

## LASER FLASH PHOTOLYTIC DETERMINATION OF TRIPLET YIELDS VIA SINGLET OXYGEN GENERATION

S. K. CHATTOPADHYAY, C. V. KUMAR and P. K. DAS

*Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556 (U.S.A.)*

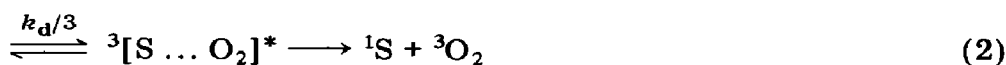
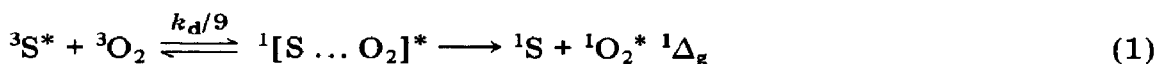
(Received June 28, 1983; in revised form September 3, 1983)

### Summary

The efficiency  $\phi_{\Delta}$  of the generation of singlet oxygen  $^1\text{O}_2^*$  via oxygen quenching of triplets of a number of substrates of photochemical and photo-biological interest was studied by 337.1 nm laser flash photolysis using 1,3-diphenylisobenzofuran as the monitor for  $^1\text{O}_2^*$ . For all-*trans* retinal and two polyenals related to retinal as lower and higher homologues the  $\phi_{\Delta}$  data agree well with the triplet yields reported in the literature, suggesting that mechanisms involving charge transfer or spin exchange (at twisted configurations) leading to non-production of  $^1\text{O}_2^*$  are unimportant in the oxygen quenching of the triplets of these polyenes. Similar conclusions are also drawn for pyrene-1-aldehyde and tris(bipyridine)ruthenium(II) triplets where observation of quantitative production of  $^1\text{O}_2^*$  suggests energy transfer to be the dominant pathway. In support of some previous reports, the singlet oxygen yield in benzophenone triplet quenching by oxygen in benzene is found to be much less than unity (0.4).

### 1. Introduction

The spin statistical aspects of triplet quenching by oxygen are as follows:



When energy transfer (eqn. (1)) is the sole mechanism for the quenching of a triplet  $^3\text{S}^*$  by oxygen, it would be expected that (i) the quenching rate constant  $k_q^T$  would approach a maximum value of one-ninth of the diffusion-controlled rate  $k_d$  and (ii) singlet oxygen  $^1\text{O}_2^*$   $^1\Delta_g$  would be produced quantitatively as a result of the quenching. In many instances, however,

alternative mechanisms have been recognized, namely charge transfer and spin exchange, both of which are embodied in eqn. (2). The involvement of these interactions is manifested in the observations that  $k_q^T$  is greater than  $k_d/9$  and approaches  $k_d/3$  (eqn. (2)) and that the efficiency of singlet oxygen generation is less than unity. Some examples of molecular systems where the three principal mechanisms have been implicated in triplet quenching by oxygen are aromatic hydrocarbons [1, 2] (energy transfer), indoles and aromatic carbonyl compounds [3, 4] (charge transfer), and stilbene [3, 5, 6] and  $\beta$ -carotene [7] (spin exchange). It should be noted that inefficient energy transfer in the cases with  $k_q^T \approx k_d/9$  has also been attributed [8] to the favorable competition of intersystem crossing in the singlet encounter complex  $^1[S \dots O_2]^*$  with its spin-allowed dissociative process (eqns. (1) and (2)). In contrast, observation of  $k_q^T > k_d/9$  in the cases where quantitative production of  $^1O_2^*$  is achieved has been explained in terms of re-encounter amplification of encounter quenching probability [9].

In this paper we present the results of a laser flash photolysis study of singlet oxygen generation during the oxygen quenching of a number of triplets of photochemical and photobiological interest. The systems under study include all-*trans* retinal and two all-*trans* polyenals related to retinal as lower and higher homologues (*i.e.* the  $C_{17}$  and  $C_{22}$  aldehydes). 1,3-diphenylisobenzofuran (DPBF) was employed as the monitor for singlet oxygen  $^1O_2^*$ . The results show that in the case of the polyenals the production of  $^1O_2^*$  via triplet quenching by oxygen in polar and non-polar solvents is quantitative and can be conveniently utilized for indirect estimation of the intersystem crossing quantum yields  $\phi_T$  of these systems.

