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# A Laser Photolysis Study of Triplet Lifetimes and of Triplet–Triplet Annihilation Reactions of Phthalocyanins in DMSO Solutions

## Etude des Durées de Vie du Triplet et des Réactions d'Annihilation Triplet–Triplet de Phthalocyanines dans le DMSO par Photolyse Laser

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Triplet decay of Mg and Zn phthalocyanins have been studied by laser flash photolysis as a function of concentration. The triplet decay mechanism changes from a near first order in dilute solution to an almost second order in concentrated solutions. This is interpreted in terms of triplet–triplet recombination. With the help of a reducing agent, it is shown that the triplet–triplet reaction can lead to charge separation.

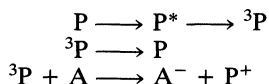
La décroissance des états excités triplet des phthalocyanines de Mg et de Zn a été étudiée par photolyse éclair laser en fonction de la concentration. Le mécanisme de décroissance

du triplet passe d'un premier ordre presque idéal en solution diluée à un quasi second ordre en solution concentrée. Ceci s'explique par une recombinaison triplet-triplet. A l'aide d'un réducteur, la réaction triplet-triplet peut conduire à une séparation de charges.

KEY WORDS: Phthalocyanines, kinetics.

The conversion of solar energy into chemical fuels usually involves a charge transfer from an excited state of a photosensitizer to an acceptor molecule. The triplet states, having a much longer lifetime than singlet states, play an important role in reactions involving charge separation and therefore energy conversion. In order to study the efficiency of these processes, the kinetics of the reaction of the excited species can be studied by the means of flash or laser photolysis.

In the most simple cases, the following reaction scheme can be written:



It is clear that in this case, the triplet should decay via a first order mechanism, and there should not be any dependence of the observed rate constants upon the concentration of  ${}^3\text{P}$  or  $\text{P}$  present in the solution. This situation is seldom encountered. Especially when the excited species have a long lifetime, several other deactivation paths may become important.

In some previous studies,<sup>1,2,3</sup> we have shown that zinc and magnesium phthalocyanine ( $\text{ZnPc}$  and  $\text{MgPc}$ ) in DMSO solutions have long lived triplets (ca. 500  $\mu\text{s}$ ). It was observed that under these conditions, the photoreduction of methylviologen could be achieved and that even in very dilute solutions, the triplet decay did not follow a simple first order kinetic law.

A variety of work has also been performed on the photoreduction of porphyrins<sup>4</sup> in aqueous media by EDTA. Dimerization of  $\pi$  radical cations of porphyrins have also been studied as a function of solvent composition.<sup>5</sup> The effect of concentration of the triplet of porphyrins and of Al and Si phthalocyanines upon lifetimes have been recently studied. The results were interpreted in terms of excimer formation.<sup>6,7</sup>

The purpose of this paper is to show that  $\text{ZnPc}$  and  $\text{MgPc}$  triplets undergo triplet-triplet annihilation when the concentration is increased. In DMSO, aprotic solvent of high dielectric constant, no

other species are formed as a function of time. A complete kinetic analysis of the phenomena has been performed. It will also be shown that these phthalocyanins can be photoreduced by mild reducing agents only when the concentration of triplet is sufficiently high. The possibility of applying these results to the problem of charge transfer to other molecules will be discussed.

## EXPERIMENTAL

Commercial phthalocyanins (Eastman Kodak) were used throughout this work. They were purified in two steps: first by a moderate heating (150°C) for several hours under vacuum, some unidentified white and yellow compounds were sublimated; the remaining product was then sublimated in small quantities at 250°C under high vacuum conditions. The UV-visible spectra of the solutions obtained with the sublimated phthalocyanine did not show evidence of the presence of impurities (like  $\text{PcH}_2$ , which is the one most likely to be found). The concentrations were calculated using  $10^5 \text{ M}^{-1} \cdot \text{cm}^{-1}$  for  $\epsilon_{675}$ , value that was previously used.<sup>1</sup> All the other reagents were of the highest purity available (Aldrich or Merck). The proper concentration of phthalocyanine was obtained by diluting a stock solution. Quartz cells having path length of 10, 5, 1, 0.5 and 0.1 cm were used. The absorbance of the dye was the same in each of these cells. These cells were attached to borosilicate vessels to allow outgassing of the solutions by the freeze-pump-thaw method ( $10^{-5}$  torr). The optical spectrum of the solutions was recorded before and after each experiment on a Beckman 5240 spectrophotometer.

