

## RADICALS PRODUCED FROM THE LASER-INDUCED PHOTOIONIZATION OF ACRIDINE IN SOLUTION

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### Summary

We report on the transient species obtained in the biphotonic ionization of acridine in aqueous solution (pH 12.3) induced by the third harmonic of a neodymium-doped glass laser. The species directly produced during the laser pulse were the hydrated electron and the acridine cation which was detected for the first time in fluid media at room temperature. The hydrated electron and the cation decayed with pseudo-first-order kinetics, leading to microsecond transients which were assigned to two different acridine neutral radicals. The acridine cation was neutralized by the  $\text{OH}^-$  present in the solution ( $k = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), leading to a radical (the "N radical") characterized by an absorption around 600 nm ( $\lambda_{\text{max}} = 595 \text{ nm}$ ;  $\epsilon_{\text{max}} \approx 5000 \text{ M}^{-1} \text{ cm}^{-1}$ ). The hydrated electron reacted efficiently with unexcited acridine ( $k = 4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) to give a hydrogenated radical (the "C radical") which showed a broad absorption in the visible region around 500 nm ( $\lambda_{\text{max}} = 510 \text{ nm}$ ;  $\epsilon_{\text{max}} \approx 4000 \text{ M}^{-1} \text{ s}^{-1}$ ).

### 1. Introduction

Considerable interest has been developing for many years concerning the mechanism of the photoionization of organic molecules in fluid solution, using continuous irradiation and the flash photolysis technique [1]. More recently, excitation of polyatomic molecules has been shown to generate biphotonic phenomena [2]. In particular, it has been established in a number of studies that the laser-induced photoionization of aromatic compounds in fluid media also occurs via a biphotonic process [3 - 8].

In a recent laser flash investigation [9] it was found that acridine (Ac) in aqueous solution is photoionized under excitation in its first excited singlet state. The mechanism of the hydrated electron  $e^-_{\text{aq}}$  formation was determined using the third harmonic of a neodymium laser (353 nm), and it was concluded that acridine is photoionized via a consecutive two-photon process. The relative population of the possible intermediates (the first

excited singlet  $S_1^*$  and the lowest triplet T states) was varied by changing the laser pulse duration with respect to the  $S_1^*$  lifetime and by experiments using the heavy atom effect to enhance the triplet population. The results indicated that the intermediate states are both  $S_1^*$  and T; however, the  $S_1^*$  pathway was shown to be more efficient than the T pathway.

In this paper we report on the transient species obtained from the photoionization of acridine in alkaline solution. The species directly produced during the laser pulse are  $e^-_{aq}$  and the acridine cation  $Ac^+$ , whereas two neutral radicals are formed as a consequence of secondary reactions. The observed nanosecond and microsecond transient absorptions are spectrally and kinetically consistent with the formation of two different acridine radicals, one due to the reaction of  $e^-_{aq}$  with acridine and the other to the reaction of  $Ac^+$  with  $OH^-$  present in the solution.

## 2. Experimental section

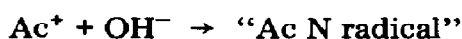
The exciting light source was an  $Nd^{3+}$ -doped glass laser (CGE model VD 231) emitting at 1058 nm. The third harmonic (353 nm) generated by means of potassium diacid phosphate crystals was used in the present work at an energy of 1 - 10 mJ. A Pockels cell (CGE, DL 11) limited the pulse duration to 6 ns full width at half-maximum intensity. Relative values of the laser energy were obtained by measuring a small fraction of the UV laser beam deflected to a calibrated photodiode (ITT, 4000 S20 UVG). The laser beam was projected onto one side of a 10 mm  $\times$  10 mm silica cell containing the sample. A frosted plate of silica was placed close to the cell to homogenize the laser beam. Transient absorptions were monitored at right angles to the excitation. Kinetic spectrophotometry of the transients was carried out using a xenon flash lamp (replaced by an Osram XBO 75 W/2 lamp for decays longer than 20  $\mu s$ ), a high intensity monochromator (Jarrel Ash;  $f = 0.25$  m; bandwidth, 2 nm), a photomultiplier (RCA 1P28 and HTV R 928 in the UV and visible ranges and HTV R 406 in the IR range) and a double-beam oscilloscope (Tektronix 7844). The time response of the detection system was 1 - 2 ns.

