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THE BEHAVIOUR OF TRIPLET BENZOPHENONE IN MICELLAR SOLUTIONS: EVIDENCE FOR AN EXCIPLEX MECHANISM?

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Summary

The study of benzophenone in sodium dodecyl sulphate micellar solutions leads to the substantiation of a transient species which can be attributed neither to a triplet state nor to a ketyl radical. From the results of laser spectroscopy and luminescence experiments, it is postulated that a triplet state, an exciplex (in which triplet benzophenone is the acceptor), a radical pair and a free ketyl radical that has escaped from the micelle are involved in the overall relaxation process of this transient.

1. Introduction

A considerable amount of research is continuously being devoted to the photophysics and the photochemistry of benzophenone (BP). In point of fact, everything should be known about this compound!

In organic solvents the primary processes involved in the photochemistry of this aryl ketone are now largely understood; these processes are rationalized in terms of the electron distribution of the lowest triplet state. In the classic case of unsubstituted BP this state exhibits a dominant $n\pi^*$ character and the primary reaction is reputedly hydrogen abstraction leading to a ketyl radical [1].

Beyond this well-known and well-documented behaviour, some points still remain unclarified [2]. Among these, the exact part played by the photoproducts generated during laser investigations, either by the laser itself or by the analysing light [3], appears to be the cause of many misinterpretations or at least of many apparently inconsistent results. Moreover, we must bear in mind that all these proposals are only supported by experiments capable of providing nothing more than overall results. In fact the quantum yields and other available kinetic information on primary processes refer to quenching experiments in which the primary step is viewed as a radical hydrogen abstraction from the quencher by the $n\pi^*$ triplet.

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In addition, the case of the interaction of BP with amines carrying an abstractable hydrogen has also been extensively investigated and reviewed. It is generally accepted that the first step is the transfer of an electron from the amine to BP forming a charge transfer (CT) complex [4 - 6] which then decays either by proton transfer to the ketyl and amine radicals or, after spin inversion and back transfer of the electron, to the ground state BP and amine. Evidence for an ultrashort-lived CT complex has recently been obtained by picosecond spectroscopy [7].

It is thus likely that the primary quenching rate constant of the BP triplet might well be very different from the photoreduction rate constant.

Now, the same type of kinetic sequence has been invoked to account for the apparently surprising results obtained when ^{3}BP is quenched by hydrocarbons. In this case the rate constants of triplet quenching and photoreduction differ by several orders of magnitude [8 - 12]. This observation supports the belief that a reversible "complex" is formed between the triplet BP and the quencher. Since this type of behaviour also occurs in perfluorobenzene, a medium in which no abstractable hydrogen is available from the solvent [8 - 13], the question of the nature of that "complex" arises.

This paper is concerned with some original results obtained in pure aqueous and micellar solutions of BP. Our purpose is to show how and to what extent the temporal behaviour of ^{3}BP is affected by compartmentalization.

2. Experimental details

Time-resolved spectroscopy experiments were performed at room temperature using two types of apparatus in which the exciting source was either a mode-locked laser with a time resolution of about 2 ns or a giant pulse ruby laser with $\tau_r \approx$ 20 ns (Laboratory of Professor Grätzel, Ecole Polytechnique Fédérale de Lausanne). The analysis and exciting lights were in a crossed-beam arrangement. Ultimately, the detection system was able to detect transient absorbances as weak as 2×10^{-3} in the submicrosecond time scale. In order to prevent any steady state photolysis of the sample, a glass filter with a sharp cut-off around 415 nm was present between the analysing source and the sample. The difficulty of avoiding the generation of small amounts of steady state photoproducts means that the results reported below for transient absorptions measured within the UV spectrum of ground state BP (350 - 400 nm) are unreliable. This problem will be considered again in Section 4.

Dissolved oxygen was removed from the solutions by bubbling argon through them. Commercial grade BP (Fluka) was recrystallized three times from ethanol–water mixtures (melting point, 48 °C). Sodium dodecyl sulphate (SDS) (Aldrich) was washed with ether and then recrystallized three times from 96% ethanol.