All photolysis experiments were made by using a laser flash system which consisted of an  $\text{XeCl}^*$  excimer laser (SOPRA) giving pulses of 15 ns duration at 308 nm with 200 mJ per pulse used to pump a dye laser. A three-stage dye laser (oscillator, preamplifier, amplifier) was used with cresyl violet (Radiant dyes) in ethanol solution (SOPRA). The wavelength used was 675 nm and 2 mJ of energy could be obtained although experiments with lower energies were also performed. The laser beam was made as colinear as possible with the analysis beam axis ( $\text{Ca} \cdot 5^\circ$ ).

The detection system was made of a xenon arc light source (250 W, Applied Photophysics), a monochromator (Jobin-Yvon H-20), and a

photomultiplier (Hamamatsu, R928). Data acquisition was performed by using a digital storage oscilloscope (Philips PM3315, 124 MHz) attached to a MINC-1123 calculator (Digital Corp.) for data storage and processing. Kinetic analysis was made by the use of a Fortran non-linear damped least square adjustment program.<sup>8</sup> Each decay curve was defined by 225 data points.

## RESULTS

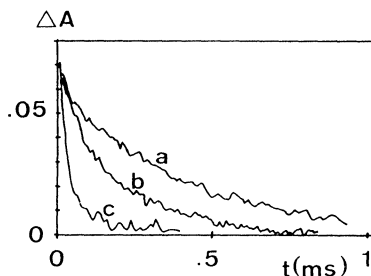
It was first checked that DMSO solutions of phthalocyanins followed BEER's law on a one hundred-fold range of concentrations (optical pathlength of the cells varied from 10 to 0.1 cm). From the shape of the optical spectrum in the region of the absorption maximum and also because no variations were observed when the concentration was modified, it was assumed that these solutions contained monomeric form of the dye. In all of the cases studied, the absorbance of the dye was of about 2 at the maximum (675 nm), which corresponds to concentrations ranging from  $2 \times 10^{-6}$  M to  $2 \times 10^{-4}$  M.

The initial absorbance of the triplet formed by the laser flash was almost independent of the path length of the cell used. Therefore, it is reasonable to consider that the initial concentration of the triplet  $[^3\text{P}]_0$  was varied by a factor of one hundred. The values of the extinction coefficient of the triplet of PcZn were those given by Linqvist<sup>9</sup> ( $\epsilon = 3.6 \times 10^4$  at 484 nm). The initial triplet concentrations in these conditions are given in Table I. As it is shown on Figure 1, the decay of the triplet is strongly dependent upon the concentration. Furthermore, the kinetics are a mixed first and second order.

**Table I**

$[\text{PcZn}]_0$	$[^3\text{PcZn}]_0$	$l$	$k_1$	$k_3/\epsilon l^*$	$k_3$
M	M	cm	$\text{s}^{-1}$		$\text{M}^{-1} \text{s}^{-1}$
$2 \cdot 10^{-4}$	$2.8 \cdot 10^{-5}$	0.1	$5050 \pm 100$	$7.8 \cdot 10^5 \pm 0.2$	$2.8 \cdot 10^9$
$2 \cdot 10^{-5}$	$1.4 \cdot 10^{-6}$	0.5	$3300 \pm 200$	$1.2 \cdot 10^5 \pm 0.06$	$2.1 \cdot 10^9$
$2 \cdot 10^{-5}$	$2.8 \cdot 10^{-6}$	1.0	$2900 \pm 300$	$5.4 \cdot 10^4 \pm 0.2$	$1.9 \cdot 10^9$
$4 \cdot 10^{-6}$	$3.4 \cdot 10^{-7}$	5.0	$2550 \pm 300$	$2.0 \cdot 10^4 \pm 0.2$	$3.5 \cdot 10^9$
$2 \cdot 10^{-6}$	$2.8 \cdot 10^{-7}$	10.0	$2250 \pm 200$	$0.9 \cdot 10^4 \pm 0.4$	$3.2 \cdot 10^9$

\* Measured at 480 nm.



