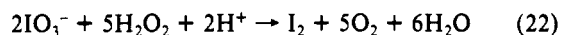


during the course of this work, can only influence concentrations of O_3 , NO_x , or iodine species when NO_3 , I_2 , and I are present simultaneously in significant amounts in the atmosphere. Iodine species exist in highest concentrations in air masses with a marine history, whereas $[NO_3]$ is greatest over continental areas, so that the reactions studied in this work are expected to be important in coastal regions only. As yet, the emissions of I_2 , HOI , or I from the ocean surface believed to occur^{4,62} are not well quantified and have not been included in tropospheric models. If the action of ozone at the sea surface does indeed release I_2 to the atmosphere, as suggested by Garland and Curtis,⁴ then there is a nighttime source of I_2 . The iodine either will react with NO_3

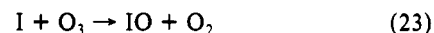


or will deposit on aerosols or the sea surface. For a typical concentration of NO_3 in the boundary layer of 2.5×10^7 molecules cm^{-3} ,⁶³ the atmospheric lifetime for removal of I_2 by reaction with NO_3 is about 7.5 h compared with lifetimes of 1 day for dry deposition and irreversible attachment to aerosol particles.¹¹ Thus, it appears that, during the night, the reaction between NO_3 and I_2 may be the dominant process for removal of I_2 . However, the figures used for the rate of deposition must be treated with caution, as the chemistry of iodine on or in aerosols is poorly defined,¹⁰ and it is possible that I_2 is released by processes such as



occurring in cloud droplets.⁶⁴

Reaction 1a constitutes a nighttime source of iodine atoms and, therefore, a route for the consumption of O_3 via the reaction sequence



The rate of reaction between I and NO_3 ($k_2 = 4.5 \times 10^{-10}$ cm^3 molecule⁻¹ s⁻¹) can be used to calculate a lifetime for removal of I (again using $[NO_3] = 2.5 \times 10^7$ molecules cm^{-3}) of 100 s, compared with a lifetime for removal against reaction with O_3 (typical concentration of 6.25×10^{11} molecules cm^{-3}) of 1.6 s, so that, as for the daytime, I is mainly removed by reaction with ozone. Our new work thus indicates that the main influence of NO_3 on atmospheric iodine chemistry is likely to be through the reaction with I_2 rather than the interactions with atomic iodine. The consequences of reaction 1 are loss of I_2 and a possible nighttime consumption of O_3 .

Acknowledgment. A.C.H. thanks the Gassiot Committee of the Meteorological Office for a research training studentship under the auspices of which this research was conducted. We also thank Drs. P. Biggs and C. E. Canosa-Mas for practical and other assistance and Mr. P. S. Monks for his computer expertise.

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A Nanosecond Laser Flash Photolysis Study of Intramolecular Reactions in the Erythrosin B/CTAB Aqueous System

Lucia Flamigni

Istituto F.R.A.E.-C.N.R., Via de' Castagnoli, 1, 40126 Bologna, Italy (Received: October 23, 1991; In Final Form: December 30, 1991)

Both "fast", occurring within 1 μ s after excitation, and "slow" reactions, occurring in the hundreds of microseconds time scale, were observed following erythrosin B triplet formation in the cationic micellar system cetyltrimethylammonium bromide (CTAB). The "fast" events are shown to occur in multiply occupied micelles and are assigned to bimolecular reactions. The "slow" ones, which have not been studied in detail, are due to first-order deactivation processes of the triplet occurring in singly occupied micelles. The effects of the excitation intensity and occupancy on the fast triplet decay, radical formation, and subsequent geminate recombination have been studied. The triplet disappears with observed rate constants ranging from 5.5×10^6 to 3.6×10^6 s⁻¹ while the formation of radicals has rate constants varying from 3.3×10^7 to 9.1×10^6 s⁻¹. Both in triplet decay and in radical formation the increase in rates occurs by increasing the excitation energy and occupancy. The identification of the precursor(s) of radicals is discussed. The geminal radical recombination has a rate constant of 2.1×10^6 s⁻¹.

Introduction

Transient intermediates obtained upon light absorption in xanthene dyes in homogeneous solutions have been the object of intense investigations since the early days of flash photolysis.¹⁻¹⁰ Time-resolved luminescence studies on these systems appeared

later as a consequence of the short lifetime of the singlet state, requiring subnanosecond resolution.¹¹⁻¹³

Because of the wide applications of these dyes in several fields (solar energy conversion, laser dyes, biological markers, singlet oxygen photosensitizers, photoinitiators of polymerization, etc.), the interest in such compounds is still very lively. More recently, studies aimed at understanding the behavior of such dyes in heterogeneous systems like micelles,¹⁴⁻²⁵ polymers,²⁶⁻²⁸ vesicles,²⁹

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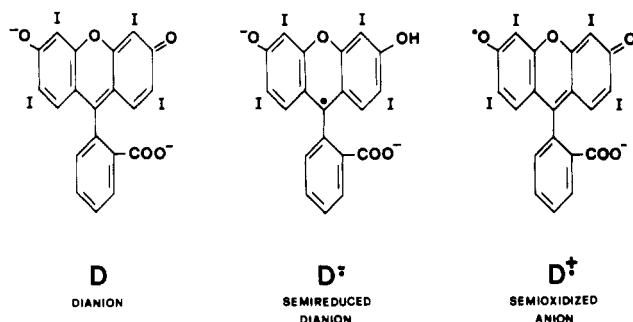
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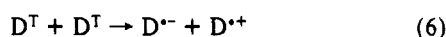
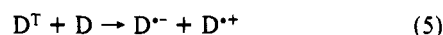
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Langmuir-Blodgett films,³⁰ semiconductor-electrolyte interface,^{31,32} and inclusion complexes with cyclodextrins³³⁻³⁵ appeared. Nevertheless, the elucidation of the primary steps following light absorption in homogeneous solutions continues to be the object of several studies.^{25,36-44}



