Available online at www.sciencedirect.com
ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 188 (2007) 293–297
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

A laser flash photolysis study of dibenzothiophene sulfoxide and benzo[*b*]naphtho[2,1-d]thiophene-11-oxide

Nanci C. de Lucas*, Ana Carla C. Albuquerque, Ana Carolina A.S. Santos, Simon J. Garden, David E. Nicodem

Laboratório de Espectroscopia Resolvida no Tempo, Departamento de Química Orgânica, Instituto de Química,
Universidade Federal do Rio de Janeiro, Ilha do Fundão, Rio de Janeiro 21945-970, Brazil

Received 11 October 2006; received in revised form 8 December 2006; accepted 18 December 2006
Available online 21 December 2006

Abstract

The photodeoxygenation reaction of dibenzothiophene sulfoxide (**1**) and of benzo[*b*]naphtho[2,1-d]thiophene-11-oxide (**3**) have been studied by nanosecond laser flash photolysis. Laser irradiation of **1** using sensitization with benzophenone leads to formation of a transient with absorption at 380 nm and a lifetime of around 140 ns. Triplet sensitized steady state irradiation of **1** indicates that the triplet state is not responsible for the direct photodeoxygenation.

Laser flash photolysis of **3** leads to the formation of a transient with a maximum absorption at 445 nm and a lifetime of around 3 μs. This transient was characterized as the triplet **3** by quenching with β-carotene. Quenching experiments indicate that the triplet energy is less than 56 kcal/mol.

Keywords: Laser photolysis; Sulfoxide; Triplet state

1. Introduction

Polyaromatic thiophenes are components of petroleum [1], and when petroleum is exposed to solar irradiation, as is the case when there is accidental or chronic release of petroleum into the marine environment, these thiophenes can be rapidly oxidized to the corresponding sulfoxides in a photochemical process [2]. These sulfoxides are photoactive, and result in the formation of free radicals, and consequently, they may play a role in the photochemical weathering of petroleum. The need to know more about this photochemical process motivated the present study.

The photodeoxygenation of aromatic sulfoxides has been known for over 30 years [3,4], and continues as an active area of research. Recently, Jenks and co-workers showed that the photolysis of dibenzothiophene sulfoxide (**1**) produces dibenzothiophene (**2**) and oxidized solvent but with a very low quantum yield (Scheme 1) [5,6]. It was suggested that along with **2**, an intermediate was also produced that was capable of oxidizing the solvent. These results are consistent with a mechanism involving simple S–O bond cleavage generating the thiophene and atomic oxygen O(^{3}P) and are consistent with the chemistry observed for gas phase atomic oxygen, the known reactivity of O(^{3}P), and the measured quantum yields.

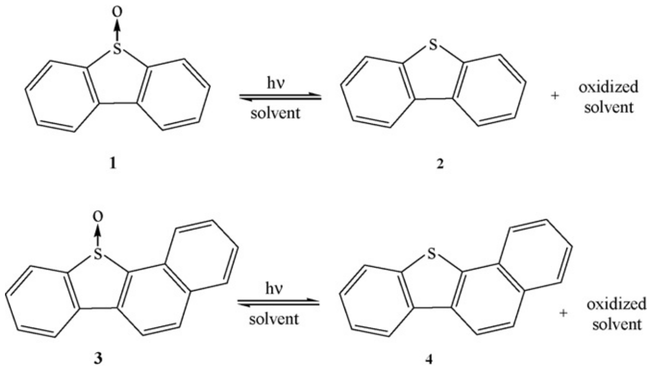
Greer and co-workers reported that the photolysis of benzo[*b*]naphtho[2,1-d]thiophene-11-oxide (**3**), also generated an intermediate capable of oxidizing the solvent [7]. Their data are similar to the results found for **1**. In a more recent paper, this group found that sulfoxide deoxygenation was a potentially clean method for O(^{3}P) production and hydrocarbon oxidation [8].

