ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 101 (1996) 29–32

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

An investigation of the triplet state properties of 1,8-naphthalimide: a laser flash photolysis study

A. Samanta [†,*], B. Ramachandram, G. Saroja
School of Chemistry, University of Hyderabad, Hyderabad 500 046, India

Received 11 March 1996; accepted 29 April 1996

Abstract

The triplet state of 1,8-naphthalimide has been studied by the laser flash photolysis technique. The triplet–triplet absorption spectrum and the decay kinetics of the triplet state have been investigated in benzene, acetonitrile and 2-propanol. It is shown that, unlike phthalimide, 1,8-naphthalimide does not undergo photoinduced hydrogen abstraction reactions with protic solvents. Quantitative data on various triplet state parameters such as molar extinction coefficient of the triplet–triplet absorption, triplet yield and energy have been obtained. The behaviour of the compound towards some electron-rich substances have been studied and the rate constants have been evaluated.

Keywords: 1,8-Naphthalimide; Triplet state parameters; Photo-electron transfer reaction; Flash photolysis

1. Introduction

Despite the fact that imides undergo a variety of photochemical reactions [1,2], a number of them are synthetically quite useful; very little is known about the mechanistic details of these transformations. The photophysical behaviour of the first excited singlet state of *N*-alkylphthalimides and *N*-alkyl and aryl naphthalimides have been studied using fluorescence measurements [3–10]. This state in unsubstituted imides is characterized by low fluorescence quantum yield [10]. Substitution of one of the hydrogen atoms in the six-membered ring by an amino group, however, results in dramatic enhancement in fluorescence lifetime and yield due to intramolecular charge transfer phenomenon [11,12]. As far as the unsubstituted imides are concerned, the weak fluorescence of phthalimide (**1**) is presumably due to the n–π^* nature of the lowest excited singlet state which favours both photochemical reactions and intersystem crossing. We have recently shown that a less reactive π–π^* state is the lowest excited singlet state in 1,8-naphthalimide (**2**); although this participates in the electron transfer reactions with aromatic hydrocarbons and amines, facile recombination of the products does not lead to any observable photochemistry from this state [10]. It was found that the fluorescence quantum yield and lifetime did not increase much when the lowest state is changed from n–π^* in phthalimide to π–π^* in naphthalimide. Thus, it is apparent that because of short singlet lifetime of **1** and **2** a majority of the photochemical reactions of naphthalimide, or aromatic imides in general, take place from the triplet state. It is surprising, however, that the behaviour of the triplet states of even simple imides is not known notwithstanding its important role in photochemical transformations. Also, very few mechanistic studies on imides have been made [13]. It is for this reason that we have undertaken a laser flash photolysis study on **2**. The main objective of this work is to determine various parameters related to the triplet state such as triplet–triplet absorption spectra, triplet yield, triplet energy and study the reactivity of the triplet towards electron-rich compounds.

2. Experimental details

1,8-Naphthalimide (Aldrich) was recrystallized twice from ethanol before use. Thioxanthone, benzophenone, biphenyl, naphthalene, 2,5-dimethyl-2,4-hexadiene (DMHD) and triphenylamine (TPA) were all obtained from Aldrich and recrystallized from ethanol. Triethylamine (TEA) was distilled under reduced pressure. The nitroxide radical, 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTMP), was obtained from Aldrich and recrystallized twice from cyclohexane. Ferrocene was used without any further

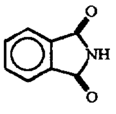
---

[†] Also at Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA.

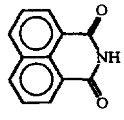
[*] Corresponding author. All correspondence to the University of Hyderabad.

PII S1010-6030(96)04392-4

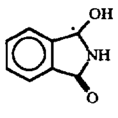
purification. The solvents were purified by standard procedures. The laser flash photolysis system has been previously described [14,15].



