

SENSITIZATION AND QUENCHING OF NAPHTHOQUINONE PHOTOREDUCTION*

J. RENNERT and P. GINSBURG

Department of Chemistry, City College of Cuny, New York, N.Y. 10031 (U.S.A.)

(Received November 19, 1974)

Summary

The quantum efficiency of the photoreduction of 1,4-naphthoquinone was determined at the long wavelength tail of the n, π^* absorption band (436 nm). This confirmed that the efficiency is indeed within less than 1% identical for excitation in either the π, π^* or n, π^* absorption band and that internal conversion $\pi\pi^* - n\pi^*$ takes place with unit efficiency, the n, π^* excited molecule being the reactant in the primary photochemical reaction. Furthermore with photosensitization by acridine yellow and attenuation of the efficiency by anthracene, the former having a higher and the latter having a lower lying triplet state than the quinone, it was shown that the reactive $n\pi^*$ state was a triplet. The demonstration of complexation of the quinone in the ground state with either the sensitizer or the quencher suggests that, even if small, this interaction facilitates energy transfer to or from the photosensitive material.

Introduction

Rennert *et al.* [1] had concluded that since the quantum yields of 1,4-naphthoquinone photoreduction at 313 nm and 405 nm were almost the same and that since these wavelengths corresponded to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively, photoreduction took place in the n, π^* state reached *via* either direct transition, or by a 100% efficient internal conversion from the higher lying π, π^* state.

Sensitization of thymine dimerization by Lamola [2] and quenching of phenanthraquinone photoreduction by Carapelluci *et al.* [3] suggested that energy transfer experiments would shed light on the multiplicity of the n, π^* excited state in 1,4-naphthoquinone photoreduction.

*This paper describes a part of the research performed by P. Ginsburg in partial fulfillment of the requirements for the Ph.D. at the City University of N.Y.

Materials and equipment

1,4-Naphthoquinone (J. T. Baker, practical grade) was purified by extraction with petroleum ether in a Soxhlet extractor. After precipitation, it was collected by filtration and was then recrystallized three times from methanol. It was further purified by sublimation under high vacuum.

2-Propanol (J. T. Baker G.C.-spectroscopic) was used as supplied.

Anthracene (Aldrich, zone refined), and acridine yellow, *i.e.*, 2,7-dimethyl-3,6-diaminoacridine (Pfaltz and Bauer, greater than 99%) were used as a quencher and sensitizer respectively.

The apparatus used for irradiation has been previously described [4]. Solutions were stirred during irradiation with a built-in magnetic stirrer so that accumulation of absorbing photoproduct within the path of the beam was avoided.

The YSI-Kettering radiometer probe used as the detector was calibrated by ferrioxalate actinometry [5].

Experimental quantum yields of photoreduction

The conclusions of Rennert *et al.* [1] were confirmed upon irradiation of degassed (2×10^{-5} Torr) solutions of 1,4-naphthoquinone 2-propanol at 334 nm, corresponding to the $\pi \rightarrow \pi^*$ peak, and at 436 nm, the highest possible wavelength for $n \rightarrow \pi^*$ exposure, where it was assured that $\pi \rightarrow \pi^*$ transitions were negligible. At 334 nm for a 3.23×10^{-4} M solution the quantum yield was 0.93 and for a 3.04×10^{-5} M solution it was 0.89. At 436 nm for a 3.58×10^{-3} M solution it was 0.90. Within the experimental error the quantum yields were independent of wavelength and of concentration. It was confirmed that the n , π^* state is the photochemically reactive state.

