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Benzophenone Triplet Properties in Acetonitrile and Water

Reduction by Lactams

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The technique of time resolved laser flash spectroscopy has been used to study the photophysical and photochemical properties of the lowest triplet of benzophenone in water and acetonitrile. New estimates have been obtained for the triplet extinction coefficient, unimolecular and bimolecular rate constant of decay in both solvents, as well as a determination of the quantum yield of ketyl formation in pure water and the rate constants of hydrogen abstraction from various lactams in both solvents. Evidence for hydrogen abstraction from water by a triplet of benzophenone is found. Correlation between rate constants of hydrogen abstraction from lactams by the lowest benzophenone triplet and their ionization potential is discussed. Reversibility of these hydrogen abstractions is considered.

The absorption spectrum, the lifetime and the oxidizing nature of the ${}^{3}n\pi^{*}$ lowest excited triplet state of benzophenone has been extensively studied.¹

The present report describes some results of a further investigation of the photophysical and photochemical properties of the ${}^{3}n\pi^{*}$ triplet state of benzophenone in water and acetonitrile. We have estimated, for the first time, the extinction coefficient of the T-T transition in water and acetonitrile and the quantum yield of benzhydryl (the neutral benzophenone ketyl radical) formation in pure water. We have also obtained the unimolecular and bimolecular rate constant of the triplet decay in water and acetonitrile, taking into account an important triplet-triplet annihilation neglected by previous determinations. Furthermore, we have determined the rate constants of hydrogen abstraction by the ${}^{3}n\pi^{*}$ benzophenone lowest triplet from various lactams in acetonitrile and water. These molecules appear as more efficient reductants than alcohols.

EXPERIMENTAL

MATERIALS AND METHODS

Time resolved laser flash spectroscopy experiments were performed at room temperature on an apparatus built in our laboratory and described previously.² The laser wavelengths used for excitation were 265 and 353 nm $(35 \times 10^{-9} \text{ s})$. Exciting (laser) and analysing (Xe) flashes were in a crossed beam arrangement. Transient absorption was observed in the sample along 1 cm within the first mm of solution excited by the laser. The slice of solution observed was the optical image of the monochromator slit through a lens of magnification unity. Transient optical densities were normalized to correct for variation in excitation intensity. This normalization was performed by deflecting 10 % of the exciting light to an ITT diode (F 4000, rise time 0.5 ns). The detection system used an automatic back-off already described ³ and was able to measure absorbance as small as 10^{-3} . The analysing Xe flash gives a light intensity constant to 0.1 % for 20 μ s. A Pyrex filter with a cut off around 300 nm was present between the sample and the analysing light. For each experiment a fresh sample of the solution, deaerated by bubbling with Ar, was used.

Acetonitrile (Merck uvasol) was used as supplied. Water was freshly double distilled. 2-Pyrrolidone (Fluka), N-methyl-2-pyrrolidone (Prolabo) and 2-piperidone (Fluka) were distilled and the centre fraction was used. ε -Caprolactam (Fluka) was recrystallised from hexane and 2-oxazolidone (Fluka) was recrystallised from benzene. Benzophenone (Prolabo) was crystallised three times from EtOH. Benzhydrol was prepared by reduction of benzophenone by lithium aluminium hydride in diethylether and crystallised from light petroleum.

Ionization potentials of the lactams were determined by photoelectron spectroscopy with a Perkin-Elmer PS 18 instrument. We thank Dr. Y. Henry (Laboratoire de Chimie de l'Ecole Polytechnique, 91120 Palaiseau) for these determinations.

PHOTOPHYSICAL PROPERTIES OF THE LOWEST TRIPLET OF BENZOPHENONE, ³B

DETERMINATION OF THE TRIPLET EXTINCTION COEFFICIENT ε_T

Two comparative methods were used to estimate the extinction coefficient of the T-T transition.

