Available online at www.sciencedirect.com

Journal of Photochemistry and Photobiology A: Chemistry 162 (2004) 225–229

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Laser flash photolysis study of the photochemistry of isatin and *N*-methylisatin

M.T. Silva, J.C. Netto-Ferreira*

Departamento de Química, Universidade Federal Rural do Rio de Janeiro, Antiga Rio-São Paulo km 47, Seropédica, 23851-970 Rio de Janeiro, Brazil

Received 12 February 2003; received in revised form 4 August 2003; accepted 23 August 2003

Abstract

Rate constants for the quenching of isatin (**1**) and *N*-methylisatin (**2**) by hydrogen and electron donors were measured by the laser flash photolysis (LFP) technique in benzene solution. For **1**, rate constants ranging from $1.5 \times 10^5\,M^{-1}\,s^{-1}$ (for toluene) to $5.9 \times 10^9\,M^{-1}\,s^{-1}$ (for 1,4-diazabicyclo[2.2.2]octane, DABCO) were obtained. Slightly lower rate quenching values were obtained for *N*-methylisatin, which probably indicates an increase in the charge-transfer (CT) character of its triplet state. The lack of dependence of the quenching rate constants of **1** and **2** with the substituent, in the case where substituted phenols were employed as quenchers, indicates that for the two isatins the primary process in the quenching reaction is electron transfer followed by a fast proton transfer, leading to the formation of the corresponding phenoxyl radicals. From the quenching rate constants by *trans*- and *cis*-stilbene, a value between 49.3 and 54.3 kcal/mol was estimated for the triplet state of isatin, whereas for *N*-methylisatin the E_T is estimated to be <49.3 kcal/mol.

Keywords: Isatins; Hydrogen abstraction; Electron transfer; Laser flash photolysis

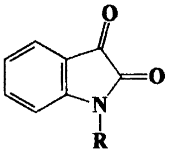
1. Introduction

In the last years, the chemistry of vicinal polycarbonyl compounds has received remarkable attention due to its wide application for analytical and synthetic purposes [1]. Although the presence of two carbonyl groups in isatin makes it an attractive target to synthetic organic chemists [2,3], little is known about its photochemical reactivity.

Isatin (**1**) does not show fluorescence or phosphorescence emission in a variety of solvents and upon excitation it undergoes very fast intersystem crossing to the triplet state. In oxygen saturated solution the irradiation of isatin leads to the formation of isatoic acid anhydride [4]. This triplet state is capable of abstracting hydrogen from toluene, *p*-xylene or cumene, yielding the pinacol isatide [4]. The photochemical reaction of isatin in the presence of 1,3-cylohexanedione leads to the formation of an a spiro derivative [5], whereas the irradiation of isatin and 5-fluorisatin with pyrazolone gives ring expanded heterocyclic compounds derived from the cleavage of the amide bond [5].

Irradiation of *N*-alkylisatins in degassed alcohols leads to a chemoselective reaction to afford 3-hydroxy-*N*-methyloxindole, as a primary product, and *N*-methyloxindole [6]. Like the reactions of isatin with hydrogen donors [4,5], it has been proposed that the primary photochemical process involves hydrogen abstraction from the solvent to generate a semidione radical.

This work shows the results of laser flash photolysis (LFP) studies of the reaction of isatin (**1**) and *N*-methylisatin (**2**) in the presence of several quenchers, including hydrogen and electron donors.



1: R = H
2: R = Me

2. Experimental

2.1. Materials

The solvents employed were Aldrich Spectrograde and were used as received. Isatin, *N*-methylisatin, triethylamine, ethyl 2-hydroxyethyl sulfide, 1,4-diazabicyclo[2.2.2]octane (DABCO), 4-cyanophenol, 4-chlorophenol, 4-*tert*-butyl-

---

* Corresponding author.
E-mail address: jcnetto@ufrrj.br (J.C. Netto-Ferreira).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/S1010-6030(03)00383-6

phenol, 4-methoxyphenol, 1,4-dimethoxybenzene, *cis*-stilbene, *trans*-stilbene, 1,4-cyclohexadiene, and β-carotene were purchased from Aldrich and purified when necessary.