Quenching of 1,4-naphthoquinone photoreduction by anthracene

Dienes, trienes and polycyclic aromatics are frequently used as triplet quenchers in photochemical reactions because they have high singlet energies ($> 10^2$ kcal/mol) and low triplet energies (in the order of 50 kcal/mol). It was found that *trans*-piperylene reacts with 1,4-naphthoquinone in the dark, presumably *via* a Diels-Alder reaction. Therefore, dienes and trienes were not found suitable for further tests as possible triplet quenchers. Polycyclic aromatics were thought to be more stable in the presence of 1,4-naphthoquinone. Lewis and Kasha [6] determined from its phosphorescence spectrum that the triplet energy of anthracene was 42 kcal. Anthracene was the lowest molecular weight polycyclic aromatic with a lower triplet energy and a higher singlet energy than 1,4-naphthoquinone.

For a degassed solution containing 2:1 anthracene/1,4-naphthoquinone in 2-propanol no quenching was observed. A higher ratio of anthracene to 1,4-naphthoquinone could not be used because of the

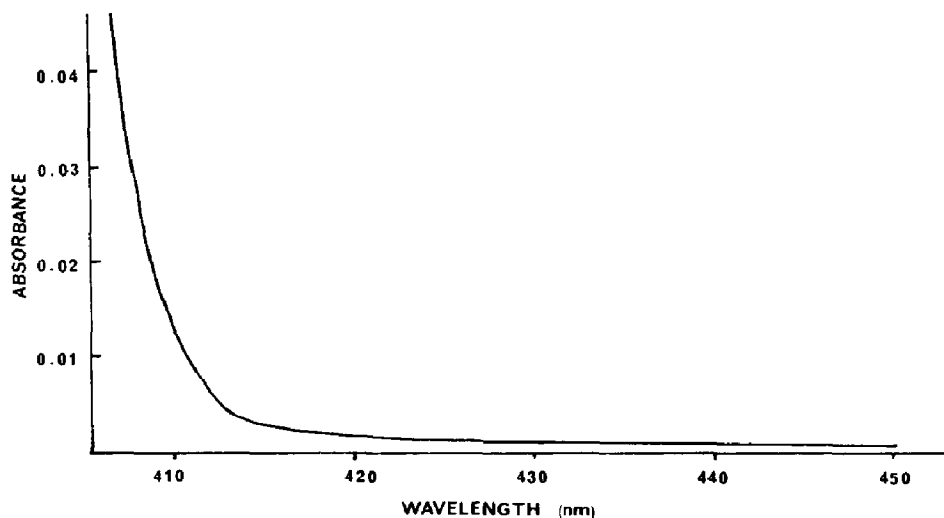


Fig. 1. Tail absorption in the visible spectrum of $2.28 \times 10^{-2} M$ anthracene in 4:1 benzene/isopropyl alcohol.

limited solubility of anthracene in 2-propanol. As anthracene was much more soluble in benzene than in 2-propanol, a mixed solvent system consisting of 4:1 benzene/2-propanol was chosen. A degassed solution $2.46 \times 10^{-3} M$ in 1,4-naphthoquinone and $2.28 \times 10^{-2} M$ in anthracene and a degassed solution containing the same concentration of 1,4-naphthoquinone only were irradiated by 436 nm where the absorbance of anthracene is negligible (Fig. 1). 1,4-Naphthalenediol, identified by its fluorescence spectrum, precipitated from each and settled to the bottom of the cell. Quantum yields were determined by measuring the absorbance decrease at 422.0 nm corresponding to disappearance of 1,4-naphthoquinone. In determining the number of Einsteins absorbed correction was made for complex formation (see below). The number of mol of 1,4-naphthoquinone reacted for the solution containing anthracene was 2.06×10^{-6} for 6.49×10^{-6} Einsteins absorbed. In the absence of anthracene 2.55×10^{-6} mol reacted for 6.94×10^{-6} Einsteins absorbed. The quantum efficiencies were 0.32 in the presence of anthracene and 0.37 in the absence of anthracene.

