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Triplet State Lifetime of Anthracene in Benzene Solution**

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Dedicated to Professor Albert Weller on the occasion of his 65th birthday

Abstract: The decay kinetics of the triplet state absorption of anthracene in benzene have been measured in conditions of laser flash photolysis, as a function of anthracene concentration and of laser light intensity. It is concluded that concentration quenching of triplet state anthracene by ground state anthracene is the major bimolecular deactivation process.

The lifetime of electronically excited states plays a most important role in the actual efficiency of photochemical processes. A photochemical reaction may be very inefficient in terms of its quantum yield Φ_r even though the reaction rate constant k_r may be large, because of the competing photophysical processes of deactivation of the excited state which can be represented by a deactivation rate constant k_d:

$$\Phi_r = \frac{k_r}{k_r + k_d}$$

The lowest triplet excited states of organic molecules M are of special importance in bimolecular photochemical reactions, since such states are expected to have relatively long lifetimes (of the order of ms to s), long enough to lead to reactive encounters in liquids of low viscosity even when the partner (ground state) species N is present in low concentration

$$^3M^* + N \rightarrow P$$

It is however well known that the triplet state lifetimes of many aromatic molecules measured in solution are much shorter than the phosphorescence lifetimes, or the lifetimes measured in highly viscous media or solid matrices such as organic glasses at low temperatures[1]. Thus the lifetime of the triplet state (T_1) of anthracene (**A**) is only some 80 µs in ethanol or cyclohexane at room temperature as measured in conventional or laser flash photolysis experiments, whereas it is 26 ms in an acrylic glass and even longer in low temperature frozen matrices[2].

The reason for the dramatic shortening of the triplet state lifetime in low viscosity liquids has been ascribed to a variety of factors such as quenching by residual molecular oxygen[3], quenching by unspecified impurities in the solvent or in the an-

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thracene sample itself[4], or concentration quenching of $^3A^*$ by ground state A[5]. In this paper we report a study of the lifetime of the triplet state of A in benzene at extremely low concentrations, in conditions of laser flash photolysis. The unambiguous result is that concentration quenching is the decisive process.

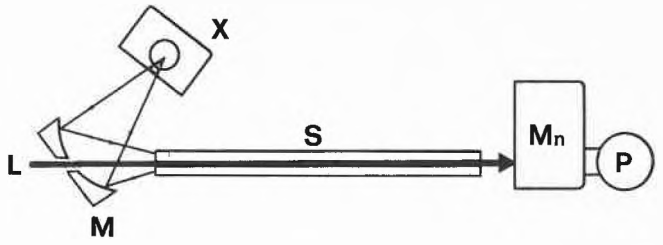

Fig. 1. Outline of the optical arrangement of the flash photolysis experiment using long pathlength cells. X: xenon arc (monitoring light source); L: laser beam; M: spherical mirror with central hole; S: glass sample cell of pathlength l; Mn: monochromator; P: photomultiplier.

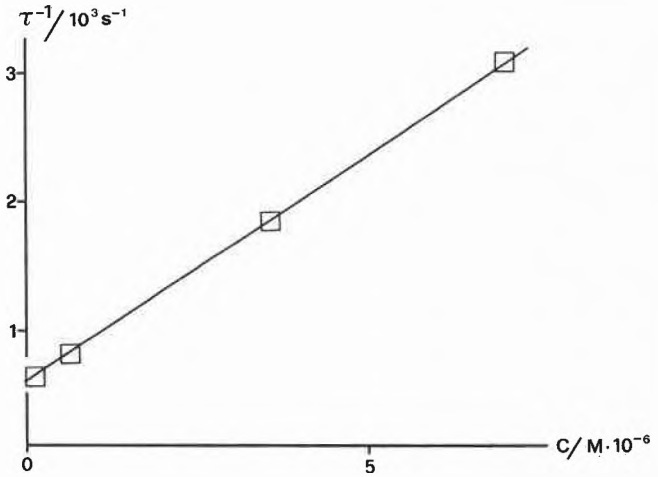

Fig. 2. Observed reciprocal triplet state lifetimes at various anthracene concentrations c.

Experimental

Solutions of anthracene (A) of very low concentrations can be used if the cell pathlength l can be made large enough to give a reasonable absorbance at the excitation wavelength. The third harmonic of a Nd-YAG laser (JK model 2000) at $\lambda = 355$ nm has been used in this work; the molar decadic extinction coefficient of A is $8.68 \cdot 10^3$ M^{-1} cm^{-1} at this wavelength, so that concentrations of A down to $\approx 10^{-8}$ M could be used in a cell of 1 m optical pathlength.

