ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 137 (2000) 125–129

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Effect of excitation energy on the photochemical reaction of 2-(bromomethyl)naphthalene in solution

Sadayuki Watanabe, Mika Nagano, Tadashi Suzuki, Teijiro Ichimura*

Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro-ku, Tokyo 152-8551, Japan

Received 30 May 2000; received in revised form 9 August 2000; accepted 31 August 2000

Abstract

The photochemical reaction of 2-(bromomethyl)naphthalene (2-BMN) in acetonitrile solution was studied with nanosecond laser flash photolysis. There appeared two peaks at 380 and 415 nm in the transient absorption spectrum obtained at a 248 nm excitation, while a 308 nm excitation gave only one peak (380 nm), which is due to naphthylmethyl radical. The absorption at 415 nm is attributed to the T–T absorption of 2-BMN by means of triplet photosensitization with benzophenone. The excitation energy effect on the reaction reveals the different relaxation and reaction dynamics of the S_1 and S_2 states, which are discussed in terms of a dissociative and non-dissociative triplet state. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: 2-(Bromomethyl)naphthalene; Excitation energy effect; Transient absorption

1. Introduction

Photoexcitation of haloaromatic compounds is known to give rise to carbon–halogen (C–X) bond dissociation generating the aryl radical and a halogen atom. The radical is considered to be important on organic chemical synthesis. The dynamics of the dissociation processes has been extensively studied with flash photolytic techniques, ultrafast spectroscopy, mass spectroscopy, and magnetic resonance spectroscopy [1–5].

Photoexcited halomethylnaphthalene is also known to produce naphthylmethyl radical. Hilinski et al. [1] reported on the photodissociation of 1- and 2-(halomethyl)naphthalenes in room-temperature hexane solutions studied by means of picosecond emission and absorption spectroscopy. Emission spectra resulting from 1- and 2-naphthylmethyl radicals were observed with the 355 nm laser excitation. A broad absorption was observed for the 1-naphthylmethyl radical with a maximum near 365 nm and for the 2-naphthylmethyl radical with a maximum near 380 nm. Excitation of the (halomethyl)naphthalene at 266 or 299 nm into the $S_2(\pi,\pi^*)$ state results in dissipation through two channels: (1) internal conversion to the $S_1(\pi,\pi^*)$ state followed by fluorescence and (2) intersystem crossing (ISC) to an upper triplet state which is itself, or crosses to, a dissociative (σ,σ^*) triplet state that leads to homolysis of C–X bond.

Kawai et al. [2] measured the time resolved ESR spectrum of 1-naphthylmethyl radical produced by 1-(chloromethyl)naphthalene (1-CMN) with 308 nm excitation. They proposed the following photodissociation mechanisms of 1-CMN:

1. Upon the excitation into the S_1 state, the main dissociation channel opens in the triplet state.
2. Direct evidence for the dissociation from the triplet state was obtained by the sensitization.
3. Low vibrational levels in the T_1 state dissociate.

Slocum and Schuster [3] reported on the photolyzes of 1-CMN and 1-(bromomethyl)naphthalene (1-BMN) with 266 nm excitation. They observed similar transient absorption bands at 422 and 426 nm, both of which were assigned to T–T absorption based on triplet quenching experiments with tetramethyldiazetidine dioxide. Tokumura et al. [4] reported on the photolysis of 2-(chloromethyl)naphthalene (2-CMN) with 248 nm excitation by means of transient absorption spectroscopy. This spectrum had two peaks at 380 and 415 nm. On the other hand, Weir et al. [5] also measured the spectrum with 308 nm excitation. The transient absorption spectrum had only one peak at around 380 nm. There is a discrepancy between these spectra. The reaction mechanism was not clearly understood.

There would be the effect of excitation energy on reaction and relaxation processes of 2-(halomethyl)naphthalene,

---

* Corresponding author.
E-mail address: tichimur@chem.titech.ac.jp (T. Ichimura).

PII: S1010-6030(00)00368-3

which are different from 1-(halomethyl)naphthalene. In this work, in order to elucidate the effect of excitation energy on the reaction and relaxation processes of 2-BMN, we carried out nanosecond laser photolysis at 308 and 248 nm as well as triplet photosensitization by benzophenone.