Complex formation of 1,4-naphthoquinone with anthracene and with acridine yellow

It was observed that a solution containing 1,4-naphthoquinone and anthracene in 4:1 benzene/2-propanol showed spectral differences from a solution containing 1,4-naphthoquinone only (Fig. 2), and that when nearly saturated solutions of 1,4-naphthoquinone and anthracene in a mixed solvent of 2:1 methylcyclohexane/toluene is frozen in liquid nitrogen, the resultant glass appears reddish rather than yellow. These observations suggested complex formation.

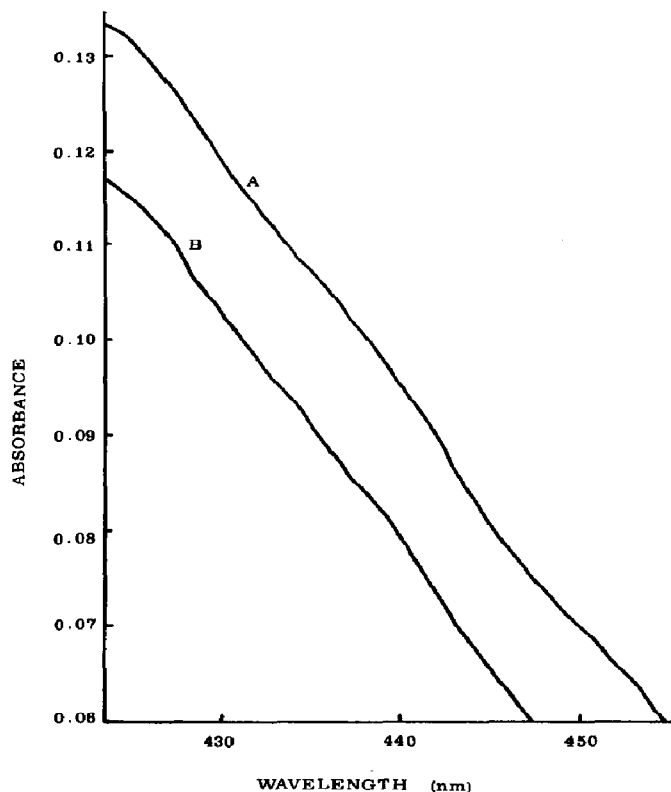


Fig. 2. Tail absorption in the visible spectrum of (B) 1,4-naphthoquinone alone and (A) in the presence of anthracene in 4:1 benzene/isopropyl alcohol.

The composition of the complex formed by 1,4-naphthoquinone and anthracene in 4:1 benzene/2-propanol was determined by Job's [7, 8] method (Fig. 3). Solutions of $2.28 \times 10^{-2} M$ 1,4-naphthoquinone and $2.28 \times 10^{-2} M$ anthracene were mixed. x ml of the 1,4-naphthoquinone solution were added to $(1 - x)$ ml of the anthracene solution. y shows the values of the difference between the measured absorbance, at 450.0 nm, and that calculated from the absorbance at the same wavelength of the pure 1,4-naphthoquinone solution assuming no reaction on mixing the two solutions. The peak at $x = 0.5$ indicated that 1:1 complex was formed.

An equation derived by Brittain *et al.* [9], when applied to the case of 1,4-naphthoquinone and anthracene in 4:1 benzene/2-propanol becomes:

$$\frac{Q_i l}{A_{\text{obs}} - A_{\text{obs}}^f} = \frac{1}{K_a(\epsilon_{QA} - \epsilon_Q)} \frac{1}{D_i} + \frac{1}{(\epsilon_{QA} - \epsilon_Q)}$$

where l is the path length, Q_i is the initial concentration of the quinone, A_{obs} is the absorbance observed, A_{obs}^f is the absorbance of the free quinone, and K_a is the equilibrium constant for complex formation. If the left hand side of the equation is plotted (Fig. 4) against $1/D_i$, the value of K_a may be calculated from the slope of the line and the intercept of the