3. Results

3.1. *The location of benzophenone in sodium dodecyl sulphate micelles*

A series of BP solutions containing variable amounts of SDS was prepared ($0 < [\mathrm{SDS}] < 0.1$ M). Figure 1 shows the UV spectrum ($n \rightarrow \pi^*$ transition) and its blue shift as small amounts of SDS are added. The amplitude of this shift [14] and the critical micelle concentration (CMC), which can be determined colorimetrically [15], agree fairly well with values cited in the literature (Fig. 1, inset). These spectra show beyond doubt that the site of solubilization of micellized BP is the Stern layer, a region where the polarity of the microenvironment is quite high and is at least comparable with that observed in alcohols [14]. Accordingly BP must be viewed as being "anchored" in a spherical "layer" of intense electrical fields bordering on the polar head of the surfactant and close to the "fjords and icebergs" of water.

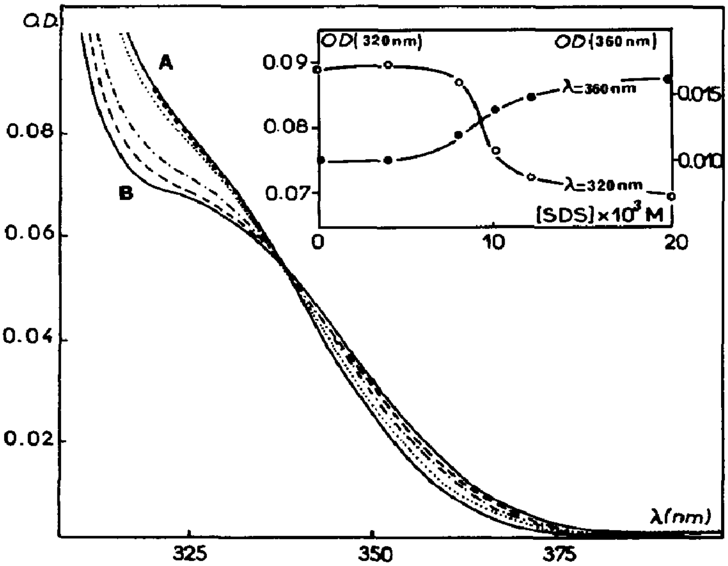


Fig. 1. UV absorption spectra of BP–SDS aqueous solutions with [BP] = 3×10^{-4} M: ——, curve A, [SDS] = 0; – – –, [SDS] = 0.004 M; ······, [SDS] = 0.008 M; —·—, [SDS] = 0.010 M; ------, [SDS] = 0.012 M; ——, curve B, [SDS] = 0.020 M.

3.2. *Transient absorption of benzophenone in micelles*

Laser excitation of a solution of BP in SDS micelles leads to transient absorptions in the visible region. A decay trace corresponding to first-order kinetics ($\tau = 420$ ns) can be seen. A weak residual absorption assigned to a long-lived transient appears after this fast decay. The fast transient is oxygen sensitive. In a recent publication Sakaguchi *et al.* [16] claimed that the fast decay corresponds to the convolution of two decays with first-order kinetics. We cannot explain this discrepancy. The absorption of these two transients is shown in Fig. 2.