**Figure 1** PcZn triplet decay for various concentrations at 490 nm (a)  $2 \times 10^{-6}$  M; (b)  $2 \times 10^{-5}$  M; (c)  $2 \times 10^{-4}$  M.

In order to analyse the data, the following mechanism was used:



The kinetic law can then be written:

$$\frac{d[^3\text{P}]}{dt} = -k \cdot [^3\text{P}] - k_2 \cdot [^3\text{P}] \cdot [\text{P}] - k_3 \cdot [^3\text{P}]^2$$

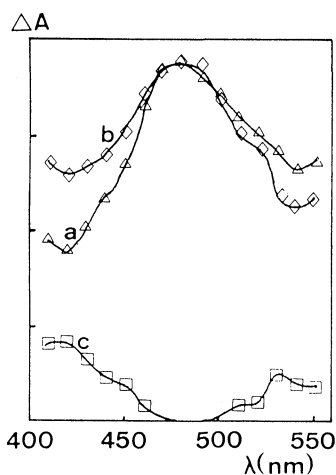
Since in most cases,  $[\text{P}] \gg [^3\text{P}]$  the first two terms can be regrouped and a pseudo first order rate constant  $k'_1 = k_1 + k_2[\text{P}]$  used. The reaction mechanism consists of two parallel reactions, one of the pseudo first-order, the other one of the second order in the triplet concentration.

If only one species is absorbing at each wavelength studied, the following rate expression can be derived:<sup>10</sup>

$$\frac{1}{A(t)} = \frac{1}{A^0} \exp(k'_1 \cdot t) + \frac{k_3}{k'_1 \cdot \epsilon_t \cdot l} [\exp(k'_1 \cdot t) - 1]$$

All the decay curves were fitted to this equation by using three adjustable independent parameters  $A_0$ ,  $k'_1$ ,  $k_3/\epsilon_t \cdot l$  in which  $\epsilon_t$  is the extinction coefficient of the triplet at each wavelength and  $l$  the optical pathlength of the cell being used. The pseudo first order rate constant  $k'_1$  should be independent of the wavelength if the mechanism is valid.

For the two phthalocyanins studied, the best results were obtained for PcZn, all other conditions being identical. Some of the results obtained at the absorption maximum of the triplet are summarized on



**Figure 2** Absorption difference spectra in the presence of ascorbic acid: (a)  $t = 0$ ; (b)  $t = 0.4$  ms; (c) difference (b) – (a).

Table I. At any given concentration, the pseudo first-order rate constant does not vary with the wavelength in the range 400–580 nm where only the triplet absorbs under our experimental conditions. A dependence upon the concentration is observed and it will be discussed below. The third adjustable parameter is obtained as the ratio  $k_3/\epsilon_t \cdot l$ ; it is therefore wavelength dependent. However by assuming that the laser pulses are reproducible and yield the same amount of triplet at each flash, the product of this parameter by the initial absorbance yields a reasonable constant value from 400 to 580 nm. The value of  $k_3$  can be calculated by using the extinction coefficient of the triplet at the maximum of  $3.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . They are reported in the last column of Table I. The agreement between the four sets of measurements is quite satisfactory. There is a gradual shift from first to second order as one goes from dilute to more concentrated solutions.

Experiments performed under the same experimental conditions with MgPc yield the same kind of results although for some unexplained reasons they are much more scattered. Studies performed with relatively dilute solutions ( $l = 1 - 10$  cm) yield a first order rate constant of  $1100 \text{ s}^{-1}$  independent of the wavelength. This value is about one half of the one observed with PcZn. In concentrated solutions, this constant rises to a value of  $5000 \text{ s}^{-1}$  as it was the case of

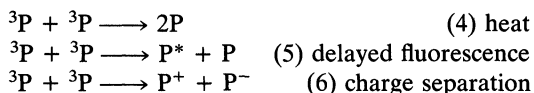
PcZn. The accuracy of this last value is somewhat limited by the fact that the reaction is almost of second order.