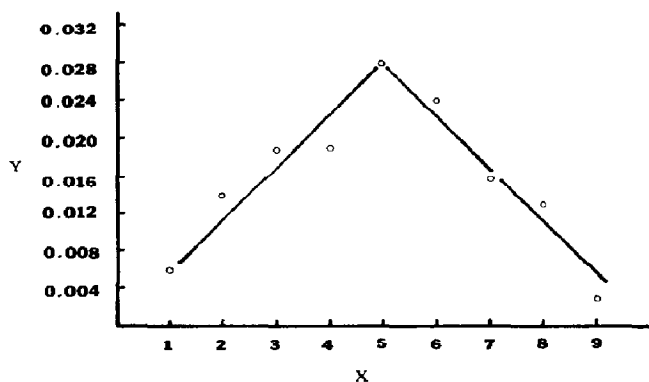


Fig. 3. Job's method plot for determination of the composition of the naphthoquinone-anthracene complex in 4:1 benzene/isopropyl alcohol.

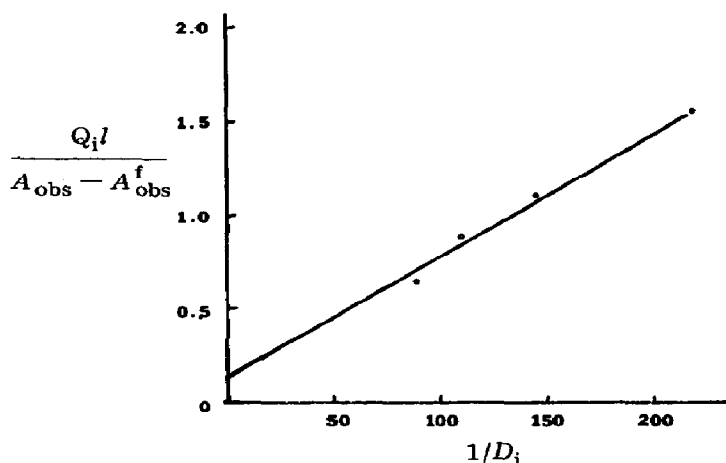


Fig. 4. Determination of the complex formation constant and absorptivity of the naphthoquinone-anthracene complex in 4:1 benzene/isopropyl alcohol.

line on the y axis. From the data in Table 1, K_a was found by the method of least squares, to be 12.8 as ϵ_Q was determined to be 0.91 at 490.0 nm, ϵ_{QA} was calculated to be 11.6. A spectrum of the complex is shown in Fig. 5.

Since $Abs = \epsilon_{QA} QA + \epsilon_Q Q_f$ where Abs is the absorbance at 490.0 nm, QA is the concentration of complex, and Q_f is the concentration of uncomplexed quinone and $QA = Q_i - Q_f$. Therefore:

$$Q_f = \frac{Abs - \epsilon_{QA} Q_i}{\epsilon_Q - \epsilon_{QA}}$$

This relation was used to determine the fraction of radiation absorbed by the uncomplexed quinone in the quenching experiment. As the initial concentration of 1,4-naphthoquinone present was known, and conversion of 1,4-naphthoquinone to 1,4-naphthalenediol was followed by absorbance decreases at 422.0 nm, it was possible to calculate the total quantity of

TABLE 1

Determination of K_a and ϵ_{QA} for the complex formed by 1,4-naphthoquinone and anthracene in 4:1 benzene/2-propanol.

Initial concentrations (M)		$A_{\text{abs}} - A_{\text{obs}}^f$	$Q_i/A_{\text{abs}} - A_{\text{obs}}^f$	$1/D_i$
A_i	Q_i			
0.00456	0.0684	0.0440	1.55	219
0.00684	0.0684	0.0650	1.05	146
0.00912	0.0684	0.0775	0.882	110
0.0114	0.0684	0.1070	0.639	87.7

By the method of least squares:

$$\text{slope} = \frac{1}{K_a(\epsilon_{QA} - \epsilon_Q)} = 0.00671; \text{intercept} = \frac{1}{(\epsilon_{QA} - \epsilon_Q)} = 0.0860.$$

