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Laser flash photolysis of 1,8-bis(halomethyl)naphthalenes

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Abstract

Transient absorption spectra were observed by the laser flash photolysis of 1,8-bis(halomethyl)naphthalenes for Cl and Br substituents. In the case of 1,8-bis(chloromethyl)naphthalene, the main transient absorption bands at 340 and 365 nm were attributed to the carbon-centred radical which was formed by bond fission of one of two C–Cl bonds. In the case of the dibromo derivative, the transient bands appeared at 435 and 350 nm. The 350 nm band was assigned to the carbon-centred radical. Because of the low reactivity to O_2 and triplet quenchers, the main transient absorption band appearing at 435 nm was attributed to the rearranged radicals. The radical structures were based on molecular orbital calculation.

Keywords: Laser flash photolysis; 1,8-Bis(halomethyl)naphthalenes; Free radicals; Photodissociation

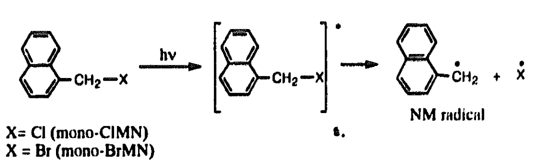
1. Introduction

Many photochemical reactions have been conducted with halomethylaromatics in order to study the energy dissipation of photochemical processes because they are good sources for the stable benzyl-type radicals when photolysed in non-polar media. Transient spectroscopic methods such as laser flash photolysis have often been employed to confirm the precursors of such radicals [1–7]. However, the halomethylaromatic compounds intensively studied so far are mostly monosubstituted derivatives. In non-polar solvents, both 1-(chloromethyl)naphthalene (mono-ClMN) and 1-(bromomethyl)naphthalene (mono-BrMN) are reported to yield naphthylmethyl (NM) radical as shown in Scheme 1 [8,9]. The excited states responsible for the bond cleavage of C–Cl and C–Br have been suggested by various investigators [10–15]; with the wavelength of the photolysis light, the excited states change from the triplet state to the singlet state.

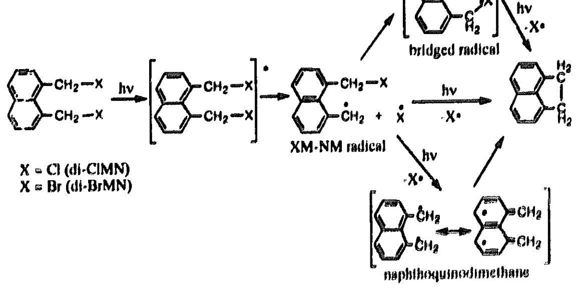
In previous papers, we have reported that acenaphthene was efficiently formed from 1,8-bis(halomethyl)-naphthalenes by laser photolysis as shown in Scheme 2 [16–18]. The yield of acenaphthene varied with the wavelength and fluence of the laser light. In general, the bromo derivative was more reactive than chloro derivatives. Such observations required of us direct observation of reaction intermediates such as carbon-centred radicals and the excited states.

In this study, we have reported the results of the laser flash photolysis of 1,8-bis(chloromethyl)naphthalene (di-ClMN) and 1,8-bis(bromomethyl)naphthalene (di-BrMN). In these cases, it is interesting that a bridged radical can participate in the reaction, which might change the characteristics of the intermediate radicals (Scheme 2). Another interest in this system is whether it is possible to observe an intermediate 1,8-naphthoquinodimethane or not [19–25].

In the present report, we have assigned the transient absorption bands of di-ClMN and di-BrMN in comparison with mono-ClMN and mono-BrMN on the basis of the reactivities of triplet quenchers. In addition, semiempirical molecular



Scheme 1.



Scheme 2.

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orbital (MO) calculations were performed in order to support the interpretation of the experimental results.

2. Experimental details

2.1. Materials

Solvents used for the transient absorption measurements were of spectroscopic grade. 1,8-bis(halomethyl)-naphthalenes were prepared from 1,8-bis(hydroxymethyl)-naphthalene by treatment with concentrated HBr or HCl at room temperature. They were used for laser flash photolysis experiments after recrystallization from benzene-hexane. 1-(halomethyl)naphthalenes were purchased from Aldrich.

2.2. Apparatus

Laser flash photolysis apparatus was a standard design with an Nd:YAG laser having pulses of ca. 6 ns duration [26–28]. The solution was photolysed with FHG light (266 nm). The time profiles were followed by a photomultiplier system in the visible region. Transient spectra were recorded with a multichannel photodiode system. The laser photolysis was performed for the solution in a rectangular quartz cell with a 10 mm optical path. The monitoring light was selected with band-path filters. Deoxygenation of the solution was performed by Ar bubbling and the O_2-saturated solution was prepared by O_2 bubbling. All the measurements were carried out at 23 °C.

