Nanosecond laser flash photolysis of acridine in organic solvents

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Abstract. A laser flash photolysis set-up is described for nanosecond time resolved study of transient species. The system described uses 30 nsec, 355-nm UV laser pulse as the photolysing source. Laser flash photolysis of acridine in various organic solvents (polar, non-polar and hydroxylic) has been carried out. The quantum yields of intersystem crossing and C-radicals (in hydroxylic solvents) have been calculated from the transient absorption measurements. The quenching of the triplet state by chloranil is efficient in all the solvents and free radical ions are formed as products only in the polar solvents. Biphotonic ionisation of acridine occurs at high laser intensities and is more efficient in hydroxylic solvents compared to benzene or acetonitrile.

Keywords. Laser chemistry; acridine; laser flash photolysis; intersystem crossing; biphotonic ionisation.

1. Introduction

Very fast chemical and physical changes in condensed systems are studied by picosecond (psec) and nanosecond (nsec) techniques which provide real time data. Usually a pulsed laser source provides the initial perturbation in the sample by absorption of laser photons and the status of the sample after the laser excitation is probed to obtain data on the evolution and decay of the intermediate species/states. In this paper, we describe a nsec laser flash photolysis set-up, which has been used to investigate the laser-induced chemistry of acridine in different organic solvents and report the results obtained.

The relaxation mechanism of the excited singlet state (S_1) of acridine depends upon the solvent (Mataga et al 1956; Kellmann 1977; Noe et al 1978; Kasama et al 1981). The four major deactivation routes of the excited singlet state, namely, fluorescence, intersystem crossing, internal conversion and photochemical reaction are strongly dependent upon the nature of the solvent. For example, the fluorescence quantum yield (ϕ_f) of acridine decreases from 0·37 in aqueous solution to 0·03 in ethanol (Bowen et al 1962), to 5×10^{-4} in benzene (Kasama et al 1981a), and to zero in n-hexane (Sundstrom et al 1977). Similarly, the photochemical reaction of the excited singlet state is sensitive to the type of solvent as indicated in steady state experiments (Whitten and Lee 1971) but the quantum yields of the primary product, namely, the C-radical of acridine have not been measured in time scales comparable to the nsec lifetime of the excited singlet state of acridine in the reactive solvents. In recent years pulsed laser techniques (psec and nsec) have been used to study the solvent dependence of intersystem crossing and internal conversion in organic solvents (Kellmann 1977; Sundstrom et al 1977). Theoretical models based on energy level diagrams have been given to account for the

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experimental data (Mataga *et al* 1956; Li and Lim 1972; Kellmann 1977; Kasama *et al* 1981b) and the picture is far from complete (Struve *et al* 1983). The excited triplet state T_3 (π, π^*) energy of acridine is shown to be independent of the solvent (Periasamy 1983). In this paper we report the results of the laser flash photolysis of acridine in various organic solvents for different photochemical reactions: triplet decay, triplet quenching and biphotonic ionisation.

2. Experimental section

The experimental set-up for the study of time resolved laser induced chemistry is shown in figure 1. The third harmonic output at 355 nm (pulse width: 15–30 nsec) from the Nd : YAG Laser (Molectron MY 35) is used to excite the sample. The light shutter (SH) controlled 'single pulse selector' generates a Q-switch pulse for the Pockels Cell and this arrangement ensures that the laser pulse arrives at the sample when the probe light from the LAMP (100 W tungsten or 150 W xenon lamp) is already present in the sample. The dielectric multilayer mirror (DMM) reflects the 355 nm $(R \approx 97\%)$ laser pulse and transmits the probe light (> 400 nm) so that the two beams pass through the circular aperture (A) (diameter: 1 to 2 mm) in front of the sample. Care is taken that a spatially uniform section of the laser beam of energy $\approx$ 1 mj passes through the aperture. In high intensity experiments the laser energy is increased and/or focussed with a lens of long
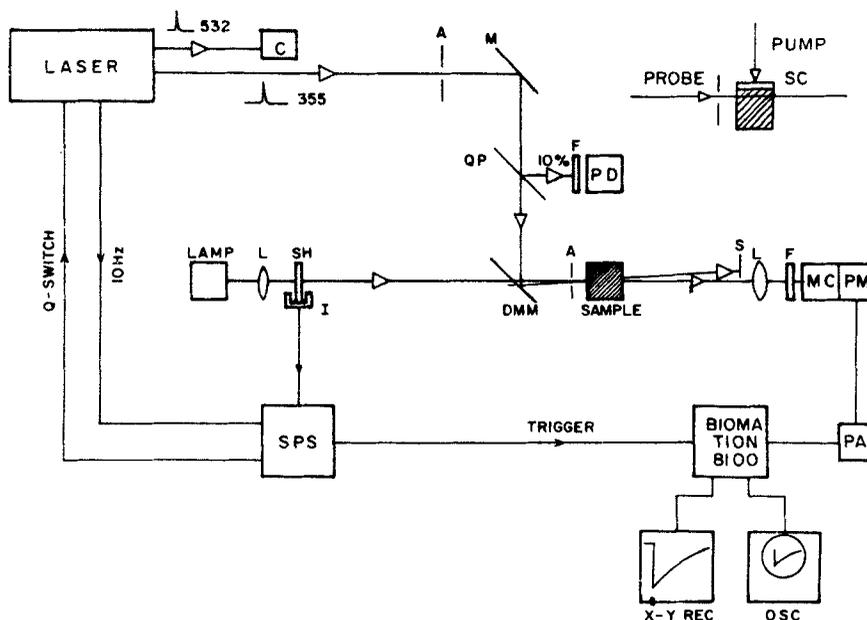
Figure 1. Experimental set-up for nsec time-resolved laser induced chemistry. The sample excitation is carried out in a direction parallel or perpendicular to the probe beam. A-aperture/slit, C-energy absorbing calorimeter, DMM-dichroic multilayer mirror, F-filter, I-interruptor, L-lens, M-mirror, MC-monochromator, PA-preamplifier, PD-photodiode, PM-photomultiplier, QP-quartz plate beam splitter, S-beam stop, SC-scatterer, SH-light shutter, SPS-single pulse selector.