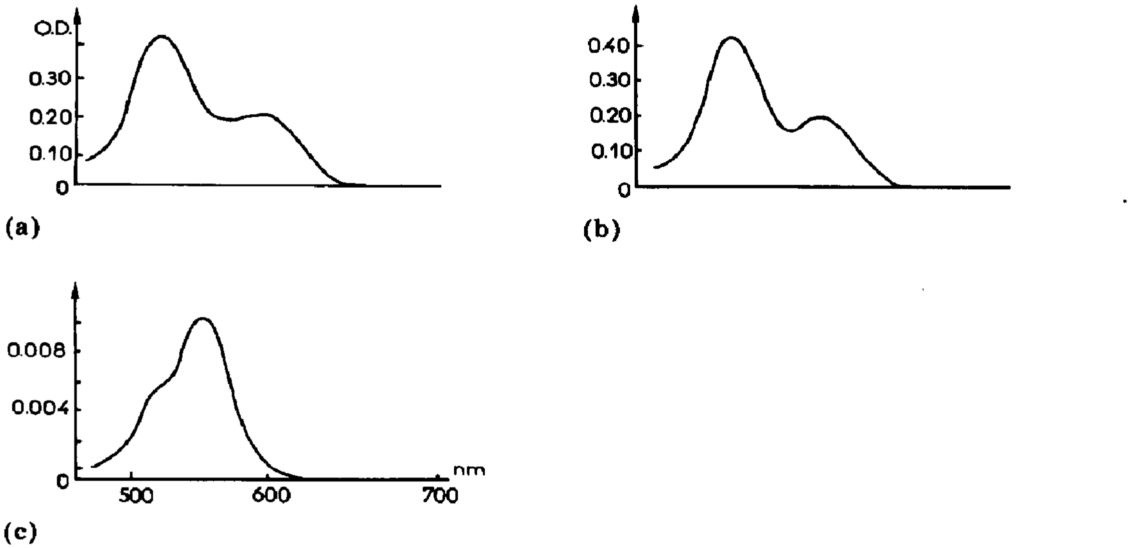


Fig. 2. Transient absorption spectra ([BP] = 3 × 10^{-4} M): (a) BP triplet in pure water; (b) BP with [SDS] = 0.1 M (spectrum at zero time); (c) BP with [SDS] = 0.1 M (residual absorption after the complete relaxation of (b)).

At this step of our investigation it seems reasonable to assign the fast and the slow components to the triplet state and the ketyl radical of BP respectively.

3.3. The effects of concentration and excitation intensity

In order to obtain information concerning the effect of concentration and light intensity on these transients and to take advantage of the wide range of available outputs delivered by the two laser devices used in this work, we investigated the main features of the excited BP reaction sequence in a micellar environment with respect to annihilation (rate constant k_{TT}) and self-quenching (rate constant k_{SQ}), two processes which are dependent on the occupancy $\langle n \rangle$ which is defined as the average number of guest molecules per micelle.

The following procedure was used: (i) a series of solutions with [BP] = 4.4 × 10^{-3} M and various SDS concentrations was tested under the same conditions of laser excitation and the transient absorption appearing in the 100 ns time scale was recorded; (ii) a solution with [SDS] = 0.1 M and an average occupancy $\langle n \rangle$ of 10 was subjected to laser excitation intensities varying over a twentyfold scale (if the recorded transient absorption is assumed to be due to triplet BP, the average number $\langle n^* \rangle$ of excited BP molecules varies from 0.1 to 2); (iii) experiment (ii) was repeated with $\langle n \rangle$ = 1 and, on the same assumption as before, with $\langle n^* \rangle$ varying from 0.02 to 0.25. The results of this study are reported in Tables 1 - 3. The unexpected conclusion is that the lifetime of the transient is not sensitive to occupancy changes.

TABLE 1

The lifetime of the transient absorption observed in deaerated micellar solutions of BP as a function of the occupancy

[SDS]	$\langle n \rangle$	τ (ns)
0.60	0.49	425 ± 20
0.17	1.93	415 ± 20
0.10	3.65	420 ± 20
0.046	7.8	415 ± 20
0.023	20.6	430 ± 20

The occupancies were calculated for a CMC of 0.009 M and an aggregation number $\bar{N}$ of 65; [BP] = 4.4×10^{-3} M.

TABLE 2

The lifetime of the transient absorption observed in micellar deaerated solutions of BP as a function of the laser intensity I/I_0

I/I_0	$\langle n^* \rangle$	τ (ns)
0.08	0.14	420 ± 50
0.16	0.30	420 ± 40
0.36	0.65	415 ± 30
0.51	0.93	420 ± 20
1	1.70	430 ± 20

The values of $\langle n^* \rangle$ were calculated for ϵ = 5800 M^{-1} cm^{-1} and $\bar{N}$ = 65; [SDS] = 0.05 M; $\langle n \rangle \approx 9.3$.

TABLE 3

The lifetime of the transient absorption as a function of the laser intensity I/I_0

I/I_0	$\langle n^* \rangle$	τ (ns)
0.08	0.02	430 ± 50
0.16	0.04	420 ± 50
0.36	0.08	410 ± 30
1	0.25	425 ± 20

[SDS] = 0.3 M; $\langle n \rangle$ = 1.