The second order rate constant of the triplet-triplet reaction was obtained in 1 cm and 0.1 cm cells. Values of  $k_3/\epsilon_t$  of  $6 \times 10^4$  and  $1.5 \times 10^5$  were respectively obtained at 480 nm. This difference cannot be explained by experimental errors.

### STUDY OF THE REACTION PRODUCTS

As long as there are no other species in the solution, kinetics can be reasonably performed in terms of a single absorbing species  $^3P$  in the wavelength range 420–550 nm.

However the products of the reaction may be:

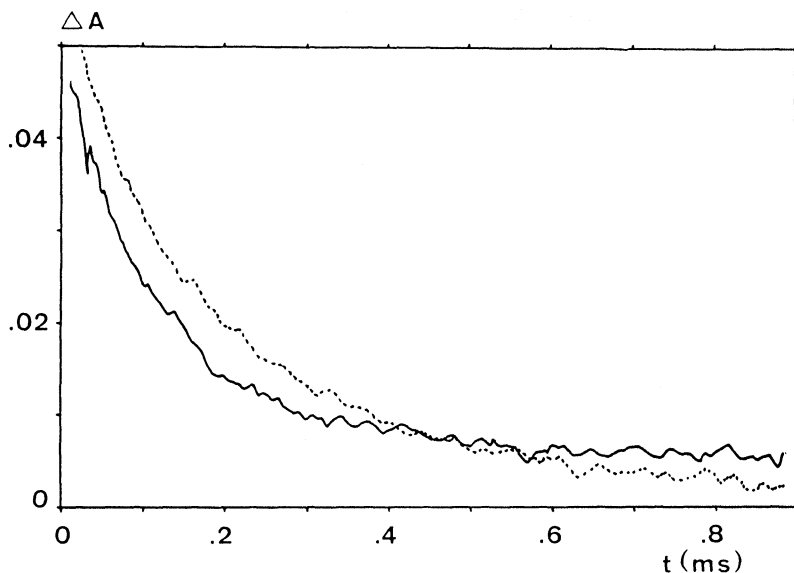


The first two reactions do not produce any new absorbing species provided that the conversion of  $P^*$  into  $^3P$  is not too efficient. The last reaction creates new absorbing species but it is reasonable to assume that the back reaction will be very fast and that in the absence of any reducing or oxidizing species, they will not interfere with the observations.

The presence of a reducing agent such as ascorbic acid, does not change anything to the first two processes but should stabilize  $P^-$  by reacting with  $P^+$  if the third reaction is important.

In dilute solutions ( $l = 5$  or  $10$  cm) of ZnPc, there are no evidences of the formation of new absorbing species as a function of time. On the contrary as the ZnPc, concentration is increased ( $l = 1$  cm or less) but at the same ascorbic acid concentration, transient spectra measured at various times after the laser pulses are different and indicate clearly the formation of a new absorbing species which may be attributed to  $ZnPc^-$ .<sup>11</sup> Typical decay curves measured at 520 nm show clearly the formation of long lived species in the presence of ascorbic acid (Figure 3). Identical results were obtained with PcMg under the same conditions or using EDTA as reducing agent.

The mechanism previously developed can still be used for the regions where  $PcZn^-$  does not absorb (ca. 480 nm). However, systematic errors occur at other wavelengths. Data obtained with two



**Figure 3** Effect of the presence of ascorbic acid on PcZn decay curves at 420 nm: — with ascorbic acid; - - - without ascorbic acid.

phthalocyanin concentrations (but with the same ascorbic acid content  $10^{-2}$  M) were analysed by a new mechanism taking into account the formation of a new absorbing species  $P^-$ :

$$\frac{d[P^-]}{dt} = k_3 \cdot [{}^3P]^2$$

$$A = \epsilon_t \cdot [{}^3P] + \epsilon_- \cdot [P^-]$$

Integrating the above formula yields an expression in which there is clearly a fourth unknown introduced as the ratio of the extinction coefficients  $\epsilon_-/\epsilon_t$  (see Annex 1). Adjustment of each individual decay curve to this equation is remarkable, no systematic deviation being observed.