Acridine (Eastman Kodak) was recrystallized three times from an ethanol-water mixture after refluxing over active carbon. The aqueous solutions were prepared from twice-distilled deionized water and were made alkaline by adding NaOH. Protolytic reactions of excited acridine were avoided by carrying out the experiments at pH 12.3 ( $pK_G = 5.5$  [10],  $pK_T = 5.6$  [11],  $pK_S = 10.6$  [10]). The acridine concentration was  $10^{-4}$  M unless otherwise stated. The samples were deaerated by bubbling argon through the solution just before the experiments.

When necessary,  $e^-_{aq}$  produced by the laser photolysis was eliminated by saturation of the solution with  $N_2O$ . For kinetic studies of the most short-lived species ( $e^-_{aq}$  and  $Ac^+$ ), it was necessary to subtract the triplet-triplet absorption [12, 13] remaining after the decay of these species from the measured optical density (the triplet-triplet absorption was con-

sidered to be constant over a few hundred nanoseconds). The absorptions of the long-lived species (radicals) were observed 40  $\mu$ s after the laser pulse; at that time,  $e^-_{aq}$  and the acridine triplet had decayed completely.

The principal uncertainty in time-resolved spectroscopic measurements of the extinction coefficients  $\epsilon$  for transient species is the concentration of these species. In the photoionization process,  $e^-_{aq}$  and  $Ac^+$  are necessarily produced in identical concentrations. Using the published  $e^-_{aq}$  spectrum [14], it was possible to calculate the  $e^-_{aq}$  concentration from the initial absorption of  $e^-_{aq}$  at 660 nm. Since the  $Ac^+$  concentration was equal to the  $e^-_{aq}$  concentration, the extinction coefficient  $\epsilon$  at 900 nm ( $\lambda_{max}$ ) was deduced from the optical density obtained at this wavelength. The kinetics showed that under our experimental conditions  $e^-_{aq}$  and  $Ac^+$  decay only by the following reactions:



Since the decay of the radicals is slow compared with their formation, the maximum concentration of these radicals could be set equal to the initial  $e^-_{aq}$  concentration. Values of  $\epsilon$  for the radicals were deduced from their respective experimental absorptions.

### 3. Results and discussion

#### 3.1. Electron decay and radical formation by reaction with acridine

On optical excitation at 353 nm of acridine in deoxygenated aqueous solution (pH 12.3),  $e^-_{aq}$  was identified by its characteristic red absorption band ( $\lambda_{max} = 720$  nm) [14] and its quenching by electrophilic agents such as  $O_2$  and  $N_2O$  [15]. In our experiments the disappearance of  $e^-_{aq}$  was monitored at 660 nm: an exponential decay was observed ( $\tau \approx 350$  ns) (Fig. 1). At low concentrations of  $e^-_{aq}$  (less than  $5 \times 10^{-6}$  M) the bimolecular reaction  $e^-_{aq} + e^-_{aq}$  may be neglected ( $k_2 = 5 \times 10^9$  M $^{-1}$  s $^{-1}$  [16]). This pseudo-first-order decay must be due to the reaction of  $e^-_{aq}$  with unexcited acridine. Indeed the  $e^-_{aq}$  decay rate was found to be directly proportional to the acridine concentration (Fig. 1) in experiments where the laser energy was adjusted to give the same low value for the initial  $e^-_{aq}$  concentration ( $3 \times 10^{-6}$  M), confirming that the decay of  $e^-_{aq}$  is controlled by the reaction of  $e^-_{aq}$  with  $Ac^+$ . From the experimental results the rate constant of this reaction was found to be  $4 \times 10^{10}$  M $^{-1}$  s $^{-1}$ , in good agreement with the results obtained for the one-electron reduction of acridine in pulse radiolysis studies [17, 18]. A high reactivity with  $e^-_{aq}$  has also been observed for a number of other *N*-heterocyclic compounds [17]. We would expect the acridine anion to be formed in the above reaction. However, no transient absorption due to this species (which has been chemically prepared [19]) could be detected even at high pH (11 - 13). The observed microsecond