The primary steps in homogeneous oxygen-free solutions, as proposed earlier by Lindqvist for fluorescein,³ applicable to all xanthenes,^{8,25,37-39,41,43} are as follows:



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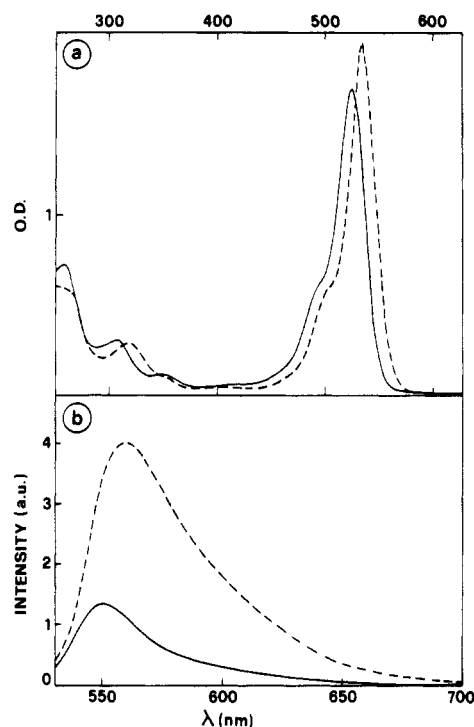
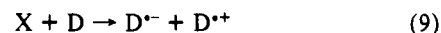


Figure 1. (a) Ground-state absorption spectra of a 19 μM EB aqueous solution (—) and of a 19 μM EB/2.2 mM CTAB aqueous solution, $\bar{n} = 0.9$ (---). (b) Emission spectra of the above solutions excited at 520 nm.

where D, D^S , and D^T stand respectively for dye ground state, excited singlet state, and triplet state; $D^{\bullet-}$ and $D^{\bullet+}$ are the semireduced and semioxidized dye radicals.

Vintgens et al.⁴³ showed that, for a rose bengal derivative, the yield and the rate of formation of radicals are dependent on the laser intensity,⁴⁵ clearly indicating the involvement of a biphotonic step in the mechanism. In accordance with the Lindqvist scheme, they identified such a step as the triplet-triplet reaction, process 6.

An alternative or additional path for the same observed phenomena in erythrosin B has been proposed to be the reaction with the ground state of a more reactive intermediate X, formed via a two-photon mechanism⁴⁶ which can be schematized as follows:



The discrimination between these two interpretations should be based on (a) comparison of the kinetics of decay of the triplet to the kinetics of formation of radicals and (b) identification of an intermediate other than the triplet and compatible with formation via a two-photon step.

These points can hardly be checked in fluid homogeneous solutions where the overlap of singlet ground and excited state⁴⁷ with triplet and radical absorptions^{1-9,36-44} and the occurrence of mixed-order and consecutive kinetics, namely reactions 5 + 6 followed by reaction 7, make the analysis quite complicated.

In an attempt to simplify, we decided to study a micellar system like CTAB where a binegatively charged solute like erythrosin B could easily locate.^{14,16,19} In this way the changes in the excitation intensity and in the population distribution, which can

(45) The accuracy of their kinetic analysis, approximating a first-order followed by a second-order reaction, namely (5) + (7), to the sum of two exponentials was intrinsically dependent (i.e. the degree of approximation increased) on the excitation intensity used, thus weakening the evidence of their results.

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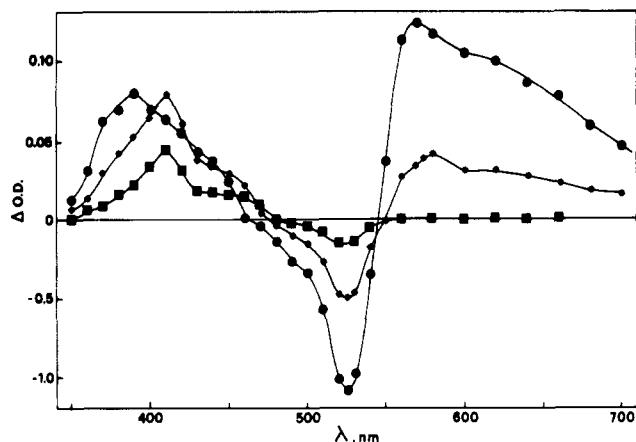


Figure 2. Transient absorption spectra detected in a 19 μM EB aqueous solution at $t = 0$ (\bullet), $t = 100 \mu\text{s}$ ($*$), and $t = 500 \mu\text{s}$ (\blacksquare) after the laser pulse. Excitation at 532 nm, 6 mJ cm^{-2} per pulse.

be achieved by tuning the ratio of solute to micelle concentration, are expected to allow the control on the order of reaction of the excited triplet. Furthermore, the geminal nature of the radical recombination in micelles would make the kinetics exponential,⁴⁸ thus simplifying the analysis.

In the present paper, a laser flash photolysis study with nanosecond resolution on erythrosin B in CTAB micellar solutions is presented where the effect of population distribution and excitation intensity on the intracellular reactions is investigated. The results obtained put forward some doubts on the current interpretation (reactions 1-7) of the processes occurring in these dyes upon light absorption.