Nag and Jenks have recently reported on the photochemistry and photophysics of halogen substituted dibenzothiophene sulfoxides [9]. There is a modest improvement in the quantum yield for deoxygenation, relative to the parent **1** which was attributed to a heavy atom effect consistent with the proposed mechanism of unimolecular S–O bond scission in which bond stretching is coupled to intersystem crossing to produce atomic oxygen O(^{3}P) from the sulfoxide singlet state. However, it is not possible to eliminate reaction from a short-lived triplet state sulfoxide. Although reaction from the triplet would presumably be reasonably endothermic it would be state allowed. It must be noted that O(^{3}P) has not actually been observed in these reactions

---

* Corresponding author. Tel.: +55 21 25627278.
E-mail address: nancicl@iq.ufrj.br (N.C. de Lucas).

1010-6030/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2006.12.026



Scheme 1.

although solvent oxidation products compatible with O(^{3}P) are seen [5–7]. We therefore report here the results of a study using laser flash photolysis of **1** and **3**, and triplet sensitized continuous irradiation of **1**, in which the triplet is generated and its lifetime measured. In this work we show that the triplet of **1** is not responsible for the direct photodeoxygenation.

2. Materials and methods

2.1. Material

The solvents, acetonitrile, 2-propanol, CCl_4, methanol and deuterated methanol (VETEC spectrograde), were used as received. Dibenzothiophene (Merck–Shuchart) and benzo[*b*] naphto[2,1-d]thiophene-11-oxide, β-carotene, 1,3-cyclohexadiene, biacetyl and biphenyl (all from Aldrich) were used as received.

2.2. Synthesis

Dibenzothiophene sulfoxide (**1**) was prepared by in situ oxidation of dibenzothiophene with dimethyldioxirane. $NaHCO_3$ (1.302 g, 15.5 mmol), water (30 mL), acetone (50 mL) and dibenzothiophene (1.837 g, 5 mmol) were combined. Oxone (3.074 g, 5 mmol) was added in small portions over a period of 30 min. The reaction mixture was stirred at room temperature during 24 h. Water (100 mL) was then added and the mixture extracted with ethyl acetate (3 × 50 mL). Drying, filtering and removal of the solvent gave 1.9 g of crude product. The crude product was chromatographed on a column of silica eluting with dichloromethane. The product was then recrystallized from ethanol (848 mg, 42%), mp = 189–190 °C (mp$^{\text{lit}}$ = 186–187.5 °C) [10].

Compound **3** has been previously reported but without characterization [7]. Compound **3** was prepared analogously and was obtained in 18% yield after chromatographic separation on silica from the sulfone using CH_2Cl_2 as eluent. When mCPBA was used as the oxidant in CH_2Cl_2 compound **3** was obtained in 38% yield after chromatographic purification. mp = 165–170 °C with degradation. IR: 3050, 2924, 1583, 1471, 1140, 1053, 1016, 860, 818 and 761. ^{1}H NMR ($CDCl_3$): 8.45 (1H, d, J = 8 Hz), 8.04 (2H, d, J = 8 Hz), 7.90 (1H, d, J = 8 Hz), 7.84 (2H, d, J = 8 Hz) and 7.40–7.70 (4H, m). ^{13}C NMR: 118.9, 122.2, 124.1, 127.4, 127.5, 129.0, 129.2, 129.5, 130.8, 132.6, 133.8, 134.1, 135.7, 137.5, 140.6 and 145.5.

2.3. Steady state irradiation

A solution of **1** (2×10^{-3} M) and benzophenone (3×10^{-3} M) in acetonitrile was placed in a 10 mm Pyrex cell and deoxygenated by bubbling with oxygen-free nitrogen for 10 min. This solution was irradiated by a 1000 W Oriel high-pressure mercury lamp through 1 cm of lime glass as a filter to eliminate wavelengths below 350 nm. The reaction was analyzed by GC–MS (Shimadzu model QP2010S) using a 30 m DB-5column (J&W Scientific). Analysis after 1 h of irradiation showed no formation of the product **2**. Photolysis of benzophenone in 2-propanol was used as an actinometer [11].