2.2. General techniques

UV-Vis spectra were recorded in a Varian Cary 3E. LFP experiments were carried out on an Edinburgh Analytical Instruments LP900. Samples were contained in a 10 mm × 10 mm cell made from Suprasil quartz tubing and were deaerated by bubbling with oxygen-free nitrogen for 20 min. The samples were irradiated either with the third harmonic (λ = 355 nm, ∼5 ns, 40 mJ per pulse) of a Nd/YAG Surelite laser, or with an Excimer laser from Lumonics EX-510 (λ = 308 nm, ∼5 ns, 80 mJ per pulse). Sample concentration was chosen in order to give an absorption at the wavelength of excitation of 0.3. Stock solutions of quenchers in the same solvent employed in sample preparation were prepared so that it was only necessary to add microliter volumes to the sample cell in order to obtain appropriate concentrations of the quencher.

3. Results and discussion

The ground state absorption spectrum for isatin and *N*-methylisatin in benzene shows a strong and sharp absorption at 296 nm and a broad band with maximum at 404 nm. A slight red shift is observed in the long wavelength absorption for both isatins in going from benzene to acetonitrile (from 404 to 414 nm). This is an indication that there is some charge-transfer (CT) interaction in the excited singlet state of isatin and *N*-methylisatin. Fig. 1 shows the ground state absorption spectra for *N*-methylisatin in benzene and in acetonitrile.

Laser excitation of a deaerated benzene solution of isatin (**1**) leads to the formation of a transient with strong absorptions at 320 and 420 nm (Fig. 2). This transient decays by mixed first and second-order kinetics with an apparent lifetime around 2.5 μs.

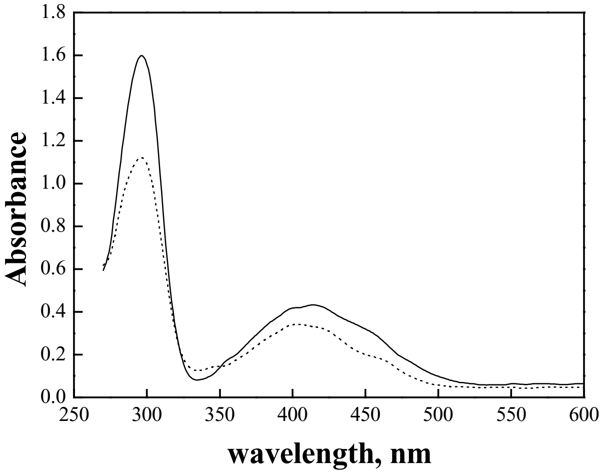


Fig. 1. Ground state absorption spectra for *N*-methylisatin in benzene (···) and in acetonitrile (—).

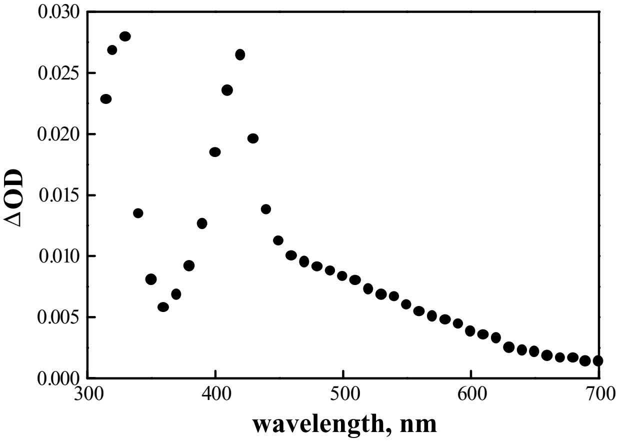


Fig. 2. Transient absorption spectrum obtained on 308 nm excitation of isatin (**1**) in benzene 2 μs after the laser pulse.