Experimental Section

Erythrosin B (EB), Aldrich, was purified by column chromatography according to literature methods.²⁶ In agreement with a previous report,⁴⁹ the ϵ_{526} of the purified product in water was $90\,000 \text{ M}^{-1} \text{ cm}^{-1}$. Water was purified by passage through a Millipore Milli-Q system. Cetyltrimethylammonium bromide (CTAB) from Carlo Erba, RP grade, was used as received.

Absorption spectra were measured by a Perkin-Elmer Lambda 5 spectrophotometer. Emission spectra were obtained with a Spex-Fluorolog-2 fluorimeter.

Laser flash photolysis was performed by using the second harmonic ($\lambda = 532 \text{ nm}$) of a Nd:YAG laser (JK Lasers HY750, 18-ns pulse duration). The energy ranged from 10 to 0.7 mJ cm^{-2} per pulse. The laser-induced transient transmission changes were monitored perpendicular to the laser beam by a Xe arc lamp. The light transmitted by the sample (10-mm optical path) was monochromated with 4-nm resolution and detected by an Hamamatsu R936 photomultiplier. A Tektronix R7912 transient digitizer in conjunction with a Digital PDP11/23 microcomputer was used to acquire and process the signals by standard iterative nonlinear procedures. The goodness of fit between experimental points and applied mathematical function was judged on the basis of the reduced χ^2 and of the distribution of residuals along the time axis. The error on the rate constants is estimated to be $<15\%$. The overall instrumental response time is $<20 \text{ ns}$. Micellar solutions were shortly bubbled with nitrogen and kept under a constant, high flux of gas. To prevent concentration changes due to water evaporation, nitrogen was passed through a water trap. Experiments were carried out at room temperature.

Results

When CTAB is added to an aqueous EB solution, modifications occur both in the absorption and in the emission spectrum. Figure

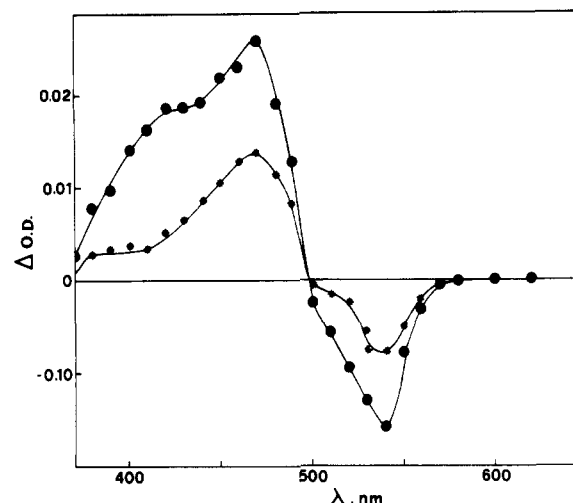


Figure 3. Transient absorption spectra detected in a 19 μM EB/0.5 mM CTAB aqueous solution at $t = 0$ (\bullet) and $t = 50 \mu\text{s}$ ($*$) after the laser pulse. The concentration of CTAB is below the critical micelle concentration. Excitation at 532 nm, 6 mJ cm^{-2} per pulse.

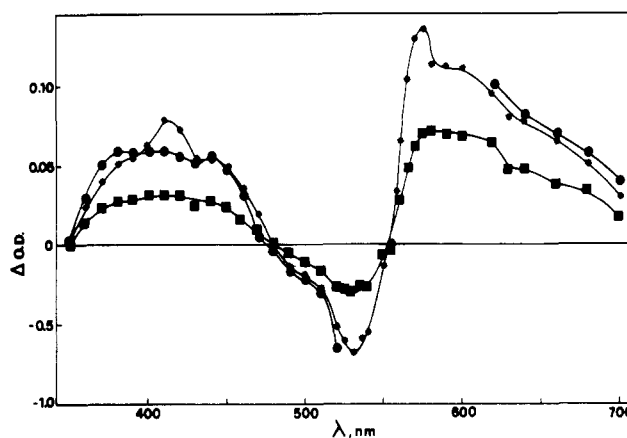


Figure 4. Transient absorption spectra detected in a 19 μM /2.2 mM CTAB aqueous solution, $\bar{n} = 0.9$, at $t = 0$ (\bullet), $t = 80 \text{ ns}$ ($*$), and $t = 820 \text{ ns}$ (\blacksquare) after the laser pulse. For data points from 530 to 610 nm at $t = 0$, see text. Excitation at 532 nm, 6 mJ cm^{-2} per pulse.

1a shows the absorption spectrum of 19 μM EB in CTAB micellar solution compared to that of 19 μM EB in water. The emission spectra of the same solutions are shown in Figure 1b.

Figure 2 shows the transient absorption changes of EB (19 μM) in water, detected at the end of the laser pulse, and its time evolution. The spectrum shows a strong bleaching on the visible band of the ground state ($\lambda = 526 \text{ nm}$) and absorption on both sides of the negative signal. In accordance with previous data on this²⁰ and similar dyes,^{1-10,36-44} the absorption from 560 nm onward is assigned solely to the triplet state while the 350-470-nm part of the spectrum is attributed to the triplet plus the bands of the semireduced (410 nm) and semioxidized (ca. 460 nm) radicals whose formation is shown by the time evolution of the transient absorption.