For each concentration of phthalocyanine studied, the first order rate constant did not change upon the investigated wavelength range (400 to 560 nm). However  $k'_1$  depends upon the triplet concentration: a value of  $3800 \pm 400 \text{ s}^{-1}$  was obtained in dilute solutions; it rose to  $6400 \pm 500 \text{ s}^{-1}$  in solutions five times more concentrated. The second order rate constant did not change upon addition of ascorbic acid.



## DISCUSSION

Triplets of MgPc and of ZnPc (as well as the one of ClAlPc) do not react with DMSO. On the contrary,<sup>6</sup> the triplet of ClAlPc in ethanol solutions readily reacts with the solvent to form a stable radical cation. Similar comparisons were not made in this work, since ZnPc and MgPc are insoluble in alcohols.

Triplet decay is strongly concentration dependent and some relatively large effects are observed upon the pseudo first order rate constant. By using the data reported in Table I a rough estimation of the real first order rate constant can be made  $k_1 = 2200 \text{ s}^{-1}$  and  $k_2 = 2 \cdot 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$ . This latter value is not diffusion controlled, but is large enough to explain some differences in the lifetime values reported by different laboratories. The method used in this work allowed us to vary the initial concentration of the dye by a factor of 100 while keeping initial triplet absorbances of the same order of magnitude. The initial triplet concentration can also be varied by changing the power of the laser through the use of absorbing filters. We have verified that this did not change the values of  $k_1$  and  $k_2$ .

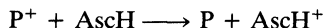
The role of triplet-triplet recombination becomes more and more important as the concentration is increased. For the highest concentrations studied, triplet decay was almost second order. On the contrary to what was observed in benzene with zinc tetraphenyl porphyrin,<sup>5</sup> no new species were formed after the flash. Therefore, the assumption that triplet-triplet reaction led to excimer formation was not taken into consideration here.

In some similar systems, the delayed fluorescence induced by reaction 5 was observed. In the case of zinc octaethylporphyrin,<sup>12</sup> fluorescence having a lifetime of 5 ms have been observed. The second order rate constants obtained by these authors were of the same order of magnitude as the ones we measured from the triplet lifetimes. The same phenomenon has also been observed for SiPc in benzene or cyclohexane solutions.<sup>7</sup> We have not been able to verify the importance of this reaction in our case.

As it was previously observed in very dilute solutions of PcZn in DMSO<sup>1</sup> in the presence of ascorbic acid, there are no reactions of photoreduction of the phthalocyanine by ascorbic acid. The optical absorption spectrum of deaerated Zn or MgPc in presence of ascorbic acid is not modified upon illumination. On the contrary, some porphy-

rins<sup>4</sup> or some Zn tetra 2,3 pyridino porphyrazines<sup>13</sup> are easily reduced in the same conditions.

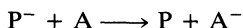
In more concentrated solutions, the presence of P<sup>-</sup> at relatively long times is due to the reaction 6 followed by:



which leaves only the radical anion in the solution.

From the kinetic analysis, it seems clear that for phthalocyanines in DMSO solution, the reaction 6 is a very important mode of triplet deactivation since no modification of  $k_3$  is required to fit the decay curves in the presence of P<sup>-</sup>.

In most experiments involving charge transfer from PcZn or PcMg triplets to an acceptor such as methyl viologen, it was assumed that the triplet reacted directly with the acceptor. The donor was then used to regenerate the photooxidized dye. This is correct in dilute solutions since we have shown that there are no reactions between triplet species and the reducing agent. However, as the concentration becomes larger than 10<sup>-5</sup> M, new reaction paths become important and the main reaction becomes the triplet-triplet one. In this case, the reduced form of the acceptor may stem from the reaction:



since the  $E^0(P/P^-) = -0.89 \text{ V/SCE}^{14}$  is sufficient to reduce most of the acceptors commonly used. Such a mechanism indicates that in sufficiently concentrated solutions, in the presence of a weak electron donor, a strong reducing species may be formed. It is then possible, if a proper catalyst is found, that interesting reactions could occur without the help of an auxiliary electron transfer agent.

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