These results are quite different from those obtained in homogeneous solutions. With the aim of explaining this significant observation, the decay rates of the lowest triplet of BP in pure water were recorded with special care in order to determine to what extent the bimolecular processes affect the triplet decay. Although studies of this problem are recurrently undertaken, the data reported are at variance owing to the insufficient precision of experiments performed in concentration ranges that are too narrow. Of course experimental conclusions are often called into question by the introduction of new techniques or different procedures [17 - 19]. Thus the use of laser sources to excite either the $\pi \rightarrow \pi^*$ (265 nm) transition or the $n \rightarrow \pi^*$ (347 or 353 nm) transition might well introduce spurious effects.

The approach used in the present work is well known [18]. It is based on a kinetic treatment which involves only the determination of the initial decay rate of the triplet which can be written

$$\frac{d[^3BP]}{dt} = k_{sp}[^3BP] + k_{SQ}[^3BP][BP] + k_{TT}[^3BP]^2$$

or

$$\frac{d}{dt}\ln[^3BP] = k_{sp} + k_{SQ}[BP] + k_{TT}[^3BP]$$

where k_{sp}, k_{SQ} and k_{TT} are the rate constants for spontaneous decay, self-quenching and triplet–triplet annihilation respectively. Thus k_{TT} can be defined as the slope of the straight line obtained by plotting the initial rate constant $\{d(\ln[^3BP])/dt\}_{t=0}$ against the initial triplet concentration $[^3BP]_0$; the intercept represents the pseudo-unimolecular rate $k_I = k_{sp} + k_{SQ}[BP]$ (Fig. 3). The same kind of kinetic analysis was repeated with several concentrations of ground state BP and the parameter k_I was then plotted against [BP] (Fig. 4). Here the slope corresponds to k_{SQ} and the intercept at infinite dilution is k_{sp}.

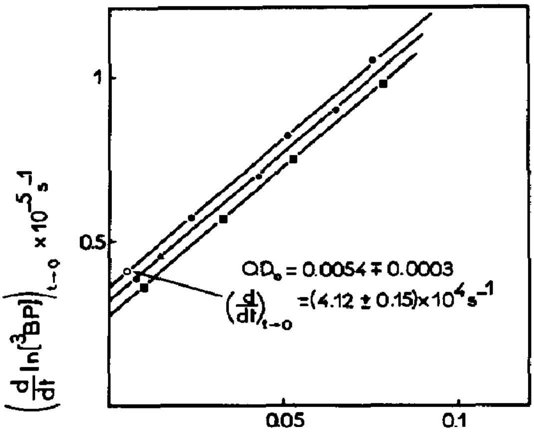


Fig. 3. The initial decay rate constants of BP plotted against the initial optical density OD_0 measured at 520 nm: ■, [BP] = 10^{-4} M; ●, [BP] = 2×10^{-4} M; ○, [BP] = 3×10^{-4} M; λ_{exc} = 347 nm; $OD_0 = \epsilon_{TT} l [^3BP]_0$ with $\epsilon_{TT}^{520} = 5800 \pm 400$ M^{-1} cm^{-1} [18] and l = 0.5 cm.

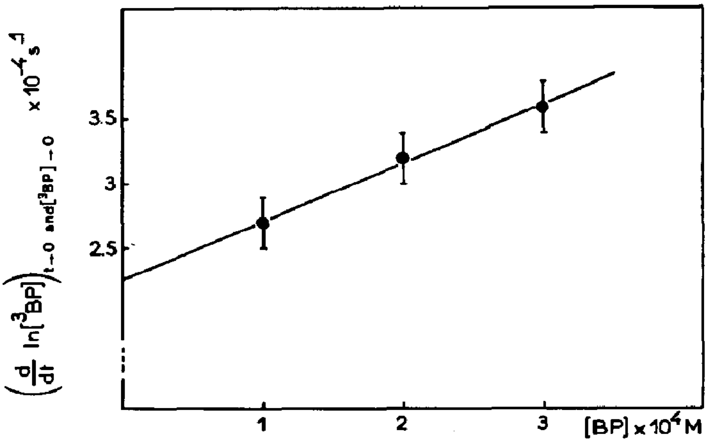


Fig. 4. The limit of the initial decay rate constant of triplet BP at $[^3BP] = 0$ plotted against the ground state concentration.