(a) The first method compared the $\varepsilon_{\rm T}$ of ³B in water with the extinction coefficient of the ketyl radical in water determined in previous pulse radiolysis experiments.⁴

The optical density, $OD_{T}^{520}({}^{3}B)$, observed at 520 nm due to the benzophenone triplet formed immediately after the flash was compared with the optical density, $OD^{520}(\dot{B}H)$, due to the long-lived ketyl radical observed after completion of the triplet decay in conditions such that the benzophenone triplet was decaying only by its reaction with a reducing molecule present in large concentration:

$$^{3}B+LH \rightarrow HBH+L.$$
 (1)

Fig. 1 shows a typical oscillogram observed at 520 nm showing the photoreduction of ³B by the lactam LH. The lifetime of the triplet (³B) was reduced by more than a factor ten in presence of LH. The initial concentration of ³B can then be considered as equal to the total concentration of ketyl radical (BH) formed. The BH radical spectrum which we observe is identical to the classical BH radical spectrum in aqueous solution.⁴ Therefore the radical L does not absorb in the 300-600 nm region. Thus it is possible to determine

$$\varepsilon_{\rm T}^{520} = \varepsilon^{520}({}^{\bullet}{}^{\bullet}{\rm H}) \frac{OD^{520}({}^{\circ}{}^{\bullet}{\rm B})}{OD^{520}({}^{\bullet}{\rm B}{\rm H})}$$

with $\varepsilon^{540}(\dot{B}H) = 3220 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} 4$ and thus $\varepsilon^{520}(\dot{B}H) = 2150 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. $OD^{520}(\dot{B}H)$ is ³B the optical density observed immediately after the flash, and $OD^{520}(\dot{B}H)$ is the optical density observed after completion of the triplet decay.

Using, as reducing agent, 0.3 mol dm⁻³ pyrrolidone or 0.2 mol dm⁻³ valerolactam in water and 1 mol dm⁻³ pyrrolidone, 0.3 mol dm⁻³ valerolactam, 1 mol dm⁻³ caprolactam and 1 mol dm⁻³ oxazolidone in acetonitrile, it was thus possible to determine $\varepsilon_T^{520}({}^{3}B) = 5750 \pm 400 \text{ dm}^{3} \text{ mol}^{-1} \text{ cm}^{-1}$ in water and $\varepsilon_T^{520}({}^{3}B) =$ $6500 \pm 400 \text{ dm}^{3} \text{ mol}^{-1} \text{ cm}^{-1}$ in acetonitrile with the hypothesis that $\varepsilon^{540}(BH) =$ $3220 \text{ dm}^{3} \text{ mol}^{-1} \text{ cm}^{-1}$ in acetonitrile as the ketyl radical absorption profiles in water and acetonitrile are very similar. Fig. 2 shows the triplet absorption spectrum and the ketyl radical absorption spectrum observed in water when formed through reaction (1). This spectrum is identical to the classical ketyl spectrum and it is not perturbed by any absorption by the L radical resulting from the oxidation of the lactam which should absorb further in the u.v. as it is a non-conjugated molecule.

(b) The second method for the determination of $\varepsilon_{\rm T}$ compares the optical density of the benzophenonone triplet, observed in a dilute aqueous solution of benzophenone, $OD_{\rm T}^{520}(^{3}{\rm B})$ observed at 520 nm, with the optical density of naphthalene



FIG. 1.—Dual beam oscilloscope traces showing the photoreduction of benzophenone triplet (³B) by 2-pyrrolidone (LH) in water, at 520 nm (upper trace 50 mV per div, time scale 200 ns per div) and the monitoring diode signal (lower trace 5 V per div, time scale 200 ns per div). Benzophenone $= 10^{-4}$ mol dm⁻³, 2-pyrrolidone = 0.3 mol dm⁻³.



FIG. 2.—Transient absorption spectra observed after flash excitation of 10^{-4} mol dm⁻³ benzophenone in presence of 0.1 mol dm⁻³ 2-pyrrolidone in water. Lowest triplet, +; ketyl radical, •.

triplet observed in a diluted solution of naphthalene in cyclohexane, $OD_T^{414}({}^{3}N)$ at 414 nm. Using similar OD of the ground state at excitation for both solutions, it is possible to assure that both solutions will absorb the same number of photons if the depletion of the ground state is small.⁶. ⁷

$$\varepsilon_{\rm T}^{520}({}^{3}{\rm B}) = \frac{OD_{\rm T}^{520}\,{}^{3}{\rm B}}{OD_{\rm T}^{414}\,{}^{3}{\rm N}} \times \Phi_{\rm T}\,{}^{3}{\rm N} \times \frac{1}{\Phi_{\rm T}\,{}^{3}{\rm B}} \tag{I}$$

Assuming that the triplet quantum yield of benzophenone is unity in water as it is unity in benzene,⁸ that the $\phi_{\rm T}$ for naphthalene is 0.75 ⁶ and $\varepsilon_{\rm T}^{414}({}^{3}{\rm N}) = 24500$ in cyclohexane,⁹ relation (I) gives $\varepsilon_{\rm T}^{220}({}^{3}{\rm B}) = 5800 \pm 400$ dm³ mol⁻¹ cm⁻¹, very similar to the extinction coefficient determined by the previous method. This value is the first one determined in water and acetonitrile. A previous work ⁹ had given $\varepsilon_{\rm T}^{532} =$ 7600 dm³ mol⁻¹ cm⁻¹ in benzene.