The transient spectrum detected at the end of the laser pulse and its time evolution for a 19 μM EB micellar solution 0.5 mM in CTAB (below the critical micelle concentration) is reported in Figure 3. In these conditions no micelle formation is expected; nevertheless, a very strong effect on the transient spectrum is produced. No triplet is detected, since no absorption is shown around 600 nm, a modest bleaching of the visible ground-state band is produced, and a low optical density, compared to that of aqueous solution, is shown only in the region of the radical's absorbance, from 350 to 500 nm. Formation of the radical species occurs during the pulse, and it cannot be time-resolved. The decay consists of a rapid, kinetically complex part, with a mean lifetime of approximately 500 ns, and a slow part, extending over tens of microseconds. The recovery of the bleaching follows the same

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TABLE I: Optical Density Changes Measured for Radical D^{•-} at 420 nm, Ground-State D at 520 nm, and Triplet-State D^T at 620 nm at Several Excitation Energies and Mean Occupancy Numbers; Fraction of Fast Component for D and D^T Also Reported

\bar{n}	$I, \text{mJ cm}^{-2}$	D ^{•-}	D		D ^T	
		$\Delta\text{OD}'_0$	$\Delta\text{OD}_{\text{tot}}$	$\Delta\text{OD}_0/\Delta\text{OD}_{\text{tot}}$	$\Delta\text{OD}_{\text{tot}}$	$\Delta\text{OD}_0/\Delta\text{OD}_{\text{tot}}$
0.3	10	0.062	-0.570	0.29	0.093	0.27
	6	0.047	-0.564	0.27	0.099	0.22
	2	0.043	-0.479	0.27	0.093	0.24
	0.7	0.024	-0.344	0.19	0.063	0.15
0.9	10	0.109	-0.630	0.55	0.089	0.49
	6	0.099	-0.536	0.46	0.082	0.47
	2	0.085	-0.554	0.47	0.081	0.43
	0.7	0.032	-0.376	0.30	0.053	0.31
2.3	10	0.082	-0.443	0.79	0.052	0.68
	6	0.080	-0.408	0.79	0.046	0.63
	2	0.074	-0.388	0.75	0.052	0.67
	0.7	0.058	-0.312	0.67	0.043	0.56

complex pattern as the radical decay.

The same 19 μM EB concentration in different CTAB solutions above the critical micelle concentration (cmc), with mean occupancy numbers \bar{n} ([EB]/[micelles]) of 0.3, 0.9, and 2.3, has been studied at different excitation intensities. In Figure 4 the spectrum relevant to the solution with $\bar{n} = 0.9$ and laser energy density 6 mJ cm^{-2} is shown. Absorption data from $\lambda = 530$ to $\lambda = 610$ nm at the end of the laser pulse are missing in the spectrum because of a strong emission signal originating from the micellized EB singlet which superimposes the absorption. The emission is completely over, and the electronics has fully recovered 80 ns after the end of the flash.

The spectra have features similar to the ones in water: ground-state bleaching (535 nm), triplet absorption at $\lambda > 560$ nm and extending all over the red side, and underlying triplet absorption on the UV side of the bleaching with superimposed maxima of the semireduced (410 nm) and semioxidized (ca. 460 nm) radicals.

At variance with water solution, it has to be noted that a peculiar peak at 570 nm seems to disappear faster than the underlying triplet. In water this band is probably overshadowed by the superposition of the absorption of the other species. Unfortunately, for the above-mentioned complication due to the strong emission, this spectral region is not suitable for detailed kinetic determinations. Nevertheless, an upper limit of 100 ns can be derived for the lifetime of the species.

The kinetics in CTAB solutions is different from the one in water; the triplet decay shows a biexponential time evolution with a fast component which is over in about 500 ns and a slow one, extending over hundreds of microseconds, very sensitive to the deaeration procedure. A similar biexponential evolution is shown by the ground-state recovery. On the short-wavelength side of the spectra, the formation of radicals takes place in about 100 ns followed by a decay which is over in a microsecond and leaves a residual absorption which survives with the same time constant as the "slow" part detected at other typical wavelengths. The "slow" class of events is assigned to EB residing in singly occupied micelles (see later). These phenomena have been widely treated in the literature,^{16,19,25b} and they are beyond the interest of the present paper.

Kinetic analyses at 420, 520, and 620 nm were performed as typical wavelengths to follow radical, ground-state, and triplet-state time evolution. The choice of the last two wavelengths, which do not correspond to the maxima of the bands, was done to avoid the strong emission signal which could distort the early part of the optical density (OD) time evolution. Kinetic determinations were also performed at 475 nm, where the semioxidized form absorbs; the kinetic treatment gave results in complete agreement with the one derived for the semireduced radical. Therefore, the rate constants reported for the semireduced radical D^{•-} are also representative of the time evolution of the semioxidized species D^{•+}. Optical densities vs time were fitted by single exponentials or linear combinations of exponentials; as already mentioned in the Introduction, formal second-order reactions become first order in a restricted environment;⁴⁸ therefore, no approximation is in-

TABLE II: Rate Constants of the Intracellular Formation and Decay of Radical (D^{•-}) Recovery of the Ground State (D) and Decay of the Triplet (D^T) at Several Excitation Energies and Mean Occupancy Numbers