2. Experimental

Transient absorption spectra were measured with a conventional laser flash photolysis system consisting of a XeCl excimer laser (Lumonics TE-860-4; 308 nm, 110 mJ/pulse, 10 ns pulse duration) or a KrF excimer laser (COMPex 102; 248 nm, 350 mJ/pulse, 50 ns pulse duration) and a steady-state Xe lamp (Ushio UXL-300DO; 300 W) as a monitoring light source. The monitoring light was passed through a monochromator (Nikon P-250) and was detected with a photomultiplier tube (Hamamatsu R928). The transient signals were fed to a digital oscilloscope (Sony Tektronix TDS380P; 2 GS/s) and analyzed by computer. The signals were averaged over 100 laser shots. The sample solution was flowed through a cuvette of 40 mm optical path length in order to remove the influence of photoproduct. Absorption spectra were measured with a double beam spectrometer (Jasco Ubest V-550).

2-BMN (Aldrich, GR grade) was used from a freshly opened bottle. Benzophenone (Tokyo Kasei, GR grade) was recrystallized from methanol. Acetonitrile (Kanto Chemical, GR grade) was used without further purification. All samples were deaerated by bubbling with Ar gas (purity 99.95%) that was saturated by acetonitrile vapor for half-an-hour before use. All measurements were carried out at room temperature.

3. Results and discussion

Figs. 1a and 2a show transient absorption spectra of 2-BMN in acetonitrile with laser excitation wavelength

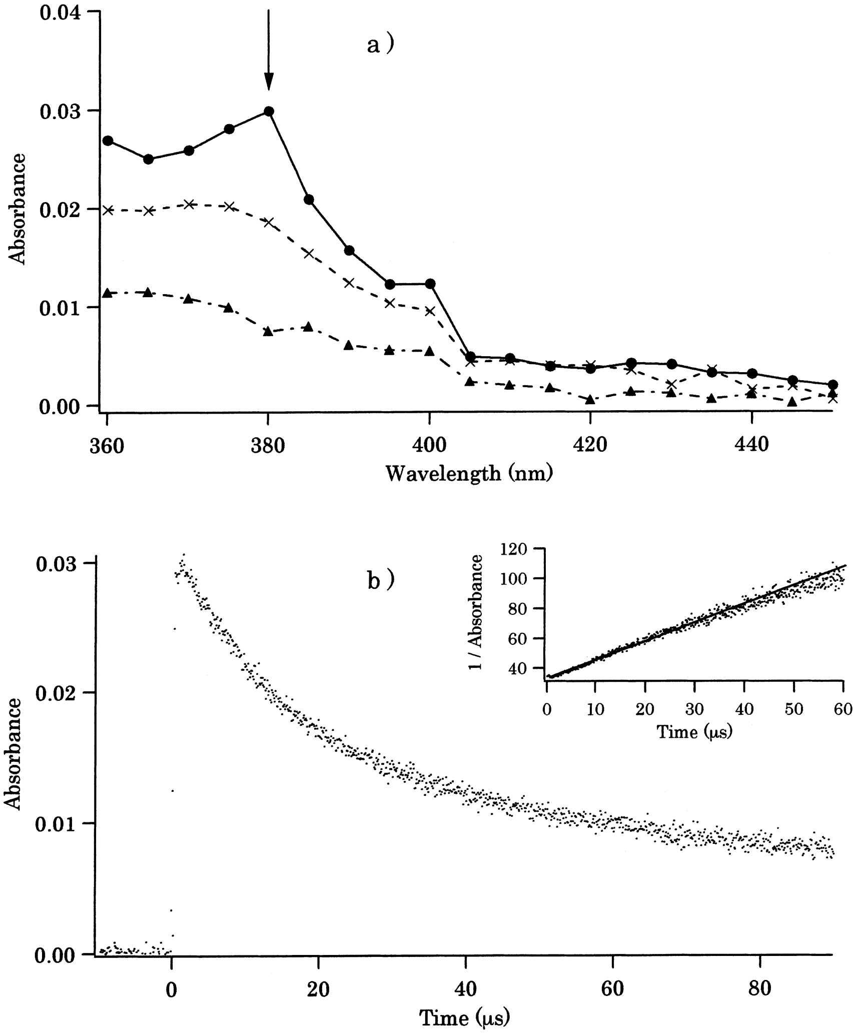

Fig. 1. (a) Transient absorption spectra of 2-BMN in acetonitrile at 1.5 μs (●), 16.1 μs (×) and 89.9 μs (▲), after the 308 nm excitation. The peak is observed at 380 nm. (b) The time profile of the absorption monitored at 380 nm. The reciprocal plots of the absorbance against time are shown in the inset.

