

Efficiency of singlet oxygen generation from the triplet states of nitrophenyl ethers

Miquel Mir^a, Lisinka M.G. Jansen^a, Francis Wilkinson^{a,1}, Jose L. Bourdelande^b,
Jordi Marquet^{b,*}

^a Department of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

^b Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

Received 7 February 1997; received in revised form 10 November 1997; accepted 11 November 1997

Abstract

The bimolecular rate constants for oxygen quenching, $k_{O_2}^T$, and the quantum yields of singlet oxygen production, ϕ_{Δ} , for 4-nitroveratrole, 4-nitroanisole and 3-nitroanisole triplet states in air-equilibrated deuterated water and acetonitrile solutions were determined where possible from nanosecond laser flash photolysis and time-resolved $O_2(^1\Delta_g)$ phosphorescence measurements. The results show that the efficiency of singlet oxygen production, f_{Δ}^T , for 4-nitroveratrole and 3-nitroanisole is moderately high and is related with the nature of the low-lying triplet state and that 4-nitroanisole is not able to sensitize singlet oxygen under these conditions. © 1998 Elsevier Science S.A.

Keywords: Nitrophenyl ether; Oxygen quenching; Acetonitrile solution

1. Introduction

Nitroaromatic compounds are cytotoxic, it has been proposed that their cytotoxicity is due to the generation of reactive oxygen species such as superoxide radical anion, singlet oxygen and hydrogen peroxide [1]. Despite this, very few data concerning nitrobenzene derivatives can be found in a recent extensive compilation of the quantum yields for the photosensitized formation of singlet oxygen in fluid solution [2]. The photophysics and photochemistry of nitroaromatic compounds is scarcely studied because, generally, they exhibit neither fluorescence nor phosphorescence and their triplet lifetimes are relatively short [3–6]. In this context, it is desirable to have more information about the effect of molecular oxygen on the photophysical behaviour of these compounds. We chose nitrophenyl ethers as model compounds because their photophysics [7,8] and photochemistry [9–18] is relatively well-known. Nitrophenyl ethers have close lying n, π^* and π, π^* triplet states [7,19] and therefore it is possible to study the effect of the nature of the low-lying triplet state of nitroaromatic compounds on the formation efficiency of singlet oxygen.

2. Experimental details

The nitrophenyl ethers studied (4-nitroveratrole, 4NV; 4-nitroanisole, 4NA; and, 3-nitroanisole, 3NA), perinaphthenone and benzophenone were used as received from Aldrich. The structures of the nitrophenyl ethers used are depicted in Fig. 1. Acetonitrile (Aldrich spectrophotometric grade) and D_2O (Aldrich) were used as received. Distilled water was used for preparing aqueous solutions.

Kinetic absorption measurements were carried out using a LKS50 instrument from Applied Photophysics with a Q-switched Nd:YAG laser (Spectron Laser System, UK) at 355 nm with a pulse width of 9 ns and an energy pulse of 10 mJ.

For singlet oxygen luminescence measurements, the third harmonic (355 nm) of a Lumonics HY200 Q-switched Nd:YAG laser (8 ns, 15 mJ pulse⁻¹) was employed as the excitation source. Time-resolved singlet oxygen luminescence at 1270 nm was detected using a Judson germanium photodiode (J16-85P-RO5M)-amplifier (PA100) combination as described previously [20]. The phosphorescence was detected at right angle to the exciting beam through a silicon cutoff filter.

Solutions were prepared in 1-cm² fluorescence quartz cells with absorbances at 355 nm of between 0.3 and 0.5. Deoxygenated solutions were obtained by bubbling nitrogen through the solutions for 30 min.

* Corresponding author. E-mail: iqr3@cc.uab.es

¹ Also corresponding author.

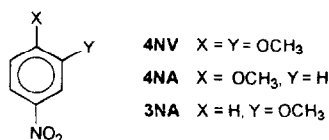


Fig. 1. Structures and abbreviations for the compounds studied in this work.