\bar{n}	$I, \text{mJ cm}^{-2}$	$k', 10^6 \text{ s}^{-1}$		$k, 10^6 \text{ s}^{-1}$	
		D ^{•-}	D ^{•-}	D	D ^T
0.3	10	9.1	2.3	2.9	5.0
	6	11.1	2.0	2.9	3.6
	2	10.0	2.3	3.2	3.8
	0.7	11.1	2.3	2.9	4.8
0.9	10	14.2	2.3	2.8	4.8
	6	11.1	2.3	2.9	4.5
	2	11.1	2.1	2.6	3.7
	0.7	11.1	2.0	2.5	3.8
2.3	10	33.3	2.0	3.3	5.5
	6	16.7	1.9	3.0	4.2
	2	14.3	2.0	3.0	3.6
	0.7	10.0	2.0	2.7	3.6

duced. At 520 and 620 nm the optical densities were fitted by the expression

$$\Delta\text{OD} = \Delta\text{OD}_0 e^{-kt} + \Delta\text{OD}_\infty$$

Therefore, $\Delta\text{OD}_{\text{tot}} = \Delta\text{OD}_0 + \Delta\text{OD}_\infty$ represents the total change in optical density at $t = 0$; ΔOD_∞ represents the change in optical density at $t = \infty$, i.e. the OD relevant to the "slow" part of the decay; k is the observed rate constant of the process. At 420 nm the optical densities were fitted by the expression

$$\Delta\text{OD} = \Delta\text{OD}'_0 e^{-k't} + \Delta\text{OD}''_0 e^{-k''t} + \Delta\text{OD}_\infty$$

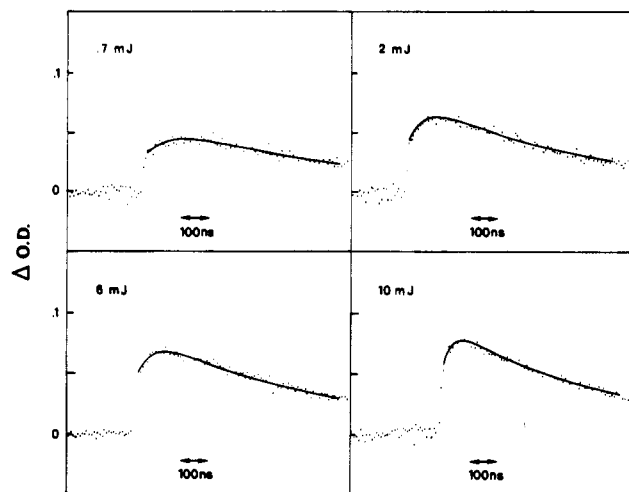
which describes two consecutive first-order reactions, where $\Delta\text{OD}'_0$ and $\Delta\text{OD}''_0$ represent the value at $t = 0$ of the single exponentials and ΔOD_∞ is the optical density at $t = \infty$ for the time domain of interest, and it is the optical density relevant to species which follow "slow" processes. k' and k'' represent the rate constant of the two consecutive reactions, i.e. formation and decay of the radical.

In Table I are reported the optical densities derived at the three typical wavelengths for 19 μM EB/CTAB solutions with mean occupancy of 0.3, 0.9, and 2.3 at several excitation intensities. For D^{•-} is reported the $\Delta\text{OD}'_0$, i.e. the extrapolated to zero-time optical density relevant to the radical decay, as derived from the fittings; for D and D^T are reported the total optical densities, OD_{tot} , and the fraction of fast to total component at $t = 0$, $\Delta\text{OD}_0/\Delta\text{OD}_{\text{tot}}$. It can be noticed that the fast component for D recovery and for D^T decay increases both with the occupancy and with the laser intensity. The correspondence between the fast components for D and D^T is fairly good. A net decrease in the total optical density can be noticed at the highest energies for the occupancy number 2.3, more remarkable for the triplet than for the bleaching.

In Table II are reported the rates measured according to the above kinetic equations in the different conditions at the three typical wavelengths. From the table it is clearly derived that the rate of formation of the radical is at least twice faster than the

TABLE III: P_i , the Probability That a Micelle Hosts i Molecules As Calculated by the Poisson Distribution Law, and p_i , the Probability That an Occupied Micelle Hosts i Molecules

\bar{n}	P_0	P_1	P_2	P_3	$P_{>3}$	p_1	$p_{>1}$	$p_{>3}$	Y
0.3	0.74	0.22	0.03	0.01		0.85	0.15		0.27
0.9	0.40	0.36	0.16	0.05	0.03	0.60	0.40	0.05	0.54
2.3	0.10	0.23	0.26	0.20	0.20	0.26	0.74	0.23	0.80

**Figure 5.** Experimental points and computed fits for the OD changes vs time measured at 420 nm at different laser energies for a 19 μM EB/1.4 mM CTAB solution ($\bar{n} = 2.3$).

decay of the triplet for every laser intensity and mean occupancy number. Furthermore, the rate of $\text{D}^{\cdot-}$ formation increases considerably by increasing the intensity of excitation, at least at high occupancy numbers, from 10×10^6 to $33 \times 10^6 \text{ s}^{-1}$. The decay of the triplet is slower, with rate constants slightly increasing with the excitation energy, from 3.6×10^6 to $5.5 \times 10^6 \text{ s}^{-1}$. In Figures 5 and 6 are shown experimental points and computed fits for ΔOD vs time of a 19 μM /1.4 mM CTAB solution ($\bar{n} = 2.3$) respectively at 420 nm ($\text{D}^{\cdot-}$) and 620 nm (D^{\cdot}). Both the decay of the radicals and the recovery of the ground state are fairly constant over all conditions with rate constants respectively of 2.1×10^6 and $2.9 \times 10^6 \text{ s}^{-1}$.

