at 610 nm (Fig. 2c) with a rate constant value ($5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), close to the value determined from the decay at 420 nm. This confirms the cationic nature of the transient species formed in DCE.

The decay of $\text{ADH}^{\bullet+}$ at 420 nm was monitored for various concentrations of triethyl amine (TEA). It was observed to accelerate in presence of TEA (Fig. 3) and increased with increasing concentrations of TEA. The bimolecular rate constant was determined to be $3.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Ethanol, which is a relatively inefficient positive charge scavenger, accelerated the decay of $\text{ADH}^{\bullet+}$ at 420 nm only slightly and the bimolecular rate constant was determined to be $0.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The transient absorption, both in presence of TEA and ethanol, decreased

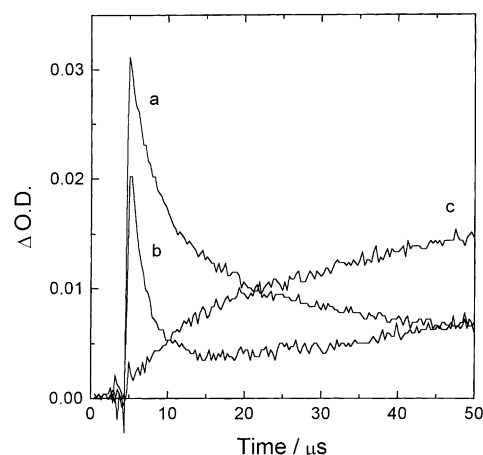


Fig. 2. Absorption–time profiles obtained on pulse radiolysis of N_2 -saturated solution of ADH ($5 \times 10^{-3} \text{ mol dm}^{-3}$) in DCE at 420 nm in (a) absence and (b) presence of TMPD ($3 \times 10^{-5} \text{ mol dm}^{-3}$) and (c) at 610 nm, dose = 15 Gy per pulse.

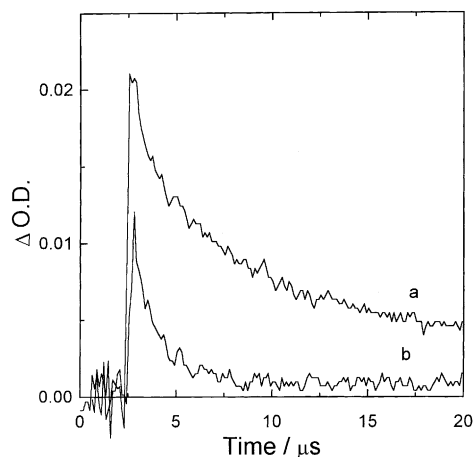
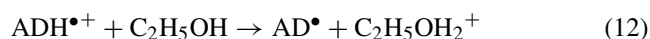
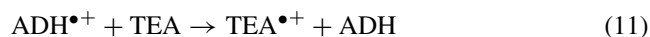


Fig. 3. Absorption–time profiles obtained on pulse radiolysis of N_2 -saturated solution of ADH ($5 \times 10^{-3} \text{ mol dm}^{-3}$, $\lambda = 420 \text{ nm}$) in (a) absence and (b) presence of TEA ($2 \times 10^{-4} \text{ mol dm}^{-3}$), dose = 15 Gy per pulse.

appreciably without formation of any new transient absorption band in 420–650 nm region. The transient absorption, which is quenched by TEA and ethanol is attributed to the solute radical cation ($ADH^{\bullet+}$).



While TEA acts as a positive charge scavenger (reaction 11), ethanol can also compete with the formation of solute radical cation and therefore can prevent the efficient formation of solute radical cation (reaction 13). Since the time resolved studies have not shown the formation of any new band, indicating that AD^{\bullet} may not be absorbing in 420–650 nm region.

3.2. Formation of triplet states

Fig. 4 shows the transient absorption spectrum obtained on pulse radiolysis of N_2 -saturated solution of ADPh ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$) in benzene, which exhibits an absorption band at 590 nm decaying by first-order kinetics with $k = 1.5 \times 10^5 \text{ s}^{-1}$ (Table 2). The absorption was quenched in aerated solution and the band may therefore be assigned to

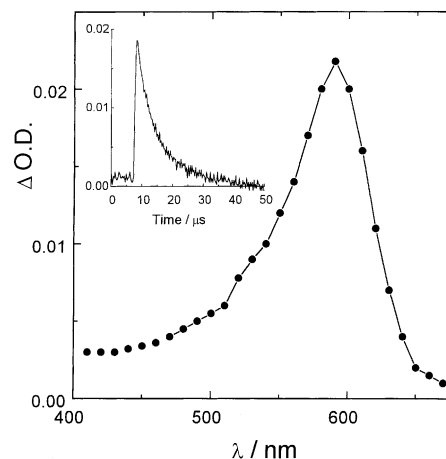


Fig. 4. The transient absorption spectrum obtained on pulse radiolysis of N_2 -saturated solution of ADPh ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$) in benzene 2 μs after the pulse. Inset shows absorption–time profile at 590 nm, dose = 15 Gy per pulse.

dye triplets formed on energy transfer from benzene triplets (reaction 14).