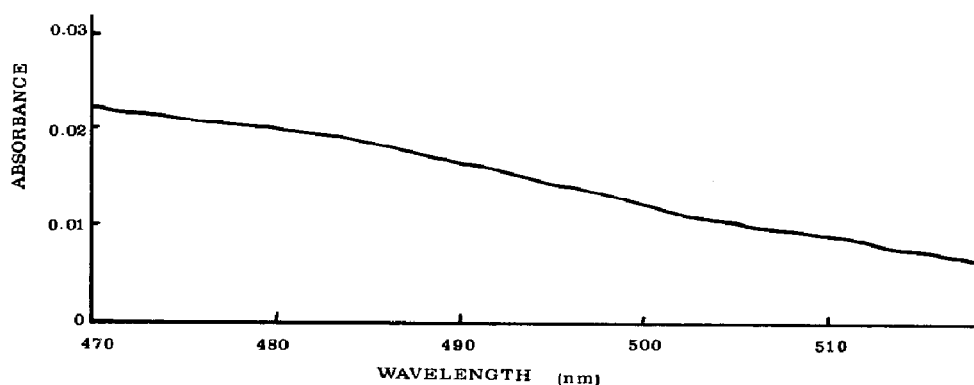


Fig. 5. Visible absorption spectrum of 6.84×10^{-2} formal naphthoquinone and 2.28×10^{-3} formal anthracene *vs.* an equal concentration of naphthoquinone in 4:1 benzene/isopropyl alcohol.

1,4-naphthoquinone present, after an irradiation. Measurement of the absorbance at 490.0 nm enabled a calculation, using the equation derived above, of the concentration of uncomplexed quinone. The absorptivity of 1,4-naphthoquinone in the irradiation apparatus was calculated from the initial fraction of radiation absorbed by the solution containing 1,4-naphthoquinone only. It was then possible to calculate the absorbance of the uncomplexed 1,4-naphthoquinone in the irradiated solution, and thus the quantity of radiation absorbed by the uncomplexed quinone could also be calculated.

Spectra were taken of 2-propanol solutions of 6.3×10^{-4} M acridine yellow and 9.6×10^{-4} M 1,4-naphthoquinone in a split cell, before and after mixing. The small differences (Table 2) suggest that in the acridine yellow and 1,4-naphthoquinone solutions discussed before, very little complex was formed, and that its absorbance at 436 nm was negligible. However, when an ethanol solution (both acridine yellow and 1,4-naphthoquinone are more soluble in ethanol than in 2-propanol) 10^{-2} M in both

TABLE 2

Absorbance changes of 2-propanol solutions of 1,4-naphthoquinone and acridine yellow upon mixing

Wavelength (nm)	Absorbance before mixing	Absorbance change upon mixing
490.0	0.097	+0.006
458.0	1.296	-0.004
436.0	0.882	0.000
331.0	1.215	+0.003

Concentrations: 9.6×10^{-4} M 1,4-naphthoquinone; 6.3×10^{-4} M acridine yellow

acridine yellow and 1,4-naphthoquinone is frozen in liquid nitrogen, the resultant glass appears reddish. In order to check if complex formation occurred in solution, in the case of more concentrated solutions than those described before, stock solutions of 3.53×10^{-2} M 1,4-naphthoquinone in ethanol and 3.32×10^{-2} M acridine yellow in ethanol (both nearly saturated) were prepared. Each solution was added to an equal volume of ethanol to give a solution of one-half the concentration. Equal volumes of the stock solutions were combined to give a third solution. Spectra of these three solutions were obtained, using 0.05 nm path length cells, and it was found that the spectrum of the solution containing both quinone and dye differed only slightly from the spectrum obtained by adding the spectra of the quinone and dye solutions (Table 3). It was concluded that very little complex formation occurred in this case as well.