1



2



3

3. Results and discussion

Upon laser excitation at 337.1 nm, degassed acetonitrile solution of **2** produces transient species with absorption maxima at 360 and 470 nm that decay with first-order kinetics on a microsecond time scale. The transient absorption spectrum is shown in Fig. 1. The first-order fit to the decay measured at 470 nm yielded a lifetime of 9 μs for the transient. A similar decay behaviour at 360 nm indicates that both the absorption bands arise from a single species. The bleaching at 330 nm corresponds to the ground-state absorption maximum of the compound [10]. A similar absorption spectrum is obtained in non-polar solvent such as benzene. The band maxima are observed at 355 and 460 nm and the lifetime of the transient species is measured to be about 10 μs in benzene. To determine the nature of the transient we have carried out quenching studies with oxygen and ferrocene. Both are known to be efficient quenchers for the triplet state [16]. For quenching experiments, the decay times τ at 470 nm were measured as a function of quencher concentration [Q]. The observed lifetimes τ are related to quencher concentration [Q] by the following equation

$$\tau^{-1}=\tau_0^{-1}+k_q[Q] \qquad (1)$$

where τ_0 is the lifetime of the transient in the absence of quencher. k_q is obtained as a slope of the plot of τ^{-1} against [Q]. A representative plot for ferrocene quenching based on Eq. (1) is shown in Fig. 2. k_q (ferrocene) is obtained as 1.4×10^{10} M^{-1} s^{-1}. The diffusion-controlled quenching constant indicates that the transient species must be the triplet of **2**. This is supported by the oxygen quenching studies in which lifetimes were measured in deoxygenated and oxygen saturated solutions. $k_q(O_2)$ was measured to be 2.3×10^9 M^{-1} s^{-1}. Additional proof in support of the triplet nature of the transient is obtained from photolysis of a mixed solution of **2** and thioxanthone at 355 nm. The similarity of the sensitized spectrum and the spectrum obtained on direct excitation supported the triplet nature of the transient.

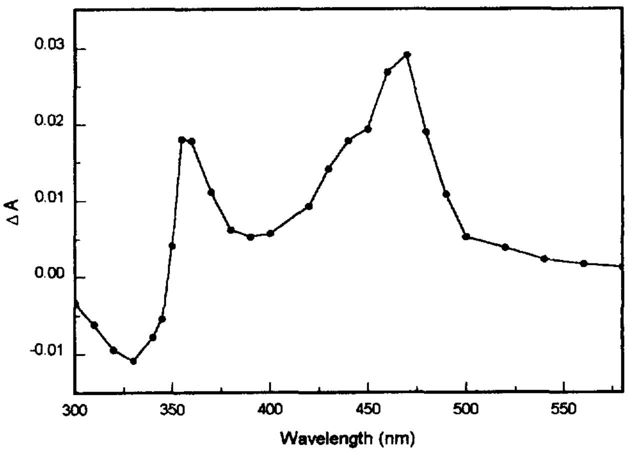


Fig. 1. Transient absorption spectrum of **2** in acetonitrile at 2.8 μs after laser excitation at 337 nm.

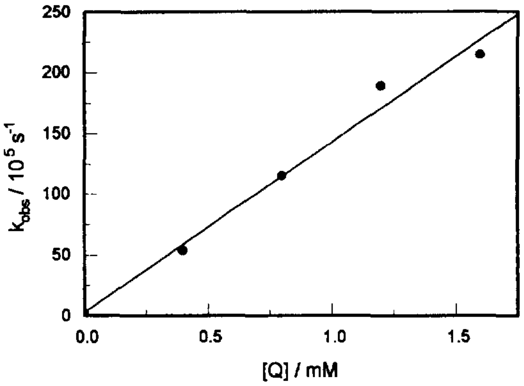
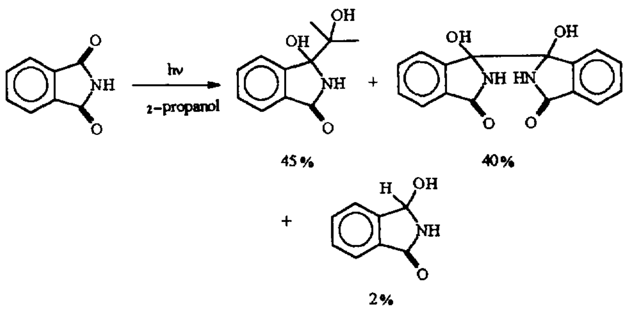


Fig. 2. Plot of the observed rate constants for the triplet decay of **2** vs. ferrocene concentrations in acetonitrile.