focal length. Constancy of the shot-to-shot laser energy is monitored either by measuring the unused 532 nm laser output of the Nd:YAG laser or by detecting a fraction of the 355 nm output using a photodiode (Hamamatsu R 1193U). The angular separation of the pump and probe beams is kept at $\approx$ 2 degrees. The divergence of the probe beam is adjusted to the minimum so that the overlap of the two beams within the sample is complete. The laser pulse emerging through the sample is stopped by a beam stop (s) and only the probe light enters the monochromator. Scattered laser light and fluorescence from the sample are cut out or minimised by suitable colour filters (F). In an alternate arrangement shown in top of figure 1, the pump laser beam excites the sample transversely where a ground quartz plate (sc) scatters the laser beam for uniform excitation. The probe light is detected by the photomultiplier (1P28, 5 dynodes) and the output fed to a preamplifier (time constant: 1 μsec, and unity gain) to offset the photocurrent, so that temporal changes in intensity after laser photolysis could be recorded at high sensitivity. The transient analog signal is fed to a waveform digitizer (Biomation 8100) and displayed on an oscilloscope and recorded on an x–y recorder. Fast transient decay has been recorded with 50 ohm termination at the anode of PM and a fast preamplifier (time constant: 20 nsec).

Acridine (BDH, England) was recrystallised from ethanol-water six times. Chloranil was recrystallised from benzene four times. All the solvents are either spectrograde or analar grade. 2-Propanol was of electronic grade quality. The samples were degassed by bubbling argon (99·99 %) gas through a syringe needle inserted into the sample taken in a quartz cuvette (1 cm × 1 cm) and another syringe needle serving as a vent. The rubber stopper into which the needles are pierced provided an air-tight seal for the cuvette. The kinetic decay of acridine in acetonitrile was analysed using a sealed sample prepared in vacuum after repeated freeze-pump-thaw cycles for degassing. The absorption spectra of the samples were recorded in a Cary 17D spectrophotometer.

3. Results

3.1 *The triplet-triplet absorption: spectrum and decay*

The absorption spectrum of acridine in acetonitrile is shown in figure 2 ($S_n \leftarrow S_0$). The degassed sample was photolysed by the 355 nm laser pulse ($\approx$ 1 mj) and the difference absorption spectrum of the transient species at 5 μsec after excitation is shown in figure 2 ($T_n \leftarrow T_1$). The difference absorbance ΔA is equal to $-\log(1 - \Delta I/I_0)$ where I_0 is the intensity of the probe beam before laser excitation and ΔI is the change in intensity after laser excitation; ΔI is positive if the intensity decreases ($\varepsilon_T > \varepsilon_G$), and vice versa. Since the absorption spectrum of acridine ($S_n \leftarrow S_0$) does not overlap with that of the transient species in the region > 400 nm, the difference absorption spectrum is the true absorption spectrum of the transient species.

The transient species is inferred to be the triplet state of acridine for the following reasons: (i) The growth of the transient species occurs in about 20 nsec (figure 2, inset) which is comparable to the exciting laser pulse width. Since acridine is non-fluorescent in acetonitrile, the singlet excited state is assumed to be very short-lived and the triplet state is formed immediately after the nsec laser excitation. (ii) The lifetime of the transient species is several microseconds which is typical of the triplet state lifetime. (iii) The transient species is sensitive to the presence of oxygen in the sample. No transient absorption is observed when acridine sample is not degassed. (iv) The triplet
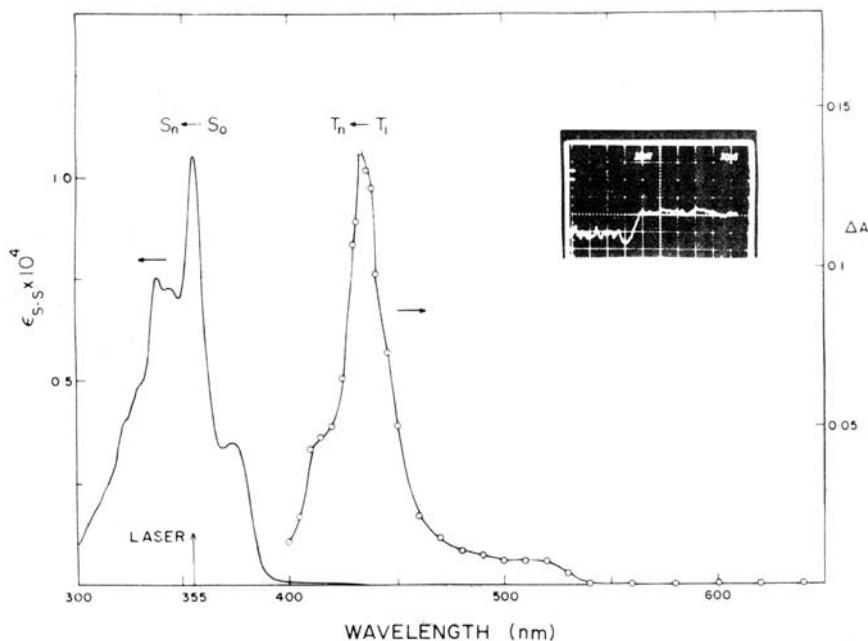
Figure 2. Absorption spectra of the singlet ground state $(S_n \leftarrow S_0)$ and the triplet state $(T_n \leftarrow T_1)$ of acridine $(1 \times 10^{-4}$ M) in acetonitrile. Inset: Temporal intensity profile at 434 nm showing that triplet growth is completed within 30 nsec after laser excitation Scale: X $-$ 20 nsec/div; Y $-$ 10 mv/div; $I_0 \cdots 100$ mV.

state of acridine is also efficiently quenched by an electron acceptor quencher, namely, chloranil. (v) The triplet-triplet absorption spectrum of acridine in acetonitrile shown in figure 2 is in close agreement with the spectrum obtained in benzene (Kellmann and Lindquist 1967); namely a prominent absorption peak at 434 nm, a shoulder at 410 nm and a weak absorption band at 520 nm.