## 2. Experimental details

Benzophenone (Aldrich), 2-acetonaphthone (Aldrich), pyrene-1-aldehyde (Pfaltz & Bauer), DPBF (Aldrich) and tris(bipyridine)ruthenium(II) chloride (G. Frederick Smith Chemical Co.) were recrystallized from aqueous ethanol or water. All-*trans* retinal (Sigma) was purified by column chromatography (silica gel; petroleum ether + 10% diethyl ether eluent) followed by recrystallization from *n*-hexane. The preparation and purification of the  $C_{17}$  and  $C_{22}$  aldehydes have been described in a previous publication [10]. The solvents (cyclohexane (Matheson, Coleman and Bell), benzene (Aldrich) and methanol (Aldrich)) were of spectroscopic grade.

The description of the laser flash photolysis apparatus is available elsewhere [11, 12]. All our experiments were carried out using laser pulses (337.1 nm; 8 ns; 2 - 3 mJ) from a Moletron UV-400 nitrogen laser system for excitation. Rectangular quartz cells with path lengths of 1 or 2 mm along and optically flat faces across the monitoring light were used for the actinometric experiments. Quartz cells of path length 3 mm were also used for some kinetic measurements of DPBF depletion. The direction of the laser beam was at an angle of about  $20^\circ$  to that of the monitoring light. Suitable

Corning and Balzer filters were placed in the path of the analyzing light (in front of the photolysis cell) in order to select a narrow spectral region at 390 - 430 nm for registering the consumption of DPBF by singlet oxygen.

### 3. Results

In the present study the triplet substrates were generated by direct absorption of laser light (337.1 nm) followed by intersystem crossing in oxygen-saturated solutions. The substrates were deliberately chosen with very short singlet lifetimes (subnanosecond) so that the singlet state quenching by oxygen was negligible under the conditions of the experiments and singlet oxygen produced in the system could be ascribed solely to triplet quenching. The important steps which need to be considered for kinetic analysis are as follows:



The sets of equations (4) and (5), (6) - (8), and (9) and (10) represent triplet formation, triplet decay (under quenching by oxygen) and singlet oxygen reaction kinetics respectively, and the related processes occur on subnanosecond, nanosecond and microsecond time scales respectively. The equation

$$\frac{-\Delta(\text{OD})_{\infty}^{\lambda_1}}{\Delta(\text{OD})_0^{\lambda_2}} = \frac{\epsilon_{\text{D}}^{\lambda_1}}{\epsilon_{\text{A}}^{\lambda_2}} \frac{\phi_{\text{T}}^{\text{S}}}{\phi_{\text{T}}^{\text{A}}} \frac{k_7[{}^3\text{O}_2]}{\tau_{\text{T}}^{-1} + (k_7 + k_8)[{}^3\text{O}_2]} \frac{k_{10}[\text{DPBF}]}{k_9 + k_{10}[\text{DPBF}]} \quad (11)$$

relates the negative change  $\Delta(\text{OD})_{\infty}^{\lambda_1}$  in optical density due to total DPBF depletion monitored at a wavelength  $\lambda_1$  in the region of its ground state absorption to the positive end-of-pulse change  $\Delta(\text{OD})_0^{\lambda_2}$  in optical density due to the benzophenone (or fluorenone) triplet in benzene monitored at its absorption maximum  $\lambda_2$ ; the latter serves as the actinometer and is observed in separate experiments under conditions of optical matching at the laser excitation wavelength (337.1 nm). In eqn. (11)  $\epsilon_{\text{D}}^{\lambda_1}$  and  $\epsilon_{\text{A}}^{\lambda_2}$  denote the molar extinction coefficients of the ground state absorption of DPBF at  $\lambda_1$  and the triplet-triplet absorption of the actinometer at  $\lambda_2$  respectively and

$\phi_T^S$  and  $\phi_T^A$  are triplet yields with the superscripts S and A designating the substrate and the actinometer respectively. We have determined the yield  $\phi_\Delta$  of singlet oxygen experimentally using the expression

$$\phi_\Delta = \phi_T^A \frac{-\Delta(\text{OD})_\infty^{\lambda_1}}{\Delta(\text{OD})_0^{\lambda_2}} \frac{\epsilon_A^{\lambda_2}}{\epsilon_{\text{DPBF}}^{\lambda_1}} \frac{k_q^T [{}^3\text{O}_2] + \tau_T^{-1}}{k_q^T [{}^3\text{O}_2]} \frac{k_{\text{obs}}^D}{k_{\text{obs}}^D - k_9} \quad (12)$$