The bimolecular rate constant for energy transfer from benzene triplet to dye, as determined by formation kinetic studies at 590 nm was $7.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. These studies have been carried out with other acridine(1,8)dione dyes and the nature of the transient absorption spectra are shown in Figs. 5 and 6 and the kinetic parameters are shown in Table 2. The nature of the transient absorption spectrum and decay kinetics was similar in all the cases. The yield of ADH triplet (see text) was much lower than that of ADPh and ADMe (Table 2). The spectral and kinetic parameters of the transient absorption bands (Figs. 4–6) also matched with those obtained on laser flash photolysis of acridine(1,8)dione dyes in various solvents and thus support the assignment of absorption bands to triplet states [14].

3.3. Decay kinetics of triplet states

The decay kinetics of dye triplets were seen to depend on solute and initial concentration of the triplet produced on pulse radiolysis. Therefore, in addition to the normal first-order decay of the triplets to the ground state (reaction 15), other possible processes contributing to the decay might

Table 2
Kinetic and spectral parameters of the triplets of acridine(1,8)dione dyes

Dye	λ_{max} (nm)	ϵ_{max} ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	Decay, k (s^{-1})	G (triplet)	E_T (kJ mol^{-1}) ^a
ADPh	590	1.4×10^4	1.5×10^5	0.9	221.2
ADMe	610	1.1×10^4	2.1×10^5	1.1	216.1
ADH	600	–	5.5×10^5	0.1	223.7

^a From [14].

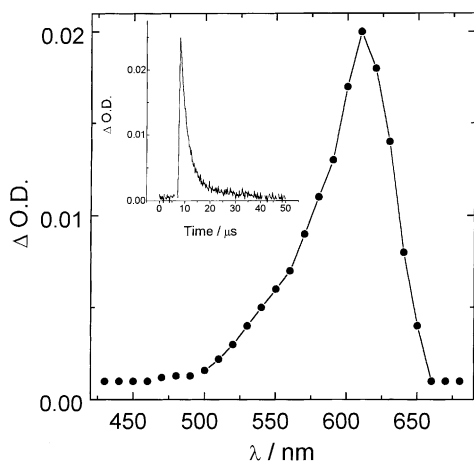
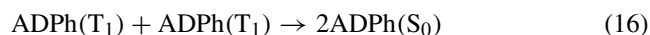


Fig. 5. The transient absorption spectrum obtained on pulse radiolysis of N_2 -saturated solution of ADMe ($1.3 \times 10^{-3} \text{ mol dm}^{-3}$) in benzene $2 \mu\text{s}$ after the pulse. Inset shows absorption–time profile at 610 nm, dose = 15 Gy per pulse.

be triplet–triplet annihilation (reaction 16) and quenching of the triplet by the ground state (reaction 17).



The self quenching rate constant (k_{TS}) for the ADPh triplet decay has been determined on monitoring its decay at 590 nm for various concentrations of ADPh (0.3 – 2.9) $\times 10^{-3} \text{ mol dm}^{-3}$ using the same low dose (11.2 Gy). The pseudo-first-order rate constant for triplet decay was observed to decrease with a decrease in the solute concentration (Fig. 7A) The quenching rate constant determined from the linear plot of k_{obs} versus solute (Fig. 7A) concentration gave

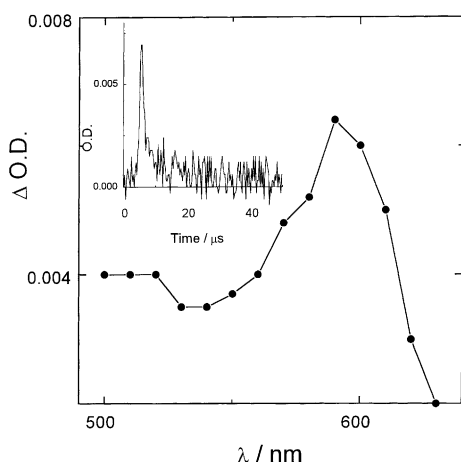


Fig. 6. The transient absorption spectrum obtained on pulse radiolysis of N_2 -saturated solution of ADH ($1.2 \times 10^{-3} \text{ mol dm}^{-3}$) in benzene $2 \mu\text{s}$ after the pulse. Inset shows absorption–time profile at 600 nm, dose = 15 Gy per pulse.