The temporal decay of the triplet state of acridine (inset figure 3) depends upon the relaxation mechanism of the triplet state. In the absence of external triplet quenchers in the sample the triplet decay generally follows a three-route mechanism (Pekkarinen and Linschitz 1960; Parker 1968) and the temporal decay is analysed on that basis:

$$T \rightarrow G; k_1 \tag{1}$$

$$T + G \rightarrow 2G; k_2 \tag{2}$$

$$T + T \rightarrow 2G; k_3. \tag{3}$$

T and G are the triplet state and ground state species. k_1, k_2 and k_3 are the rate constants of the reactions (1), (2) and (3) respectively. The temporal decay of the triplet state is analysed by a least-squares method described in appendix I and the rate constants k_1, k_2 and k_3 are obtained. The following rate constants were obtained for the triplet decay of acridine in acetonitrile: $k_1 = (3 \pm 1.5) \times 10^2$ sec^{-1}, $k_2 = (8 \pm 2) \times 10^7$ M^{-1} sec^{-1}, $k_3 = (8 \pm 1) \times 10^9$ M^{-1} sec^{-1}. The experimentally observed temporal decay of the triplet and the computed curve for the above rate constants are shown in figure 3.
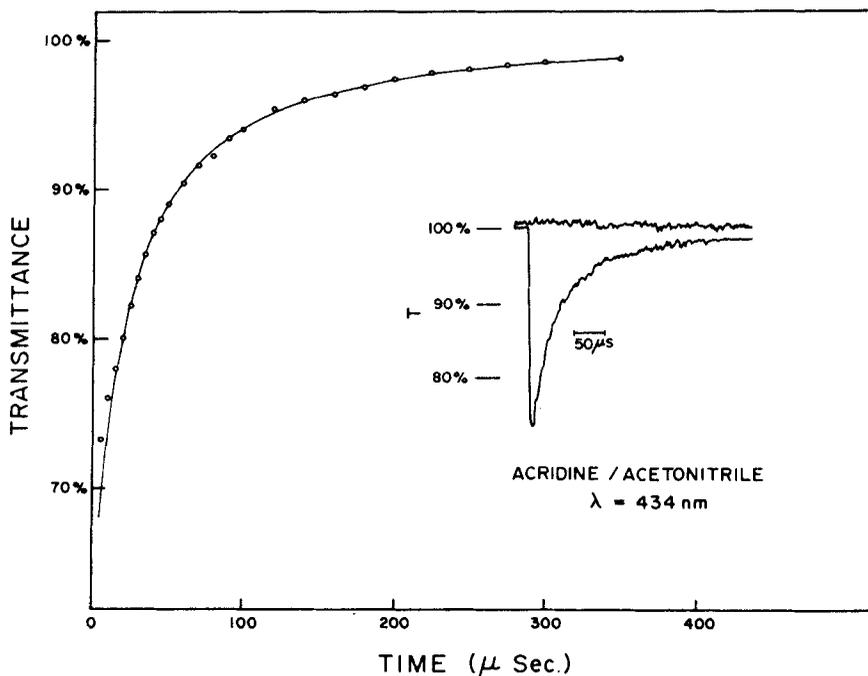
Figure 3. The computer fit according to the three-route mechanism for the triplet decay in acetonitrile. Circles are data taken from the decay curve and the solid line is the computed best fit for the following values: $(k_1 + k_2 C_0) = 3\cdot5 \times 10^3 \text{ sec}^{-1}$ and $l\varepsilon_T/(k_3 - k_2) = 3\cdot7 \times 10^{-6}$ sec.

3.2 *Relative triplet absorbance in different solvents*

The UV (355 nm) excitation of acridine produces the excited singlet state. The triplet state of acridine is formed by intersystem crossing which is one of the deactivation routes of the singlet excited state. The determination of the absolute yield of intersystem crossing using transient absorption data requires an accurate value of the fraction of laser energy absorbed by the sample, which is usually difficult to estimate, and the molar extinction coefficient of the triplet state. In laser excitation experiments it is usual to estimate the absolute triplet yield by comparison with a suitable reference system. In the case of acridine the variation of triplet yields in different solvents is estimated by measuring the relative triplet absorbance under identical excitation conditions.

Samples of acridine in various solvents are prepared such that the absorbance at 355 nm is 0·2 when measured in the cuvette used for laser excitation. This ensures that when excited by the laser pulse the same fraction of laser energy is absorbed in each sample. The incident laser energy is checked for shot-to-shot constancy and hence the number of excited singlet states produced by laser excitation is identical in each sample. The triplet-triplet absorption maximum occurs at different wavelengths in different solvents (table 1). The triplet absorbances at their respective maxima (*eg* at 434 nm in acetonitrile) are measured immediately after the laser excitation. The measured values of the triplet absorbance (ΔA) for these samples are given in table 1. The variation of

Table 1. $T-T$ absorption maximum (λm), Triplet absorbance at λm (ΔA), k_q, k_d and (k_q/k_d).

Solvent	λm (nm)	$\Delta A^{(a)}$ $x (1 \pm 0.1)$	$10^{-9}k_q^{(b)}$ $(M^{-1} sec^{-1})$	$10^{-9}k_d^{(c)}$ $(M^{-1} sec^{-1})$	(k_q/k_d)
Acetonitrile	434	0·155	4·8 ± 0·3	18	0·27
DMSO	440	0·072	1·5 ± 0·2	3·5	0·43
Benzene	442	0·124	3·6 ± 0·3	10	0·36
CCl$_4$	442	0·093	5·8 ± 0·2	6·9	0·84
Methanol	437	0·073	4·2 ± 0·2	11	0·38
2-Propanol	440	0·095	2·3 ± 0·2	2·9	0·79
t-Butanol	436	—	1·1 ± 0·1$^{(d)}$	1·4$^{(d)}$	0·79$^{(d)}$

(a) Absorbance of acridine at 355 nm is 0·2 in all the solvents (b) T = 22°C (c) k_d = 8 RT/3000 η (d) T = 25°C.