$k_q^T$  in this equation is the overall bimolecular rate constant for substrate triplet quenching by oxygen and is equal to  $k_7 + k_8$ .  $k_{\text{obs}}^D$  is the observed pseudo-first-order rate constant for the reaction of  ${}^1\text{O}_2^*$  with DPBF (measured from the kinetics of depletion) and is equal to  $k_9 + k_{10}[\text{DPBF}]$  in the absence of any other competing reactions, namely with the substrates (see later). Comparison of eqns. (11) and (12) gives

$$\phi_\Delta = \frac{k_7}{k_7 + k_8} \phi_T^S \quad (13a)$$

$$\phi_\Delta = \gamma_\Delta \phi_T^S \quad (13b)$$

Except for the tris(bipyridine)ruthenium(II) complex, the triplet substrates under study were characterized by long lifetimes ( $\tau_T > 5 \mu\text{s}$ ) and in oxygen-saturated solutions ( $[{}^3\text{O}_2] \approx 10^{-2} \text{ M}$ )  $\tau_T^{-1}$  was much less than  $k_q^T [{}^3\text{O}_2]$ . The metal-to-ligand charge transfer triplet excited state of the ruthenium(II) complex has a lifetime of 790 ns in degassed methanol (measured from luminescence decay at 630 nm) and the rate constant for its quenching by oxygen in this solvent is  $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Thus in oxygen-saturated methanol the unimolecular decay of the triplet of the complex (*i.e.* reaction (6)) constituted only 7% of overall decay (*i.e.* combined reactions (6) - (8)).

Data concerning the decay of  ${}^1\text{O}_2^*$  (*i.e.*  $k_9$ ) and the rate constant  $k_{10}$  for its reaction with DPBF were obtained from the intercepts and the slopes of linear plots of the observed pseudo-first-order rate constants  $k_{\text{obs}}^D$  for the depletion of DPBF against DPBF concentrations (0.05 - 0.5 mM). For these experiments, 2-acetonaphthone was used as the sensitizer in air-saturated solutions. The data in the three solvents, which are summarized in Table 1, are in reasonable agreement with many of those reported in the literature [13]. It should be noted that the relative consumption of DPBF in a flash photolysis experiment was kept small (10% or less of the original [DPBF]) by attenuating the laser intensity so that the kinetics of depletion could be approximately described by first-order processes with observed rate constants given by  $k_9 + k_{10}[\text{DPBF}]$ . In other words, the small time-dependent decrease in [DPBF] during depletion was ignored.

Some potential complications in the measurement of  $\phi_\Delta$  based on the expression for it in eqn. (12) and on the photoprocesses represented by eqns. (4) - (10) should be considered. First, the triplet energies  $E_T$  of all the substrates under consideration are greater than or close to the triplet energy of DPBF (34 kcal mol<sup>-1</sup> [14]); hence the latter is expected to quench  ${}^3\text{S}^*$  in competition with oxygen, producing DPBF triplets which would be quenched

TABLE 1

Kinetic data concerning decay of singlet oxygen and its reaction with 1,3-diphenylisobenzofuran

<i>Solvent</i>	$k_9^a$ ( $\times 10^4 \text{ s}^{-1}$ )	$k_{10}^b$ ( $\times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ )
Cyclohexane	5.0	3.4
Methanol	10.0	8.1
Benzene	4.0	8.0

<sup>a</sup> Reciprocal of singlet oxygen lifetime (eqn. (9)); error,  $\pm 10\%$ .

<sup>b</sup> Rate constant for reaction of singlet oxygen with DPBF; error,  $\pm 15\%$ .