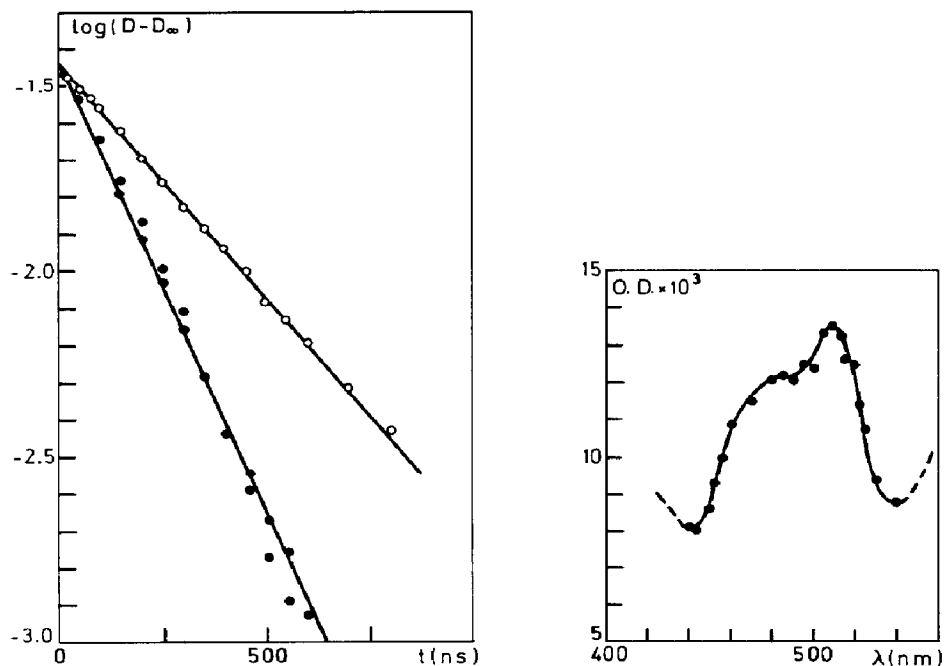
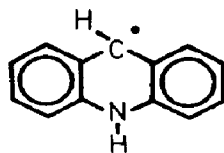


Fig. 1. Decay kinetics of  $e^-_{aq}$  at 660 nm after the laser photolysis of argon-saturated solutions (pH 12.3) with different initial concentrations of acridine ( $D_\infty$ , optical density of the acridine triplet): ○,  $10^{-4}$  M; ●,  $2 \times 10^{-4}$  M.

Fig. 2. The absorption spectrum of the neutral hydrogenated acridine radical  $\cdot\text{AcH}$  ("C radical") recorded 40  $\mu\text{s}$  after the laser pulse (argon-saturated acridine solution ( $10^{-4}$  M; pH 12.3)).

transient absorption spectrum after the reaction of  $e^-_{aq}$  with acridine (Fig. 2) presents a broad band in the visible region with a maximum at 510 nm and an  $\epsilon_{\text{max}}$  of  $4000 \text{ M}^{-1} \text{ cm}^{-1}$ . This absorption is consistent with the spectrum of the neutral radical  $\cdot\text{AcH}$  ("C radical")



which has been obtained previously in the photoreduction of acridine in hydrogenated solvents [20, 21]. In addition, the transient species was found to be efficiently quenched by  $\text{O}_2$ , in agreement with the reactivity of carbon-centred radicals towards  $\text{O}_2$  [20, 22]. This  $\cdot\text{AcH}$  radical has also been observed after reduction of aqueous acridine solution by  $e^-_{aq}$  in pulse radiolysis studies at high pH (12 - 14) [17, 18]. Support for this assignment was derived from electron spin resonance studies of radicals produced by the one-electron reduction of pyridine and identified as pyridinyl radicals [23]. Similar results have been obtained with other heterocyclic compounds such

as phenazine and other diazines [17]. These observations indicate that the  $pK$  of the acridine "C radical" is above 14.

### 3.2. Decay of the cation and formation of a neutral radical

Simultaneously with  $e^-_{aq}$ , another species is formed during the laser pulse. Its transient absorption shows a broad band with a maximum at 900 nm. This spectrum is similar to that of the species obtained by the  $\gamma$  irradiation of acridine in butyl chloride (BuCl) at low temperature (77 K) and identified as the acridine cation [24]. Indeed, although cations of *N*-heterocycles have never been prepared chemically, it has been established that they are produced by irradiation in BuCl at 77 K according to the method used to obtain cations of aromatic compounds [25]. From the previous observations the absorption spectrum shown in Fig. 3 (recorded 50 ns after the pulse) is then assigned to the acridine radical cation  $Ac^+$ . For the absorption maximum located at 900 nm,  $\epsilon \approx 8000 \text{ M}^{-1} \text{ cm}^{-1}$ . The cation absorption follows an exponential decay ( $\tau \approx 170 \text{ ns}$  at pH 12.3).

