ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 107 (1997) 165–167

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Bianthrone photophysics and photochemistry: solvent heavy-atom-induced triplet state formation

David E. Nicodem [a],*, M. Fernanda V. da Cunha [b]

[a] *Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro 21945-970, Brazil*
[b] *Instituto de Química, Universidade Federal Fluminense, Niterói 24210-150, Brazil*

Received 2 September 1996; accepted 11 December 1996

Abstract

The cyclization of bianthrone to helioanthrone in toluene occurs from the singlet state, since the quantum yield of intersystem crossing in this solvent is very low or zero. In bromoform, the triplet is formed and in the presence of oxygen generates singlet oxygen with a quantum yield of 0.42. A transient absorbing at 720 nm with a lifetime of 19 μs is also observed in this solvent and is attributed to the excited triplet state. © 1997 Elsevier Science S.A.

Keywords: Bianthrone; Photocyclization; Singlet oxygen; Triplet state

1. Introduction

The photocyclization of bianthrone (**I**) to helioanthrone (**III**) is thought to involve the conrotatory electrocyclization of the lowest excited singlet of **I** to generate initially the dihydrohelioanthrone (**II**) as an intermediate [1,2] (see Fig. 1). Although this is reasonable on theoretical grounds, and a transient absorption attributed to **II** has been observed using flash photolysis, the only experimental evidence to support cyclization through the singlet state is the lack of suppression by molecular oxygen [3]. However, this criterion is insufficient to rule out cyclization via the triplet state since oxygen quenching may not compete efficiently with rapid triplet state cyclization. Even if cyclization occurs via the singlet state, the triplet state may also be reactive if formed.

There have been a number of low-temperature studies of bianthrone and its derivatives in which the triplet state has been observed, but these provide no information on the nature of the excited state responsible for cyclization [4–9]. At low temperature, cyclization is no longer observed. Instead, bianthrone fluoresces and intersystem crosses, generating a triplet which phosphoresces and generates a long-lived photochromic isomer identical to the known thermochromic form. In some cases, an unidentified transient is also observed originating from the triplet [6–8] which has been suggested to be a biradical [9].

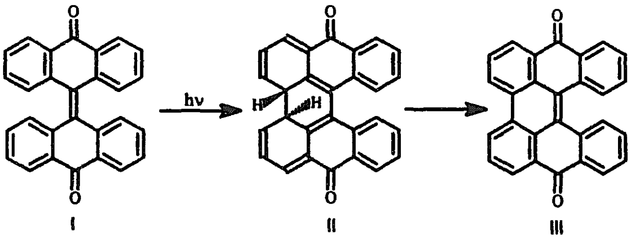

Fig. 1. The photocyclization of bianthrone (**I**) to helioanthrone (**III**) via dihydrohelioanthrone (**II**) as an intermediate.

At room temperature, it still remains to be shown whether or not cyclization is truly a singlet state reaction and whether or not the triplet state is formed. The objective of this work is to define the manifold through which cyclization occurs using heavy-atom-induced intersystem crossing.

2. Experimental details

Bianthrone (Aldrich) and 2,3-dimethyl-2-butene (TME) (Aldrich) were used as received. Bromoform (Vetec) was distilled immediately before use. Helioanthrone used as a reference was synthesized following the literature procedure [10,11].

Quantum yields were measured by following the formation of helioanthrone using its absorbance at 450 nm where bianthrone does not absorb. Conversions were kept below 20%. The filtered radiation of a 450 W medium-pressure mercury

---

* Corresponding author. E-mail: nicodem@iq.ufrj.br.

1010-6030/97/$17.00
PII S1010-6030(96)04618-7

lamp (Hanovia) in a merry-go-round was employed. The 405 nm wavelength mercury line used to irradiate bianthrone was isolated by passing the radiation through 5 cm of 1.0×10^{-3} M crystal violet solution. Potassium ferrioxalate was used as actinometer [12,13]. The samples were degassed by at least four freeze–pump–thaw cycles on a high vacuum line followed by sealing in Pyrex ampoules.