3. Results

Time-resolved triplet–triplet transient absorption spectra were obtained for 4NV, 4NA and 3NA in water and for 4NV and 3NA in acetonitrile by nanosecond laser flash photolysis at 355 nm (see Figs. 2–4). Wavelengths below 400 nm were not recorded due to overlap with the ground state absorption in this region. Transient decays were independent of the monitoring wavelength and could be fitted, in all cases, by a single exponential function decay indicating that they arise from single transient species (see Table 1) The lifetime of the transients was affected noticeably by the presence of oxygen except in the case of 4NA in acetonitrile where the transient decay rate constant was $1.5 \times 10^7 \text{ s}^{-1}$ irrespective of whether the solution was air-equilibrated or deoxygenated. Assignment of the transients to the corresponding triplet states was made on the basis of the comparison with literature data for

4NV in water [11] and in acetonitrile [11,22], and for 3NA in water [7,17]. The similarity of the transient spectra for 4NA and 4NV and 3NA in water suggests that the transient observed for 4NA in water is also due to absorption by its triplet state. The triplet state of 4NA in acetonitrile could not be observed with our nanosecond equipment presumably because it has a short lifetime (nitroaromatic triplets with a low-lying state of n, π^* character have been reported to have lifetimes in the picosecond time domain, Ref. [23]).

It is worth noting the differences in the triplet spectra for 4NV and 3NA in going from water to acetonitrile. These differences had already been reported for 4NV [24] and were attributed to the presence or absence of hydrogen bonds between the solvent and the π, π^* triplet state molecules of 4NV. It has been reported that only nitroaromatic triplets with π, π^* character form hydrogen bonds, whereas n, π^* triplet states do not [7,8,25,26]. The same behaviour is observed for 3NA as depicted in Fig. 3.

The quenching rate constant of the triplet states by molecular oxygen, $k_{O_2}^T$, were evaluated for 4NV and 3NA in air-equilibrated water and acetonitrile from Eq. (1):

$$k_{O_2}^T = (k - k_{TD}) / [O_2] \quad (1)$$

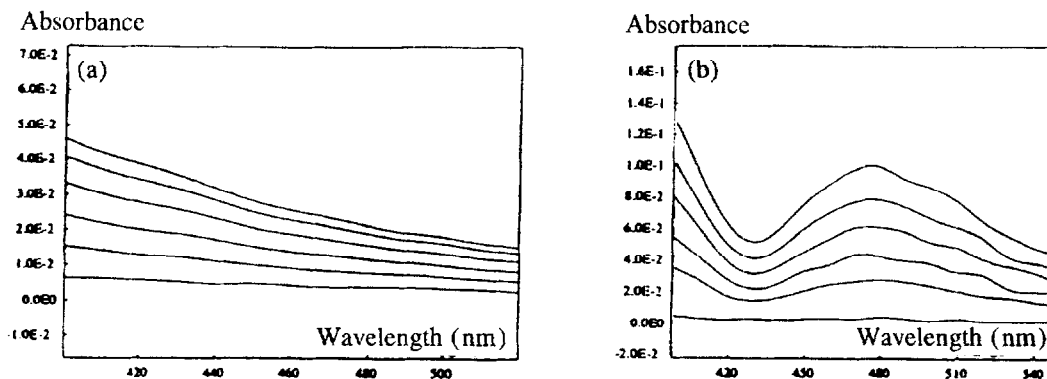


Fig. 2. (a) Transient absorption spectra of an air-equilibrated solution of 4NV in water. From top to bottom: 3.2×10^{-7} , 8.8×10^{-7} , 1.8×10^{-6} and 3.2×10^{-6} s after the laser flash. (b) Transient absorption spectra of an air-equilibrated solution of 4NV in acetonitrile. From top to bottom: 3.2×10^{-8} , 1.2×10^{-7} , 2.0×10^{-7} , 3.2×10^{-7} , 4.8×10^{-7} , and 1.4×10^{-6} s after the laser flash.