As  $Ac^+$  decays, a new transient appears which presents a broad band with a maximum at 595 nm and  $\epsilon_{595} \approx 5000 \text{ M}^{-1} \text{ cm}^{-1}$  (Fig. 4). In Fig. 5 the decay curve of the cation is drawn as  $\log(D - D_\infty)$  versus time where  $D$  is the observed optical density at 900 nm and  $D_\infty$  is the optical density due to the acridine triplet which absorbs in the IR region and is considered constant over a few hundred nanoseconds. Around 600 nm an absorption is present after the laser pulse because the acridine triplet also absorbs in this region. This triplet absorption is considered constant over the rise time of the new transient. The total absorbance  $D'$  at time  $t$  reaches a constant level  $D'_\infty$  at

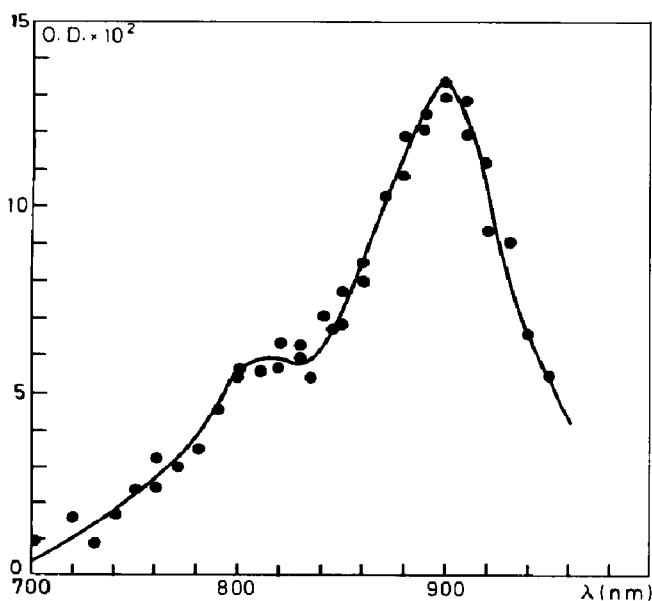


Fig. 3. The absorption spectrum of the acridine radical cation  $Ac^+$  recorded 50 ns after the laser pulse ( $N_2O$ -saturated acridine solution ( $10^{-4} \text{ M}$ ; pH 12.3)).

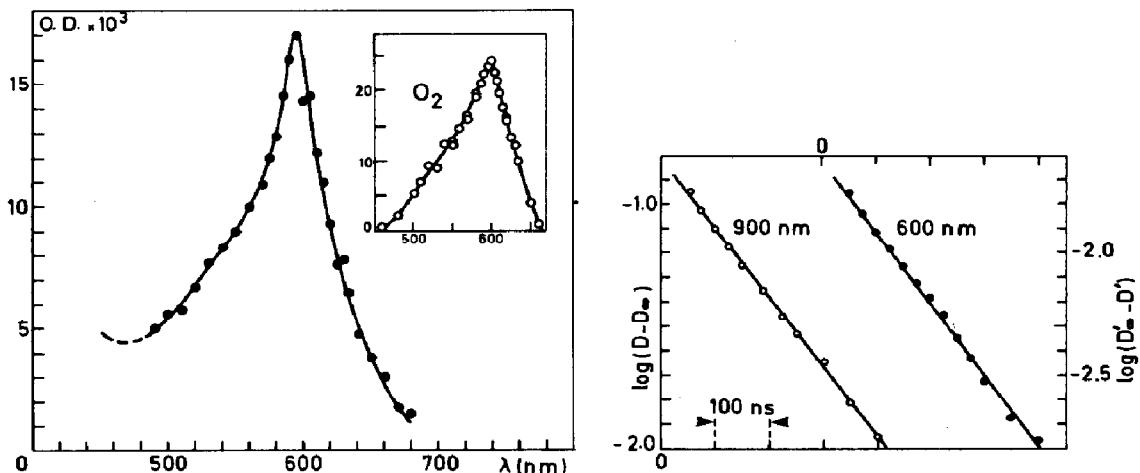
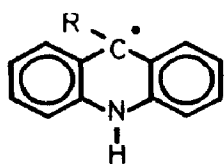


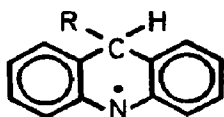
Fig. 4. The absorption spectrum of the neutral acridine radical  $\cdot\text{Ac.OH}$  ("N radical") recorded  $40 \mu\text{s}$  after the laser pulse (argon-saturated acridine solution ( $10^{-4} \text{ M}$ ; pH 12.3)). The inset is the absorption spectrum observed in  $\text{O}_2$ -saturated solution  $4 \mu\text{s}$  after the laser pulse.