by oxygen to generate  $^1\text{O}_2^*$ . However, under the conditions of our experiments, DPBF concentrations (0.05 - 0.2 mM) were a factor of 50 - 200 smaller than the oxygen concentration (about 0.01 M); thus even if the rate constant for the quenching of  $^3\text{S}^*$  by DPBF is five times greater than that for the quenching by oxygen, competitive formation of DPBF triplets and the resultant contribution to  $^1\text{O}_2^*$  generation would be small and negligible. Second, there are possibilities that the substrates in the ground state would react with  $^1\text{O}_2^*$  in competition with DPBF; we have ignored these possibilities on the basis of the fact that the  $k_{\text{obs}}^D$  values measured at similar DPBF concentrations with 2-acetonaphthone, various substrates and DPBF itself as the sensitizers agreed with one another reasonably well. Specifically, in experiments with benzophenone as the substrate, the concentration of benzophenone used was relatively high (about 0.05 M). In view of the large value ( $1.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [15]) reported for the rate constant for the reaction of benzophenone with  $^1\text{O}_2^*$  in benzene, we measured the kinetics of DPBF depletion in air-saturated benzene containing benzophenone at varying concentrations (7.5 - 75 mM) and DPBF at a constant concentration (1.1 mM). The observed rate constants for depletion were found to be constant ( $(1.4 \pm 0.1) \times 10^5 \text{ s}^{-1}$ ) within experimental error and did not show any increasing trend with increasing benzophenone concentration in the given range. This result rules out a large rate constant for the interaction of  $^1\text{O}_2^*$  with benzophenone in the ground state and is compatible with the recently reported values of less than  $3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  in benzene [9] and  $4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  in Freon-113 [16]. Third, DPBF itself absorbed a non-negligible fraction (5% - 20%) of laser photons. Although the intrinsic triplet yield of DPBF is very small [14], singlet quenching [17] by oxygen results in the formation of  $^1\text{O}_2^*$  as well as DPBF triplet (via enhanced intersystem crossing), and the latter, in turn, acts as a source of  $^1\text{O}_2^*$ . In order to correct for this, blank laser flash experiments were carried out with DPBF alone at the same concentrations as those used for experiments in the presence of the substrates; the observed change in optical density due to DPBF depletion, appropriately corrected for the difference in ground state absorptions of DPBF (at 337.1 nm) when used alone and when used in the presence of substrates, was

subtracted from  $\Delta(\text{OD})_{\infty}^{\lambda_1}$  before its use in eqn. (12) for the calculation of  $\phi_{\Delta}$ . Fourth, with  $\text{C}_{22}$  aldehyde ( $E_T \approx 28.9 - 35.4 \text{ kcal mol}^{-1}$  [18]) there was the possibility that it would efficiently quench DPBF triplet produced via direct partial absorption of laser photons under oxygen-enhanced conditions; again this was considered to be unimportant in view of the high concentration (about 0.01 M) of oxygen in comparison with the low  $\text{C}_{22}$  aldehyde concentrations used (0.1 - 0.2 mM).

A representative kinetic trace for the depletion of DPBF due to the reaction with  $^1\text{O}_2^*$  and its fit into first-order kinetics are shown in Fig. 1. Data concerning  $\phi_{\Delta}$  based on two to four independent determinations for each substrate are presented in Table 2. The following triplet-related parameters of the actinometers were used in the computation: benzophenone in benzene,  $\phi_T^A = 1$  and  $\epsilon_A^{\lambda_2} = 7.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 532 nm [19, 23, 25]; fluorenone in benzene,  $\phi_T^A = 0.93$  and  $\epsilon_A^{\lambda_2} = 6.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 440 nm [23, 26].

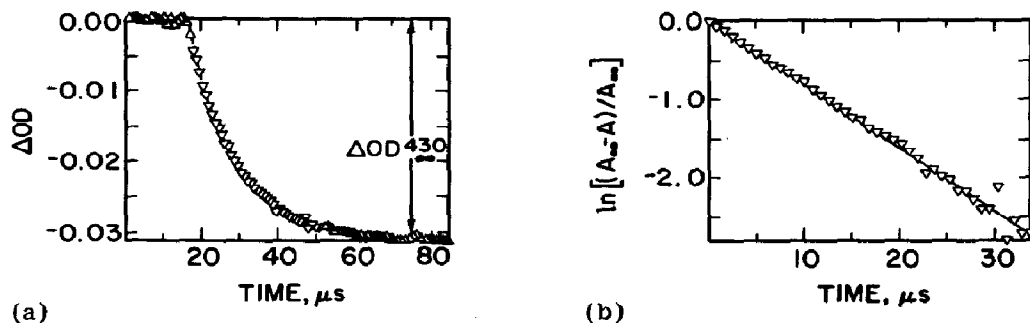


Fig. 1. (a) A representative kinetic trace for the depletion of DPBF by reaction with singlet oxygen observed in an oxygen-saturated benzene solution of 0.025 M benzophenone and 0.05 mM DPBF contained in a photolysis cell of path length 3 mm; (b) fit of the data in (a) to first-order kinetics for depletion.