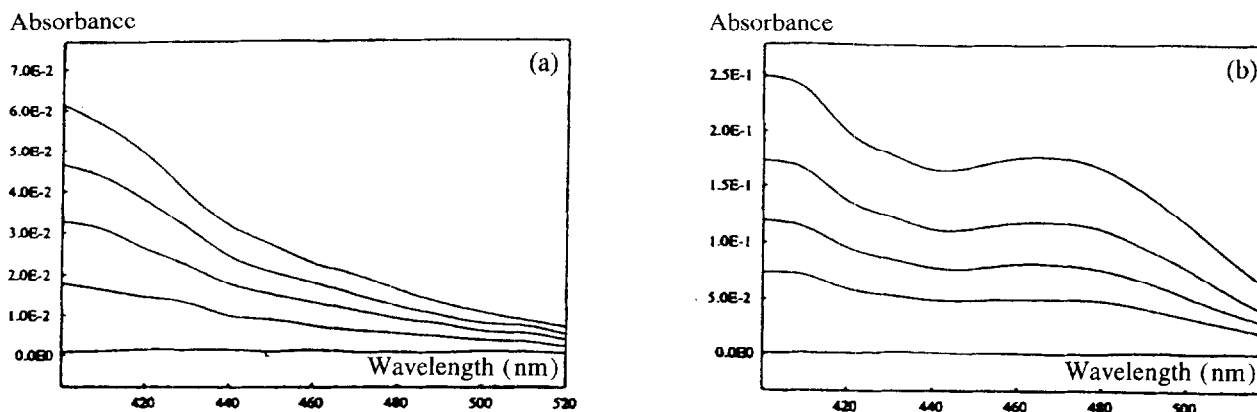


Fig. 3. (a) Transient absorption spectra of an air-equilibrated solution of 3NA in water. From top to bottom: 1.0×10^{-7} , 4.0×10^{-7} , 8.0×10^{-7} , 1.5×10^{-6} , and 5.0×10^{-6} s after the laser flash. (b) Transient absorption spectra of an air-equilibrated solution of 3NA in acetonitrile. From top to bottom: 2.3×10^{-8} , 3.3×10^{-8} , 4.3×10^{-8} , 5.5×10^{-8} and 2.5×10^{-7} s after the laser flash.

Table 1
Photophysical Properties of 4NV and 3NA in acetonitrile and water

| | k (s ⁻¹) ^a | k_{TD} (s ⁻¹) ^b | $k_{O_2}^T$ (dm ³ mol ⁻¹ s ⁻¹) | $P_{O_2}^0$ | ϕ_{Δ} | $\phi_1 \times f_{\Delta}^T$ |
|-------------------------|-------------------------------------|--|--|-------------|-----------------|------------------------------|
| 4NV in ACN | 3.0×10^6 | 4.5×10^5 | 1.3×10^9 | 0.85 | 0.44 | 0.52 |
| 3NA in ACN | 3.8×10^7 | 3.0×10^7 | 4.2×10^9 | 0.21 | 0.07 | 0.3 |
| 4NV in D ₂ O | 4.5×10^5 | 1.2×10^5 | 1.3×10^9 | 0.73 | 0.27 | 0.37 |
| 3NA in D ₂ O | 6.0×10^5 | 2.3×10^5 | 1.4×10^9 | 0.62 | 0.35 | 0.56 |

^a $[O_2]$ is 1.9×10^{-3} M and 0.27×10^{-3} M in air-equilibrated acetonitrile and water solutions, respectively [21].

^b Deoxygenated solution by bubbling nitrogen during 30 min.

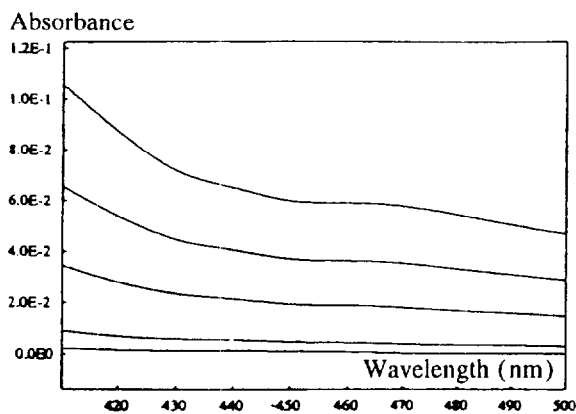


Fig. 4. Transient absorption spectra of an air-equilibrated solution of 4NA in water. From top to bottom: 2.4×10^{-8} , 5.6×10^{-8} , 1.0×10^{-7} , 2.0×10^{-7} and 1.0×10^{-6} s after the laser flash.

where k_{TD} and k are the rate constants for the triplet decay in the absence and presence of molecular oxygen at concentration $[O_2]$. Decay rate constants were measured at the maximum of the $T-T$ absorption spectra in each case. The oxygen concentrations in air-equilibrated solvents (20°C) were taken to be 0.27×10^{-3} mol dm⁻³ and 1.9×10^{-3} mol dm⁻³ in water and acetonitrile [21], respectively. The values obtained for k , k_{TD} and $k_{O_2}^T$ are collected in Table 1.