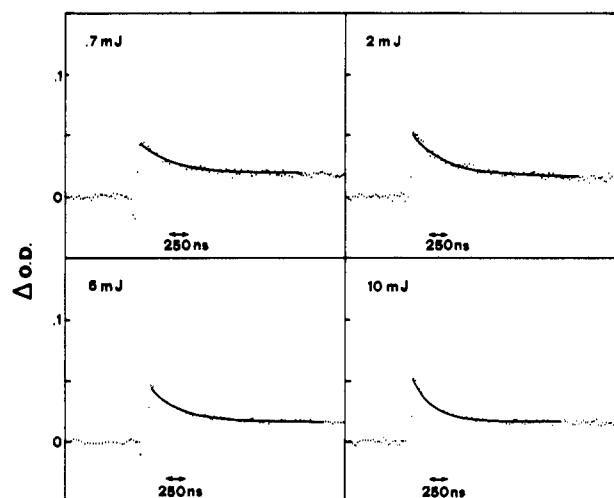
Experiments performed on solutions containing 10 μM EB and CTAB concentration adjusted to provide the same values of mean occupancy numbers gave results in complete agreement with those reported above for the 19 μM EB solution.

Discussion

The binegatively charged EB molecule is expected to locate in the cationic micelle, as shown by previous reports on xanthene dyes.^{14,16,19,25b} The determined escape constant for EB in this system has been reported to be quite low, $0.25 \times 10^3 \text{ s}^{-1}$.¹⁹ The here reported results can be fully explained in terms of a complete location of EB and of all the intermediates, at least on the time scale of interest, in the micellar phase. This is not surprising since, besides the hydrophobic interaction, Coulombic attraction is also operative for all the species considered. (Also $\text{D}^{\cdot+}$, the semi-oxidized species, is actually a negative ion.)

The solubilization of EB in the micelles produces the changes detected in the absorption spectrum, where the increase in ϵ can be assigned to the disaggregating ability of micelles while the bathochromic shift could indicate that the molecule is located in a less polar environment, in agreement with previous results.^{12,25} The remarkable increase in the emission yield of EB when dissolved in micellar solutions as compared to water, in agreement with previous reports on similar systems,^{14,25b} can be correlated to the decrease of the nonradiative rate constant of the emitting state when located in the micellar environment depending on the reduced hydrogen-bonding ability of this medium.¹²⁻¹⁴

The effect of CTAB addition on the EB triplet state properties is dramatic even at pre-micellar concentration, as can be seen from Figure 3. The formation of dye-rich pre-micellar aggregates is a well-established phenomenon. (See, for example, refs 16 and

**Figure 6.** Experimental points and computed fits for the OD changes vs time measured at 620 nm at different laser energies for a 19 μM EB/1.4 mM CTAB solution ($\bar{n} = 2.3$).

25b and literature cited therein.) This could easily explain the lack of accumulation of triplets, prevented by fast singlet and triplet quenching reactions in the aggregates. The heavy atom effect due to the Br^- counterion in close contact with EB could also play a role in increasing the decay rate of the triplet. The formation of radicals occurring during the pulse with a low yield and the complex nonexponential radical recombination can as well be explained by the high inhomogeneity of the system.

For concentrations of CTAB above the critical micelle concentration, a quantitative analysis is possible. By using $\text{cmc} = 9.2 \times 10^{-4}$ and a mean aggregation number of 60,⁵⁰ the mean occupancy number \bar{n} ($[\text{EB}]/[\text{micelles}]$) can be calculated. By applying a proper distribution law, the probability that a micelle contains i solute molecules, P_i , can be derived. In Table III are reported the P_i calculated according to the Poissonian distribution⁵¹ for the mean occupancy numbers of interest and p_i , the probability that an occupied micelle hosts i EB, where $p_i = P_i / (1 - P_0)$.

The species formed in the flash photolysis of EB in CTAB micellar solutions appear to be the same as those formed in pure water, as can be seen from comparison of Figures 2 and 4. If the different ground-state absorption of the two solutions at the excitation wavelength is taken into account ($I_a^{\text{H}_2\text{O}}/I_a^{\text{CTAB}} = 0.75$), the triplet yield in micellar solutions appears to be remarkably lower.⁵² This fact is in agreement with the decrease of the intersystem crossing rate constant, as expected by passing from a more to less polar environment.^{12,13}

From a closer inspection of the optical densities (Table I), the following considerations can be made. At the lowest excitation energy used, 0.7 mJ cm^{-2} , the number of absorbed photons in the volume of analyzed solution is about one-third of the number of EB. In this situation, very likely no more than one EB per micelle is excited, and there is a good agreement between the fraction of multiple occupancy ($p_{>1}$) and fast component reported in the

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(51) The Poisson distribution is the most commonly used to calculate the occupancy in micellar systems: $P_i = (n^i e^{-n}) / i!$

(52) By assuming Φ_{isc} of EB in water = 1 and a similar ϵ_{620} for the triplet in water and micellar solutions, a Φ_{isc} of 0.75 can be calculated for micellized EB triplet.