Similar behavior was observed upon excitation of *N*-methylisatin (**2**) in benzene. In this case, absorption bands centered at 330, 420 and 530 nm were observed. This transient also shows a decay with mixed first and second-order, from which an apparent lifetime of 6.4 μs was obtained (Fig. 3).

The transients obtained in the irradiation of **1** and **2** were assigned to their triplet state because they are quenched by β-carotene at a diffusion controlled rate constant, with the concomitant formation of the later triplet at 535 nm.

Rate constants for the quenching of isatin (**1**) and *N*-methylisatin (**2**) triplet by a variety of quenchers were measured by LFP, in benzene. The addition of quenchers that could act as electron or hydrogen donor leads to a shortening of the triplet lifetime of the isatins. Such shortening of the triplet lifetime of isatin and *N*-methylisatin was also observed for quenchers such as *trans*- and *cis*-stilbene,

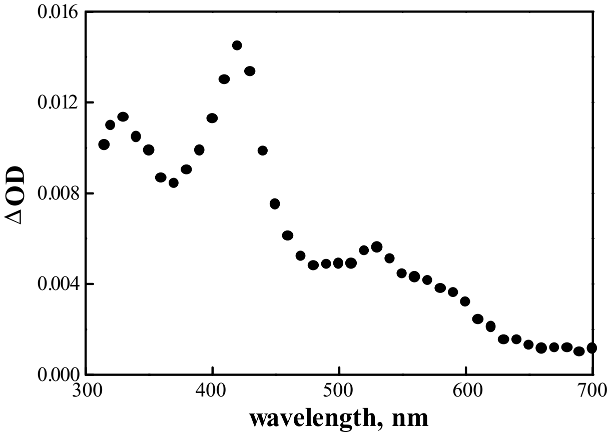


Fig. 3. Transient absorption spectrum obtained on 308 nm excitation of *N*-methylisatin (**2**) in benzene 2 μs after the laser pulse.

Table 1
Second-order rate constants for the quenching of the triplets of **1** and **2** in benzene

Quencher	k_q ($M^{-1}\,s^{-1}$)[a]	
	1	**2**
Triethylamine	1.9×10^9	1.4×10^8
Ethyl 2-hydroxyethyl sulfide	1.5×10^7	2.7×10^6
DABCO	5.8×10^9	5.8×10^9
2-Propanol	3.1×10^6	1.9×10^5
Phenol	3.5×10^9	3.7×10^9
4-Cyanophenol	3.2×10^9	3.4×10^9
4-Chlorophenol	4.0×10^9	3.9×10^9
4-*Tert*-butylphenol	4.5×10^9	5.1×10^9
4-Methoxyphenol	5.2×10^9	5.7×10^9
Cis-stilbene	3.7×10^8	7.4×10^7
Trans-stilbene	1.7×10^9	5.7×10^8
Toluene	1.4×10^5	1.0×10^5
1,4-Cyclohexadiene	6.6×10^6	6.8×10^5

[a] Estimated to be accurate to ±10%.