Hydroperoxide concentrations were measured by oxidation of iodide and measurement of the triiodide formed using the literature procedure [14].

A Beckman DU-6 UV–visible spectrophotometer was used for absorption measurements. An Edinburgh Analytical Instruments LP900 time-resolved spectrometer was employed for transient absorption experiments. The third harmonic of a Continuum Nd/YAG laser (355 nm) was used as the excitation source. Singlet oxygen emission experiments were performed using instrumentation at the Center for the Study of Early Events in Photosynthesis at Arizona State University which has been described previously [15]. For these experiments, excitation was performed at 420 nm, the laser intensity was maintained below 1 mJ per pulse and the sample and reference cells were matched for absorbance.

3. Results and discussion

Cyclization of bianthrone to helioanthrone occurs equally well in the presence or absence of oxygen [1,2]. This would be adequate evidence for cyclization from the singlet state if it could be shown that the triplet state was formed, and was quenched by oxygen. If, however, the triplet is not observed, the lack of quenching by oxygen could be due to cyclization either from a singlet state or a short-lived triplet. In this case it would need to be shown that, if formed, the triplet lives long enough to be quenched by oxygen. Then the lack of oxygen quenching would confirm the reaction via the singlet.

The approach to the problem used here was to study the formation of singlet oxygen. The bianthrone triplet energy is estimated to be 54 kcal mol^{-1} [8] and a singlet energy of 63 kcal mol^{-1} was extracted from the low-temperature fluorescence emission spectrum [16]; the singlet–triplet energy separation is therefore 9 kcal mol^{-1}. Considering this energy separation, it would be expected that intersystem crossing would be relatively fast and that singlet oxygen would be formed only from the triplet, since oxygen quenching of the singlet state would not be capable of generating singlet oxygen [17]. The production of singlet oxygen would then show that the triplet was indeed formed and quenched by oxygen and would validate the oxygen quenching experiments.

Singlet oxygen formation was investigated in two ways. In the first, TME was added and the singlet oxygen produced was "measured" by analyzing the quantity of hydroperoxide formed by the reaction of singlet oxygen with TME [18,19]. However, since the photocyclization of bianthrone produces dihydrobianthrone, which is oxidized by molecular oxygen to give bianthrone and hydrogen peroxide [1,2], some hydroperoxide will also be formed by this route and does not involve singlet oxygen. When the irradiation is carried out in aerated toluene, the quantum yield of formation of hydroperoxides is 0.28 ± 0.02. Irradiation in the absence of oxygen, followed by opening of the ampoules to air and analysis of hydroperoxides, also gives a quantum yield of 0.28 ± 0.01; therefore all the hydroperoxide produced can be attributed to the oxidation of the dihydrobianthrone formed as a consequence of cyclization with essentially no contribution from singlet oxygen.

The formation of singlet oxygen was also probed by looking for the emission of singlet oxygen at 1270 nm following laser flash excitation of bianthrone at 420 nm in aerated toluene. No singlet oxygen emission was observed. Under the same conditions, dibenzopyrenequinone (DBPQ), used as a reference [20,21], gave a strong signal. (The value actually found was 0.8 using a value of 0.7 for the quantum yield of singlet oxygen formation by tetraphenylporphine (TTP) in CCl_4 [20,21]. Using a value of 0.86 for TTP in CCl_4 gives a quantum yield of 1.01 for DBPQ [22].) Given the sensitivity of the instrument used and the signal intensity in the case of DBPQ, it is estimated that the bianthrone-sensitized formation of singlet oxygen is less than 0.05.

These results are consistent with either a low value of intersystem crossing to the triplet state or the formation of a very short-lived triplet state for bianthrone in toluene at room temperature.

3.1. Heavy-atom solvent effects

It was decided to use a heavy-atom-containing solvent, in this case bromoform, to induce intersystem crossing [23]. If it could be shown that the triplet state is indeed formed in bromoform and has a lifetime sufficiently long to be quenched by oxygen, forming singlet oxygen, the lack of oxygen quenching and singlet oxygen formation in toluene would be good evidence for the lack of intersystem crossing and for a singlet mechanism of cyclization.