2.4. Laser flash photolysis

The laser flash photolysis (LFP) experiments were carried out on an Edinburgh Analytical Instruments LP900, which has been previously described [12]. Samples were contained in a 10 mm × 10 mm cell made from Pyrex tubing and were dearated by bubbling with oxygen-free nitrogen for about 10 min. The samples were irradiated with a Nd/YAG Surelite II laser, using the third harmonic (λ = 355 nm, ∼4–6 ns, ≥40 mJ/pulse).

3. Results and discussion

Dibenzothiophene sulfoxide (**1**) does not absorb at the 355 nm laser wavelength. We therefore used benzophenone (Bz) sensitization to generate the triplet of **1**. Irradiation of a degassed acetonitrile solution of benzophenone led to the formation of a transient with absorption at 520 nm and a lifetime of around 1 μs. This absorption is in agreement with the literature value for the benzophenone triplet (Fig. 1) [13].

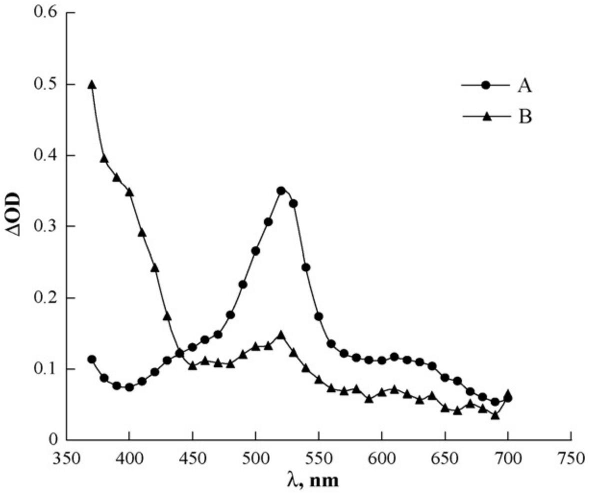


Fig. 1. Transient absorption spectrum recorded after 355 nm laser excitation of: (A) benzophenone in acetonitrile, 1.5 μs after the laser pulse and (B) 1×10^{-3} M of benzophenone and 1×10^{-4} M of **1** in acetonitrile 1.5 μs after the laser pulse.

Irradiation of a degassed acetonitrile solution of benzophenone in the presence of **1** led to a shortening of the triplet lifetime of benzophenone and the formation of a new transient with absorption at 370 nm (Fig. 1). The analogous sulfide triplet, **2**, absorbs at 380 nm [14].

The triplet decay of benzophenone followed pseudo-first-order kinetics in the presence of **1**. The experimentally observed pseudo-first-order kinetics rate constant, k_{obs}, is related to the quenching rate constant, k_{s}, according to Eq. (1),

$$k_{\mathrm{obs}} = k_0 + k_{\mathrm{s}}[\mathbf{1}] \tag{1}$$

k_0 is a decay rate constant of the triplet in the absence of **1**, and [**1**] the sulfoxide concentration. A plot of the rate of decay of triplet benzophenone as a function of the concentration of **1** was linear as expected from Eq. (1), from which one can determine the value of k_{s}. The second-order rate constant for the quenching of the benzophenone triplet by **1** was found to be $(9.39 \pm 0.26) \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ (Fig. 2).