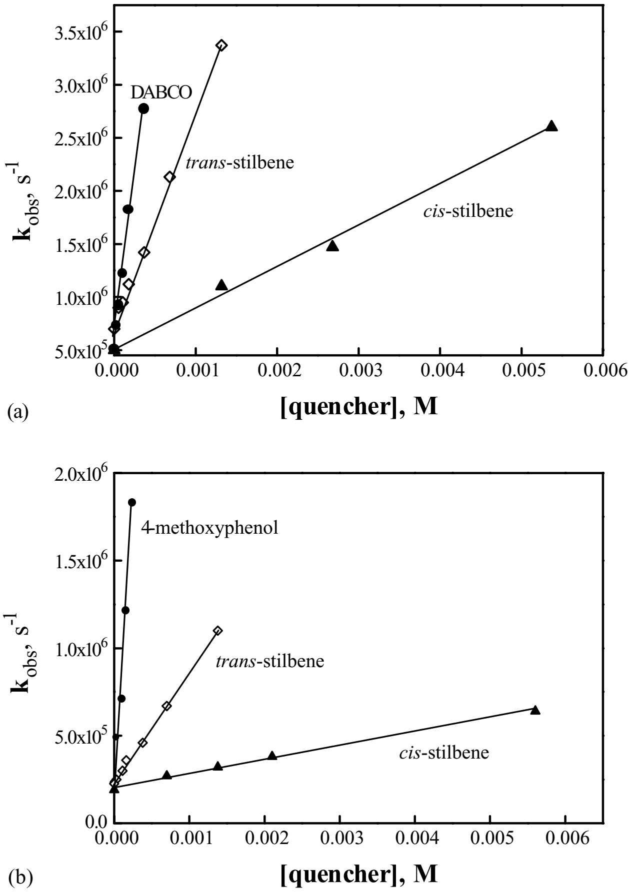


Fig. 4. (a) Quenching plots for the triplet of **1** by DABCO, *cis*-stilbene and *trans*-stilbene in benzene ($\lambda_{exc} = 355$ nm, $\lambda_{mon} = 420$ nm). (b) Quenching plots for the triplet of **2** by 4-methoxyphenol, *cis*-stilbene and *trans*-stilbene in benzene ($\lambda_{exc} = 355$ nm, $\lambda_{mon} = 420$ nm).

in which the quenching process can occur by energy transfer. The decay of these triplets, monitored at their maxima absorptions (420 nm), followed pseudo-first-order kinetics in the presence of all quenchers employed. The experimentally observed pseudo-first-order kinetic rate constant (k_{obs}) is related to the quenching rate constant (k_q) according to Eq. (1) (Stern–Volmer equation), where k_0 is the decay rate constant of the triplet in the absence of quencher and $[Q]$ the quencher concentration:

$$k_{obs} = k_0 + k_q[Q] \tag{1}$$

Plots based on this equation for the quenching of triplets of **1** and **2** by various quenchers were found linear, from which one can determine k_q values (Table 1). For example, Fig. 4a shows quenching plots for **1** by DABCO, *cis*-stilbene and *trans*-stilbene, in benzene, whereas Fig. 4b shows similar plots for *N*-methylisatin in the presence of 4-methoxyphenol, *cis*-stilbene and *trans*-stilbene.

The addition of the electron donor 1,4-dimethoxybenzene to the triplet of **1** or **2** results in the formation of an intense signal at the monitoring wavelength of their triplets, with the resulting spectra showing intense absorption maxima at 450 and 490 nm (Fig. 5). This transient was assigned to the cation radical of 1,4-dimethoxybenzene because a similar transient has been detected in dichloromethane and acetonitrile solutions [7,8]. Since both the triplet state of isatin (and *N*-methylisatin) and of 1,4-dimethoxybenzene show intense absorption in the 420 nm region, the kinetics at this wavelength after addition of the quencher was complex enough to prevent a reasonable measurement of the corresponding quenching rate constants for **1** and **2**.

Phenoxyl radicals were easily detected when the irradiation of **1** and **2** was performed in the presence of phenols. In this case, the absorption due to the phenoxyl radical was observed in the 370–440 nm region, depending on the substituent, which is in full agreement with those previously described for phenoxyl radicals [9,10]. A representative spectrum employing 4-methoxyphenol as the quencher of the isatin triplet is shown in Fig. 6. The rate constants for the reactions of **1** and **2** with phenols are consistent with the contribution of an electron transfer process to the triplet