Fig. 5. A comparison of the formation kinetics of the "N radical" at 600 nm ( $\bullet$ ) with the decay kinetics of  $\text{Ac}^+$  at 900 nm ( $\circ$ ): at 900 nm,  $D_\infty = D_{\text{T}}$  (the optical density of the acridine triplet); at 600 nm,  $D_\infty' = D'_{\text{R max}} + D'_{\text{T}}$  (the sum of the optical densities of the transient and of the acridine triplet).

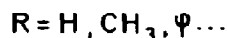
$t_\infty$  (approximately 500 ns), which is the sum of the optical densities of the transient R at its maximum concentration ( $D'_{\text{R max}}$ ) and of the acridine triplet ( $D'_{\text{T}}$ ):  $D_\infty' = D'_{\text{R max}} + D'_{\text{T}}$ . The expression  $D_\infty' - D' = D'_{\text{R max}} - D'_{\text{R}}$  (where  $D'_{\text{R}}$  is the optical density of R at time  $t$ ) thus corresponds to the build-up of the transient to its maximum value. As shown in Fig. 5, the plot of  $\log(D_\infty' - D')$  versus  $t$  is parallel to that of  $\log(D - D_\infty)$  versus  $t$  corresponding to the cation; clearly the transient rise time and the cation decay time agree well with each other. When the solution is made more basic (the  $\text{OH}^-$  concentration being varied from  $10^{-2}$  to  $10^{-1} \text{ M}$ ) the cation lifetime is reduced and the rate of the formation of this transient increases linearly with the  $\text{OH}^-$  concentration. Since the formation kinetics of this new species are consistent with the exponential decay kinetics of the  $\text{Ac}^+$  cation for different concentrations of  $\text{OH}^-$ , the transient is assumed to result directly from the neutralization of the  $\text{Ac}^+$  cation by the  $\text{OH}^-$  present in the solution ( $k = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). The absorption at 595 nm can thus be assigned to a neutral radical of Ac ( $\tau \approx 100 \mu\text{s}$ ). However, this radical is different from the radical resulting from the reaction of  $e^-_{\text{aq}}$  with acridine. Its absorption spectrum is red shifted compared with that of the  $\cdot\text{AcH}$  radical and it is unaffected by oxygen (as shown in the inset of Fig. 4) in contrast with  $\cdot\text{AcH}$ . The existence of two neutral radicals is well established from spectroscopic and electron spin resonance studies [21, 22, 26]. One is described as the "C radical" (I) and the other as the "N radical" (II):



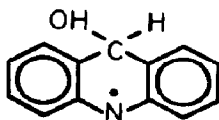
( I )



( II )



The spectra of these two radicals are different: the "C radical" has an absorption around 500 nm whereas the "N radical" absorption is located at 560 - 600 nm (depending on the R substituent). Furthermore, this radical is nearly unreactive towards  $O_2$  while the "C radical" is very sensitive to  $O_2$  ( $k \approx 10^9 M^{-1} s^{-1}$  [20]). On these grounds the radical resulting from the neutralization of the cation is assumed to be the "N radical", with an OH group attached to the *meso*-carbon.



#### 4. Conclusion

In the present paper we reported a detailed study of the chemical reactions that occur after the biphotonic laser-induced ionization of acridine. It was demonstrated that  $e^-_{aq}$  reacts very efficiently with unexcited acridine, giving the neutral hydrogenated (carbon-centred) radical instead of the acridine anion. The acridine radical cation was detected for the first time in fluid solution and its absorption spectrum and extinction coefficient were determined. The cation was shown to undergo neutralization in alkaline media, leading to the formation of a neutral nitrogen-centred radical. Thus, both a neutral "C radical" and a neutral "N radical" of acridine are formed as a consequence of secondary reactions in the photoionization of acridine.

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