ΔA is proportional to the variation of the intersystem crossing yield in different solvents (§4.1).

3.3   Triplet quenching by chloranil

The triplet state of acridine is quenched by chloranil, as indicated by the reduction of the triplet lifetime when the quencher is present at low concentrations. The decay of the triplet state in acetonitrile is non-exponential and dominated by the triplet-triplet annihilation route (3). The measured lifetime (decay of triplet absorbance to $(1/e)$ of peak value of the triplet state) in 10^{-5} M solution of acridine is in the range of 70–100 μsec. In the presence of chloranil $([Q] = 5·2 \times 10^{-5}$ M) the lifetime of the triplet state of acridine decreases to 4 μsec and the absorbance decay curve is exponential. This shows that in the presence of the quencher the triplet decay is dominated by the quenching reaction. The quenching rate constant is calculated from the measured lifetime (τ) and the quencher concentration $[Q]$:

$$k_q = [Q]/\tau. \tag{4}$$

The efficiency of a quenching reaction is indicated by comparing the quenching rate constant with the diffusion limited rate constant calculated for the solvent using the expression given below (Rohatgi-Mukherjee 1978):

$$k_d = 8 RT/3000 \, \eta, \tag{5}$$

where R is the gas constant, T is the absolute temperature and η is the viscosity in poise. The measured value of k_q and the calculated value of k_d in various solvents are given in table 1. The value of (k_q/k_d) ranges from 0·27 to 0·84. Considering that the value of k_d is based on a model which is strictly true only for spherical molecules it may be assumed that the triplet quenching by chloranil is efficient and occurs upon the first encounter of the triplet species and the quencher.

The mechanism of the quenching of the triplet state of acridine by chloranil depends upon the solvent. In benzene and CCl$_4$ the triplet acridine is efficiently quenched by chloranil and both the molecules are in the ground state after quenching. No transient species are detectable in these solvents which can be attributed to the products of the triplet quenching reaction. However, in acetonitrile the triplet quenching reaction is accompanied by products of long life-time. Figure 4 shows the temporal intensity decay
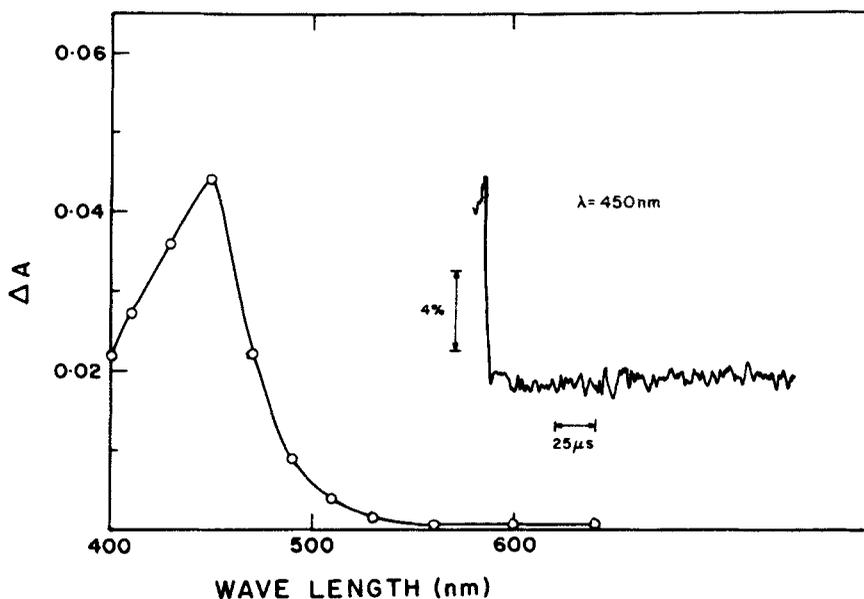
Figure 4. The transient absorption spectrum obtained when acridine $(5\cdot3 \times 10^{-5}$ M) in acetonitrile is laser excited in the presence of chloranil $(1\cdot1 \times 10^{-3}$ M). At this quencher concentration the triplet state is completely quenched in less than 500 nsec. The growth and decay of acridine anion at 450 nm is also shown (inset).

of the products at 450 nm (inset) and the absorption spectrum of the products in the region 400–640 nm. The prominent absorption band in the 400–500 nm region is attributed to the chloranil anion radical $(Q^{\dot-})$ and the structureless absorption extending upto 640 nm is attributed to the acridine cation radical $(A^{\dot+})$ (Sakiguchi *et al* 1980). Thus, the triplet quenching in acetonitrile occurs by electron transfer from the triplet state of acridine to the chloranil. The quenching of the triplet acridine by chloranil in alcohol solvents (methanol, *t*-butanol, 2-propenol) is also accompanied by the formation of products, but in these solvents the electron transfer reaction is likely to be accompanied by fast protonation reaction.

