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PIGMENT COLOR RESEARCH REPORT

PHOTOCHEMISTRY OF QUINACRIDONE DERIVATIVES

Period Covered MARCH 3, 1969 - OCTOBER 3, 1969

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SUBJECT: PHOTOCHEMISTRY OF QUINACRIDONE DERIVATIVES

PERIOD COVERED: MARCH 3, 1969 - OCTOBER 3, 1969

SUBMITTED BY: PETER A. WRIEDE DATE SUBMITTED: 9/24/70

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ABSTRACT

The photochemical degradations of quinacridone (QA) and quinacridonequinone (QAQ) in N,N-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) have been investigated. Reaction of QA in aerated DMF solutions occurs via the triplet state and can be quenched by nickel salts. In DMSO different end products are formed but the same QA excited state seems to be involved.

QAQ was studied as colloidal dispersions in DMF and DMSO. QAQ decomposed only slowly in these solvents, but reacted readily with dienes and amines.

INTRODUCTION

It is generally believed that basic nickel carbonate and cobalt carbonate enhance the lightfastness of various quinacridones[1]. It was the intent of this study to examine the solution phase photochemistry of quinacridones, to determine what excited states were responsible for the observed photo-decomposition of QA in DMF and also to determine the effect of nickel and other metal salts on the decomposition of QA.

RESULTS AND DISCUSSION

The principal effort in this study was aimed at determining the nature of the excited state involved in the solution phase photo-degradation of QA. Since QA shows efficient solution phase fluorescence (see below), the effect of quenchers on the efficiency of photo-degradation could be compared to their effect on the QA luminescence, thereby leading to a direct determination of the possible involvement of the singlet state in QA photochemistry.

The energy of the lowest excited singlet state of QA in DMF solution is estimated to be close to 54 kCal/mole (estimated by assuming 0-0 band to lie at point of overlap of the absorption and fluorescence spectra). Because of this low singlet energy, the first excited triplet state is estimated to have an energy of close to 30 kcal/mole (based on the $\pi - \pi^*$ character of the lowest singlet state)[2]. Compounds which would be suitable diffusion controlled quenchers of the QA triplet state were difficult to find. Of the compounds which had a sufficiently low triplet energy to be able to quench QA at the diffusion controlled rate (ie. tetracene and pentacene), none were sufficiently soluble to have any effect on the rate of QA photo degradation (pentacene could only be dissolved to the extent of 10^{-6}M in DMF).

Anthracene was finally used on a triplet quencher, even though its 43 kCal/Mole triplet energy was higher than the estimated triplet energy of QA. Endothermic energy transfer is known to occur between systems in which the donor has a lower triplet energy than the acceptor. The rate of transfer is significantly reduced from 10^{10} for diffusion controlled transfer to as low as 10^5 - 10^6 for some endothermic processes.[3]

The photo degradation of QA in DMF was run in the presence of anthracene and the decomposition was inhibited. (Table I)

TABLE I

(Anthracene Concentration)	% Decomposition of QA*	ϕ°/ϕ
	73%	1.0
$3.3X10^{-3}M$	68%	1.07
$6.7X10^{-3}M$	50%	1.46
$1.0X10^{-2}M$	40%	1.82
$1.33X10^{-2}M$	34%	2.14

*QA concentration $6.3X10^{-5}M$.

From the Stern - Volmer plot[4] (Figure I) a value of 82 was obtained for $k_q \tau_{QA}$, where k_q is the rate constant for triplet quenching by anthracene and τ_{QA} is the lifetime of the QA triplet state in DMF.