2.3. Molecular orbital calculation

The MO calculations were performed with PM3 and MNDO methods using MOPAC '93.

3. Results and discussion

3.1. Assignment of transient species

The transient spectra observed by the laser flash photolysis of mono-ClMN in degassed cyclohexane with 266 nm light are shown in Fig. 1. The main transient absorption bands appeared at 345 and 360 nm with a weak broad band in the 400–450 nm region. These absorption bands decayed relatively slowly in degassed solution, while the decay rates were accelerated on addition of air. The decay at 360 nm is also shown in the figure; since a similar time profile was observed for 345 nm, both of the bands were assigned to the same species.

In Fig. 2, the time profile of the rise and decay of mono-ClMN at 360 nm and 420 nm is shown in the presence of triplet quenchers. On addition of *trans*-piperylene (triplet energy E_{T1} = 59.2 kcal mol^{-1} [29]), the decays of the 365 nm and 420 nm bands were not accelerated, while the 420 nm band decayed rapidly in the presence of ferrocene (E_{T1} = 42.8 kcal mol^{-1} [30]). Thus, the absorption band at 345 nm was attributed to the carbon-centred radical, i.e. NM radical. On the contrary, the band at 420 nm was ascribed to the triplet state, whose E_{T1} is between 43 and 59 kcal mol^{-1}; the value is consistent with the reported E_{T1} = 59.6 kcal mol^{-1} of 1-methylnaphthalene [29]. These assignments are in good accord with previous reports [10–13]. The observed lifetime of the triplet state (0.5–0.7 μs) was also similar to that reported previously [11,12].

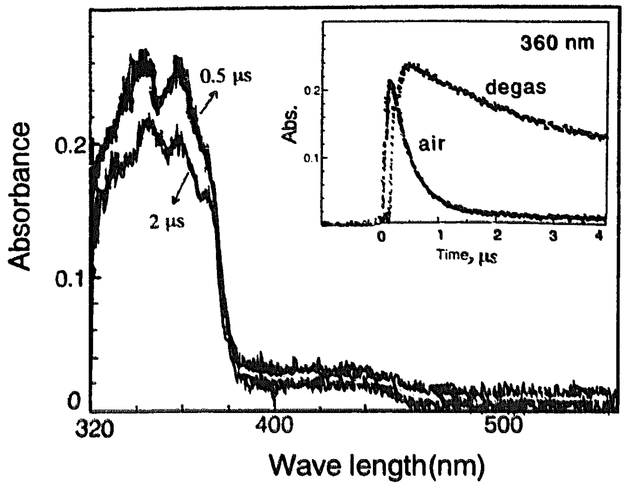

Fig. 1. Transient absorption spectra observed after laser photolysis of mono-ClMN (1 mM) with 266 nm light in degassed cyclohexane. Decay profiles at 360 nm in the absence and presence of O_2 (2.1 mM) are also shown.

In the absence of the triplet quenchers (Fig. 2), the rise of NM radical was completed before the consumption of the triplet state at the 420 nm band. This finding suggests that the NM radical was not always formed through the triplet state of mono-ClMN. This is in agreement with the conclusion derived by Slocum and Schuster who concluded that some of the photocleavage occurs from the excited singlet state [10].

In the time profile at 360 nm band (Fig. 1), a rapid rise and decay were observed for air-saturated solution

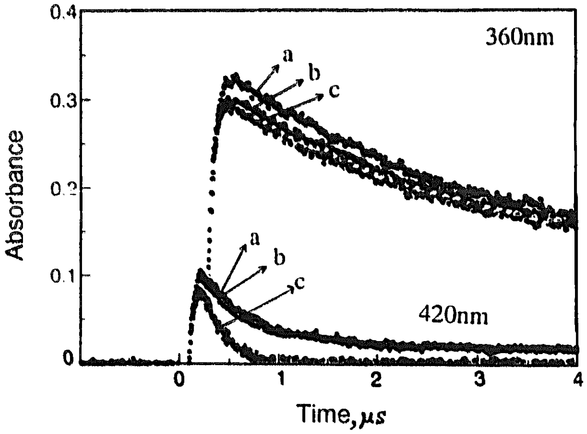

Fig. 2. Time profiles at 360 and 420 nm obtained from mono-ClMN in degassed solution in the absence of triplet quencher (curves a) and in the presence of *trans*-piperylene (0.5 mM) (curves b) and ferrocene (0.5 mM) (curves c).