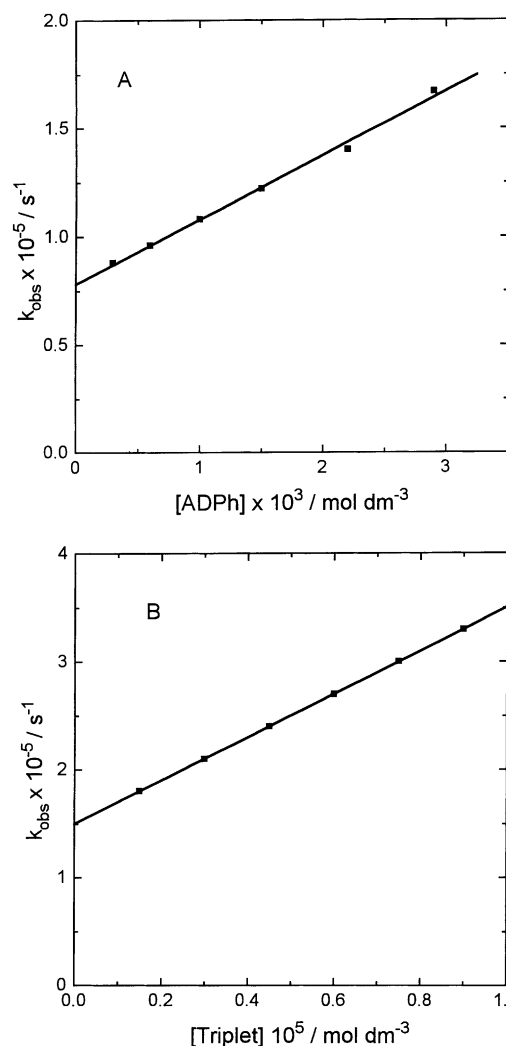


Fig. 7. Variation of ADPh triplet decay as a function of solute concentration (A) and triplet concentration (B).

a value of $3.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Table 3). The value of the rate constant obtained by extrapolation of the linear plot to zero solute concentration was found to be $0.78 \times 10^5 \text{ s}^{-1}$, which can be taken as the value of triplet decay rate constant (k_T). The inverse of k_T should be the actual lifetime ($\tau = 12.8 \mu\text{s}$) of ADPh triplet decay in the absence of reactions 16 and 17. The triplet–triplet annihilation rate constant (k_{TT}) was determined by monitoring the decay of ADPh triplet decay as a function of pulse dose rate at a constant solute concentration ($0.3 \times 10^{-3} \text{ mol dm}^{-3}$). The value of lifetime decreased from 6.6 to 2.8 μs when the dose was increased

Table 3

Triplet–triplet (k_{TT}) and self quenching (k_{TS}) rate constants for acridine(1,8)dione dyes

Dye	$k_{TT} (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$k_{TS} (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	$\tau (\mu\text{s})$
ADPh	2.1×10^{10}	3.0×10^7	12.8
ADMe	1.3×10^{10}	2.9×10^7	9.6

Table 4

Comparison of kinetic and spectral parameters of the triplets of acridine(1,8)dione dyes produced on pulse radiolysis and laser flash photolysis^a

Dye	λ_{\max} (nm)		Decay, k (s^{-1})	
	PR	LFP ^b	PR	LFP ^b
ADPh	590	610	1.5×10^5	7.7×10^5
ADMe	610	630	2.1×10^5	3.1×10^5
ADH	600	610	5.5×10^5	6.6×10^5

^a PR: pulse radiolysis; LFP: laser flash photolysis.

^b From [14].

from 16 to 96 Gy. The concentration of the initially formed triplet was determined from its molar extinction coefficient value ($1.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (see text). The value of k_{TT} was determined from the slope of the linear plot of k_{obs} versus triplet concentration (Fig. 7B) and was determined to be $2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Table 3). The triplet–triplet annihilation (k_{TT}) and self quenching rate constant (k_{TS}) for ADMe dye were also determined and are shown in Table 3. Due to very small absorption of ADH dye, the decay kinetic studies could not be carried out for ADH dye. The triplet–triplet annihilation rate determined for some of the organic compounds was also in this range [24,25].