The decay of the band at 370 nm also followed pseudo-first-order kinetics which varied with the concentration of **1** (Fig. 3). For this process, a second-order rate constant of $(8.35 \pm 0.20) \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ was found. The rate constant of the growth of the signal at 370 nm is $7 \times 10^6\ \mathrm{s}^{-1}$ and does not change with the concentration of **1**. The rates of decay of the transients at 520 and 370 nm have the same dependence on the concentration of **1** and are the same within experimental error. This is true even though the transient at 370 nm grows in while the transient at 520 does not. If we assume that the transient at 370 nm is the triplet of **1**, then these results can be understood if the kinetics are inverted. This happens when the rate of formation of a transient is slower than its rate of decay [15]. The decay of the signal will then follow the kinetics of its precursor while its growth will be controlled by its lifetime. In this case, the rate of the growth at 370 nm corresponds to the triplet lifetime of **1** and is 143 ns. This kinetic behavior was simulated using the kinetic scheme (Eqs. (2)–(4)) which generate Eqs. (5) and (6) [16], and the experimental rate constants. The resulting curve adequately follows the experimental data (Fig. 4).

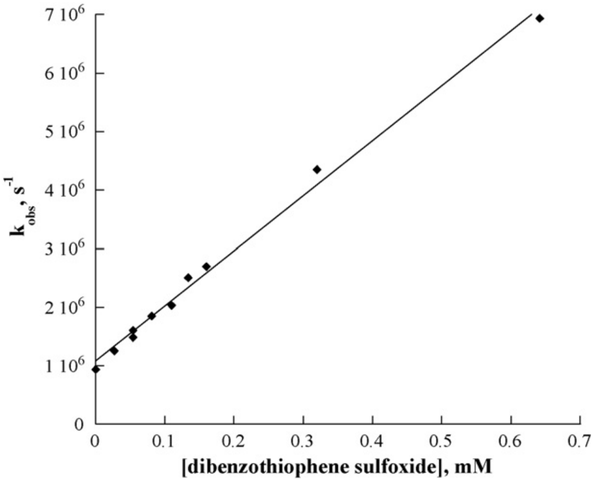


Fig. 2. A quenching plot of the triplet of benzophenone by **1** ($\lambda_{\mathrm{mon}} = 520$ nm, $\lambda_{\mathrm{exc}} = 355$ nm, in acetonitrile, [benzophenone] = 1×10^{-3} M).

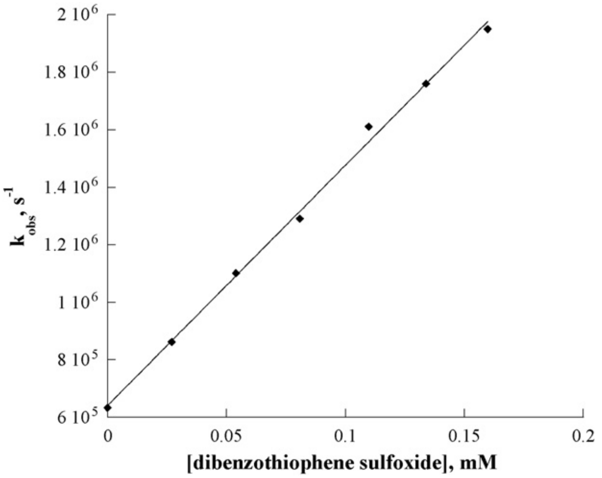


Fig. 3. Quenching plot of the 370 nm band by **1** in acetonitrile, [benzophenone] = 1×10^{-3} M.

$${}^3\mathrm{Bz}^* \xrightarrow{k_{\mathrm{d}}} \mathrm{Bz} \tag{2}$$

$${}^3\mathrm{Bz}^* + \mathbf{1} \xrightarrow{k_{\mathrm{s}}} \mathrm{Bz} + {}^3\mathbf{1}^* \tag{3}$$

$${}^3\mathbf{1} \xrightarrow{k_{\mathrm{x}}} \mathbf{1} \tag{4}$$

$$\frac{\mathrm{d}\,{}^3\mathrm{Bz}^*}{\mathrm{d}t} = {}^3\mathrm{Bz_0}^* - k_{\mathrm{d}}\,{}^3\mathrm{Bz}^* - k_{\mathrm{s}}\,{}^3\mathrm{Bz}^*\mathbf{1} \tag{5}$$

$$\frac{\mathrm{d}\,\mathbf{1}}{\mathrm{d}t} = k_{\mathrm{s}}\,{}^3\mathrm{Bz}^*\,\mathbf{1} - k_{\mathrm{x}}\,{}^3\mathbf{1}^* \tag{6}$$