DECAY RATE CONSTANTS OF THE LOWEST TRIPLET T₁

The rate constants of the benzophenone lowest triplet were determined in water and acetonitrile for different laser intensities and different ground state concentrations of benzophenone. The higher the laser intensity, the higher is a second-order component of the benzophenone triplet decay. This does not seem to be due to a reaction of a molecule of benzophenone in the lowest triplet state ³B with a molecule of benzophenone in the ground state ¹B. In fact for similar triplet concentrations the triplet decay is similar and independent of the ground state concentration between 5×10^{-5} mol dm⁻³ (265 nm excitation) and 10^{-2} mol dm⁻³ (353 nm excitation) for acetonitrile solutions and between 2×10^{-4} and 2×10^{-5} mol dm⁻³ for aqueous solutions (265 nm excitation). The second-order component of the triplet decay is in fact due to a triplet-triplet annihilation. It is possible to determine a bimolecular rate constant $k_{\rm TT}$ for the triplet-triplet annihilation defined as the slope of the straight line obtained by plotting the initial observed rate constant of the triplet decay against the initial triplet concentration [³B]₀:

$$\frac{\mathrm{d}}{\mathrm{d}t}\ln\left[{}^{3}\mathrm{B}\right]\mathrm{initial} = k_{\mathrm{T}} + k_{\mathrm{TT}}\left[{}^{3}\mathrm{B}\right]_{\mathrm{0}}$$

where $k_{\rm T}$ is the pseudo unimolecular decay, being the ordinate at $[{}^{3}B]_{0} = 0$.

Table 1 reports the values found in the present work for $k_{\rm T}$ and $k_{\rm TT}$ in water and acetonitrile from the experimental data of fig. 3(a)-b). Note that the unimolecular decay rate constant $k_{\rm T} = 2.5 \times 10^4 \, {\rm s}^{-1}$ in water is larger than the values $k_{\rm T} = 10^4 \, {\rm s}^{-1}$ which can be calculated from the oscillograms of previous microsecond flash experiments performed either by Ledger and Porter¹ or by Charlier and Hélène⁵ for benzophenone in water. The same kind of discrepancy had already been noticed

Table 1.—Unimolecular $k_{\rm T}$ and bimolecular $k_{\rm TT}$ rate constants of benzophenone triplet ${}^{3}\phi_{2}$ C=O decay in water and acetonitrile

	$k_{\rm T}/{\rm s}^{-1}$	$k_{\mathrm{TT}}/\mathrm{dm^3}\mathrm{mol^{-1}}\mathrm{s}$	⁻¹ reference
water	$2.5 imes 10^4$ 10^4	0.5×10 ¹⁰ 0	this work (1)
acetoni	itrile 7×10^4	0.7×10 ¹⁰	this work

for the triplet decay rate constant of benzophenone in benzene measured with a microsecond conventional flash photolysis set-up¹¹ and a nanosecond laser flash photolysis set-up.¹²



BENZOPHENONE TRIPLET PROPERTIES

A possible cause for this discrepancy has already been given : the error introduced by the tail of the microsecond conventional flash leading to an apparent longer lifetime of the triplet.¹² With very high concentrations of benzophenone $(10^{-2}-3 \text{ mol dm}^{-3})$ in benzene evidence has been found for a quenching of benzophenone triplet by benzophenone ground state ¹³ with a rate constant $k_{TG} = 1.6 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. We have not observed this kind of triplet quenching between 5×10^{-5} and 10^{-2} mol dm⁻³ in water. The large $k_{TG} = 1.8 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ observed in water by other authors ¹ might be due to triplet-triplet annihilation.