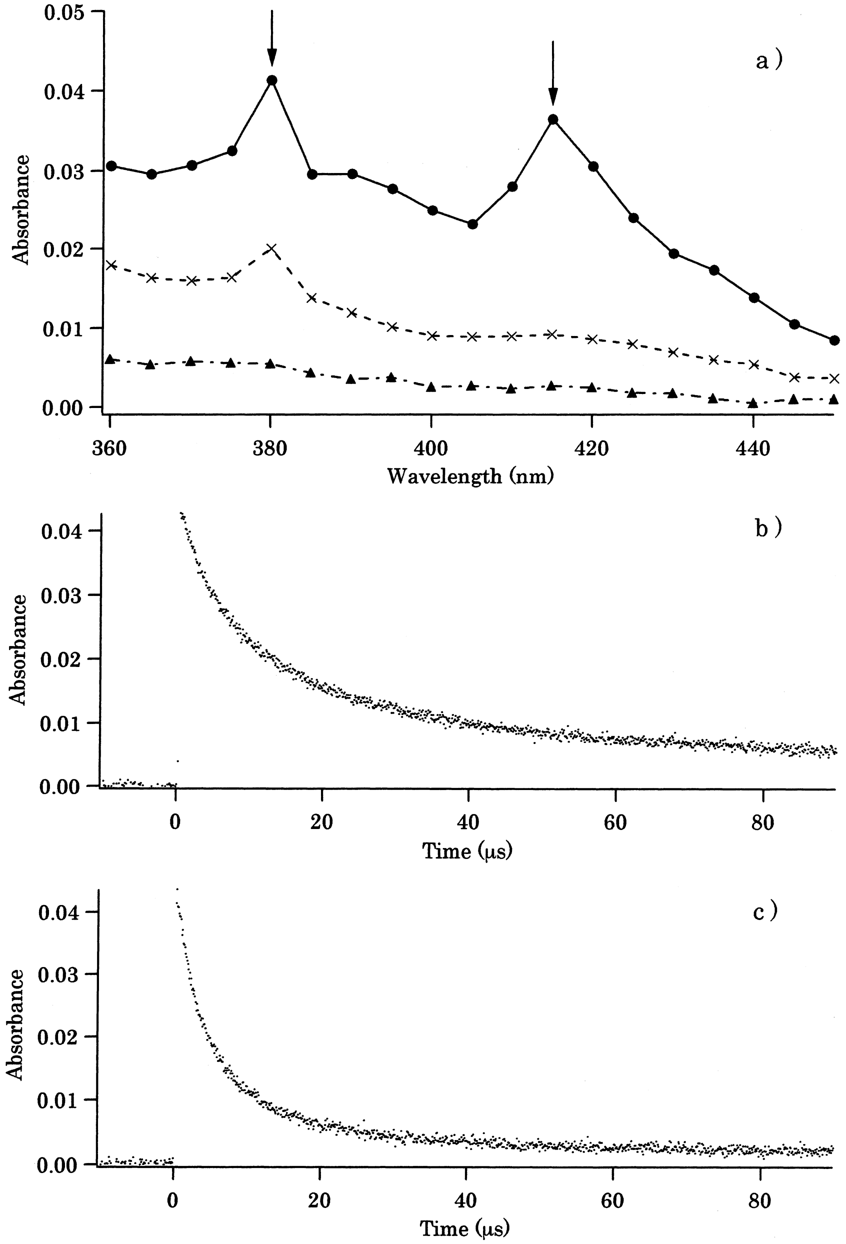

Fig. 2. (a) Transient absorption spectra of 2-BMN in acetonitrile at 1.0 μs (●), 13.1 μs (×) and 89.9 μs (▲), after the 248 nm excitation. Two peaks are observed at 380 and 415 nm. The time profiles of the absorption were monitored at (b) 380 and (c) 415 nm.

of 308 and 248 nm, respectively. The structured band at around 380 nm appeared immediately after the laser excitation, and decayed with a second-order rate (described below). The spectral feature was identical with that reported for 2-naphthylmetyl radical, which was produced by the photolysis of 2-CMN [5].