Although the 370 nm transient could be due to electron transfer this process was considered less likely. Sensitized reduction of **1** has been observed using electron donors and a mechanism involving electron transfer was suggested [17]. In this case, the benzophenone triplet would be oxidized to the cation radical.

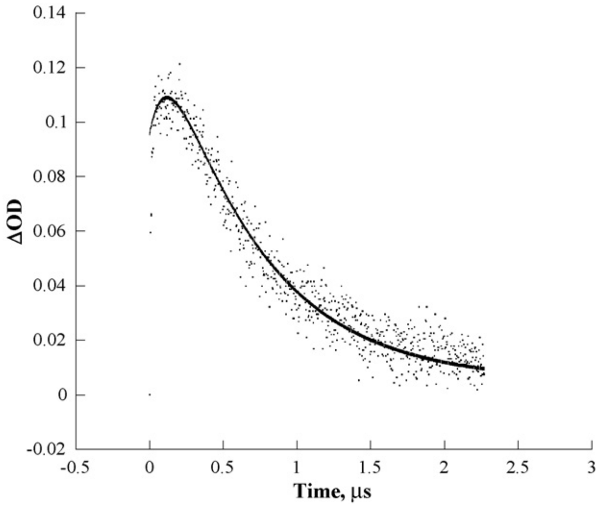


Fig. 4. Simulated and experimental data of the kinetic trace at 370 nm obtained after excitation of 2×10^{-3} M of **2** and 3×10^{-3} M of benzophenone in acetonitrile solution. The simulated trace is represented by the solid line through the experimental data.

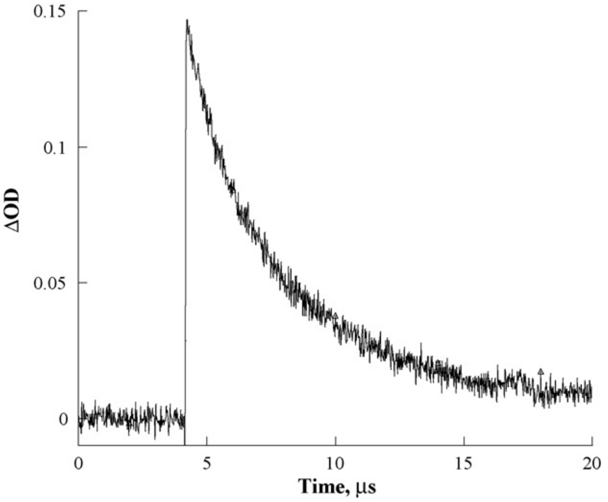


Fig. 5. Kinetic trace at 380 nm obtained after excitation of 2×10^{-3} M of **2** and 3×10^{-3} M of benzophenone in acetonitrile solution.

Although this is known to occur when the quencher is a strong electron acceptor such as MV^{++} [18], the rate constant for this reaction is smaller than that observed in the present study, since **1** is a much weaker electron acceptor an even lower rate constant would be expected. Due to the nearly diffusion controlled rate constant observed, this process was considered unlikely.

Alternatively, if electron transfer occurred from **1** to the benzophenone triplet then the transient at 370 nm could be assigned as the cation radical of **1**. Consequently, one would expect the formation of the benzophenone anion radical, a transient that has been previously reported to have a strong absorption at 630 nm [19]. However, no such transient was observed in these experiments thus excluding this process (Fig. 1).