The spectral and kinetic parameters for the triplets of acridine(1,8)dione dyes produced on pulse radiolysis and laser flash photolysis are shown in Table 4. A red shift of 10–20 nm was seen in the λ_{\max} of the triplets. This may be due to the solvent effect, as the pulse radiolysis studies were carried out in benzene whereas laser flash photolysis studies are in methanol [14]. Except for ADPh dye, the decay rate constants of the triplets produced by both the methods were comparable. The small difference may arise due to different nature of the solvent, contribution of triplet–triplet and self quenching of dye triplets produced by both the methods.

3.4. Energy transfer studies

The confirmative evidence for the formation of dye triplets could be obtained on energy transfer to or from a known triplet which is already well characterized [26]. The decay (Fig. 8a) of the transient band of biphenyl triplet ($\lambda = 360 \text{ nm}$, $E_{\text{T}} = 274 \text{ kJ mol}^{-1}$, $\varepsilon_{\text{T}} = 27100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) produced on pulse radiolysis of N_2 -saturated solution of biphenyl ($4 \times 10^{-2} \text{ mol dm}^{-3}$) was observed to decay faster (Fig. 8b) on addition of low concentration of ADPh ($1\text{--}4 \times 10^{-4} \text{ mol dm}^{-3}$) and the bimolecular rate constant was determined to be $3.8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Table 5). The time-resolved studies showed the formation of a transient absorption band with $\lambda_{\max} = 590 \text{ nm}$ (Fig. 8c). The nature of the transient absorption spectrum matched with that shown in Fig. 4 and assigned to dye triplet. The extinction coefficient (ε_{T}) value for dye triplet ($T_1 \rightarrow T_n$) absorption was determined by energy transfer method as suggested by Amouyal et al. [27] and the

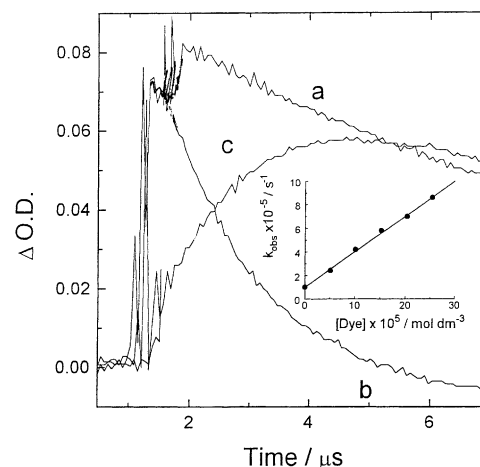


Fig. 8. Absorption–time profiles obtained on pulse radiolysis of N_2 -saturated solution of biphenyl ($4 \times 10^{-2} \text{ mol dm}^{-3}$, $\lambda = 360 \text{ nm}$) in absence (a) and presence of ADPh ($4 \times 10^{-4} \text{ mol dm}^{-3}$) (b), and at 590 nm (c). Inset shows variation of first-order rate constant with ADPh concentration, dose = 15 Gy per pulse.

value is given in Table 2. Using this value of molar absorptivity, the G value of the triplet states produced on pulse radiolysis has been determined (Table 2). The transient absorption band of *p*-terphenyl triplet ($\lambda = 460 \text{ nm}$, $E_{\text{T}} = 244 \text{ kJ mol}^{-1}$, $\varepsilon_{\text{T}} = 90000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and benzophenone triplet ($\lambda = 525 \text{ nm}$, $E_{\text{T}} = 287 \text{ kJ mol}^{-1}$, $\varepsilon_{\text{T}} = 6500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) were also observed to decay faster in the presence of low concentrations of ADPh and the time-resolved studies showed the formation of transient absorption bands of ADPh triplet. The energy transfer rate constant values are given in Table 5. The transient absorption band of anthracene triplet ($\lambda = 430 \text{ nm}$, $E_{\text{T}} = 178 \text{ kJ mol}^{-1}$, $\varepsilon_{\text{T}} = 71500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) produced on pulse radiolysis of N_2 -saturated solution of anthracene ($4 \times 10^{-2} \text{ mol dm}^{-3}$) was not affected on addition of low concentration of ADPh, indicating the absence on energy transfer from anthracene triplets to ADPh, and suggesting that the E_{T} of ADPh triplet is more than that of anthracene