TABLE IV: Experimental and Calculated ΔOD at $\lambda = 420$ nm

\bar{n}	$I, \text{mJ cm}^{-2}$	ΔOD_{tot}		ΔOD_{∞}	
		exp	calc	exp	calc
0.3	10	0.059	0.044	0.033	0.032
	6	0.056	0.047	0.037	0.036
	2	0.050	0.044	0.034	0.033
	0.7	0.030	0.030	0.024	0.025
0.9	10	0.074	0.042	0.020	0.022
	6	0.067	0.039	0.020	0.020
	2	0.050	0.038	0.020	0.022
	0.7	0.033	0.025	0.019	0.017
2.3	10	0.057	0.024	0.009	0.008
	6	0.049	0.022	0.008	0.008
	2	0.041	0.025	0.008	0.008
	0.7	0.031	0.020	0.007	0.009

table for D recovery and D^T decay. This means that the fast component can be assigned to the intramicellar reaction $D^T + D$, occurring in micelles loaded with more than one EB. By increasing the excitation energy, more EB can be excited and the intramicellar reaction $D^T + D^T$, consuming two triplets per multiply occupied micelle, starts to contribute to the triplet depopulation. Accordingly, the weight of the fast component increases with the energy. At the highest energy used all EB are converted to triplets, as can be deduced by the saturation effect, and the by far prevailing reaction is $D^T + D^T$. The probability Y that a single EB triplet decays by the latter reaction has been calculated⁵³ and reported in Table III. The agreement between Y and the weight of the fast component at the highest energy is fairly good, and it can be safely assumed that the reaction observed at 10 mJ cm^{-2} is the triplet-triplet reaction $D^T + D^T$.

The reduction in ΔOD_{tot} for D and D^T at the highest occupancy and energies used can be ascribed to singlet quenching reactions which have been observed in the similar systems CTAB/rose bengal.¹⁴ The occurrence of singlet quenching reactions, not leading to triplet state at high occupancy, could explain some slight discrepancy between calculated probabilities and fast components found for the occupancy number $\bar{n} = 2.3$. If the reduction in OD of Table I (ca. 30%) is compared to the EB population distribution of Table III, it can be inferred that the above-discussed singlet quenching reactions become important for occupancies > 3 .

For optical density data at 420 nm, additional difficulties are related to spectral overlap of radical and triplet and, as known from the 620-nm optical density data, to the fact that the triplet decays with "fast" and "slow" processes.

On the basis of a $\epsilon_{620}/\epsilon_{420}$ for D^T of 2.1,⁵⁴ the ΔOD_{∞} expected at 420 nm from the contribution of the surviving triplet can be calculated from the ΔOD_{∞} at 620 nm. By applying the same ϵ ratio to the ΔOD_{tot} measured at 620 nm, the ΔOD_{tot} at $t = 0$ and 420 nm ($\Delta OD'_0 + OD''_0 + \Delta OD_{\infty}$) should be obtained provided that only the triplet species is present immediately after the laser pulse. In Table IV are reported the measured and calculated optical densities at 420 nm for several laser intensities and mean occupancy numbers. It is clear that the ΔOD_{∞} at 420 nm can be accounted for completely by the residual absorption of the "slow" triplet, indicating that there is no radical escape from the geminal recombination in the micelle. On the contrary, the calculated values for ΔOD_{tot} at $t = 0$ are lower than the experimental, the discrepancy being more severe at higher occupancies and energies. This can be explained by the production of radicals during the pulse, a process that could escape the resolution of our apparatus. Formation of radicals via singlet reactions in dye-rich micelles¹⁴ at high laser intensities could be responsible for such fast formation.

(53) Y is calculated by the empirical expression $2(P_2 + P_3)/(P_1 + P_2 + P_3)$. The assumptions are (a) that in triply EB loaded micelles only two D^T can react and (b) that micelles loaded with more than 3 EB are ineffective in this respect giving singlet reactions (see text).

(54) Determined in EB/CTAB solutions with occupancy $\bar{n} = 0.05$. In this case $p_{>1} = 0.02$ and very few radicals are expected to be formed.

The fittings of the optical density vs time allow one to derive the rates of the various processes, listed in Table II. The radical reaction rate ($2.1 \times 10^6 \text{ s}^{-1}$) is of the order expected for a geminate process of a triplet-derived, radical pair⁵⁵ which requires the crossing from triplet to singlet state prior to recombination.

The triplet deactivation rate is in agreement with a reported rate constant of $5 \times 10^6 \text{ s}^{-1}$ for the triplet decay of the xanthene dye selenopyronine in SDS micelles.²² The increase in the rate with the excitation intensity can be assigned to the increasing contribution of the reaction $D^T + D^T$ which, in spite of the molecularity two, can be described by an exponential law.⁴⁸ The recovery of the ground state, described as a single exponential, is characterized by a rate of $2.9 \times 10^6 \text{ s}^{-1}$, resulting from the superposition of the two processes regenerating the ground state, i.e., radical decay and triplet decay, too close to each other to be separated by kinetic analysis.

The formation of the radicals is in all conditions at least twice faster than the triplet decay. The discrepancy increases at higher intensities, particularly evident at the highest occupancy. The increase of the apparent first-order formation of the radical production could be explained by an increasing contribution by a faster process, operative at high occupancies and excitation energies. The possibility that this is the $D^T + D^T$ reaction is inconsistent with the fact that when we detect mainly this process, i.e. at 10 mJ cm^{-2} , no important increase in the triplet decay rate occurs. This lead to the conclusion that the two ways of decay of the triplet can only be minor components in the formation of radicals.

The above results could be understood by admitting that the formation of the radicals is due, at least in part, to a species different from the triplet. In this case the kinetic treatment used at 420 nm is incorrect, and the sum of three exponentials (decay of triplet, formation and decay of radicals) should be used instead. Given the difficulty in the present experimental conditions to determine with some useful precision all the pertinent parameters, we prefer the simplified approach, which clearly informs us that the processes producing the radical are not, or not only, the same processes depopulating the triplet.