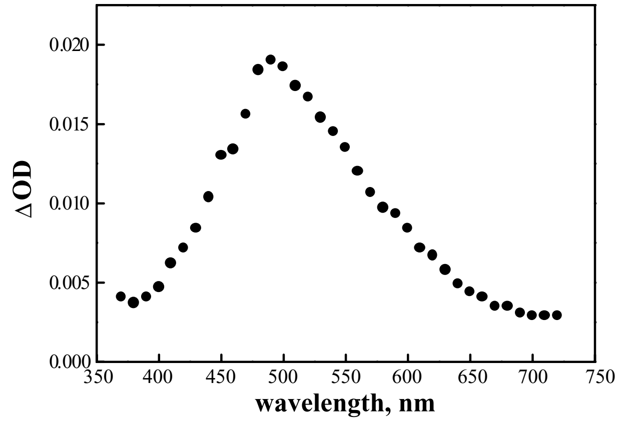


Fig. 5. Transient absorption spectrum obtained on 355 nm excitation of isatin (**1**) and 2.3×10^{-3} M of 1,4-dimethoxybenzene in benzene solution, 0.75 μs after the laser pulse.

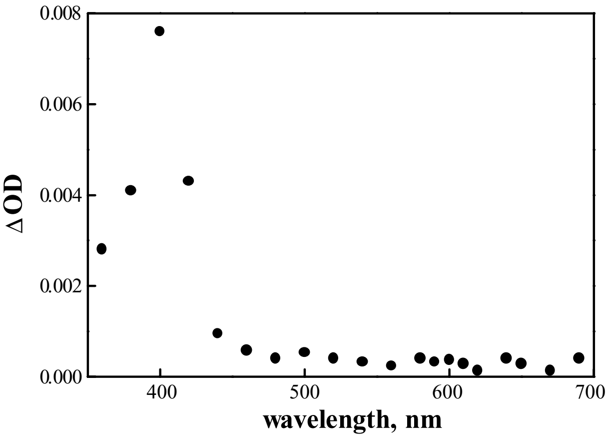


Fig. 6. Transient absorption spectrum obtained on 355 nm excitation of isatin (**1**) and 1.4×10^{-3} M of 4-methoxyphenol in benzene solution, 0.75 μs after the laser pulse.

quenching (Table 1). These quenching rate constants are quasi identical since the very fast process is close to diffusion controlled rates for all phenols. Thus, the quenching of these triplets with phenols may involve an initial electron transfer process followed by a fast proton transfer, ultimately leading to the formation of the corresponding phenoxyl radicals [11].

The configuration that describes the excited state of aromatic carbonyl compounds bearing strong electron releasing groups involves nearly complete transfer of an electron from the heteroatom on the substituent to the carbonyl group. This electron transfer reduces the electrophilicity of the carbonyl oxygen in the excited state, making it more nucleophilic. States which are best described by such a model are called charge-transfer states. Although both $\pi\pi^*$ and CT states involve mainly π type orbitals, in the $\pi\pi^*$ state the π and π^* electrons are generally considered to occupy similar or the same region of space, but in the CT state the π and π^* electrons may be located in different regions of space, thereby producing a charge separation. This implies a decreasing of reactivity of these excited states towards hydrogen abstraction, which is influenced by the ketone structure, solvent and other experimental variables [12–15]. It has been reported that $n\pi^*$ transition of isatin has some CT character due to n nitrogen electrons [4]. Thus, the minor reactivity of *N*-methylisatin towards hydrogen donors, such as 1,4-cyclohexadiene and 2-propanol, can be attributed to a remarkable CT character of its excited state, when compared to **1**. The rate constants observed with phenols confirm the involvement of different mechanism for these reactions.