Table 5

Energy transfer rate constants for various donors to different dyes

Donor	Acceptor	Rate constant $\times 10^{-9}$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)
Biphenyl	ADPh	3.8
<i>p</i> -Terphenyl	ADPh	2.1
Benzophenone	ADPh	4.8
Biphenyl	ADMe	3.1
<i>p</i> -Terphenyl	ADMe	2.8
Benzophenone	ADMe	4.1
Anthracene	ADPh	–
ADPh	Anthracene	5.1
Biphenyl	ADH	–
<i>p</i> -Terphenyl	ADH	–
Benzophenone	ADH	0.7
CA	ADH	2.0

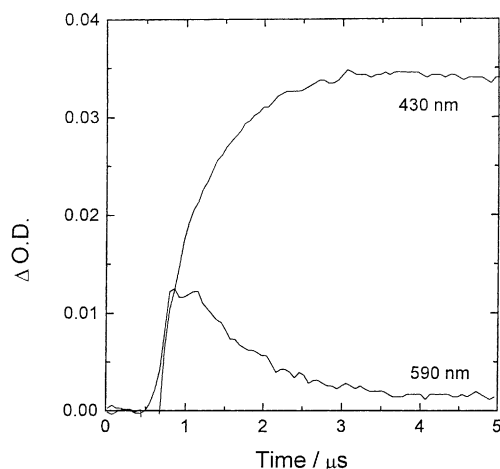
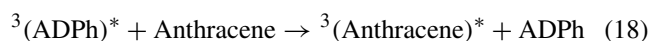


Fig. 9. Absorption–time profiles obtained on pulse radiolysis of N_2 -saturated solution of ADPh ($3.5 \times 10^{-3} \text{ mol dm}^{-3}$) containing anthracene ($5.5 \times 10^{-5} \text{ mol dm}^{-3}$) at 430 and 590 nm.

triplet. On the other hand the transient absorption band at 590 nm, formed on pulse radiolysis of N_2 -saturated solution of ADPh ($3.5 \times 10^{-3} \text{ mol dm}^{-3}$) in benzene was observed to decay faster on addition of low concentration of anthracene (Figs. 4 and 9) with a growth at 430 nm (Fig. 9). Time-resolved studies showed the formation of a transient absorption band at 430 nm, matching with the absorption spectrum of anthracene triplet and confirming the formation of anthracene triplet on energy transfer from ADPh triplets to anthracene (reaction 18).



Therefore, these studies suggest that E_T of ADPh is between 178 and 244 kJ mol^{-1} . The E_T of ADPh, determined by laser flash photolysis experiments (221.2 kJ mol^{-1}) [14] is within the above mentioned limit.

The energy transfer studies were also carried out with ADMe dye and the rate constant values are given in Table 5. In each case the nature of the transient absorption spectrum obtained on energy transfer from the donor to the dye was similar to that shown in Fig. 5 and thus support the assignment of the spectra to the dye triplets.

The decay of the transient absorption band of biphenyl and *p*-terphenyl triplets were not affected on addition of low concentration of ADH dye. This may be due to very low yield of ADH triplets formed on pulse radiolysis of N_2 -saturated solution of ADH in benzene.

3.5. Triplet sensitized electron/ H^+ transfer reactions

In absence of any dye, the benzophenone triplet ($\lambda = 525 \text{ nm}$) decay by first-order kinetics with $k = 8.2 \times 10^5 \text{ s}^{-1}$ and time resolved studies do not show any new absorption band on decay (Fig. 10a and b). In presence of low

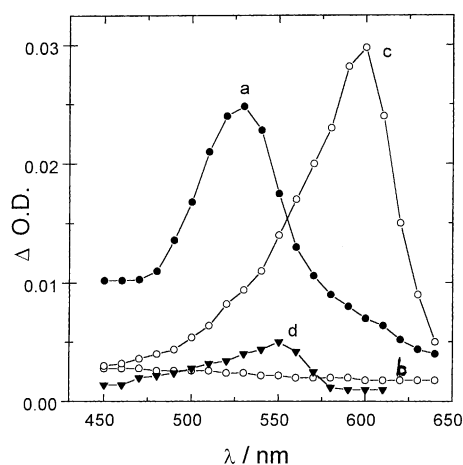
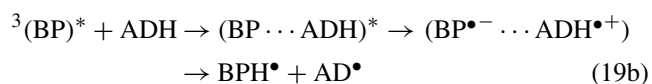