3.4 *C-radical formation in alcoholic solvents*

The transient absorption spectra and the temporal decay of 355 nm laser excited acridine indicates that the triplet state is the only product in acetonitrile, benzene, DMSO and CCl$_4$. However, in alcoholic solvents transient species other than the triplet state are also formed upon laser excitation. The transient absorption spectrum of acridine in 2-propanol at 200 nsec after laser excitation is shown in figure 5. The spectrum shows no significant change upto 5 μsec. The spectrum at 375 μsec is significantly different from the initial spectrum; the prominent triplet absorption band at 440 nm has disappeared at 375 μsec. The absorption spectrum given by the dashed line in the figure is due to the longlived transient species formed in this solvent. Intense absorption bands are observed in 260–290 nm region with a local maximum at 278 nm, and in the 350–370 nm region. The absorption band in the 350–370 nm region appears weak in the difference absorption spectrum because of the ground state absorption in this
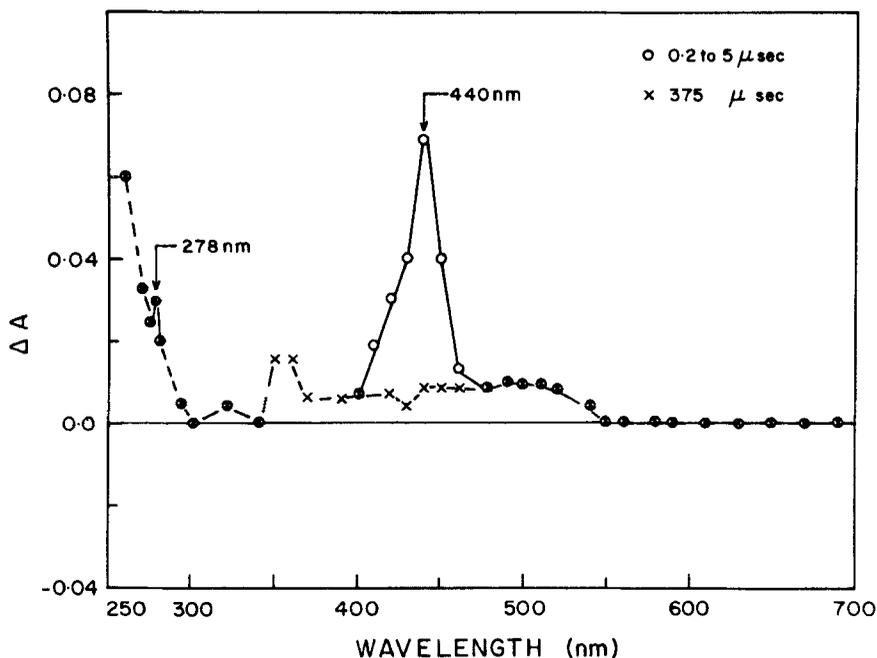
Figure 5. The transient absorption spectrum of acridine (1×10^{-4} M) in 2-propanol at 0·2–5 μsec and at 375 μsec after laser excitation. The spectrum at 375 μsec is due to the C-radical of acridine (dashed line).

wavelength region. The band appearing in the 480–520 nm region belongs to the same species. Similar transient absorption spectra were obtained when acridine in methanol was laser-excited. The spectrum of this transient species is identical to that of the semireduced, carbon-centred, C-radical of acridine observed in the flash photolysis of acridine-acridan mixture in benzene (Kira and Koizumi 1969; Zanker and Prell 1969). The temporal growth of the absorption at 278 nm due to the C-radical is identical to the temporal growth at 440 nm due to the triplet (figure 6) and hence it is inferred that the precursor of both the transient species is the excited singlet state.

3.5 *Biphotonic excitation of acridine*

Laser excitation of acridine in non-hydroxylic solvents (acetonitrile and benzene) produces the triplet state of acridine when the laser energy is low (< 10 mj/cm^2). When the laser energy is increased the triplet state concentration (absorbance) does not increase linearly and a saturation value for the triplet concentration is reached at higher laser energies (figure 7). The saturation value of triplet concentration is only a fraction (0·1 to 0·5) of the initial concentration of acridine and hence the complete depletion of molecules in the ground state by laser excitation is ruled out. We conclude that a second photon of the laser pulse is absorbed by the triplet state and this biphotonic process gives rise to the saturation behaviour shown in figure 7.

Biphotonic excitation of acridine in benzene and acetonitrile produces new transient species absorbing in the region > 550 nm and the absorbance is less than 0·01. Although the lifetime of this species is long (> 1 msec) the low yield of this species has
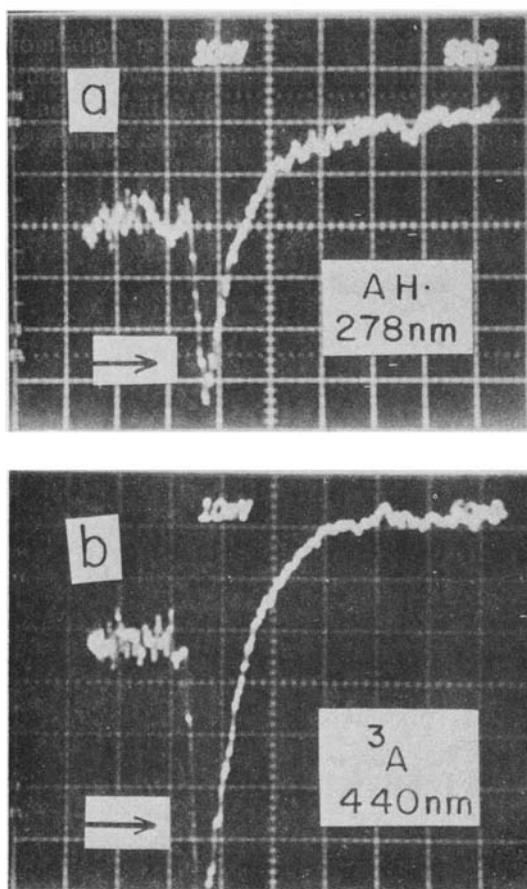
Figure 6. The temporal growth profile of C-radical at 278 nm (**a**) and that of triplet at 440 nm (**b**). The time constant of detector-amplifier electronics is ≈ 100 nsec. The fast transient appearing in the beginning shown by the arrow is due to laser scatter and/or fluorescence from the sample. Scale: X − 50 nsec/div; Y − 10 mV/div; $I_0 = 120$ mV (278 nm) and 150 mV (440 nm).

not been helpful in identification of the transient species. It is assumed that biphotonic ionisation would have occurred in these solvents and the species absorbing in the region > 550 nm could be the acridine cation and the weak absorption spectrum due to the anion would be submerged in the triplet spectral region (400–500 nm).