The quantum yields of singlet oxygen production for 4NV, 4NA and 3NA in water and in acetonitrile were determined where possible by relative measurements of the time-resolved singlet oxygen luminescence (0,0 vibronic band of the ¹O₂ phosphorescence centred at 1270 nm). The time-resolved phosphorescence signal at 1270 nm was recorded following 355 nm laser excitation of each solution at variable laser intensities. The solutions were matched at 355 nm (± 0.002 absorbance units) for each nitrophenyl ether and for a standard reference compound in each solvent used. Luminescence decays obtained by signal averaging 6 traces were fitted using a single exponential function in order to obtain the initial luminescence intensity (L_{Δ}) at time $t=0$ (e.g., see Fig. 5). The fast decay of the detector signal after the laser pulse excitation which was observed for all compounds examined is due to the laser scattered light shortly after the laser pulse and was not considered in the analysis decay. Plots of $L_{\Delta}(t=0)$ vs. laser intensity were linear within the incident laser intensity range used. ϕ_{Δ} values were calculated from Eq. (2):

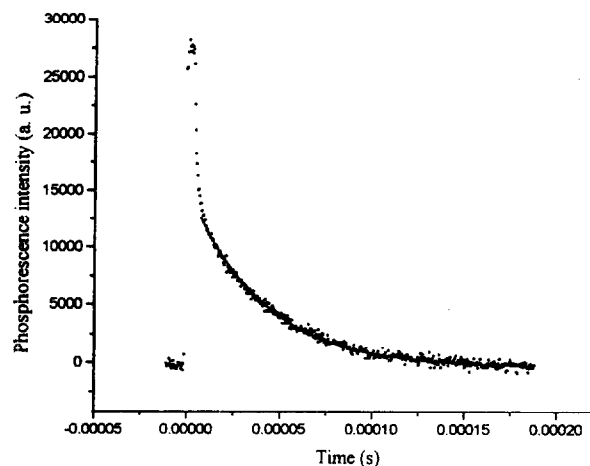


Fig. 5. ¹O₂ phosphorescence decay at 1270 nm for an air-equilibrated solution of 4NV in acetonitrile with monoexponential fit and plot of residuals. The fast decay shortly after the laser pulse was not considered in the analysis decay (see text).

$$\frac{\phi_{\Delta}(S)}{\phi_{\Delta}(S_{st})} = \frac{L_{\Delta}(S)_{t=0}}{L_{\Delta}(S_{st})_{t=0}} \quad (2)$$

where S is the sensitizer under study and S_{st} is a suitable standard sensitizer which ϕ_{Δ} is known.

Benzophenone was used as a standard in acetonitrile taking its reported [27] value for ϕ_{Δ} as 0.38. D₂O was used as a solvent instead of H₂O, because the lifetime of singlet oxygen in H₂O (3.1–5.0 μ s) [28] is too short to measure accurately the ¹O₂* decay using our equipment, whereas that in D₂O (55–68.5 μ s) [28] is much longer. Due to its low solubility in water we could not use benzophenone as a standard in this solvent, instead we made measurements relative to perinaphthenone. Although ϕ_{Δ} for perinaphthenone in D₂O has not been reported, ϕ_{Δ} values have been measured in a range of different solvents² [2] including benzene, CCl₄, H₂O and CD₃OD and have shown to be in a narrow range (0.93–0.98). We took $\phi_{\Delta} = 0.95$ for perinaphthenone in D₂O.

² See Ref. [29]. We thank the referee for the suggestion of this reference.

The values of ϕ_{Δ} obtained for 4NV and 3NA in acetonitrile and in D₂O are collected in Table 1. No ¹O₂* phosphorescence could be detected for 4NA either in D₂O or in acetonitrile. The singlet oxygen phosphorescence lifetime which we observed in the experiments with benzophenone in acetonitrile was 73 μs and in the experiments for 4NV and 3NA this was reduced to 67 and 47 μs, respectively. In D₂O the lifetime of singlet oxygen was reduced from 66 μs with perinaphthenone to 60 and 54 μs with 4NV and 3NA, respectively. The reduction of the singlet oxygen phosphorescence lifetime was due presumably to the quenching of singlet oxygen by nitrophenyl ethers in their ground states.