Three cells have been used for different concentrations of A, of pathlenghts 0.1, 0.5, and 1 m, all of 7 mm diameter to fit the laser beam diameter of 6 mm. The monitoring light was focussed on to the end window of the cell by means of a spherical mirror provided with a 10 mm diameter hole for the laser beam (Fig. 1).

The monitoring light from a 150 W xenon arc lamp could be passed through the long cylindrical cells by taking advantage of the light-guide effect which depends on the difference between the refractive indices of the solvent and of the surrounding glass. This made it necessary to use a solvent of relatively high refractive index such as benzene (cyclohexane or ethanol do not give a satisfactory light-guide effect in long glass cells). Under these conditions the monitoring light passes through the solution by multiple reflection and can be collected at the other end of the cell into a monochromator set at a maximum of the $^3A^*$ absorption at $\lambda = 420$ nm. The concentration of $^3A^*$ can be determined from the absorbance since the $T_1 \rightarrow T_n$ extinction coefficient is known to be $45.5 \cdot 10^3$ M^{-1} cm^{-1} [6].

The sample cells were fitted with a degassing reservoir and an adaptor to the vacuum line; all samples are degassed by the usual freeze-pump-thaw-shake procedure until no residual gas pressure could be detected at 10^{-6} Torr. It is probably more difficult to eliminate oxygen from benzene than from other solvents since it is known that O_2 forms weak complexes with many aromatic molecules; the degassing procedure was therefore repeated six times in these experiments.

Since in conditions of laser flash photolysis the number of photons can be large compared to the number of molecules, the laser pulse intensity could be reduced by means of liquid filters of 4-hydroxybenzophenone in ethanol. The actual pulse energy was measured by means of the JK lasers energy monitor; the unfiltered pulse had an energy of 10 mJ.

Signal detection and processing: The monitoring light at 420 nm was detected by a photomultiplier EMI 9785 and displayed on a storage oscilloscope. It was then digitized by a vidicon camera and the data were transferred to a computer (Acorn BBC or PDP 11/34) for numerical analysis[7].

Samples: Anthracene was Fluka scintillation grade, recrystallized twice from spectroscopic grade ethanol; benzene was Merck UV grade solvent, used without further purification. The purity of the anthracene sample was checked by gas chromatography, and the overall level of impurities could be put as no higher than 0.1%. No fluorescence other than that of anthracene could be detected over the wavelength region up to 900 nm.

Table 1. Initial triplet state concentration $[^3A^*]_0$ and triplet state lifetime τ for different laser pulse energies.

Filter transmission (%)	$[^3A^*]_0$ (mol L^{-1})	τ (ms)
100	$1.52 \cdot 10^{-8}$	1.2
87.5	$1.32 \cdot 10^{-8}$	1.3
42.5	$6.47 \cdot 10^{-9}$	1.2
22.9	$3.86 \cdot 10^{-9}$	1.1

Table 2. Initial triplet state concentration $[^3A^*]_0$ and triplet state lifetime τ for different anthracene concentrations [A].

[A] (mol L^{-1})	$[^3A^*]_0$ (mol L^{-1})	τ (μs)
$6.87 \cdot 10^{-6}$	$1.66 \cdot 10^{-7}$	320 ± 13
$3.44 \cdot 10^{-6}$	$1.09 \cdot 10^{-7}$	540 ± 40
$5.50 \cdot 10^{-7}$	$1.42 \cdot 10^{-8}$	1200 ± 70
$2.74 \cdot 10^{-8}$	$6.28 \cdot 10^{-9}$	1550 ± 120

Results and Discussion

When a solution of A of concentration $5.5 \cdot 10^{-7}$ M is flashed with pulses of energies ranging from 10 mJ down to 2.3 mJ it is found that the initial absorbance of $^3A^*$ follows linearly the pulse energy, and that the triplet state lifetime stays constant at 1.2 ms within experimental error (Table 1).

This shows that there is no saturation effect in these conditions (such as would be reached if nearly all the molecules would be excited to the triplet state). At the highest pulse energy the ground state depopulation is of only around 3%.

The triplet decay follows first order kinetics in every case from the very start of the trace, and no delayed fluorescence could be detected.