The triplet of dibenzothiophene (**2**) was also studied. It is known that this triplet absorbs at 380 nm [14]. The same methodology used to generate the triplet of **1** was used to study the triplet of **2**. Both triplet lifetimes could then be compared under the same conditions. Decay of the transient at 380 nm produced by the benzophenone sensitized formation of the triplet of **2** is shown in Fig. 5. In this case, a triplet lifetime of 3.4 μs was found.

Jenks and co-workers used isoprene, cyclopentadiene and molecular oxygen to look for quenching of the deoxygenation reaction [5]. Although the maximum concentration of oxygen used was only 1×10^{-3} M due to saturation, the other quenchers were used at greater concentrations. Considering the triplet energies of isoprene and cyclopentadiene (60 and 58.1 kcal/mol, respectively) relative to the triplet energy of **1** (61 kcal/mol) [20], then diffusion controlled quenching would not be expected. However, at the maximum concentration of quenchers used by Jenks and co-workers it would be expected that shortening of the triplet lifetime of **1** would have occurred and that the deoxygenation would have been quenched.

Although sensitized deoxygenation of **1** is known, using acridine and chrysene [4], these sensitizers have both singlet and triplet energies lower than that of **1**, and therefore a mechanism via energy transfer is improbable.

Considering the short lifetime of the triplet of **1** and doubts about the mechanism of the literature quenching experiments, it was decided to measure the quantum yield for formation of **2** from **1** using benzophenone as the sensitizer under conditions in which only benzophenone was irradiated. While the formation of **2** from **1** would not prove that the unsensitized reaction followed a triplet mechanism it would show that it was possible. A mixture of benzophenone and **1** at the same concentration used in the laser flash photolysis experiments was irradiated for a time sufficient to produce a conversion of about 20% using the quantum yields observed by Jenks and co-workers [5]. Under these conditions, no formation of **2** was observed. It is therefore concluded that, the triplet state is not involved in the deoxygenation when **1** is directly excited. If it were, the sensitized irradiation would give the same or greater quantum yield of reduction. If **1** efficiently formed the triplet and reacted from the triplet, the quantum yield should be the same. If reaction is from the triplet but this is inefficiently formed under direct irradiation, the sensitized reaction should give a larger quantum yield. Sensitized irradiation may still generate products with a lower quantum yield or involving a different mechanism.

*3.1. Laser flash photolysis of **3***

Irradiation of a degassed acetonitrile solution of **3** led to the formation of a transient with a maximum absorption at 445 nm and a lifetime around 3 μs (Fig. 6). This transient is quenched by oxygen and β-carotene. When β-carotene was used, this transient was quenched with the formation of a 510 nm band corresponding to the β-carotene triplet (Fig. 7) [13]. The initial transient was characterized as the triplet of **3**.

The triplet of **3** was quenched by 1,3-cyclohexadiene, biacetyl and biphenyl, quenchers with different triplet energies in order to gain information with respect to the triplet energy of **3**. The triplet decay followed pseudo-first-order

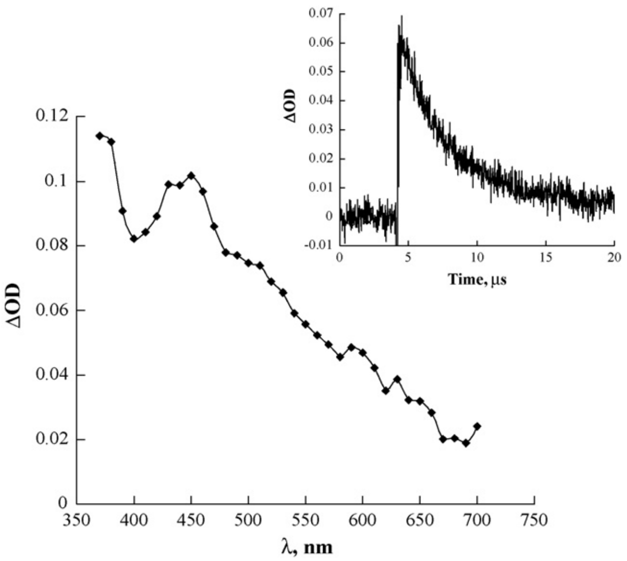


Fig. 6. Transient absorption spectrum recorded after 355 nm laser excitation of **3** (0.14 μs after the laser pulse) in acetonitrile. *Inset*: Decay at 445 nm.