The biphotonic ionisation occurs more efficiently in hydroxylic solvents such as water (Kellmann and Tfibel 1982) where acridine is also fluorescent. Kellmann and Tfibel (1980) have confirmed that the biphotonic ionisation is more efficient through the excited singlet state. In agreement with these findings we have observed that the biphotonic ionisation is more efficient in 2-propanol (compared to acetonitrile or benzene). Figure 8 shows the absorption spectrum of the transient species produced in 2-propanol. The spectral band appearing in the 560–640 nm region is absent at low laser energies and this is attributed to the acridine cation radical.
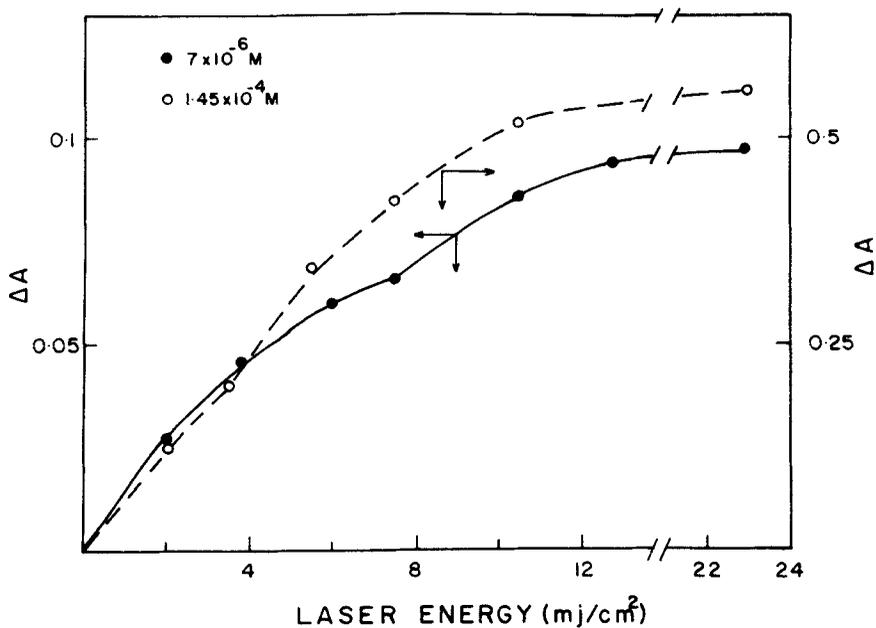
Figure 7. Non-linear dependence of triplet absorbance on laser energy. Sample: Acridine in benzene. Concentration: 7×10^{-6} M (●—●—●) and 1.45×10^{-4} M (O--O--O).
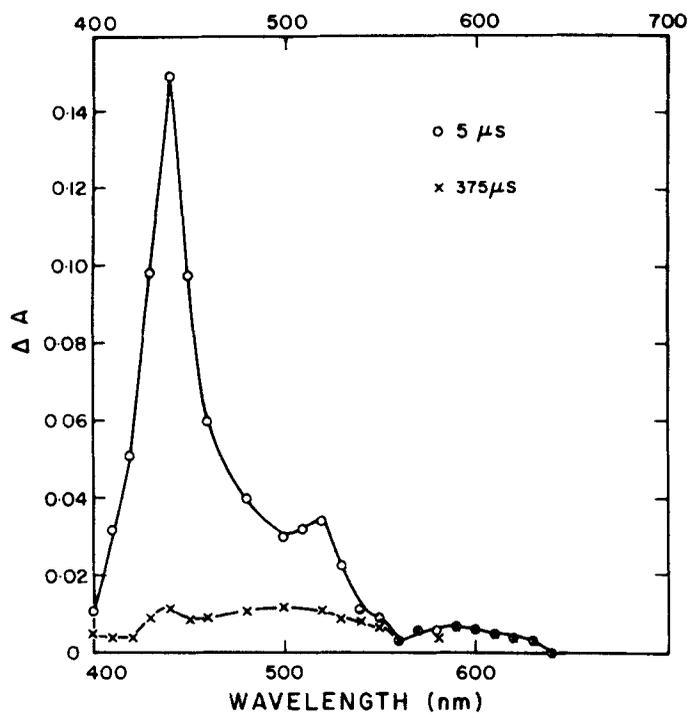

Figure 8. The transient absorption spectra of acridine in 2-propanol under conditions when biphotonic ionisation occurs. The spectral band in the 560–640 nm region is attributed to the acridine cation radical.

4. Discussion

4.1 *Electronic relaxation of the excited singlet state* (S_1)

The electronic relaxation mechanism of the excited singlet state of acridine is solvent dependent. Theoretical calculation (Goodman and Harrel 1959) predicts that the $^1(n, \pi^*)$ state of acridine is lower than $^1(\pi, \pi^*)$ state by 0·16 eV. In solution the solvent interaction, notably the hydrogen bonding interaction, perturbs the (n, π^*) and (π, π^*) energy levels affecting the energy separation between them. Thus in the hydrogen bonding solvents $^1(\pi, \pi^*)$ state is substantially lower in energy compared to $^1(n, \pi^*)$ state (Kasama *et al* 1981a, b) and acridine fluorescence intensity is strong. In inert solvents, acridine fluorescence is either weak or absent (Kasama *et al* 1981; Bowen *et al* 1962; Mataga and Tsuno 1959) indicating that the non-radiative mechanism becomes dominant through the lower $^1(n, \pi^*)$ state or through a vibronic coupling of close-lying $^1(n, \pi^*)$ and $^1(\pi, \pi^*)$ states (Li and Lim 1972). The non-radiative decay of the excited singlet state leads to a triplet state (intersystem crossing) or to the singlet ground state (internal conversion). In some reactive solvents like ethanol, 2-propanol, etc (Kira *et al* 1966; Whitten and Lee 1971) the photochemical reaction of the excited singlet state (mainly through the $^1(n, \pi^*)$ state) has to be considered as a non-radiative route of decay of S_1. Experimental data of the quantum yields of fluorescence (ϕ_f), the triplet state (ϕ_{isc}), the photochemical reaction (ϕ_r) and internal conversion (ϕ_{ic}) for acridine in different types of solvents have been used in estimating the relative importance of the different routes of deactivation of S_1 in each solvent (Kellmann 1977; Kasama *et al* 1981b).