4. Discussion

In general, the quantum yield of singlet oxygen production, ϕ_{Δ} , is given by the sum of contributions due to the oxygen quenching of S₁ and T₁ states. In view of the very short singlet state lifetimes of nitroaromatic compounds (the lifetime of the singlet nitrobenzene is about 10⁻¹² s [19,26]), we can expect that only triplet states contribute to the formation of singlet oxygen.

The quantum yield of singlet oxygen production, ϕ_{Δ} , from a triplet state is given by Eq. (3):

$$\phi_{\Delta} = \phi_T P_T^{O_2} f_{\Delta}^T \quad (3)$$

where ϕ_T is the triplet quantum yield in the presence of oxygen, $P_T^{O_2}$ is the proportion of triplet molecules produced which are quenched by O₂ and f_{Δ}^T is the fraction of triplet molecules quenched by O₂ which give ¹O₂*.

It is known that the photochemistry of nitroaromatic compounds depends on the nature of the low-lying triplet state [3–6,30,31] but nothing is known about its effect on the efficiency of singlet oxygen generation. In some cases the efficiency of singlet oxygen generation, f_{Δ}^T , depends on the nature of the triplet state [32–35]. Thus, the lower efficiency of singlet oxygen generation by n,π* states compared to π,π* states has been suggested as an experimental criterion for the differentiation between both states. For example with aromatic ketones, f_{Δ}^T is 0.3–0.4 for n,π* triplets [33] while f_{Δ}^T is 0.8–1.0 for π,π* triplets [33] and it does not depend much on the solvent polarity or viscosity [36] for a particular kind of triplet state. On the contrary, in a very recent paper Nau et al. [37] showed that this correlation is not universal and that is not applicable, for example, to azoalkanes.

As pointed out above, nitrophenyl ethers have close lying n,π* and π,π* triplet states. The nature of their lowest triplet states depends on the substituents in the aromatic ring, on the polarity of the solvent and on the existence of hydrogen bonds with the solvent [3–8,25,26]. Nitroaromatic triplet states with π,π* character are stabilized by hydrogen bond formation in protic solvents [7,8], whereas the n,π* triplet states do not form hydrogen bonds [8,25,26]; and, therefore, the π,π* state often becomes the lower state in protic solvents [7,8]. Triplet states of n,π* configuration are short-lived

(lifetime shorter than 10⁻⁹ s, [23]) and the electron hole is localized on the nitro group [7,8,19]. Triplet states of π,π* configuration have longer lifetimes and their excitation is delocalized on the phenyl ring [7,8,19]. When there is a small energy gap between the n,π* and π,π* states a strong vibronic coupling between these states can occur and the properties of the lowest triplet would have contributions due to both states [13].

The triplet lifetimes of 4NV and 3NA in water (see Table 1) indicate that they may be considered as states with strong π,π* character. This is in agreement with the presumably formation of hydrogen bonds between these triplets and the solvent [7,8,25,26]. In acetonitrile, their shorter lifetimes suggest that the T₁ states have already a contribution of the n,π* state and that is higher for 3NA than for 4NV (see triplet lifetimes in Table 1). In fact, Resonance Raman Spectroscopy studies by Van Eijk et al. [13] of the triplet of 4NV in acetonitrile showed only minor changes in the electron distribution in the phenyl ring with respect to the ground state suggesting that the triplet has significant n,π* character. For 4NA, the triplet lifetime suggests a π,π* state with considerable n,π* character in water; and, the absence of a detectable triplet state in acetonitrile in our nanosecond laser flash photolysis experiments suggests a low-lying triplet of n,π* character in this solvent.

According to Eq. (3), the quantum yield of singlet oxygen production, ϕ_{Δ} , depends on: ϕ_T , the triplet quantum yield; $P_T^{O_2}$, the proportion of triplet molecules quenched by O₂; and, f_{Δ}^T , the fraction of triplet molecules quenched by O₂ which give ¹O₂*. Triplet quantum yields for 4NV ($\phi_T = 0.31$), 4NA ($\phi_T = 0.37$) and 3NA ($\phi_T = 0.34$) have been reported in methanol (see Refs. [10,11] for the case of 4NV and Ref. [38] for 4NA and 3NA). However ϕ_T of 4NV and 4NA are not known in water or in acetonitrile. ϕ_T for 3NA has been estimated as > 0.5 in acetonitrile [7] but no estimate is available for the value in water. The similarity of ϕ_T for the three compounds in methanol suggest that these closely structurally related compounds would have similar ϕ_T values in a particular solvent. The proportion of excited triplet states quenched by oxygen, $P_T^{O_2}$, may be evaluated using the k_{TD} and k values obtained from the laser flash photolysis experiments in absence and presence of molecular oxygen, respectively. Thus, $P_T^{O_2}$ may be evaluated from Eq. (4) (see Ref. [2]):

$$P_T^{O_2} = (k - k_{TD})/k \quad (4)$$

and thus, the products $\phi_T \times f_{\Delta}^T$ can be calculated from Eq. (3). The obtained values are collected in Table 1.