On excitation of bianthrone in bromoform, the emission of singlet oxygen at 1270 nm could be readily seen (Fig. 2),

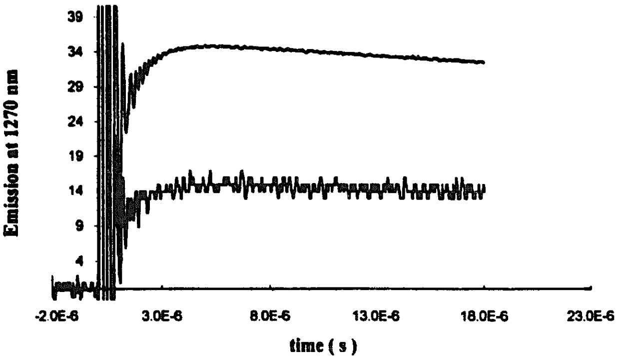

Fig. 2. Time-resolved singlet oxygen emission at 1270 nm. Top trace is the averaged signal (100 shots) using dibenzopyrenequinone (DBPQ) in bromoform as the sensitizer. Bottom trace is the signal from a single laser pulse using bianthrone in bromoform as the sensitizer.

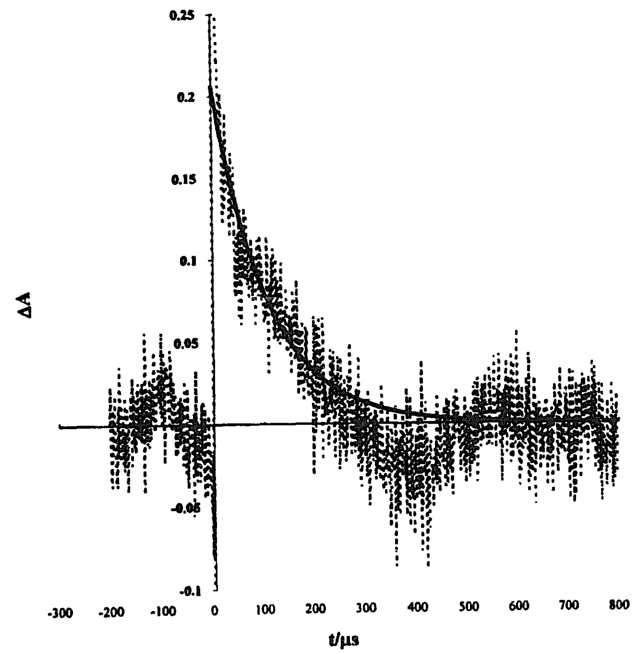

Fig. 3. Transient absorption at 720 nm produced by exciting bianthrone in bromoform (at 355 nm).

and a quantum yield of singlet oxygen of 0.42 was found by comparison with DBPQ used as a reference (see above) [20–22] in the same solvent. It is assumed that the quantum yield for DBPQ-induced singlet oxygen formation is the same (unity) in both toluene and bromoform. In order to obtain reproducible results, it was necessary to flash each bianthrone sample only once. After the first flash, a long-lived, strongly yellow transient was formed which was more efficient at generating singlet oxygen than was bianthrone. This may well be the photochromic form observed at low temperature [8].

Laser flash photolysis of degassed samples of bianthrone (6.0×10^{-5} M) in bromoform gave a transient absorption at 720 nm. This showed a very short rise time (less than the 20 ns observable with the instrument used) and a first-order decay of 19 μs (Fig. 3). When samples dissolved in toluene were subjected to the same analysis, no transient in the region of 720 nm could be observed. A triplet state absorbing at 720 nm has previously been observed at low temperature [8], and it is reasonable to assume that the room-temperature transient observed in bromoform is also the triplet excited state.