#### 4. Discussion

Among the substrates listed in Table 2, the polyenals are of special interest as far as singlet oxygen generation via triplet quenching is concerned. This is because, by analogy with olefins [27, 28], we would expect twisted geometries to be involved in the triplet decay processes and the triplets with twisted configuration would be quenched by oxygen by a spin exchange mechanism resulting in inefficient energy transfer. A recent study by Smith [29] has shown that the yield of singlet oxygen from the interaction of the all-*trans* retinol triplet with oxygen is 0.25; arguments based on an analysis of the relative rates of triplet-sensitized isomerization in the presence and absence of oxygen have led to the conclusions that spin exchange with a triplet in a twisted configuration is relatively unimportant in the case of all-*trans* retinol and that the charge transfer interaction (eqn. (2)) at the transoid

TABLE 2

Rate constants for triplet quenching by oxygen and efficiency of singlet oxygen generation

Triplet substrate	Solvent	$k_q^T$ ( $\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ )	$\phi_\Delta^a$	$\phi_T^S^b$
Benzophenone	Benzene	2.3	0.39	1.0 [19]
Pyrene-1-aldehyde	Cyclohexane	1.8	0.87	0.78 [20]
	Benzene	1.9	0.68	0.57 [20]
Tris(bipyridine)ruthenium(II) complex	Methanol	1.6	0.83	0.95 <sup>c</sup> [21]
C <sub>17</sub> aldehyde	Cyclohexane	3.3	0.72	0.66 [22]
	Methanol	4.0	0.42	0.41 [22]
All- <i>trans</i> retinal	Cyclohexane	3.7	0.66	0.4 - 0.7 [23]
	Methanol	4.6	0.20	0.12 [24]
C <sub>22</sub> aldehyde	Cyclohexane	4.7	0.48	0.54 [22]
				0.41 [18]

<sup>a</sup> Error,  $\pm 20\%$ .

<sup>b</sup> Taken from the references given. The  $\phi_T^S$  data for all-*trans* retinal are in hydrocarbon solvents, namely *n*-hexane, methylcyclohexane etc.

<sup>c</sup> In water.

triplet configuration is the dominant pathway for triplet quenching by oxygen. Our results (Table 2) with polyenals and pyrene-1-aldehyde demonstrate that  $\phi_\Delta$  data are in general slightly higher than the corresponding triplet yield  $\phi_T^S$  data taken from the literature. The discrepancies are within the experimental uncertainties of the measurements of the two parameters, however. The significance of our observation concerning  $\phi_\Delta \approx \phi_T^S$ , *i.e.*  $\gamma_\Delta^S \approx 1$ , for the polyenal triplets in both polar and non-polar solvents is that neither charge transfer nor spin exchange (at perpendicular geometries) are important as isolated channels for the oxygen quenching of the triplets of these systems. Also, we suggest that monitoring singlet oxygen production can be conveniently utilized for estimation of triplet yields of polyenals in various solvents using both steady state irradiation and laser flash photolysis techniques.

The facile donor-acceptor behavior of the metal-to-ligand charge transfer triplet excited state of the tris(bipyridine)ruthenium(II) complex is well known [12, 30]. Despite the possibility of electron transfer from this triplet,  $k_q^T$  in methanol is less than  $k_a/9$ . Also, the fact that  $\phi_\Delta$  is found to be close to the estimated intersystem crossing yield of unity [21, 31] suggests that energy transfer (eqn. (1)) is the dominant mechanism for this complex.

Quantitative aspects of the efficiency of singlet oxygen production via benzophenone triplet quenching have been a subject of controversy in recent times. An earlier laser flash photolytic observation of  $\gamma_\Delta^S = 0.56$  in benzene by Garner and Wilkinson [3], who used  $\beta$ -carotene as a probe of  $^1\text{O}_2^*$ , has been corroborated by Gorman *et al.* [8], who measured  $\gamma_\Delta^S$  to be 0.4 in

benzene using the technique of pulse radiolysis with DPBF as the  $^1\text{O}_2^*$  monitor, and by Gorman *et al.* [15], who estimated the efficiency to be 0.45 in benzene based on the steady state photolytic consumption of 2,5-di-*tert*-butylfuran. A more recent study by Stevens *et al.* [9] based on steady state measurement of quantum yields of photoperoxidation claimed that the quenching of benzophenone triplet gives  $^1\text{O}_2^*$  with 100% efficiency. Our observation of a  $\phi_\Delta$  of  $0.39 \pm 0.08$  for benzophenone strongly supports the result reported by Gorman and coworkers [8, 15]. A large systematic error in our measurements leading to underestimation of  $\phi_\Delta$  appears unlikely, particularly when it is considered that pyrene-1-aldehyde and polyenals gave  $\phi_\Delta$  values commensurate with  $\gamma_\Delta^S$  values of unity. The reason for the small  $\gamma_\Delta^S$  for benzophenone (involvement of charge transfer [4] or intersystem crossing in the collision complex [8]) is still not fully understood.