About the identity of the possible alternative reaction(s) which produce the radicals, it can be seen that the contribution to the overall rate of radical formation by such reaction increases with the excitation intensity and the occupancy. An explanation could be based on a biphotonic process producing a short-lived species which needs to rapidly find a reactant before decaying. In this case the peak reported in Figure 4 could be related to such a species. The upper limit for the lifetime is ca. 100 ns, and no more detailed kinetic investigations can be performed with some confidence, because of the overlapping emission. In these conditions the identification of the species is difficult, and more work is needed in more suitable systems. The excited singlet can be excluded on the basis of the fact that it does not absorb in this spectral region,⁴⁷ the lifetime is expected to be much shorter,¹⁴ and it would not agree with the intensity dependence discussed above. Some intermediate, possibly formed via absorption of a photon by the lowest triplet during the laser pulse, seems a plausible candidate.

Conclusions

The present study reports the detection in EB/CTAB water solutions of intramicellar electron transfer responsible for the formation of semioxidized and semireduced radicals. The rate of the radical formation, shown to increase with excitation energy and mean occupation number, was in all cases faster than the reaction(s) deactivating the triplet which were shown to be $D^T + D^T$ and $D^T + D$, depending on the intensity of excitation and occupancy. The identification of these reactions as only responsible for radical formation, as currently assumed in the literature, needs some revision in this system. On the basis of the intensity de-

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pendence of the rate of formation of radicals, the hypothesis is advanced that a biphotonic step, possibly involving the absorption of a photon by the lowest triplet, is operative in producing a state X, more reactive than the triplet. In spite of the kinetic evidence produced, no definite spectroscopic and kinetic identifications of

species X are reported.

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Role of High-Frequency and Low-Frequency Polarization of the Medium in the Kinetics of Electron Transfer and Thermodynamics of Solvation

Alexander M. Kuznetsov

The A. N. Frumkin Institute of Electrochemistry, Academy of Sciences of the USSR, Leninskii prospect 31, Moscow 117071, USSR (Received: August 26, 1991)

The behavior of high-frequency and low-frequency polarizations of the medium in the processes of electron transfer is considered in the framework of a rigorous analysis. It is shown that for the adiabatic reactions the solvation of the transition state by classical (and hence inertial with respect to transferable electron) polarization is considerably weaker than the solvation of the initial state due to delocalization of the electron density over both reactants in the former case. The solvations of the transition state and of the initial one by the high-frequency (i.e., inertialess) polarization are close to each other. Possible influence of the high-frequency polarization on the activation barrier and the role of a retardation of the polarization with respect to the electron are discussed.

I. Introduction

It is understood that the interaction of the charge with the polarization of the medium plays a great role in the processes of charge transfer in the condensed phase. The study of the dynamics of polarization in the course of these processes is a central point of the quantum mechanical theory of electron-transfer reactions, processes of the transfer of protons and atom groups.¹⁻⁸

It was assumed in first works on the theory of the electron-transfer reactions that the total polarization of the medium P_t may be split into two parts: fast (inertialess) P_e and slow (inertial) P_i .^{1,4,5} Similar to polaron theory, it was assumed that the fast polarization is characterized by much greater frequencies of fluctuations ω_f as compared to the characteristic frequency of the motion ω_e of the transferable electron. Therefore, it follows adiabatically the motion of the latter. This physical idea was used to exclude the inertialess polarization from a dynamic description of the transition process.

On the contrary, the slow polarization cannot follow the electron motion and creates a Franck-Condon barrier for its transition from a donor to an acceptor.

For electron-transfer processes in polar liquids, e.g., in water, fast (inertialess) polarization P_e in fact is related to the electronic polarization of the medium. The inertial polarization P_i is formed mainly by orientational polarization of the dipole molecules, and also by vibrational and librational polarizations, and partially by electronic polarization. Thus the electronic polarization gives a contribution to both inertialess (fast) and inertial (slow) polarizations of the medium.

It was understood in later works that the inertialess polarization plays an essential role in electron transfer.⁹⁻¹¹ It screens partially

the electric field of charged species and weakens their interaction, influencing thereby the value of a perturbation operator leading to the electron transfer. In nonadiabatic reactions this effect is involved in the value of the electron transmission coefficient. In the adiabatic reactions it is involved in the value of lowering of the potential barrier due to the resonance splitting of the potential energy surfaces.

In past years the problem of the participation of the electronic polarization in the electron-transfer reactions was under discussion in relation to two aspects:

(a) In some cases one may expect that the characteristic frequencies of a part of the electronic polarization of the medium and of the motion of the transferable electron may be comparable ($\omega_f \sim \omega_e$).¹²

(b) It is supposed that since the electronic polarization is fast, it must always be in equilibrium with the distribution of the charge in the reacting system^{12,13} and hence it may influence the value of the activation barrier for the adiabatic reactions due to the change of the solvation energy while going from the equilibrium configuration to the transitional one.¹²

The present paper is aimed at analyzing in more detail the role played by high-frequency (electronic) and low-frequency polarizations in the kinetics of electron transfer and thermodynamics of the reactant solvation. A way of rigorous decomposition of the polarization into inertial and inertialess components is presented.

II. Formulation of the Problem

A process of electron transfer is considered from a donor A to an acceptor B located at fixed distance R from each other in a polar medium. The total Hamiltonian of the system has the form

$$H = T_e + V_{eA}^0 + V_{eB}^0 + V_{eP_i} + H_{P_i} \quad (1)$$

where T_e is the kinetic energy of the transferable electron, V_{eA}^0 and V_{eB}^0 are the interactions of the electron with the donor and the acceptor, V_{eP_i} is the interaction of the electron with total

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