Thus assuming only triplet reaction

$$\phi_r^\circ = \phi_{ST} \times \frac{kr}{kr + kd}$$

and $$\phi_r = \phi_{ST} \times \frac{kr}{kr+kd+kq(An)}$$

where ϕ_{ST} = quantum yield for formation of triplet QA

kr = rate constant for decomposition process

kd = rate constant for deactivation process

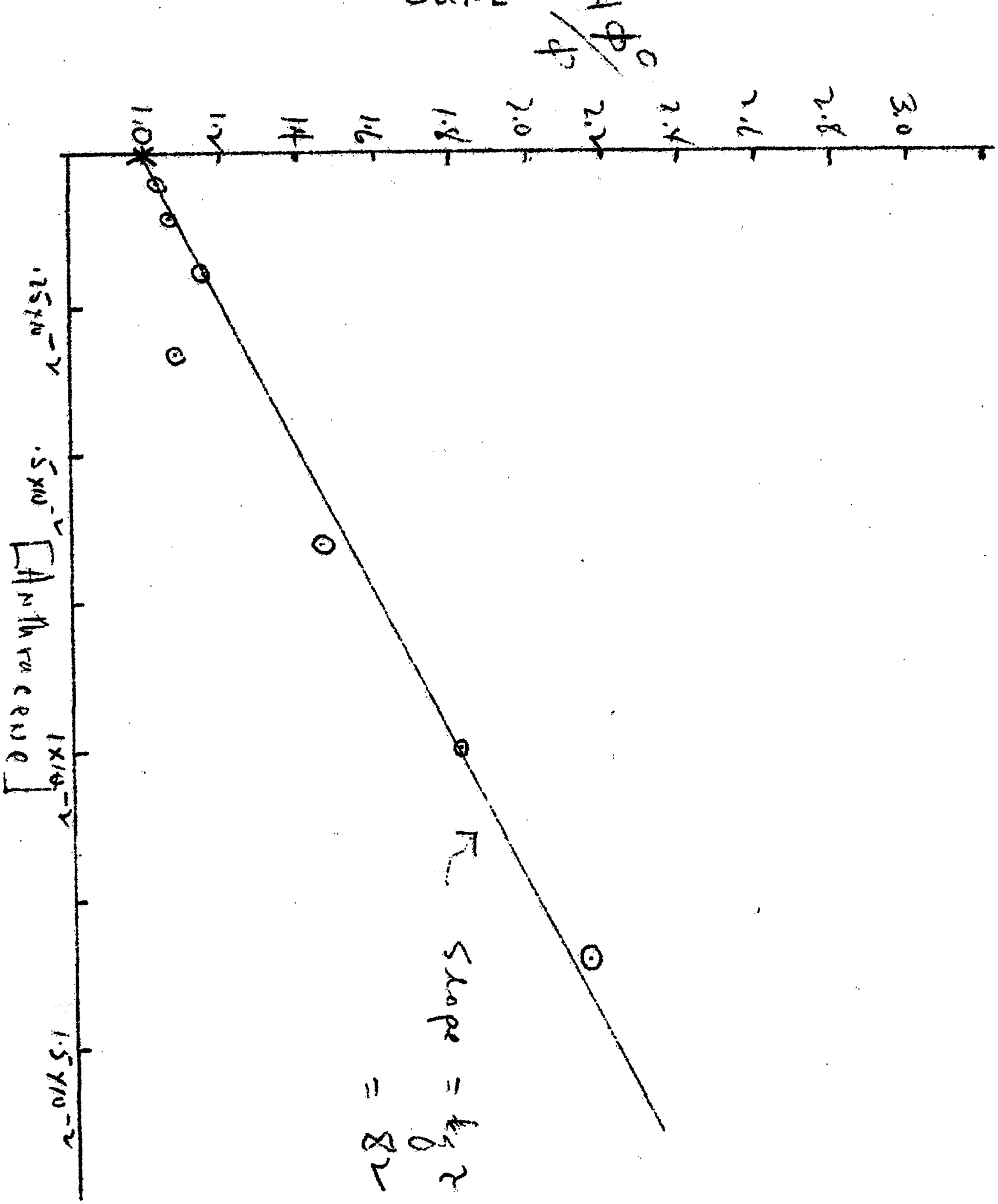
kq(An) = rate constant for quenching times Anthracene concentration.

thus $$\phi_r^\circ/\phi_r = \frac{kr+kd+kq(An)}{kr+kd} = 1 + \frac{kq(An)}{kr+kd}$$

$$\tau_{QA} = \frac{1}{kr+kd}$$

If kq were diffusion controlled ($\sim 10^{10}$) τ_{QA} could be calculated from the slope of the Stern - Volmer plot. However,

FIGURE I



Φ°/Φ
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
.25x10⁻²
.5x10⁻²
1x10⁻²
1.5x10⁻²
[Anthracene]
Slope = k_q τ
= 82

the probable endothermic nature of the quenching process does not allow us to put a value on kq, therefore τ_{QA} can not be calculated.