The quantum yields of the four different routes of deactivation of S_1 in different solvents have been estimated from our experimental data (table 2). The fluorescence quantum yield is zero in solvents where acridine is non-fluorescent and the value in 2-propanol was estimated from the relative fluorescence intensity of acridine in methanol $(\phi_f = 0.05, $ Wolff 1981) and 2-propanol. The intersystem crossing yield has been estimated from the experimentally measured ΔA values (table 1) for different solvents using (6):

$$\Delta A/(\phi_{isc}\, \varepsilon_T) = \text{constant}. \tag{6}$$

It is expected that the peak value of ε_T may not be altered significantly in different

Table 2. Quantum yields of the different deactivation routes of S_1 of acridine.

Solvent	ϕ_f	ϕ_{isc} $\times(1 \pm 0.1)$	ϕ_{ic}	ϕ_r $\times(1 \pm 0.2)$
Acetonitrile	0	1·0	0	0
DMSO	0	0·58	0·42	0
Benzene	5×10^{-4}[(a)]	0·8	0·2	0
CCl$_4$	0	0·6	0·4	0
Methanol	0·05[(b)]	0·47	0·16	0·32
2-Propanol	0·035	0·62	0·085	0·26

(a) Kasama *et al* (1981b); (b) Wolff (1981).

organic solvents (Sundstrom *et al* 1977). Hence, ϕ_{isc} is directly proportional to the measured value of ΔA. It has been estimated earlier that ϕ_{isc} in benzene is 0.73 ± 0.07 (Kellmann 1977) or 1.0 (Kasama *et al* 1981b). However, our data of relative ΔA values shows that ϕ_{isc} in benzene is likely to be smaller than in acetonitrile. The relative triplet yields are therefore calculated based on a maximum value of 1.0 for ϕ_{isc} in acetonitrile. The values so obtained are in good agreement with the reported values for methanol (0.44, Tokumura *et al* 1973) and benzene (0.73 ± 0.07, Kellmann 1977).

The quantum yields of the C-radical in 2-propanol and methanol were estimated from the measured absorbances at 278 nm (C-radical) and at 440 nm (triplet) using (7).
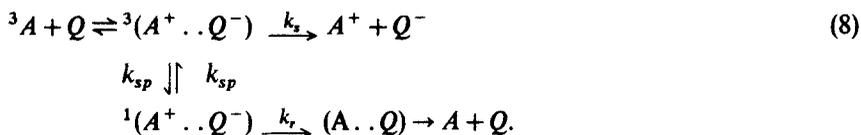
$$(\Delta A_T/\phi_{isc}\,\varepsilon_T)_{440} = (\Delta A_r/\phi_r\varepsilon_r)_{278}. \tag{7}$$

Using the value $\varepsilon_T = 2.4 \times 10^4 \text{ M}^{-1}\text{ cm}^{-1}$ (Benasson and Land 1971) and $\varepsilon_r = 2.4 \times 10^4 \text{ M}^{-1}\text{ cm}^{-1}$ (Kira and Koizumi 1969) the values of ϕ_r have been obtained. The quantum yield of internal conversion (ϕ_{ic}) has been obtained using the relation that the sum of all four quantum yields is unity.

Table 2 shows that the deactivation route of the excited singlet state of acridine is strongly solvent dependent. The most significant solvent dependence is the well-known appearance of intense fluorescence of acridine in alcoholic solvents. Even though the fluorescence is intense in alcoholic solvents the quantum yield ϕ_f remains fairly small; 0.05 in methanol and 0.035 in 2-propanol. An even larger quantum yield of C-radical is obtained in these two solvents which have not been quantitatively measured earlier. It is significant to note that ϕ_r is smaller in 2-propanol which is a better hydrogen atom donor than methanol. It appears possible that the mechanism of photoreaction in alcoholic solvents is a fast electron transfer followed by proton transfer. Further investigation is necessary to establish the mechanism of C-radical formation from the excited singlet state.

4.2 *Mechanism of triplet quenching by chloranil*

The rate constant of the quenching of the triplet state of acridine by chloranil is near the diffusion controlled limit in different types of solvents. The transient absorption spectrum after the triplet disappearance shows that long-living products are formed in polar solvents (acetonitrile and DMSO) and hydroxylic solvents (alcohols). In non-polar solvents (benzene and CCl$_4$) no product has been observed in the 400–700 nm region as a result of triplet quenching by chloranil. The following general mechanism is proposed to account for the results in polar and non-polar solvents.

$$^3A + Q \rightleftharpoons {}^3(A^+\cdots Q^-) \xrightarrow{k_s} A^+ + Q^- \tag{8}$$

$$k_{sp} \Updownarrow \ k_{sp}$$

$$^1(A^+\cdots Q^-) \xrightarrow{k_r} (A\cdots Q) \to A + Q.$$

The primary product of electron transfer quenching is the ion-pair in the triplet spin configuration in polar and non-polar solvents. Separation of the ion-pair leads to the formation of free ions. Recombination by back electron transfer in triplet ion-pair to products in singlet ground state in spin forbidden. Spin rephasing has to occur to evolve singlet ion-pair before recombination to products in the ground state. The relative rates of ion-pair separation (k_s) and spin rephasing (k_{sp}) determines the yield of the free radical ion. The spin rephasing rate constant is less sensitive to the solvent polarity since

the known mechanisms that contribute to this process, namely Δg mechanism and hyperfine interactions (Lepley and Closs 1973; Atkins and Lambert 1975) are more dependent on specific solvent interactions than on solvent polarity. However, the rate constant of ion separation (k_s) is very sensitive to solvent polarity. In polar solvents the solvation free energy of the separated ions could easily compensate for the coulombic attraction of the ions in the ion-pair. That is $k_s > k_{sp}$ in polar solvents. In non-polar solvents the separation of the triplet ion-pair becomes difficult because of the low solvation free energy of the separated ions. Since no free ions are observed in non-polar solvents, we conclude that $k_{sp} \gg k_s$.