TABLE 2.—RATE CONSTANTS	ko	(dm ³ mol ⁻¹ s ⁻¹) OF ${}^{3}\phi_{2}C=0$	REDUCTION BY	LACTAMS
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lactam	water	acetonitrile	
2-oxazolidone		2.54 × 10 ⁶	
2-pyrrolidone	10.7×10^{6}	7×10^{6}	
2-piperidone (valerolactam)	14.8×10^6	9.7×10^{6}	
e-caprolactam		1.15×10^{6}	
N-methyl-2-pyrrolidone	$34 imes 10^6$	18×10 ⁶	

DETERMINATION OF THE QUANTUM YIELD OF KETYL IN WATER

After completion of the triplet decay in aqueous solution without any reducing agent it is possible to observe a residual optical density due to a long-lived transient. Its spectrum is that of the ketyl radical. It is thus possible, knowing the extinction coefficient of the triplet and of the ketyl, to calculate a quantum yield of formation of this ketyl radical. It is important to notice that the transient optical density at 330 nm remains almost constant during the first 20 μ s, in other words the decay of ³B absorption is compensated at 330 nm by the growth of BH absorption and thus

$$\Phi_{\rm BH}^{*} = \frac{\epsilon^{330}({}^{3}{\rm B})}{\epsilon^{330}({\rm BH})} \times \Phi_{\rm T} = 0.45 \pm 0.1.$$

It is possible to calculate a similar quantum yield from the spectra observed by Ledger and Porter¹ and from the oscillogram reported by Charlier and Hélène.⁵

This quantum yield of the ketyl formation is extremely high when compared with the low quantum yield of benzophenone destruction $\approx 2 \times 10^{-2}$ reported in water.¹

photoreduction of ${}^{3}\phi_{2}$ CO by lactams (LH)

The rate constants of reduction of ${}^{3}\phi_{2}CO$, k_{Q} , are reported on table 2. They are higher the lower the ionization potential of the lactam (fig. 4). Charge transfer interaction of the type (B⁻...LH⁺) might occur in the excited state as it occurs between ketone triplets and a number of potential electron donors.¹⁴⁻¹⁸

DISCUSSION

TRANSIENT SPECTRA AND THEIR EXTINCTION COEFFICIENTS

The spectra of ³B and BH in water are shown in fig. 2 with their respective extinction coefficients. Using a bandwidth of 3 nm we have observed average ratio of 0.69 for $\varepsilon^{520}/\varepsilon^{320}$ of ³B and 0.2 for $\varepsilon^{540}/\varepsilon^{330}$ of BH in water. These ratios are

very similar to the ratios observed in water by Ledger and Porter ¹ who used a photographic method. In acetonitrile these ratios are, respectively, 0.56 and 0.165.

ORIGIN OF THE BENZHYDRYL IN AQUEOUS SOLUTION

Photoreduction of aromatic ketones lowest triplets in water has been observed previously.¹ The reaction is of great interest with respect to how water is photooxidized in chloroplasts, this being one of the most important questions in photosynthesis. In our experimental conditions the reaction ${}^{3}B+B$ or ${}^{3}B+{}^{3}B$ cannot be the source of the BH observed as the ${}^{3}B$ rate of decay is independent of (B) concentration (table 1) and (BH)/(${}^{3}B$) is independent of (${}^{3}B$).



FIG. 4.—Plot of $\log k_Q$ (rate constant of the triplet deactivation) against the adiabatic ionization potential of the lactam donor.

Ledger and Porter ¹ have suggested the following reactions :

$${}^{3}\phi_{2}c = 0 + H - 0 - H - \phi_{2}\dot{c} - 0H + \dot{0}H$$
 (2)

$$\dot{o}_{H} + \phi_2 c = 0 \longrightarrow \qquad \overset{HO}{\underset{H}{}} \sim c_0 \phi \qquad (3)$$

Their thermochemical calculation showed that reaction (2) involving a triplet was borderline. Another mechanism which would also hold for the formation of ($\dot{B}H$) might be *via* a singlet excited state of the H bonding complex ($^{1}B...H$ —OH)*.

But, if this was true, ϕ_T of benzophenone should not be unity in water. However, the assumption that $\phi_T = 1$ has allowed, by a comparative method, the determination of an ε_T very similar to the ε_T found by a method which did not involve any assumption on ϕ_T of benzophenone. Furthermore, the fact that at 330 nm the triplet absorption decay is compensated by the ketyl formation means that ³B is the precursor of BH.