The conclusion arrived at is that both annihilation and self-quenching take place in homogeneous solutions under the experimental conditions of the present study and that

$$k_{SQ} = 5 \times 10^7 \ M^{-1} \ s^{-1} \qquad k_{TT} = 5 \times 10^9 \ M^{-1} \ s^{-1}$$

whereas these bimolecular processes (triplet–triplet annihilation and self-quenching) are essentially inefficient in micellar solutions.

3.4. Gradual micellization of benzophenone

We now report some interesting results concerning the gradual micellization of BP which is observed when increasing amounts of surfactant are added to an aqueous BP solution. Accompanying effects on the behaviour of the triplet state are described.

Laser spectroscopy investigations showed that a transient absorption decaying in the 10 μs time scale was obtained in pure aqueous solutions.

Prior to micellization the transient absorption corresponding to the relaxation of triplet BP did not decay according to first-order kinetics. Owing to the presence of annihilation and self-quenching it is difficult to extract quantitative data from this type of experiment. Nevertheless, the main point to be noted is that the surfactant had little effect up to a concentration of half the CMC although the laser intensity and the ground state concentration of BP were kept constant.

In the second region (CMC/2 $<$ [SDS] $<$ 3CMC/2) an important change was observed: the transient absorption, the absorbancy of which was not significantly affected, decayed on a progressively shorter time scale. The final stage of this change corresponded to a third region where the BP was completely micellized. In this region the initial part of the decay curve was first order with $k = 2.4 \times 10^6 \ s^{-1}$, and after complete relaxation a very weak residual absorption persisted and continued to decay in the 100 μs range. A series of oscillographic traces are reproduced in Fig. 5 and show the different types of transient decay obtained relative to the steps of BP micellization. The spectra recorded at zero time and after complete relaxation of the initial transient are shown in Fig. 2.

3.5. The effect of the analysing light intensity

In the region corresponding to the $n\pi^*$ transition of BP (300 - 400 nm) the situation became more complicated. The general behaviour of the transient was identical with that observed in the visible domain as the surfactant concentration was increased. However, the kinetic analysis is much more complicated in view of the unavoidable photolysis by the analysis source which creates transient or permanent species which interfere with the laser-induced transient. We were unable to reproduce the decay curves upon which the proposals of Sakaguchi *et al.* [16] were partly based. In fact, the initial part of the decay at 330 nm which is claimed by these workers to correspond to the decay of ^{3}BP and the accompanying growth of a ketyl radical into the micelle appears to be strongly dependent on the

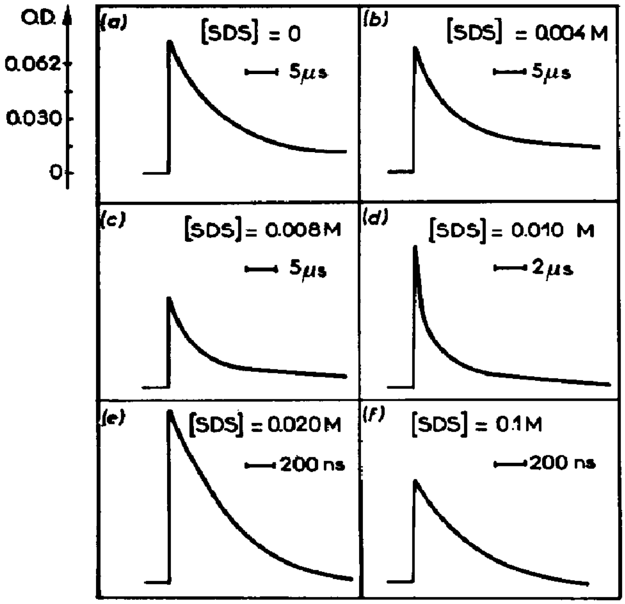


Fig. 5. Different types of transient absorption observed at λ = 525 nm in deaerated BP solutions as [SDS] is increased from 0 to 0.1 M ([BP] = 2.4 × 10^{-4} M). The ordinate scale is as given in (a) in all cases.

analysing intensity used in the laser device. In our investigation both the amplitude and the kinetics of this transient were obviously affected as can be seen in Fig. 6. Therefore reservations have to be made regarding the conclusions derived from kinetic analysis within this wavelength range.