Multiplicity of the excited state in photoreduction

The sensitizing and quenching experiments performed provide evidence that the first excited triplet state rather than the first excited singlet state is the photochemically reactive state. Irradiation of a mixture of 1,4-naphthoquinone and acridine yellow, which has a higher triplet energy than 1,4-naphthoquinone, but a lower singlet energy, resulted in sensitization of 1,4-naphthoquinone photoreduction, and also in formation of a product of 1,4-naphthoquinone and acridine yellow. This product was shown to be formed by excited acridine yellow and ground state 1,4-naphthoquinone rather than between excited 1,4-naphthoquinone and ground state acridine yellow. Millich and Oster [10] reported that acridine yellow, in a pH 4 aqueous solution, is photoreduced in the presence of allylthiourea. The quantum yield was not reported. However, the quantum yield for photoreduction of an aqueous solution of 2×10^{-5} M 3,6-diaminoacridine and 1×10^{-2} M allylthiourea concentration at pH 4 was reported to be 1.0×10^{-2} mol/Einstein. The reaction was said to be "less proficient" at higher pH, but quantitative information was not supplied. The relatively short periods of irradiation and the neutral pH in this

TABLE 3

Absorbances of ethanol solutions of 1,4-naphthoquinone, acridine yellow and a mixture of 1,4-naphthoquinone and acridine yellow

	Wavelength (nm)			
	490.0	458.0	436.0	331.0
1. 1.77×10^{-2} M 1,4-naphthoquinone	0.002	0.004	0.005	0.342
2. 1.66×10^{-2} M acridine yellow	0.094	1.488	1.035	0.015
3. 1.77×10^{-2} M 1,4-naphthoquinone and 1.66×10^{-2} M acridine yellow	0.099	1.474	1.022	0.359
Calculated absorbance of solution 3 (sum of absorbances for solutions 1 and 2)	0.096	1.492	1.040	0.357
Difference between observed and calculated absorbances for solution 3	+0.003	-0.018	-0.018	+0.002

research apparently resulted in relatively little photoreduction of acridine yellow.

Addition of anthracene, which has a lower triplet energy than 1,4-naphthoquinone but a higher singlet energy, to 1,4-naphthoquinone in a mixed solvent system of 4:1 benzene/2-propanol resulted in quenching of the photoreduction reaction.

Complex formation with acridine yellow and anthracene

The fact that 1,4-naphthoquinone forms complexes with both anthracene and acridine yellow, although such complex formation was not significant in the sensitizing experiment performed, suggests a possible mode of interaction for energy transfer to take place. Just as 1,4-naphthoquinone and 1,4-naphthalenediol form a complex *via* interaction of their π orbitals it may be that the complexes formed between anthracene and 1,4-naphthoquinone and between acridine yellow and 1,4-naphthoquinone, as well as the energy transfer observed, are due to similar interactions.

References

- 1 J. Rennert, S. Japar and M. Guttman, *Photochem. Photobiol.*, 6 (1967) 485.
- 2 A. A. Lamola, *Pure Appl. Chem.*, 24 (1970) 599.
- 3 P. A. Carapelluci, H. P. Wolf and K. Weiss, *J. Am. Chem. Soc.*, 91 (1969) 4635.
- 4 J. Rennert and P. Ginsburg, *Mol. Photochem.*, 4 (2) (1972) 235.
- 5 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. (A)*, 235 (1956) 518.
- 6 G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, 66 (1944) 2100.
- 7 P. Job, *Ann. Chim.*, 9 (10) (1928) 113.
- 8 W. C. Vosburgh and G. C. Cooper, *J. Am. Chem. Soc.*, 63 (1941) 437.
- 9 E. F. H. Brittain, W. O. George and C. H. J. Wells, *Introduction to Molecular Spectroscopy*, Academic Press, London, 1970, pp. 102 - 106.
- 10 F. Millich and G. Oster, *J. Am. Chem. Soc.*, 81 (1959) 1357.