The inset of Fig. 1b shows plots of reciprocal absorbance against time. The plots were well fitted with the least squares' method, and the slope was determined to be $1.3 \times 10^{6}\,s^{-1}$. Therefore, naphthylmethyl radical will dissipate with a bimolecular reaction. The reaction rate constant was estimated to be $6.5 \times 10^{9}\,M^{-1}\,s^{-1}$ with an extinction coefficient of $5000 \pm 300\,M^{-1}\,cm^{-1}$ at 380 nm [6].

When 2-BMN was excited at 248 nm, another absorption peak was observed at 415 nm in the transient spectra (Fig. 2c). 1-BMN was reported to have a T–T absorption band at 426 nm [3]. In the case of 2-CMN, transient absorption observed at 415 nm was postulated to be a T–T absorption [4]. Triplet photosensitization with benzophenone was carried out in order to determine the T–T absorption spectrum of 2-BMN. Fig. 3 shows the time profile of the transient absorption spectra of a mixture of benzophenone and 2-BMN excited at 308 nm and monitored at (a) 525 or (b) 415 nm. The decay at 525 nm is mainly due to the T–T absorption of benzophenone [7], while that at 415 nm is due to not only to triplet benzophenone but also to triplet 2-BMN.

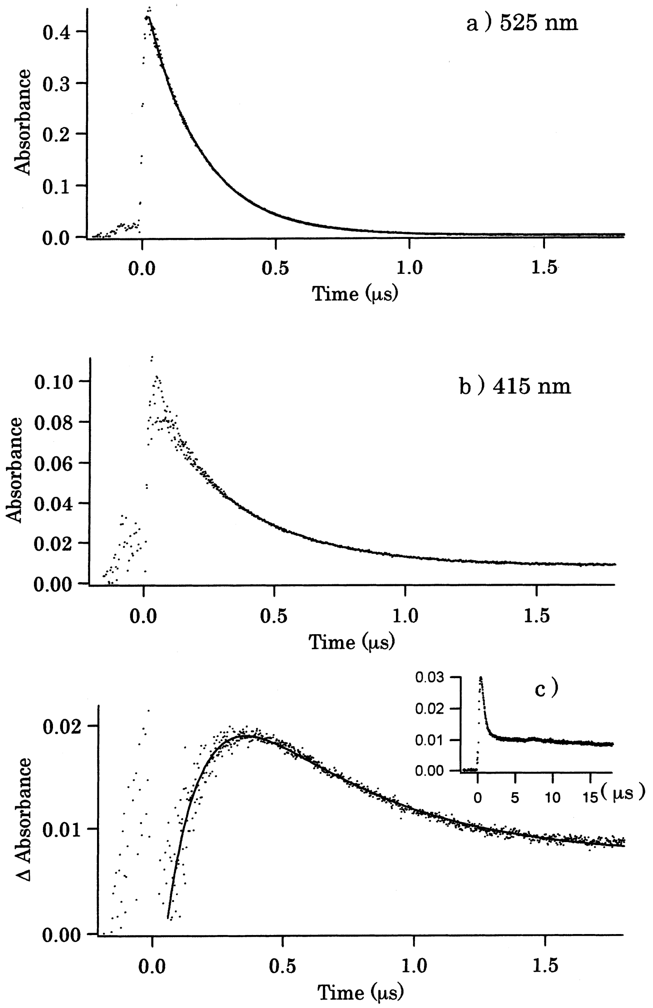

Fig. 3. Time profiles of transient absorption of 2-BMN and benzophenone monitored at (a) 525 and (b) 415 nm. (c) Time profile of only triplet 2-BMN, which was obtained by subtracting appropriate proportion of absorption at 525 nm from one of 415 nm. The inset shows longer time region.