4. Conclusions

The experiments using bromoform as the solvent show that, in this case, the triplet state is formed in competition with other reactions of the singlet state and has a lifetime sufficiently long to be quenched by molecular oxygen. The singlet oxygen experiments show that quenching does indeed take place and singlet oxygen is formed. Heavy-atom solvents, such as bromoform, are expected to induce intersystem crossing from the singlet to the triplet and to shorten the lifetime of the triplet state by inducing intersystem crossing to the ground state. It is therefore expected that the triplet lifetime in toluene would be as long as or longer than that in bromoform. Since, in toluene, the triplet was not observed by either flash photolysis or sensitized singlet oxygen generation, it is concluded that the quantum yield of intersystem crossing is very low in this solvent. It can be safely concluded that photocyclization occurs from the singlet state in toluene.

Acknowledgements

We acknowledge financial support from the "Conselho Nacional de Desenvolvimento Científico e Tecnológico" (CNPq), the "Financiadora de Estudos e Projetos" (FINEP) and the Fundação Universitária Jose Bonifácio. We also thank Dr Thomas A. Moore for access to equipment used in the singlet oxygen luminescence experiments.

References

[1] H. Brockmann, R. Mühlmann, Chem. Ber. 81 (1948) 467.
[2] H. Brockmann, R. Mühlmann, Chem. Ber. 82 (1949) 348.
[3] H.H. Richtol, L.C. Groncki, L.J. Dombronski, J. Phys. Chem. 73 (10) (1969) 3481.
[4] R. Korenstein, K.A. Muszkat, E. Fischer, Israel J. Chem. 8 (1970) 277.
[5] T. Bercovici, E. Fischer, E. Fischer, Israel J. Chem. 50 (1970) 841.
[6] T. Bercovici, E. Fischer, Helv. Chim. Acta 56 (1973) 1114.
[7] W.E. Forster, E. Fischer, J. Chem. Soc., Chem. Commun. 23 (1972) 1315.
[8] R. Korenstein, K.A. Muszkat, E. Fischer, Helv. Chim. Acta 59 (1976) 1826.
[9] T. Bercovici, R. Korenstein, G. Fischer, E. Fischer, J. Phys. Chem. 80 (1976) 108.
[10] A.E. Goldestein, J. Am. Chem. Soc. 61 (1939) 1600.
[11] R. Scholl, J. Mansfeld, Chem. Ber. 43 (1910) 1734.
[12] C.G. Hatchard, C.A. Parker, Proc. R. Soc. London, Ser. A 235 (1956) 518.
[13] D.E. Nicodem, L.M. Cabral, J.C.N. Ferreira, Mol. Photochem. 8 (1977) 213.
[14] K.D. Banerge, C.C. Budke, Anal. Chem. 36 (1964) 792.
[15] R.E. Belford, G. Seely, D. Gust, T.A. Moore, A. Moore, N.J. Cherepy, S. Ekbundit, J.E. Lewis, S.H. Lin, J. Photochem. Photobiol. A: Chem. 70 (1993) 125.
[16] R.S. Becker, E. Eahart, J. Am. Chem. Soc. 92 (1970) 5049.
[17] A.A. Gorman, M.A.J. Rodgers, in: J.C. Scaiano (Ed.), CRC Handbook of Photochemistry, vol. II, CRC Press, 1989, Chapter 10, p. 229.
[18] K. Gollnick, G.O. Schenck, Pure Appl. Chem. 9 (1964) 507.
[19] A. Nicon, J.F. Bagli, J. Am. Chem. Soc. 83 (1961) 1498.
[20] A.A. Krasnovskii, T.C. Khachaturova, N.V. Bulgarn, L.A. Polyakova, G.E. Krichevskii, Dokl. Akad. Nauk. SSR 285 (1985) 654.
[21] Y.S. Egorov, M. Maallem, A.A. Krasnovskii, T.C. Khachaturova, G.E. Krichevskii, Dokl. Akad. Nauk. SSR 315 (1990) 1152.
[22] J. Olmsted III, J. Am. Chem. Soc. 102 (1980) 66.
[23] M. Kasha, J. Chem. Phys. 20 (1952) 71.