To prove that singlet reaction was not involved in the QA photo decomposition, the effect of anthracene on QA fluorescence was studied. 1.33 $X10^{-2}M$ anthracene had no effect on QA fluorescence in DMF indicating that the reactive QA state was not the singlet.

To further confirm the QA triplet state as the reactive state, triplet sensitization was attempted using biacetyl(2,3 butanedione) as sensitizer. Biacetyl has a triplet energy of 54 kcal/mole; high enough to sensitize QA triplet formation. Sensitization of QA by biacetyl and simultaneous quenching of biacetyl photochemistry was observed (Table II).

TABLE II*

(QA)	(Biacetyl)	Decomposition % QA	Decomposition % Biacetyl
$6.7X10^{-5}M$	-	14%	-
-	0.1M	-	89%
$6.7X10^{-5}M$	0.1M	67%	-

1 hour photolysis at 4200A°

TABLE IIa*

(Biacetyl)	(QA)	%Biacetyl Decomposition
.04M	-	41%
.04M	$2.7X10^{-5}M$	33%
.04M	$4 X 10^{-5}M$	25%

*10 min. photolysis at 4200A°

THE EFFECT OF NICKEL CHLORIDE ON QA PHOTOCHEMISTRY

In an attempt to determine the effect of nickel salts on QA photo degradation in paint films, model experiments in DMF solutions were run. Nickel chloride was found to quench QA photochemistry in DMF quite efficiently (Table III).

TABLE III

($NiCl_2$)	%Decomposition QA*	Avg ϕ°/ϕ	Avg kq τ
-	60% 62%	1.00	-
$1X10^{-3}M$	20% 19% 23%	2.95	1,950
$1.5X10^{-3}M$	22%	2.76	1,170
$2.0X10^{-3}M$	19% 20% 15%	3.41	1,200
$3X10^{-3}M$	13% 13%	4.90	1,300

*QA concentration - $4.8X10^{-5}M$ in DMF.

From Table III, the average value of kq τ for $NiCl_2$ quenching of QA photochemistry is found to be - 1,400, nearly 20 times higher than that found for anthracene.

Nickel chloride was also found to quench fluorescence, but at a much reduced efficiency. The value of kq τ for singlet quenching of QA by $NiCl_2$ was ~40. This again confirms the observation that the primary reactive state of QA is not the singlet and therefore probably is the triplet excited state.

On the basis of published studies on the triplet quenching ability of nickel salts[5], it seems likely that $NiCl_2$ quenches triplet and singlet state QA in solution by complexation and subsequent deactivation. This supposition can be tested by studying the effect of other transition elements and Lanthanide elements such as Mn, Co, Cu, Cr, and Pr. No such work has yet been undertaken.

THE FLUORESCENCE EFFICIENCY OF QA.

The fluorescence quantum yield of QA was determined by the method of Parker and Rees[6]. This method compares the fluorescence intensity of the unknown material (QA) with that of a standard (Rhodamine B). Using the literature value of 0.69 for Rhodamine B fluorescence quantum yield, we observed that the

fluorescence yield of QA was 0.86± .05. This indicates that the majority of QA molecules (86%) decay by singlet fluorescence and never undergo solution phase reaction. Only 15% of excited QA molecules at any one time are in the reactive state.

PHOTOCHEMISTRY OF QA IN DMSO

The photodegradation of QA in DMSO is different than that observed in DMF. Irradiation of a solution of QA in DMSO with $\lambda \sim$ 5300A° leads to the formation of a red, non-fluorescent product with an absorption spectrum as shown in Fig. II.

The formation (and thus also the photodegradation of QA) of the red product was quenched by added Ni Cl_2, indicating that this reaction was also going through the QA triplet state.

The decomposition of QA in DMSO was found to change when irradiated with the full mercury arc (λ>3000A°). No red product was formed. The loss of QA was followed by absorption spectroscopy, and showed normal loss with no broadening of the absorption band. The solution turned colorless.

QUINACRIDONEQUINONE PHOTOCHEMISTRY

Quinacridone Quinone (QAQ) was found to be inherently less soluble than QA. Not enough could be dissolved in DMF and DMSO to study its solution photochemistry. Colloidal dispersions of QAQ could, however, be obtained by adding very small particle size QAQ (dispersion milled) to DMF or DMSO . Although these resulting mixtures looked like true solutions a beam of light passed through the solution was scattered (Tyndall effect) and repeated passes through a sintered glass funnel removed all of the QAQ from the solvent.