The influence of the direct excitation of 2-BMN on the absorption at 415 nm should be ignored because the concentration of 2-BMN was quite low (0.18 mM). Therefore, the time profile of triplet 2-BMN may be obtained by removing contribution of the T–T absorption of benzophenone at the observed wavelength of 415 nm. Fig. 3c shows the absorption time profile of triplet 2-BMN, which was obtained by subtracting on appropriate proportion of the absorption at 525 nm from that at 415 nm. The time profile shows rise and decay components. Furthermore, some residual portion was observed in longer time window (the inset of Fig. 3c). Kawai et al. [2] reported the production of 1-naphthylmethyl radical with the triplet benzophenone sensitization method by detecting the ESR signal. In general the dissociative T_m state of not only 1-(halomethyl)naphthalene but also 2-(halomethyl)naphthalene should lie near the T_1 state [1]. The residual one observed in the absorption time profile should result from 2-naphthylmethyl radical, formed via the triplet 2-BMN, which should be produced by sensitization of the triplet benzophenone. The risetime of the absorption agreed well with the lifetime of triplet benzophenone. Consequently, the absorption band appearing at 415 nm with 248 nm excitation results from the T–T absorption of 2-BMN. The result agrees with the earlier report at the T–T absorption of 2-CMN [4]. It reveals that the reaction and relaxation processes are affected by the excitation energy. The decay time was estimated to be several microsecond, which agrees within experimental error to the value of 4.3 μs observed when only 2-BMN was excited at 248 nm.

The question arises why the T–T absorption can be observed only upon excitation with the 248 nm laser. 2-BMN that is formed a vibrationally excited $S_1(\pi,\pi^*)$ state by the 308-nm laser pulse fluoresces, relaxes to the ground state through internal conversion, or undergoes ISC to the dissociative $T_m(\sigma,\sigma^*)$ state to yield a 2-naphthylmethyl radical rapidly. On the other hand, with the 248 nm excitation, 2-BMN reaches a vibrationally excited $S_2(\pi,\pi^*)$ state.

Hilinski et al. [1] proposed the following relaxation mechanism for many (halomethyl)naphthalenes. The excited molecule in the $S_1(\pi,\pi^*)$ state returns to the S_0 state by internal conversion or undergoes ISC to the $T_1(\pi,\pi^*)$ state. The T_1 state crosses to the dissociative $T_m(\sigma,\sigma^*)$ state that leads to homolysis of C–X bond. In the case of excitation to the $S_2(\pi,\pi^*)$ state with the 266-nm light, some molecules relax to the S_1 state followed by fluorescence, others undergo ISC to an upper dissociative $T'_m(\sigma,\sigma^*)$ state, also inducing the C–X bond dissociation. Therefore, the efficiency of the dissociation reaction should be larger for the 266 nm than the 308 nm excitation.

However, observation of the T–T absorption in this study suggests the formation of 2-BMN in the T_1 state upon 248 nm excitation. Furthermore, a quantitative array of radical formation was carried out with naphthalene as a standard for laser intensity. The yield of 2-naphthylmethyl radical by 248 nm excitation was surprisingly less by approximately 30% than that of 308 nm excitation, as determined by comparing the naphthylmethyl radical absorption monitored at 380 nm with the triplet naphthalene absorption monitored at 420 nm. This fact will also explain the effect of excitation energy on relaxation process of 2-BMN in the triplet manifolds. As described in a previous paragraph, the 266 nm excitation should produce 2-BMN in a low vibrationally excited S_2 state, which gives rise to the dissociative T'_m state [1]. The 248 nm excitation, however, provides a higher vibrationally excited S_2 state that undergoes ISC to an upper T_n state. The energy level of the T_n state should be higher than that of T'_m. The T_n state should transfer to the metastable $T_1(\pi,\pi^*)$ state in competition with dissociation. This mechanism is illustrated in Fig. 4.