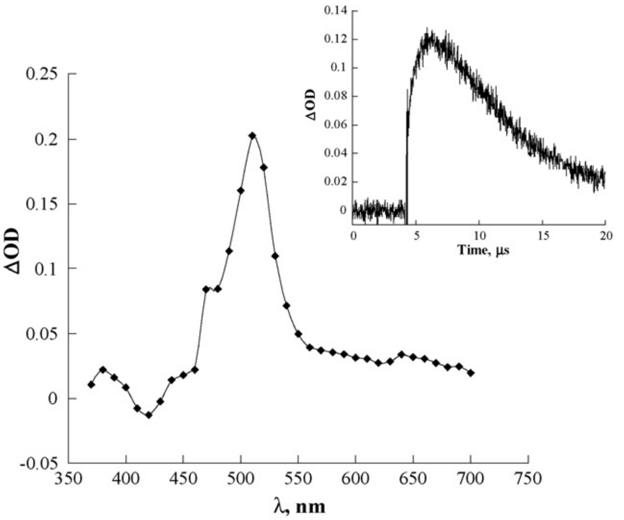


Fig. 7. Transient absorption spectrum recorded after 355 nm laser excitation of **3** (0.64 µs after the laser pulse) in the presence of β-carotene in acetonitrile solution. *Inset*: Decay at 510 nm.

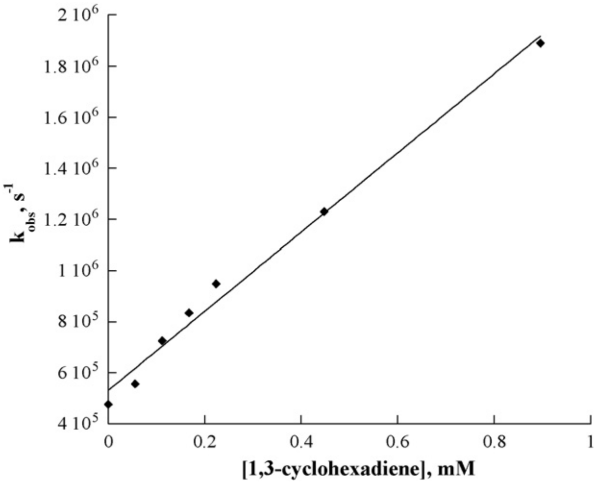


Fig. 8. Quenching plot of the triplet of **3** by 1,3-cyclohexadiene in acetonitrile, $\lambda_{mon} = 445$ nm.

kinetics in the presence of these quenchers. Stern-Volmer quenching plots were found to be linear, from which one can determine the values of the quenching rate constants for the triplet of **3**, k_s, $(1.55 \pm 0.07) \times 10^9$, $(6.56 \pm 0.54) \times 10^8$ and $(9.88 \pm 1.17) \times 10^6\, M^{-1}\, s^{-1}$ for 1,3-cyclohexadiene ($E_T = 52.4$ kcal/mol), biacetyl ($E_T = 56.4$ kcal/mol) and biphenyl ($E_T = 65.4$ kcal/mol), respectively [21]. Fig. 8 shows the quenching plot for 1,3-cyclohexadiene.

Quenching by exothermic energy transfer is expected to occur at a rate close to diffusion controlled ($10^{10}\, M^{-1}\, s^{-1}$). The rate constant for quenching by 1,3-cyclohexadiene is close to this value, biacetyl is somewhat less efficient and biphenyl is much lower. This indicates that the triplet energy is probably slightly less than 56 kcal/mol. The S–O bond dissociation energy, forming $O(^3P)$, has been estimated to be 75–77 kcal/mol using computational methods [9,22]. Considering the energy of activation necessary to achieve cleavage from the triplet state, it is unlikely that the triplet is involved in this process.