The time-resolved absorption spectra were also recorded in a polar protic solvent (2-propanol). However, apart from a minor variation in the position of the absorption maxima and lifetime, no additional transient could be seen in this medium. Phthalimides are known to undergo hydrogen abstraction reactions with alcohols [1]. With 2-propanol, phthalimide is known to form a photoadduct, a pinacol-like reduction product and a small amount of 3-hydroxyisoindolinone as shown in Scheme 1. All the products shown in Scheme 1 are expected to result from a common intermediate **3**.

However, lack of absorption due to species other than the triplet in 2-propanol suggests a less reactive π–π* singlet and triplet state of **2**. Further, enhanced fluorescence yield of **2** [10] and non-quenching of the triplet lifetime in 2-propanol clearly rules out the formation of radical similar to **3** from either the singlet or the triplet of **2**.

The extinction coefficient ϵ^N of the triplet–triplet absorption is determined by the energy transfer technique using the



Scheme 1.

triplet of thioxanthone as the energy donor. The quenching of the latter ($E_T = 65.5$ kcal mol^{-1}) [17] by **2** was assumed to be entirely dominated by the exothermic energy transfer process. Experiments were carried out in acetonitrile solutions containing both thioxanthone and **2** with 355 nm excitation. The end of the pulse absorbance change ΔA_0^R caused by thioxanthone triplet at 650 nm was compared with the absorbance change ΔA_∞^N from the triplet of **2** at 470 nm. ϵ^N was calculated from the following equation [18]:

$$\epsilon^N = \frac{\epsilon^R \, \Delta A_\infty^N k_{obs}}{\Delta A_0^R (k_{obs} - k_0)} \qquad (2)$$

where ϵ^R is the extinction coefficient of the thioxanthone triplet–triplet absorption, and k_{obs} and k_0 are the rate constants for the decay of thioxanthone triplet in the presence and in the absence respectively of **2**. A value of 3×10^4 M^{-1} cm^{-1} was used for ϵ^R at 650 nm [18].

Once the value of ϵ^N was known, the triplet yield ϕ_T^N of **2** was measured in acetonitrile using for actinometry benzophenone triplet formation ($E_T = 6500$ M^{-1} cm^{-1} at 520 nm). The end of pulse absorbance change ΔA_0^N due to the triplet of **2** at 470 nm was compared with the absorbance change ΔA_0^B due to the benzophenone triplet at 520 nm, the latter being observed in a solution optically matched at the exciting wavelength with that of **2**. The following equation was used to calculate ϕ_T^N:

$$\phi_T^N = \frac{\phi_T^B \, \Delta A_0^N \epsilon_T^B}{\Delta A_0^B \epsilon_T^N} \qquad (3)$$

A value of 1.0 was used for ϕ_T^B [19]. The triplet state parameters are presented in Table 1. It can be seen that intersystem crossing in **2** is as high as that in aromatic ketones. Further, the measured triplet yield is in agreement with the low fluorescence quantum yield of **2** ($(5–8) \times 10^{-2}$) [10]. Taking into consideration these parameters, we conclude that internal conversion between S_1 and S_0 is not a dominant mechanism of deactivation of the singlet state. This is consistent with the energy gap law of non-radiative decay processes [20].

Table 1
Triplet-state parameters of 1,8-naphthalimide [a]

λ_{max} (nm)	360, 470 ± 5
$\epsilon_T^{b,c}$ (M^{-1} cm^{-1})	10300
ϕ_T^c	0.92
τ_T (μs)	9.0
E_T (kcal mol^{-1})	52.8

[a] In acetonitrile.
[b] At 470 nm.
[c] Estimated error ± 15%.

Table 2
Half-peak oxidation potentials $E_{1/2}^{ox}$ for the quenchers, free-energy changes ΔG and bimolecular quenching constants k_q for the electron transfer processes in acetonitrile

Quencher	$E_{1/2}^{ox}$	ΔG (kcal/mole)	k_q (10^9 M^{-1} s^{-1})
Biphenyl	1.48 [b]	+ 11.5	–
Naphthalene	1.34 [b]	+ 8.3	0.02
TPA	0.59 [b]	− 9.0	1.2
TEA	0.51 [c]	− 10.8	2.1
DMHD	0.71 [d]	− 6.2	2.4
HTMP	0.41 [e]	− 13.1	3.2

[a] Vs. Ag–0.1 N Ag$^+$ in acetonitrile; $E_{1/2}^{ox}$ data measured vs. saturated calomel electrode are corrected by subtracting 0.27 V.
[b] From [22].
[c] From [23, part c, p. 6].
[d] From [23, part c, p. 5].
[e] From [24].