THE BENZOPHENONE OH ADDUCT

The presence of a shoulder at 390 nm in the transient ketyl radical spectrum only occurs in B photoreduction by water and does not show up in fig. 2 where ³B was reduced by a lactam. This shoulder at 290 nm has already been noticed by Ledger and Porter ¹ and assigned to the benzophenone $\dot{O}H$ adduct $\dot{B}OH$.

This BOH radical formed by reaction (3) does not contribute greatly to the optical density observed at 540 nm as its $\varepsilon^{540}(BOH) = 290 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1.4}$ whereas $\varepsilon^{540}(BH) = 3220 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1.4}$ Our results therefore support the mechanism of ϕ_2 CO in water described above by reaction (2) and (3) and proposed by Ledger and Porter.¹ This mechanism is also supported by the damage of OH radicals produced by reaction (2) on deoxyribose residues in DNA observed by Charlier *et al.*^{5. 10}

PHOTOREDUCTION BY LACTAMS

In the case of the reduction of the lowest ${}^{3}n\pi^{*}$ triplet of benzophenone,¹⁴ fluorenone,¹⁵ acetone ¹⁶ or trifluoro acetophenone ¹⁷ a linear correlation has been observed between the ionization potential of the donor and log k_{Q} , where k_{Q} is the rate constant of the triplet deactivation in the presence of the donor. This correlation, which we also observe (fig. 4) in the case of benzophenone photoreduction by lactams (with the exception of caprolactam) might be an indication that the reaction takes place through a charge transfer triplet exciplex.¹⁴⁻¹⁹ It is interesting to notice that this photoreduction with lactams occurs by the H atom in the α position of the N atom and that the ketyl adding with the amide radical will yield phenylethanolamides.²⁰



The higher ionization potential of amides compared with that of amines might explain the fact that photoreduction from the amides studied herein occurs only through H abstraction even in polar solvents as water and acetonitrile whereas photo-reduction by amines in polar solvents as acetonitrile can occur through electron or H transfer.¹⁸ Although the rate constants of ³B reduction by amides (table 2) are lower than by amines ¹⁸ by a factor of 10^2 - 10^3 , it is remarkable that amides are more efficient reductants of ³B than traditional H donors as alcohols:isopropanol,²¹ ethanol ¹ or benzhydrol ²² (table 3).

alcohol	solvent	$/dm^3 mol^{-1} s^{-1}$	reference
ethanol	water	1.3×10^{6}	1
isopropanol	isopropanol	2×10^{6}	21
benzhydrol	benzene	2×10^{6}	26
benzhydrol	acetonitrile	4×10^{6}	present work

TABLE 3.—RATE CONSTANTS k_0 (dm³ molecule⁻¹ s⁻¹) of ${}^3\phi_2$ C=O reduction by alcohols

REVERSIBILITY OF THE HYDROGEN ABSTRACTION IN REACTIONS (1) AND (2)

The quantum yield of formation of the ketyl in water $\phi(BH) = 0.45 \pm 0.1$ which we have observed is rather similar to what can be calculated from the transient spectra of other authors ^{1, 5} using the extinction coefficients ε (³B) determined herein and $\epsilon(BH)$ determined by Land.⁴ This quantum yield is difficult to reconcile with the very low quantum yield of benzophenone disappearance in water: $(2-5) \times 10^{-2}$ found previously ¹ in steady state photolysis.

Likewise, the quantum yield of formation of BH from the lactam oxydation by ³B reaches unity when measured by flash photolysis whereas the quantum yield of final lactam disappearance and benzophenone disappearance is 0.13²⁰ in a low continuous irradiation experiment. These long-lived BH radicals are certainly out of the cage of Frank-Rabinowitch and one possible explanation of the discrepancies between $\phi(BH) = 1$, observed in the present work by flash photolysis, and the final $\phi(-B) =$ 0.13, observed by Gramain et al.²⁰ by analysis of the final products, is that reactions (4) and (5) are reversible at least partially: CIDNP experiments ^{23, 24} confirm this reversibility, already observed through a multistep reaction in systems like benzophenone-benzhydrol.²⁵ Another possible explanation for the high yield of ketyl radicals obtained by the flash photolysis technique might be that the analysing light behaves as actinic light and that upper triplet excited states are involved in the photoreduction of benzophenone.

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