### Acknowledgment

The work described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document NDRL-2487 from the Notre Dame Radiation Laboratory.

### References

- 1 O. L. J. Gijzeman, F. Kaufman and G. Porter, *J. Chem. Soc., Faraday Trans. II*, 69 (1973) 708.
- 2 A. P. Darmanyan, *Chem. Phys. Lett.*, 96 (1983) 383.
- 3 A. Garner and F. Wilkinson, in B. Ranby and J. F. Rabek (eds.), *Singlet Oxygen*, Wiley, New York, 1978, pp. 48 - 53.
- 4 A. Garner and F. Wilkinson, *Chem. Phys. Lett.*, 45 (1977) 432.
- 5 J. Saltiel and B. Thomas, *Chem. Phys. Lett.*, 37 (1976) 147.
- 6 J. Saltiel and B. Thomas, *J. Am. Chem. Soc.*, 96 (1974) 5660.
- 7 D. R. Kearns, *Chem. Rev.*, 71 (1971) 395.
- 8 A. A. Gorman, G. Lovering and M. A. J. Rodgers, *J. Am. Chem. Soc.*, 100 (1978) 4527.
- 9 B. Stevens, K. L. Marsh and J. A. Barltrop, *J. Phys. Chem.*, 85 (1981) 3079.
- 10 P. K. Das and R. S. Becker, *J. Phys. Chem.*, 82 (1978) 2081.
- 11 P. K. Das, M. V. Encinas, R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, 101 (1979) 6965.
- 12 K. Miedlar and P. K. Das, *J. Am. Chem. Soc.*, 104 (1982) 7462.
- 13 F. Wilkinson and J. G. Brummer, *J. Phys. Chem. Ref. Data*, 10 (1981) 809.
- 14 W. G. Herkstroeter and P. B. Merkel, *J. Photochem.*, 16 (1981) 331.
- 15 A. A. Gorman, I. R. Gould and I. Hamblett, *Tetrahedron Lett.*, 21 (1980) 1087.
- 16 B. Stevens and K. L. Marsh, *J. Phys. Chem.*, 86 (1982) 4473.
- 17 B. Stevens and R. D. Small, Jr., *Chem. Phys. Lett.*, 61 (1979) 233.
- 18 R. S. Becker, R. V. Bensasson, J. Lafferty, T. G. Truscott and E. J. Land, *J. Chem. Soc., Faraday Trans. II*, 74 (1978) 2246.
- 19 A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43 (1965) 2129.
- 20 C. V. Kumar, S. K. Chattopadhyay and P. K. Das, *Photochem. Photobiol.*, 38 (1983) 142.



- 21 R. V. Bensasson, C. Salet and V. Balzani, *C.R. Acad. Sci., Sér. B*, 289 (1979) 41.
- 22 P. K. Das and R. S. Becker, *J. Am. Chem. Soc.*, 101 (1979) 6348.
- 23 R. Bensasson and E. J. Land, *Photochem. Photobiol. Rev.*, 3 (1978) 163.
- 24 R. Bensasson and E. J. Land, *Nouv. J. Chim.*, 2 (1978) 503.
- 25 R. Bensasson and E. J. Land, *Trans. Faraday Soc.*, 67 (1971) 1904.
- 26 L. J. Andrews, A. Deroulede and H. Linschitz, *J. Phys. Chem.*, 82 (1978) 2304.
- 27 H. Görner and D. Schulte-Frohlinde, *J. Phys. Chem.*, 85 (1981) 1835.
- 28 J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton and O. C. Zafiriou, *Org. Photochem.*, 3 (1973) 1.
- 29 G. J. Smith, *J. Chem. Soc., Faraday Trans. II*, 79 (1983) 1.
- 30 C. R. Bock, J. A. Connor, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan and J. K. Nagle, *J. Am. Chem. Soc.*, 101 (1979) 4815.
- 31 F. Bolleta, M. Maestri and V. Balzani, *J. Phys. Chem.*, 80 (1976) 2499.