Triplet-triplet annihilation seems therefore to be unimportant at times longer than some 10 μs following the laser pulse, and this can be understood from the triplet state concentrations: the highest concentration is of around 10^{-8} M, so that assuming a diffusion-controlled annihilation rate constant k_D of 10^{10} M^{-1} s^{-1} the initial slope $d[^3A^*]/dt$ is small compared to the first-order decay slope of $\approx 10^{-5}$ M s^{-1}:

$$\frac{d[^3A^*]}{dt} = k_D[^3A^*]_0^2 = 10^{10} \times 10^{-16} = 10^{-6}\,\text{M s}^{-1}$$

When the pulse energy is reduced the triplet concentration is even lower and triplet-triplet annihilation even less important. The effect of A concentration was then investigated with solutions prepared in cells of four different pathlenghts ranging from 2 cm to 1 m (Table 2). There is a steady increase in the triplet state lifetime as the A concentration decreases, extrapolating for zero concentration to a lifetime of around 1.7 ms (Fig. 2).

These results can now be analyzed in terms of a concentration-independent rate constant k_1 and a concentration-dependent rate constant k_2, according to the linear relationship

$$-\frac{d[^3A^*]}{dt} = k_1[^3A^*] + k_2[A]\,[^3A^*]$$

with $k_1 = 630$ s^{-1} and $k_2 = 3.6 \cdot 10^8$ M^{-1} s^{-1}.

The rate constant k_1 includes all terms which do not vary with [A] such as quenching by solvent impurities, by any residual oxygen, as well as true first order terms of unimolecular radiative and non-radiative

deactivation. The extrapolated lifetime of ^{3}**A*** is then still very much shorter than that observed in diffusionless systems, but it is difficult to establish the origin of the unimolecular or pseudo-unimolecular deactivation process. Quenching by residual oxygen still seems the most likely explanation, although it implies a repeated failure of the degassing procedure; the residual oxygen concentration should be of the order of 10^{-7} M to account for the observed rate constant k_1, far above the concentration expected from the residual gas pressure of 10^{-6} Torr (if $[O_2] = 10^{-3}$ M at the normal atmospheric pressure, it would be 10^{-9} M at 10^{-6} Torr pressure).

The concentration-dependent rate constant k_2 can cover two quite distinct quenching mechanisms which both depend on [**A**]: the quenching by impurities contained in the solute, and the quenching by the solute (ground state **A**) itself, the so-called «concentration quenching».

At the lowest concentration of **A** ($2.74 \cdot 10^{-8}$ M) the pseudo-first-order rate constant is 15 s^{-1} from the observed lifetime of 1.55 ms and the extrapolated first-order rate constant $k_1 = 630\ s^{-1}$. Assuming a diffusion limited rate constant $k = 10^{10}$ $M^{-1}\ s^{-1}$ the quencher concentration comes to $1.5 \cdot 10^{-9}$ M, that is over 5% of the concentration of **A**. Since the results of the GC analysis of the anthracene sample used in this work give an absolute limit of 0.1% for all impurities, it must be concluded that the concentration-dependent process is the quenching of ^{3}**A*** by ground state **A**. The quenching rate constant of $3.6 \cdot 10^8$ $M^{-1}\ s^{-1}$ is however substantially lower than the diffusional limit (by a factor 30 approximately).

It is of course still an open question to what extent this type of quenching may be general; it remains to be seen also if its efficiency depends on the solvent. In any case it shows that the lifetime of triplet states in solution depends on the solute concentration, and this should be given due consideration in the design of preparative photochemical experiments.

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[1] C. A. Parker: *Photoluminescence of Solutions*, Elsevier, Amsterdam (1968).
[2] R. Livingston, W. R. Ware, *J. Chem. Phys. 39* (1963) 2593.
[3] S. P. McGlynn, T. Azumi, M. Kinoshita: *Molecular Spectroscopy of the Triplet State*, Prentice-Hall, Englewood Cliffs, NJ (1969).
[4] K. H. Grellmann, H. G. Scholtz, *Chem. Phys. Lett. 62* (1979) 64.
[5] J. Langelaar, G. Jansen, R. P. H. Rettschnick, G. J. Hoytink, *Chem. Phys. Lett. 12* (1971) 86.
[6] H. Labhart, W. Heinzelmann, in J. B. Birks (Ed.): *Organic Molecular Photophysics*, Vol. *1*, Wiley, London (1973).
[7] M. Gremaud, P.-H. Chassot, P. Suppan, *Chimia 37* (1983) 379.