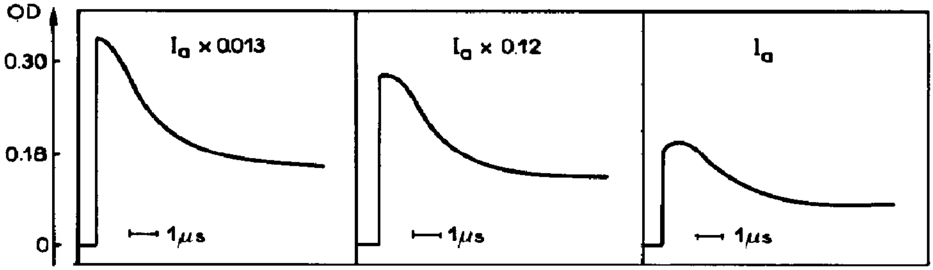


Fig. 6. The effects of the analysing light intensity I_a on the transient absorption recorded at 330 nm ([SDS] = 0.1 M; [BP] = 2.4 × 10^{-4} M). In order to keep the spectral resolution constant, the intensity was reduced by inserting two neutral filters in the analysing beam: first the filters were inserted between the sample and the detector (I_a); secondly one filter was inserted in front of the sample and the other behind it ($0.12I_a$); finally both filters were inserted in front of the sample ($0.013I_a$).

3.6. Emission spectroscopy experiments

Two additional results must also be mentioned. First, under our experimental conditions the fluorescence of the ketyl radical was not detected in micellar solutions of BP whereas it was readily observable in aqueous solutions containing small amounts of a hydrogen donor, *i.e.* isopropanol [20]. Secondly, an increase in the SDS concentration in an aqueous BP solution resulted in a dramatic decrease of the phosphorescence intensity as soon as the CMC was reached. This emission vanished completely at concentrations greater than 5CMC in agreement with the results reported by Braun *et al.* [21]. (From the signal-to-noise ratio of the detection system, the phosphorescence quantum yield is estimated to become lower than 10^{-6}.)

3.7. *Growth of the transient*

The growth of the transient absorption detected in micellar solutions was studied at 520, 540 and 630 nm with picosecond excitation (pulses with a halfwidth of 300 ps) and true nanosecond detection (a rise time τ_r of 1.2 ns). The growth time of this transient was observed to be shorter than the time response of the detector and its absorption remained strictly constant over the 10 ns time scale (Fig. 7).

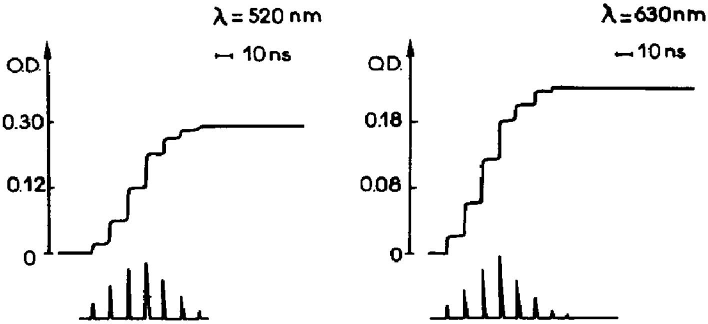


Fig. 7. Growth of the transient absorption observed in deaerated micellar solutions of BP ([BP] ≈ 4.4×10^{-3} M; [SDS] = 0.1 M). The rise time τ_r of the detector was less than 1.2 ns.

4. Discussion

The results of investigations of bimolecular interactions of triplet BP with either excited or ground state BP show that compartmentalization into micelles results in an apparent inhibition of both these deactivation routes. It is inferred that the solubilization site of BP is strongly defined and that, at this site and within the 100 ns time scale, the transient state generated by the laser pulse behaves quite independently of other micellized BP. This would denote either a very strong interaction with the host site of the BP (sufficient to render impossible the formation of a collisional pair with any other BP molecule inside the micelle) or a very fast reaction between an excited BP molecule and a partner which generates any products within less than 1 ns. We have attached the greatest importance to these facts in reaching our conclusions regarding the attribution of the transient absorption observed in these investigations.