Application of photothermal techniques to the present study is now underway. The photothermal techniques are powerful for studying not only non-radiative processes but also reaction processes. The information on reaction

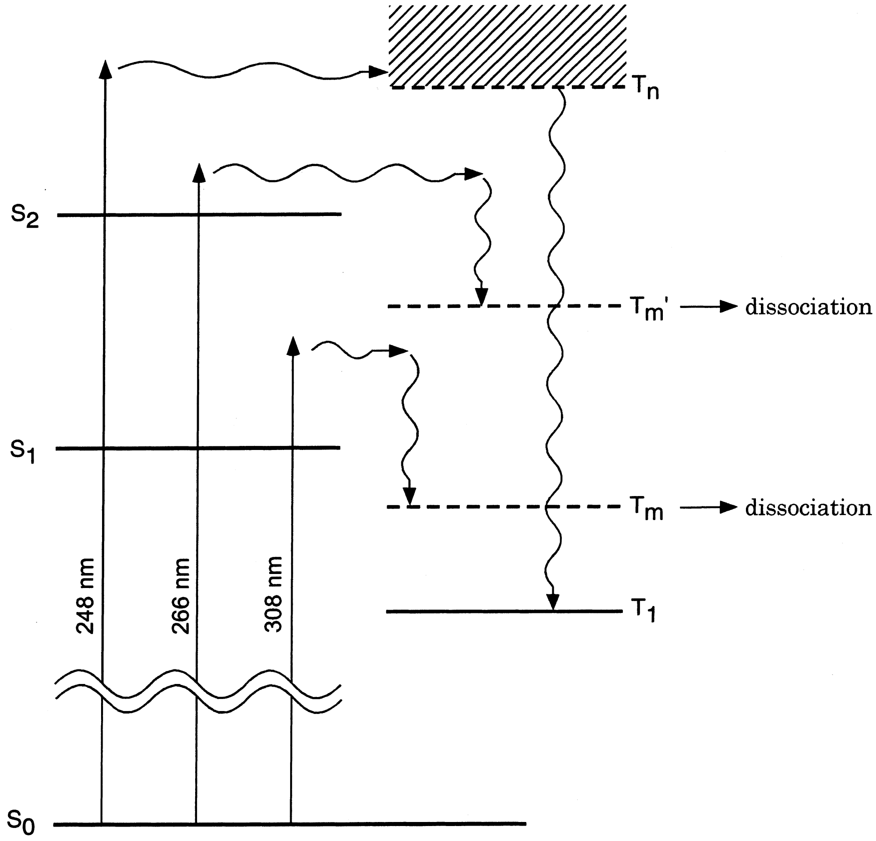

Fig. 4. A schematic diagram for reaction processes of 2-BMN after laser excitations at 308 nm (32 500 cm^{-1}), 266 nm (37 600 cm^{-1}) and 248 nm (40 300 cm^{-1}). The energies for T_1, S_1 and S_2 states are 21 300, 30 800 and 35 000 cm^{-1}, respectively. Energy levels for T_m, T'_m and T_n state are tentatively drawn. See text for detail.

quantum yield and energetics of the reaction state will be obtained.

4. Summary

We measured transient absorption spectra of 2-BMN with 308 and 248 nm excitation. With the 248 nm excitation, the T–T absorption of 2-BMN was observed at 415 nm, while it could not be observed by the 308 nm excitation. 2-BMN excited into the $S_1(\pi,\pi^*)$ state by 308 nm laser pulse undergoes ISC rapidly to the dissociative $T_m(\sigma,\sigma^*)$ state to yield 2-naphthylmethyl radical. On the other hand, 248 nm excitation is found to provide a higher vibrationally excited $S_2(\pi,\pi^*)$ state that undergoes ISC to an upper T_n state. The T_n state is transferred to the metastable $T_1(\pi,\pi^*)$ state in competition with the dissociation yielding the radical.

References

[1] E.F. Hilinski, D. Huppert, D.F. Kelley, S.V. Milton, P.M. Rentzepis, J. Am. Chem. Soc. 106 (1984) 1951.
[2] A. Kawai, T. Okutsu, K. Obi, Chem. Phys. Lett. 174 (1990) 213.
[3] G.H. Slocum, G.B. Schuster, J. Org. Chem. 49 (1984) 2177.
[4] K. Tokumura, M. Udagawa, M. Itoh, Phys. Org. Chem. 31 (1986) 79.
[5] D. Weir, L.J. Johnston, J.C. Scaiano, J. Phys. Chem. 92 (1988) 1742.
[6] M. Yamaji, Gunma University, private communication.
[7] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, 2nd Edition, Marcel Dekker, New York, 1993.