Fig. 10. Transient absorption spectra obtained on pulse radiolysis of N_2 -saturated solution of benzophenone ($2 \times 10^{-2} \text{ mol dm}^{-3}$) in benzene 0.6 (a) and 8 μs (b) after the pulse in absence of dye. 8 μs after the pulse in presence of ADPh ($3 \times 10^{-4} \text{ mol dm}^{-3}$) (c) and ADH ($3.5 \times 10^{-4} \text{ mol dm}^{-3}$) (d).

concentration of ADPh, time resolved studies showed the formation of a new transient absorption band at 595 nm (Fig. 10c), matching with ADPh triplet (Fig. 4). In presence of ADH, the benzophenone triplet decayed faster and the energy transfer rate constant was determined to be $7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Time resolved studies showed the formation a small transient absorption band at 550 nm. This band (Fig. 10d) do not matches with that of ADH triplet (Fig. 6). The benzophenone ketyl radical is known to have an absorption band around 550 nm. The formation of benzophenone ketyl radical could be considered to have taken place with H^\bullet atom transfer from ADH to benzophenone triplet either directly (reaction 19a) or via an encounter contact ion-pair complex with H^+ transfer (reaction 19b) [28].



H^\bullet atom abstraction by benzophenone is an activation energy controlled process and in ethanol as solvent it takes place with a rate constant of $1.2 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [29,30]. The rate constant observed in the present case is quite high ($7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). The formation of benzophenone ketyl radical could be explained with electron transfer and immediate proton transfer reaction (reaction 19b). As mentioned earlier, the transient absorption AD^\bullet was not seen in 450–650 nm region.

Due to high electron affinity of chloranil (CA; 2,3,5,6-tetrachloro-1,4-benzoquinone) it is known to undergo triplet (520 nm) sensitized electron transfer reaction. The transient absorption band, observed on pulse radiolysis of N_2 -saturated solution of CA ($5 \times 10^{-2} \text{ mol dm}^{-3}$) in benzene showed accelerated decay in presence of low

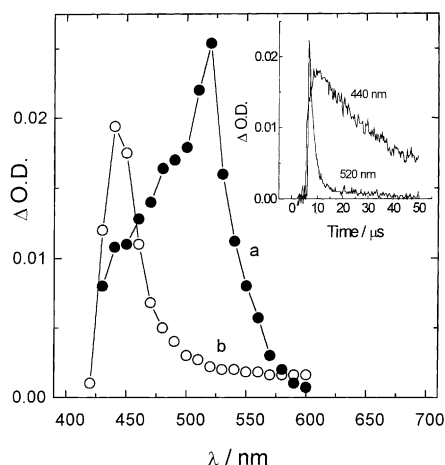
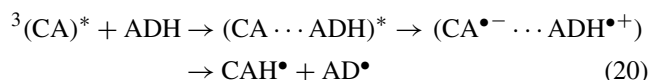


Fig. 11. Transient absorption spectra obtained on pulse radiolysis of N_2 -saturated solution of CA ($5 \times 10^{-2} \text{ mol dm}^{-3}$) containing ADH ($2 \times 10^{-4} \text{ mol dm}^{-3}$) in benzene (a) immediately and (b) $5 \mu\text{s}$ after the pulse. Inset shows absorption profiles at 440 and 520 nm.

concentration of ADH ($2 \times 10^{-4} \text{ mol dm}^{-3}$) with growth at 440 nm and a long tail in 500–600 nm region. The spectral (Fig. 11) characteristics are due to semiquinone radical (CAH^\bullet) [31]. The semiquinone radical could be considered to be formed by electron transfer and subsequent proton transfer reaction (reaction 20).



The bimolecular rate constant determined from the CA triplet decay at 520 nm as a function of ADH concentration was close to the value determined from the growth of semiquinone radical at 440 nm ($2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).

4. Conclusions

Pulse radiolysis of acridine(1,8)dione dyes in DCE showed the formation of solute radical cations and are able to undergo electron-transfer reaction with TMPD and TEA. In benzene, the transient absorption spectra are due to first excited triplet state of acridine(1,8)dione dyes. Based on energy transfer studies with well characterized triplets of different energies, the E_T of phenyl substituted acridine(1,8)dione dye is estimated to be between 178 and 244 kJ mol^{-1} . Benzophenone triplets undergo energy transfer with phenyl and methyl substituted acridine(1,8)dione dyes forming acceptor triplets. On the other hand, H substituted acridine(1,8)dione dye favor electron transfer followed by H^+ transfer reaction forming benzophenone ketyl radical.

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