In order to study the redox behaviour of the triplet state of **2** we have examined the decay kinetics of the triplet in presence of a number of electron-rich molecules such as naphthalene, biphenyl, TEA, TPA, DMHD and HTMP in acetonitrile. Even though both biphenyl and naphthalene are efficient quenchers of the singlet state of **2**, no quenching of the triplet state is observed with biphenyl. Naphthalene is found to quench the triplet of **2** with a rate constant of only 1.9×10^7 M^{-1} s^{-1}. This behaviour can be rationalized taking into consideration the free-energy changes for the quenching process by an electron transfer process using the following equation [21]:

$$\Delta G = 23.06\left(E_{ox} - E_{red} - \frac{e^2}{\epsilon r}\right) - \Delta E_{00} \qquad (4)$$

where ΔE_{00} is the triplet energy of **2**. Taking into account the redox potentials of the compounds and the triplet energy of **2** ($E_T = 52.8$ kcal mol^{-1}, determined from the origin of the phosphorescence spectrum of **2** in methanol–ethanol glass at 77 K), the calculated ΔG values (on neglect of the Coulomb term) in both cases are positive (Table 2). The negligible quenching observed with naphthalene could be due to the influence of the Coulomb term in Eq. (4) as energy transfer quenching by naphthalene ($E_T = 60.9$ kcal mol^{-1}) [17] is expected to be unfavourable. With the amines, TEA or TPA, the free-energy changes are between − 9 and 11 kcal mol^{-1} and the measured rate constants for quenching are still below the diffusion-controlled limit. Both DMHD and HTMP quench the triplet of **2** and the quenching rate constants are presented in Table 2. The quenching plots are shown in Fig. 3. The electron transfer nature of the quenching mechanism can be substantiated by the correlation of the k_q values with the oxidation potentials of the quenchers. As seen from the table, with the exception of DMHD, the quenching constants are in accordance with the ΔG values of the couples. With DMHD, however, one would have expected a k_q value slightly lower than that with TEA. Since conventional vertical energy transfer quenching by DMHD ($E_T = 59.03$ kcal mol^{-1}) [25] is not possible, the enhanced quenching could be due to some contribution from the energy transfer to a non-vertical state of DMHD. The most conclusive evidence in favour of the electron transfer mechanism of quenching is obtained by observation of the radical cations of the amines.

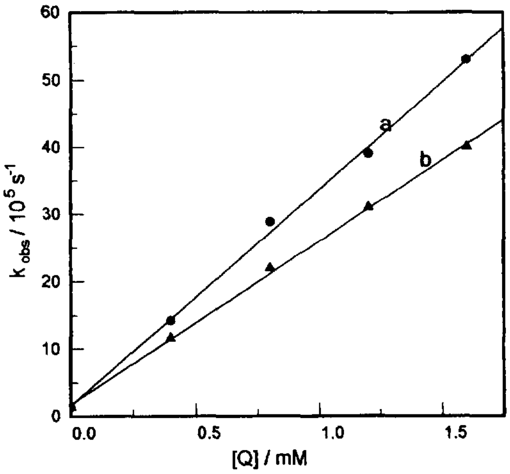


Fig. 3. Representative plots for the observed rate constants for triplet decay of 2 in acetonitrile vs. concentration: curve a, HTMP; curve b, DMHD.

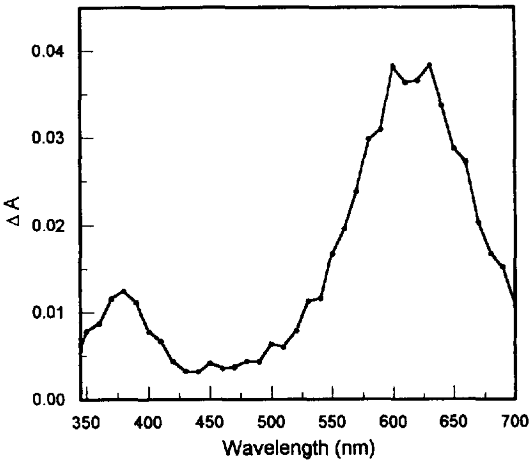


Fig. 4. Transient absorption spectrum obtained upon photolysis of acetonitrile solutions of 2 in the presence of TPA. The spectrum was recorded 12 μs after the laser flash.