4. Conclusions

Using laser flash photolysis experiments the triplet of **1** was observed by a sensitization experiment with benzophenone which led to a transient with a lifetime of around 140 ns. Triplet sensitized continuous irradiation of **1** did not show the formation of **2**, therefore it is concluded that the triplet state is not involved in the direct photodeoxygenation of **1**.

The triplet of benzo[*b*]naphtho[2,1-d]thiophene-11-oxide (**3**) was characterized by laser flash photolysis experiments which revealed a maximum absorption at 445 nm and a lifetime of around 3 µs. Quenching experiments indicate that this triplet has an energy below 56 kcal/mol.

Acknowledgements

Grants from the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação Carlos Chagas de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ).

References

[1] NAS, vol. II, National Academy Press, Washington, DC, 1985, pp. 17–38.
[2] E.B. Overton, J.R. Patel, J.L. Laseter, Oil Spill Conference, 1979, pp. 169–174.
[3] J.R. Shelton, K.E. Davis, J. Sulfur Chem. 8 (1973) 217–228.
[4] G.M. Gurria, G.H. Posner, J. Org. Chem. 38 (1973) 2419–2420.
[5] D.D. Gregory, Z. Wan, W.S. Jenks, J. Am. Chem. Soc. 119 (1997) 94–102.
[6] Z. Wan, W.S. Jenks, J. Am. Chem. Soc. 117 (1995) 2667–2668.
[7] E. Lucien, A. Greer, J. Org. Chem. 66 (2001) 4576–4579.
[8] K.B. Thomas, A. Greer, J. Org. Chem. 68 (2003) 1886–1891.
[9] M. Nag, W.S. Jenks, J. Org. Chem. 69 (2004) 8177–8182.
[10] T. Nagata, K. Fujimori, T. Yoshimura, N. Furukawa, S. Oae, J. Chem. Soc., Perkin Trans. 1 8 (1989) 1431–1435.
[11] J.N. Pitts, R.L. Letsinger, R.P. Taylor, J.M. Patterson, G. Recktenwald, R.B. Martin, J. Am. Chem. Soc. 81 (1959) 1068–1078.
[12] N.C. Lucas, J.C. Netto-Ferreira, J. Photochem. Photobiol. A: Chem. 116 (1998) 203–208.
[13] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, Marcel Dekler, Inc., New York, 1993, pp. 107–111.
[14] M. Yamaji, K. Okada, B. Marciniak, H. Shizuka, Chem. Phys. Lett. 277 (1997) 375–380.
[15] D. Gust, T.A. Moore, A.L. Moore, L. Legget, S. Liu, J.M. DeGraziano, R.M. Hermant, D. Nicodem, P. Craig, G.R. Seely, R.A. Nieman, J. Phys. Chem. 97 (1993) 7926–7931.
[16] Bz is benzophenone and $^3Bz_0{}^*$ is the initial concentration of the benzophenone triplet immediately after the laser pulse.
[17] J.W. Cubbage, T.A. Tetzlaff, H. Groundwater, R.D. McCulla, M. Nag, W.S. Jenks, J. Org. Chem. 66 (2001) 8621–8628.
[18] P.K. Das, Tetrahedron Lett. 22 (1981) 1307–1310.
[19] P.K. Das, S.N. Bhattacharyya, J. Phys. Chem. 85 (1981) 1391–1395.
[20] W.S. Jenks, W. Lee, D. Shutters, J. Phys. Chem. 98 (1994) 2282–2289.
[21] P.J. Wagner, J. Am. Chem. Soc. (1967) 2820–2825.
[22] W.S. Jenks, N. Matsunaga, M. Gordon, J. Org. Chem. 61 (1996) 1275–1283.