The results for the nitrophenyl ethers studied in this work collected in Table 1 suggest, in spite of the uncertainty in the ϕ_T values, that the efficiency of singlet oxygen generation by the triplet states, f_{Δ}^T , is moderately high, and that it is possible to relate f_{Δ}^T with the nature of the lowest triplet state as happens in the case of aromatic ketones [33] since the product of $\phi_T \times f_{\Delta}^T$ is greater for 4NV than 3NA in acetonitrile but smaller in D₂O. Thus, assuming for the reasons discussed above similar ϕ_T values in a particular solvent the efficiency

of singlet oxygen generation by the triplet states, f_{Δ}^T , is higher for 3NA than for 4NV in D₂O where both 3NA and 4NV have low-lying π, π^* triplet states; but on the contrary the values given in Table 1 suggest that f_{Δ}^T , is higher for 4NV than for 3NA in acetonitrile where the triplet state of 3NA has a stronger n, π^* character than that of 4NV (see triplet lifetimes in Table 1). In the case of 4NA, the quenching of the corresponding triplet states by O₂ is negligible under our experimental conditions due to the short triplet lifetimes both in acetonitrile and in water and therefore is not possible to evaluate its capacity as a sensitizer of singlet oxygen.

The capacity of nitrophenyl ethers as a photosensitizers of singlet oxygen in air-equilibrated solutions demonstrates that the cytotoxicity of nitroaromatic compounds can be due to the generation of singlet oxygen.

In summary, this work confirms the differences in the triplet spectra for nitrophenyl ethers in going from water to acetonitrile previously reported for 4NV [24] and shows that some nitroaromatic compounds can be moderately efficient sensitizers of singlet oxygen. The product of the efficiency of the singlet oxygen generation multiplied by the triplet quantum yield, $f_{\Delta}^T \times \phi_T$, is shown to be related to the nature of the lowest triplet. In addition, we have shown that the ground state nitrophenyl ethers quench singlet oxygen with appreciable efficiency. The nature of this quenching will be the subject of further studies in our laboratories.

Acknowledgements

Financial support from DGICYT ('Ministerio de Educación y Ciencia' of Spain) through project PB93-0895 and from CIRIT (Generalitat de Catalunya) through the project 1995SSGR00469 and for the acquisition of the LKS50 laser flash photolysis equipment (project IN92-4363) is gratefully acknowledged. We thank DGICYT also for a postdoctoral grant to M.M. and Unilever for a grant to L.M.G.J.