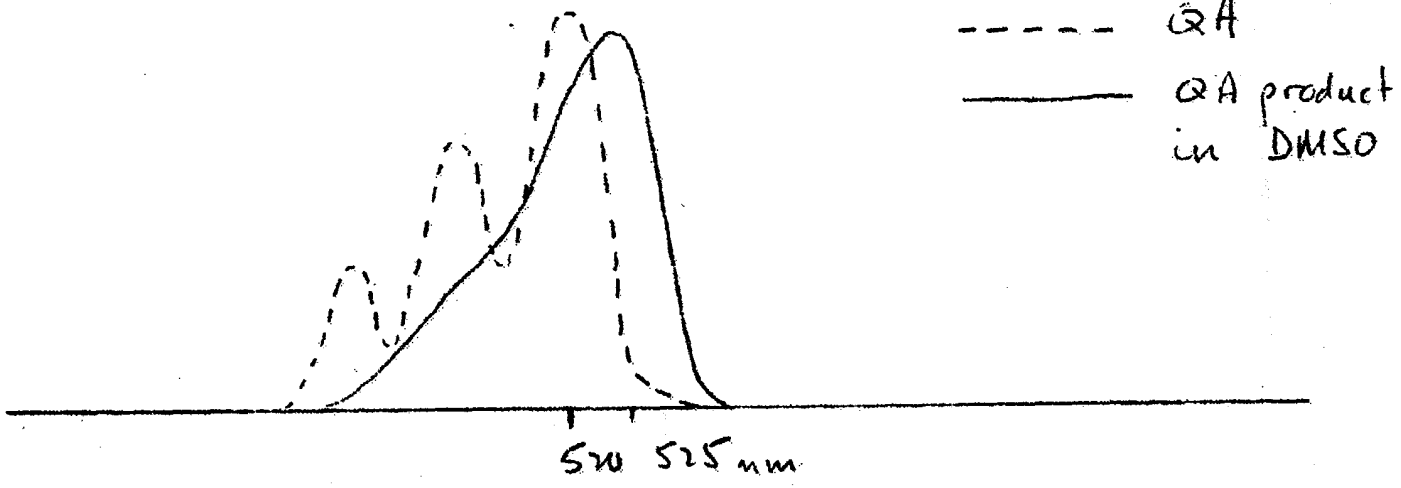
The colloidal dispersion of QAQ was irradiated (λ > 4000A°) in both DMF and DMSO. Photodegradation proceeded very slowly in DMF (6%/hr) and almost not at all in DMSO (0.5%/hr).

QAQ was irradiated in the presence of a number of hydrogen donors (ethanol, trifluoro ethanol and benzhydrol). No reaction was observed in DMSO solution.

QAQ was found to react with anthracene, 2,5 dimethyl 2,4 hexadiene and with N-methyl cyclohexylamine. The reaction with N-methyl cyclohexylamine formed a transient blue intermediate which was rapidly oxidized to an orange product (not QAQ). A similar reaction was observed with triethyl amine.

Figure II

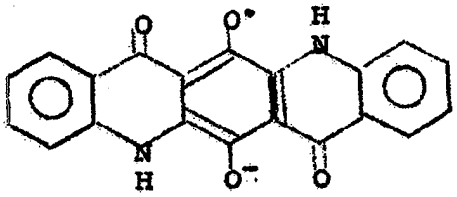
Absorption Spectra of QA + Red Photoproduct.



Photolysis of QAQ in DMSO with added triethyl amine led to the formation of a broad absorption band with λ_{max} ~590-600nm. This band disappeared after 24 hours in the dark. Little additional work was done on the QAQ system. The following observations can be made.

1. Reaction with good hydrogen donors is either non-existent or very slow.

2. QAQ readily abstracts an electron from amines to give a possible semi-quinone radical



Since these radicals have reasonable stability and lifetime formation of QAQ semi quinone radical may be the cause of the blue color. This radical may than react further with the amine cation radical, to form a reduced quinone. Alternately the reduced quinone may give rise to the blue color, which is lost by reoxidation (but not to QAQ).

Further work including ESR studies of photolyzed QAQ/amine solutions will undoubtedly help in determining the mechanism of QAQ degradation.

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