In Fig. 4 is shown the transient absorption spectrum of a mixed solution of **2** and TPA. The spectrum recorded at longer delay times is identical with reported spectrum of the radical cation of TPA [26]. The observation of the products of electron transfer reaction and their survival over a long time scale clearly indicates the ability of **2** in initiating synthetically useful photoinduced electron transfer reactions.

Acknowledgement

The research described herein is supported by the Department of Science and Technology, Government of India, and the Office of Basic Energy Sciences, Department of Energy, USA. G.S. and B.R. would like to thank the Council of Scientific and Industrial Research for fellowships.

References

[1] J.D. Coyle, in W.M. Horspool (ed.), *Synthetic Organic Photochemistry*, Plenum, New York, 1984, p. 259.
[2] P.H. Mazzocchi, in A. Padwa (ed.), *Organic Photochemistry*, Vol. 5, Dekker, New York, 1981, p. 421.
[3] A. Pardo, J.M.L. Poyato and E. Martin, *J. Photochem., 36* (1987) 323.
[4] A. Pardo, E. Martin, J.M.L. Poyato, J.J. Camacho, M.F. Brana and J.M. Castellano, *J. Photochem. Photobiol. A: Chem., 41* (1987) 69.
[5] P. Valat, V. Wintgens, J. Kossanyi, L. Biczok, A. Demeter and T. Berces, *J. Am. Chem. Soc., 114* (1992) 946.
[6] R.S. Davidson and A. Lewis, *J. Chem. Soc., Perkin Trans. II*, (1979) 900.
[7] J.H. Barlow and R.S. Davidson, *J. Chem. Soc., Perkin Trans. II*, (1979) 1103.
[8] D. Yuan and R.G. Brown, *J. Chem. Res. (M)*, (1994) 2355.
[9] P. Berci Filho, V.G. Toscano and M.J. Politi, *J. Photochem. Photobiol. A: Chem., 43* (1988) 51.
[10] A. Samanta and G. Saroja, *J. Photochem. Photobiol. A: Chem., 84* (1994) 19.
[11] T. Soujanya, T.S.R. Krishna and A. Samanta, *J. Phys. Chem., 96* (1992) 8544.
[12] T. Soujanya, R.W. Fessenden and A. Samanta, *J. Phys. Chem., 100* (1996) 3507.
[13] H. Hayashi, S. Nagakura, Y. Kubo and K. Maruyama, *Chem. Phys. Lett., 72* (1980) 291.
[14] P.K. Das, M.V. Encinas, R.D. Small, Jr. and J.C. Scaiano, *J. Am. Chem. Soc., 101* (1979) 6965.
[15] V. Nagarajan and R.W. Fessenden, *J. Phys. Chem., 89* (1985) 2330.
[16] A. Samanta and R.W. Fessenden, *J. Phys. Chem., 93* (1989) 5823.
[17] S.L. Murov, *Handbook of Photochemistry*, Dekker, New York, 1973.
[18] I. Carmichael and G.L. Hug, *J. Phys. Chem. Ref. Data, 15* (1986) 1.
[19] A.A. Lamola and S.S. Hammond, *J. Chem. Phys., 43* (1965) 2129.
[20] N.J. Turro, *Modern Molecular Photochemistry*, Benjamin–Cummings, Menlo Park, CA, 1978.
[21] D. Rehm and A. Weller, *Isr. J. Chem., 8* (1970) 259.
[22] H. Siegerman, in N.L. Weinberg (ed.), *Techniques of Chemistry*, Vol. 5, Wiley, New York, 1975, Part II.
[23] M.A. Fox and M. Chanon (eds.), *Photoinduced Electron Transfer*, Elsevier, Amsterdam, 1988.
[24] A. Samanta, K. Bhattacharyya, P.K. Das, P.V. Kamat, D. Weir and G.L. Hug, *J. Phys. Chem., 93* (1989) 3651.
[25] A.A. Gorman, I.R. Gould and I. Hamblett, *J. Am. Chem. Soc., 103* (1981) 4553.
[26] T. Shida, *Electronic Absorption Spectra of Radical Ions*, Elsevier, New York, 1988, p. 211.