References

- [1] H. Sies, H. Degroot, *Toxicol. Lett.* 64–65 (1992) 547.
- [2] F. Wilkinson, W.P. Helman, A.B. Ross, *J. Phys. Chem. Ref. Data* 22 (1993) 113.
- [3] D. Dopp, *Topics Curr. Chem.* 55 (1975) 49.
- [4] A.N. Frolov, N.A. Kuznetsova, A.V. El'tsov, *Russ. Chem. Rev. (Engl. Trans.)* 45 (1976) 1024.
- [5] Y.L. Chow, *The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives, Part 1, Supplement F, Chap. 6*, Wiley, New York, 1982.
- [6] R. Nakagaki, K. Mutai, *Bull. Chem. Soc. Jpn.* 69 (1996) 261.
- [7] C.A.G.O. Varma, F.L. Plantenga, F.L. Huizer, J.P. Zwart, Ph. Bergwerf, J.P.M. van der Ploeg, *J. Photochem.* 24 (1984) 133.
- [8] P.H.M. Van Zeijl, L.M.J. Van Eijk, C.A.G.O. Varma, *J. Photochem.* 29 (1985) 415.
- [9] J. Cornelisse, E. Havinga, *Chem. Rev.* 75 (1975) 353 and references therein.
- [10] A. Cantos, J. Marquet, M. Moreno-Mañas, A. Castelló, *Tetrahedron* 44 (1988) 2607.
- [11] L.M.J. Van Eijk, A.H. Huizer, C.A.G.O. Varma, J. Marquet, *J. Am. Chem. Soc.* 111 (1989) 88.
- [12] A. Cantos, J. Marquet, M. Moreno-Mañas, A. González-Lafont, J.M. Lluch, J. Bertrán, *J. Org. Chem.* 55 (1990) 3303.
- [13] L.M.J. Van Eijk, A.H. Huizer, C.A.G.O. Varma, *J. Photochem. Photobiol., A: Chem.* 56 (1991) 183.
- [14] E. Cayón, J. Marquet, J.M. Lluch, X. Martín, *J. Am. Chem. Soc.* 113 (1991) 8970.
- [15] M. Mir, J. Marquet, E. Cayón, *Tetrahedron Lett.* 33 (1992) 7053.
- [16] J. Marquet, A. Cantos, M. Moreno-Mañas, E. Cayón, I. Gallardo, *Tetrahedron* 48 (1992) 1333.
- [17] J.B.S. Bonilha, A.C. Tedesco, L.C. Nogueira, M.T.R.S. Diamantino, J.C. Carreiro, *Tetrahedron* 49 (1993) 3053.
- [18] J. Marquet, E. Cayón, X. Martín, F. Casado, I. Gallardo, M. Moreno, J.M. Lluch, *J. Org. Chem.* 60 (1995) 3814.
- [19] G.G. Wubbels, A.K. Halverson, J.D. Oxman, H. Van de Bruyn, *J. Org. Chem.* 50 (1985) 4499.
- [20] D.J. McGarvey, F. Wilkinson, D.R. Worrall, J. Hobley, W. Shaikh, *Chem. Phys. Lett.* 202 (1993) 528.
- [21] S.L. Murov, I. Carmichael, G.L. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York, 1993, p. 289.
- [22] K. Yokoyama, J. Nakamura, K. Mutai, S. Nagakura, *Bull. Chem. Soc. Jpn.* 55 (1982) 317.
- [23] R.W. Yip, D.K. Sharma, R. Giasson, D. Gravel, *J. Phys. Chem.* 88 (1984) 5770.
- [24] R. González-Blanco, J.L. Bourdelande, J. Marquet, *J. Org. Chem.* 62 (1997) 6903.
- [25] G.G. Wubbels, J.W. Jordan, N.S. Mills, *J. Am. Chem. Soc.* 95 (1973) 1281.
- [26] G.G. Wubbels, D.P. Susens, E.B. Coughlin, *J. Am. Chem. Soc.* 110 (1988) 2538.
- [27] F. Wilkinson, D.J. McGarvey, A.F. Olea, *J. Phys. Chem.* 98 (1994) 3762.
- [28] A.A. Gorman, M.A.J. Rodgers, in: J.C. Scaiano (Ed.), *Handbook of Organic Photochemistry, Vol. II*, CRC Press, Boca Raton, FL, 1989, p. 233.
- [29] R. Schmidt, C. Tanielian, R. Dunsbach, C. Wolf, *J. Photochem. Photobiol., A: Chem.* 79 (1994) 11.
- [30] W.C. Petersen, R.L. Letsinger, *Tetrahedron Lett.*, (1971) 2197.
- [31] N. Levy, M.D. Cohen, *Mol. Photochem.* 8 (1977) 155.
- [32] E. Oliveros, P. Suardi-Muraseco, T. Aminian-Saghafi, A.M. Braun, H.J. Hansen, *Helv. Chim. Acta* 74 (1991) 79.
- [33] A.P. Darmanyan, C.S. Foote, *J. Phys. Chem.* 97 (1993) 4573.
- [34] J. Bendig, R. Schmidt, H.D. Brauer, *Chem. Phys. Lett.* 202 (1993) 535.
- [35] C. Grewer, H.D. Brauer, *J. Phys. Chem.* 98 (1994) 4230.
- [36] A.P. Darmanyan, C.S. Foote, *J. Phys. Chem.* 97 (1993) 5032.
- [37] W.M. Nau, W. Adam, J.C. Scaiano, *J. Am. Chem. Soc.* 118 (1996) 2742.
- [38] A. Cantos, PhD Thesis, Universitat Autònoma de Barcelona, 1989.