It has been reported that isatin does not show fluorescence or phosphorescence emission under different conditions [4]. Through our kinetic study we could obtain informations about the triplet energy of **1** and **2**. The magnitude of the rate constants for the quenching of the triplet of isatin by *trans*-stilbene (E_T = 49.3 kcal/mol) [16] is consistent with the contribution of the energy transfer process to the triplet quenching. Under our experimental conditions, we obtained a value for the quenching rate constant of isatin by *trans*-stilbene in benzene closed to diffusion control (1.7×10^9 M^{-1} s^{-1}). The lower rate constant for the quenching of this triplet by *cis*-stilbene (E_T = 54.3 kcal/mol) [16] indicates that its triplet energy is located between 49.3 and 54.3 kcal/mol. For *N*-methylisatin, considerably lower values than those found for isatin for the quenching rate constants by *trans*- and *cis*-stilbene were obtained (Table 1), which indicates that for these quenchers the energy transfer process is endothermic by few kcal/mol. From these data, one can estimate a triplet energy of **2** less than 49.3 kcal/mol. The difference in the triplet energy between isatin and *N*-methylisatin can be explained again by the increasing in the CT character of the later triplet.

Surprisingly, it has been reported that the quenching rate constant of isatin by *trans*-stilbene is one order of magnitude larger than that for diffusion controlled reaction [4]. However, the discrepancy with our value can be due to the methodology employed in the literature measurement, since in the later case the quenching rate constant was estimated from the addition of a single concentration of the quencher, i.e. *trans*-stilbene, and not from a Stern–Volmer plot obtained either from steady-state irradiation or time-resolved experiments.

In conclusion, slightly lower quenching rate constants were obtained for *N*-methylisatin (**2**) ($E_T < 49.3$ kcal/mol, from energy transfer experiments) when compared to isatin (**1**) (E_T between 49.3 and 54.3 kcal/mol, from energy transfer experiments), which probably reflects an increasing in the CT character of the former triplet state. On the other hand, no dependence of the quenching rate constants of **1** and **2** with the substituent was found when substituted phenols were employed as quenchers. This indicates that in the two cases the primary process in the quenching reaction is electron transfer followed by a fast proton transfer, which results in the formation of the corresponding phenoxyl radicals.

Acknowledgements

A grant from the Fundação Carlos Chagas de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) is gratefully acknowledged. MTS thanks FAPERJ for a graduate fellowship. JCNF thanks CNPq for a research fellowship.

References

[1] M.B. Rubin, R. Gleiter, Chem. Rev. 100 (2000) 1121.
[2] M.G.A. Shvekhgeimer, Chem. Heterocycl. Comp. (Engl. Transl.) 32 (1996) 249.
[3] J.F.M. Silva, S.J. Garden, A.C. Pinto, J. Braz. Chem. Soc. 12 (2001) 273.
[4] G. Haucke, B. Seidel, A. Graness, J. Photochem. 37 (1987) 139.
[5] K.C. Joshi, R. Jain, S. Arora, Indian J. Heterocycl. Chem. 1 (1991) 95.
[6] J. Tatsugi, K. Ikuma, Y. Izawa, Heterocycles 43 (1996) 7.

[7] S. Sankararaman, J.K. Kochi, Recl. Trav. Chim. Pays-Bas (1986) 105.

[8] C.W. Chan, W.T. Wong, C.M. Che, Inorg. Chem. 33 (1994) 1266.

[9] E.J. Land, G. Porter, E. Strachan, Trans. Faraday Soc. 57 (1961) 1885.

[10] P.K. Das, M.V. Encinas, S. Steenken, J.C. Scaiano, J. Am. Chem. Soc. 103 (1981) 4162.

[11] L.M. Tolbert, CRC Handbook of Organic Photochemistry, vol. II, CRC Press, Boca Raton, FL, 1989, pp. 23–34.

[12] N.J. Turro, Modern Molecular Photochemistry, 2nd ed., Benjamin Cummings, Menlo Park, CA, 1978.

[13] N.J. Turro, J.C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, N. Schore, Acc. Chem. Res. 5 (1972) 92.

[14] J.C. Dalton, P.A. Wriede, N.J. Turro, J. Am. Chem. Soc. 92 (1970) 1318.

[15] J.C. Scaiano, J. Photochem. 2 (1974) 81.

[16] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, 2nd ed., Marcel Dekker, New York, 1993.