The hydroxylic solvents (alcohols) are also polar solvents and hence the triplet ion-pair is formed in the triplet quenching by chloranil. However, in these solvents the protonation of the free radical anion $(Q^{\pm})$ occurs fast to give the neutral free radical.

$(QH^{.})$, but the transient spectrum of $QH^{.}$ is very similar to that of $Q^{\pm}$ in aprotic solvents. Temporal decay of $QH^{.}$ indicates that $QH^{.}$ continues to grow even after the complete quenching of the triplet state of acridine. The formation of the C-radical of acridine from the singlet state in alcoholic solvents appears to contribute to the formation of $QH^{.}$ through a hydrogen atom exchange reaction (9):

$$AH^{.} \text{ (C-radical)} + Q \rightarrow A + QH^{.}. \tag{9}$$
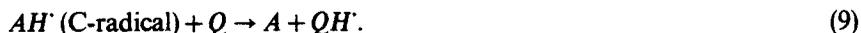
The kinetics and mechanism of triplet quenching in alcohol solvents require further investigation.

5. Conclusion

A nsec time resolved laser flash photolysis set-up is described and used for the investigation of the 355 nm-laser induced chemistry of acridine in various organic solvents. The triplet state is formed within 20 nsec of laser excitation. The triplet decay in acetonitrile is analysed on the basis of a three-route mechanism and the rate constants obtained. The quantum yields of the four major deactivation routes of S_1 of acridine are determined in various solvents which show a strong solvent dependence. In alcoholic solvents the growth rate of C-radical and triplet state of acridine after laser excitation are comparable, thereby establishing the S_1 as the precursor of the C-radical in these solvents.

The triplet state of acridine is efficiently quenched by chloranil in all the solvents. Electron transfer quenching mechanism is supported by the appearance of free-radical ions in the polar solvents.

The nonlinear dependence of triplet yield of acridine on 355 nm-laser pulse energy is interpreted to be due to a biphotonic process and the products of biphotonic ionization are unambiguously observed in alcoholic solvents.

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Appendix I

The decay of homogeneously distributed triplets according to the three-route mechanism is given by:

$$-(dC_T/dt) = k_1 C_T + k_2 C_T C_G + k_3 C_T^2 \tag{A1}$$

C_T and C_G are the concentrations of the triplet state (T) and the ground state (G). When the excitation laser pulse width is very short compared to the triplet decay time, (A1) is integrated with the initial condition $C_T = C_T^0$ at $t = 0$ (i.e. at the end of the laser pulse). The solution is written in terms of the experimentally measured transient absorbance (ΔA) at a specific wavelength, λ, as

$$\Delta A(K + \Delta A)^{-1} = \Delta A_0 (K + \Delta A_0)^{-1} \exp\{-t(k_1 + k_2 C_0)\}, \tag{A2}$$

where,

$$\Delta A = C_T(\varepsilon_T - \varepsilon_G) l, \tag{A3}$$

$$K = l(\varepsilon_T - \varepsilon_G)(k_1 + k_2 C_0)/(k_3 - k_2), \tag{A4}$$

and

$$C_0 = C_T + C_G. \tag{A5}$$

ε_T and ε_G are the molar extinction coefficients of the triplet state and the ground state at λ respectively; l is the path length in the sample in which the triplet species are present; ΔA_0 and ΔA are the measured transient absorbances at $t = 0$ and $t > 0$ respectively.

The measurement of the initial absorbance ΔA_0 at $t = 0$ is usually hindered by fluorescence or laser scatter from the sample. The following method avoids the measurement of ΔA_0 and leads to the evaluation of the kinetic constants. Equation (A2) is rewritten in a form where t *vs* $\ln(1 + K/\Delta A)$ is linear.

$$t = (k_1 + k_2 C_0)^{-1}\{\ln(1 + K/\Delta A) - \ln(1 + K/\Delta A_0)\}. \tag{A6}$$

The experimental data of t *vs* ΔA is used to calculate t *vs* $\ln(1 + K/\Delta A)$ for a particular value of K (the choice of the value of K is discussed later) and tested for a straight line fit according to (A6) by the standard least square method. The deviation of the experimental data from the linear fit for the chosen value of K is given by the parameter S_K.

$$S_K = \sum_i (t_i - m_k x_i - n_k)^2, \tag{A7}$$

where $x_i = \ln(1 + K/\Delta A_i)$, m_k and n_k are the constants of the fit for (A6) written in the form:

$$t = m_k x + n_k. \tag{A8}$$

S_K is obtained in the units of $\sec^2$. The value of K is varied in suitable increments and for an optimum value of K (*i.e.* for the best fit) S_K is minimum. The kinetic constants are obtained in the following form:

$$(k_1 + k_2 C_0) = 1/m_k, \tag{A9}$$

$$(k_3 - k_2) = l(\varepsilon_T - \varepsilon_G)/(m_k K). \tag{A10}$$

Analysis of the transient decay curves for two different values of C_0 makes it possible to evaluate k_1 and k_2. k_3 is evaluated using (A10).

The value of K could lie in the range $-\alpha$ to $+\alpha$. However, a value of $|K| \gg \Delta A_0$ indicates that the decay is exponential. Such an exponential decay indicates that $k_2 = k_3 = 0$ or $k_3 = k_2$ and the choice between the two is made by varying C_0. In practice the value of ΔA_0 is likely to be in the range of 10^{-3} to 1 and hence the value of K is initially varied in decades from 10^{-5} to 10^2. If no minimum of S_K is reached K is negative ($\varepsilon_T < \varepsilon_G$ and $k_2 > k_3$ or $\varepsilon_T < \varepsilon_G$ and $k_3 > k_2$) and the value of K is varied from -10^{-5} to -10^2 to obtain the minimum S_K. The value of K is then varied within the narrow range of two decades in smaller increments and this procedure is extended until the optimum value of K is obtained.