In order to establish the nature of the state responsible for the transient absorption the following points have to be stressed.

(1) The absorption spectrum (Fig. 2(b)) has a well-positioned maximum at 525 nm which extends up to 650 nm in the red. This shoulder is completely absent in the absorption spectrum of the ketyl radical [8, 12, 18, 22].

(2) The rate constant for quenching with oxygen (dynamic quenching) ($k_Q^{O_2} \approx 3 \times 10^{-9}$ M^{-1} s^{-1}) exceeds by more than an order of magnitude the values usually obtained for the oxygen quenching of this type of radical [23].

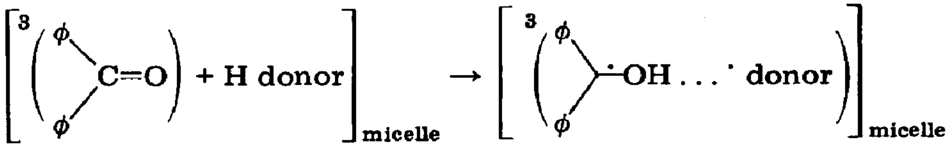
(3) It is not possible to detect any trace of fluorescence at 570 nm, an emission which is reputedly characteristic of the ketyl radical [20].

(4) The oscillograph traces corresponding to the build-up of transient absorptions at 520, 540 and 630 nm are identical, which is inconsistent with the occurrence of hydrogen abstraction within a few nanoseconds or more as was suggested by Braun *et al.* [21].

These observations indicate that the transient should not be assigned to a free ketyl radical.

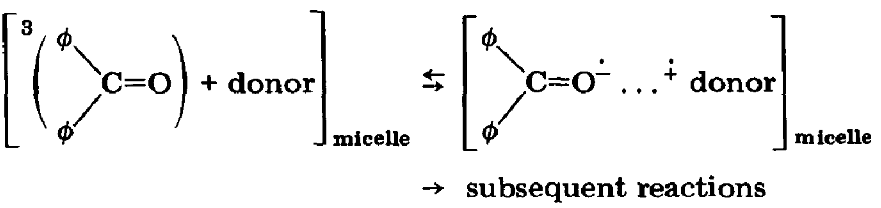
It is possible that the transient could be merely the micellized triplet of BP. However, an important experimental observation, *i.e.* that the phosphorescence of BP completely vanishes whenever micellization occurs, is inconsistent with this assumption. Therefore the explanation should be sought elsewhere.

The decay kinetics of micellized BP are reported to be affected by magnetic fields [16] which suggests that this transient exhibits a biradical pair character. Despite the reservations raised with regard to the interpretation proposed in ref. 16, this magnetic field effect appears to be beyond doubt. Therefore we propose the following reaction:



The magnetic field sensitivity and the absence of phosphorescence might well be accounted for by such a radical pair; however, this species would actually exhibit a ketyl-type spectrum which is not experimentally observed. Moreover, the transfer of a hydrogen radical in a time scale shorter than 1 ns is unlikely. (In fact BP is known to be very poorly reactive towards linear alkanes in homogeneous solutions, and the presence of large amounts of hexane, cyclohexane or dodecane in SDS micelles of BP has little effect on the lifetime of the transient.)

One way of avoiding this inconsistency is to postulate a multistep sequence of reactions in which the first event is the reversible generation of a CT complex:

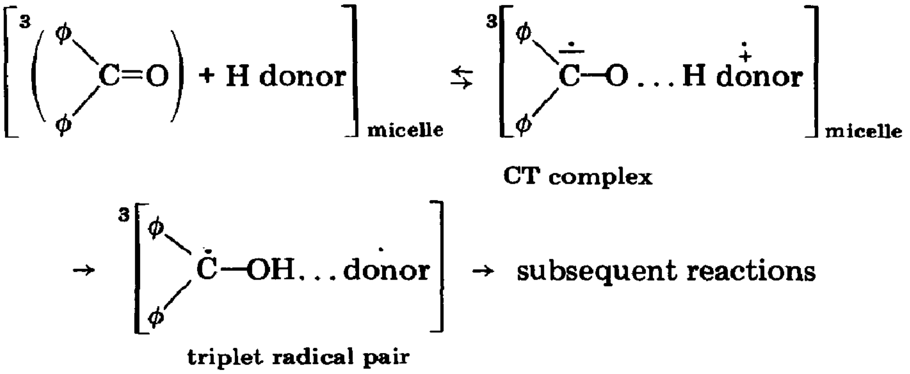


Such a CT complex mechanism, which is commonly invoked in studies of BP photoreduction by aliphatic amines, would account relatively well for the experimental observations, *i.e.* the sensitivity to magnetic fields, the absence of phosphorescence and ketyl character and the very fast build-up.

The only hitch in this picture is the difference between the experimental spectrum of the transient which has a maximum at 530 nm and the spectrum of the radical anion of BP which has a peak at longer wavelengths (720 nm in acetonitrile, 680 nm in methanol and 610 nm in water) [24]. However, since the lifetime is less than 1 ns, it is not surprising that such a CT complex, even if present in the first moment of the reaction, does not contribute significantly to the spectrum of the 400 ns transient recorded at zero time. (In fact when this type of complex is observed in a homogeneous solution it has a lifetime of no more than a few tens of picoseconds [7, 25].)

The final point to be discussed arises from work reported in refs. 21 and 26 in which the kinetics of triplet BP in SDS and in perfluorinated micelles were compared. The results reported demonstrate the apparent unreactivity of triplet BP towards sodium perfluorooctanoate, from which it was asserted that the main route of deactivation in SDS micelles is merely a one-step hydrogen abstraction from the alkyl chain of the surfactant. This reaction scheme is obviously unable to account for the experimental data reported here.

The multistep reaction sequence



is an attractive solution of this problem, on condition that the nature of the "donor" is explicit.

Although no definite hypothesis appears to be possible yet, the following points allow limits to be imposed on the problem.

(1) The overall quantum yield of the photolysis of BP in SDS micelles by laser light is particularly low ($\phi < 0.0005$), indicating among other things that an attachment reaction between BP and the surfactant is most improbable. This suggests that the surfactant chain, whatever its part in a possible CT complex, is no longer involved in the 400 ns transient, *i.e.* the triplet radical pair.

(2) The apparent indifference towards the charge on the surfactant excludes any participation of its polar head in the sequence of reactions generating the 400 ns transient. (BP exhibits exactly the same behaviour in SDS anionic and cetyltrimethylammonium chloride cationic micelles.)

(3) A significant difference between SDS and the perfluorinated micelles used by Braun *et al.* [21] has not been taken into account: whereas SDS forms micelles with $\bar{N} \approx 65$ in which water can be regarded as a molecule with properties very different from those of the intermicellar medium [27], the fluorinated surfactant aggregates with very low $\bar{N}$ [28] and hence the remarks regarding water properties do not hold [29]. Therefore water may play an important part in the sequence of reactions occurring with SDS micelles which would be related to the "different properties" conferred by compartmentalization in SDS micelles.

Thus the first event of the sequence would be the essentially reversible generation of a CT complex involving the alkyl chain of the surfactant; in a subsequent step it might also undergo proton capture from its vicinity. This sequence is seemingly tantamount to a hydrogen radical abstraction.

Accordingly, depending on the different rate constants of these processes, two schemes are plausible: either the exciplex behaves identically in micellar environments and in homogeneous solutions and the ketyl-type reaction sequence requires the mediation of a biradical with a lifetime in the 100 ns time scale or owing to micellization the lifetime of this exciplex is much longer than in the homogeneous solution and the transient is then due to the CT complex. In the first case the residual absorption assigned to a small amount of free ketyl radical outside the micelle results from decoupling of the ketyl radical pair and the escape of a free ketyl from the micelle; in the second case this free ketyl arises from decoupling of the triplet exciplex, the escape of a radical anion and fast proton capture in the intermicellar medium.

Computer calculations designed to elaborate this mechanistic approach are in progress and will be reported elsewhere in more detail. Some important implications for the emulsion polymerization of acrylic monomers initiated by carbonyl compounds have just been published [30].

Acknowledgments

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