($[O_2]=2.1$ mM) [29]. From the decay the reaction rate constant $k(O_2)$ of NM radical with O_2 was evaluated to be 3.7×10^9 M^{-1} s^{-1}. This value is similar to that reported for carbon-centred radicals such as the benzyl radical [31].

In the time profiles of the NM radical in Fig. 2, there is a time lag (0.5 μs) between the trigger time of the laser pulse and the time at which the NM radical concentration reaches a maximum, while the time lag of the triplet state is short (0.25 μs). On addition of O_2, however, the time lag of the NM radical becomes small as seen in Fig. 1. At the present time, the reason why the long time lag is observed only for the NM radical in deoxygenated solution is not clear; such a time lag is not always observed in time profiles of the later figures as shown subsequently. It may be necessary to exclude the effect of the fluorescence or scattered light on the time profiles immediately after the laser pulse.

Transient absorption spectra observed by the laser photolysis of di-ClMN in degassed cyclohexane are shown in Fig. 3. The transient absorption bands that appeared at 370 and 340 nm seemed to decay on the same time scale, suggesting the same species. These bands decayed rapidly on the addition of air to the solution; the decay at 340 nm is also shown in Fig. 3. On the contrary, neither of the decay rates was accelerated on addition of triplet quenchers such as ferrocene and piperylene. Therefore, both of the transient absorption bands at 370 and 340 nm were assigned to the carbon-centred radical (ClM–NM radical in Scheme 2). Since the reactivity of the ClM–NM radical to O_2 is similar to that of the NM radical as listed in Table 1, the radical centre may not interact with the remaining Cl atom.

We can also exclude the possibility of assigning these transient bands to 1,8-naphthoquinodimethane, which is reported to exhibit a strong absorption band at 340 nm and a weak band at 500 nm [32], because the lifetime of 1,8-naphthoquinodimethane is ca. 100 μs which is longer than the observed lifetime (7 μs) from the time profile in Fig. 3. The absorption band of Cl_2 (330 nm with $\epsilon=60$ M^{-1} cm^{-1} [33]) is in the same region as the observed transient bands; however, ϵ of the Cl_2 band at 330 nm may be too small to be observed from the transient absorption spectra.

In the case of mono-BrMN (Fig. 4), the main transient absorption band appeared in the long wavelength region (at 440 nm) accompanied by a band at 360 nm. The decay rate of the 360 nm band was lower than that of the 440 nm band in degassed solution. A rapid rise and decay of the 360 nm band was also observed in air-saturated photolysis, similar to that of mono-ClMN. Furthermore, on addition of O_2 to the solution, both of the bands exhibited two decay components. One component decayed rapidly for both the bands on addition of O_2, while the other remained unchanged as shown in the time profiles of Fig. 4.

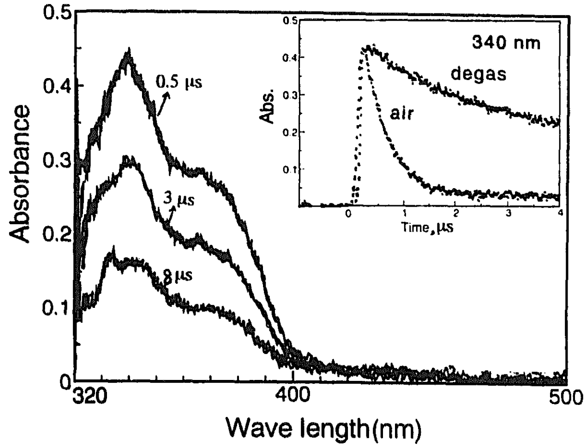

Fig. 3. Transient absorption spectra observed after laser photolysis of di-ClMN (1 mM) with 266 nm light in degassed cyclohexane. Decay profiles at 340 nm in the absence and presence of O_2 (2.1 mM) are also shown.

Table 1
Reaction rate constants k [a] for the reactions with radical quencher and triplet state quenchers in cyclohexane

Compound	λ_{max} (nm)	$k(O_2)$ [b] (M^{-1} s^{-1})	k(1,3-CHD) [c] (M^{-1} s^{-1})
Mono-ClMN	360	3.7×10^9	No reaction
Di-ClMN	340	3.0×10^9	No reaction
Mono-BrMN	360	2.9×10^9	No reaction
	440	1.7×10^9	2.0×10^9
Di-BrMN	350	0.7×10^9	No reaction
	435	No reaction	No reaction

[a] Each value may contain the experimental error of ± 15%.
[b] Diffusion-controlled rate constant k_d in cyclohexane is calculated to be 5.6×10^9 M^{-1} s^{-1}.
[c] 1,3-Cyclohexadiene.

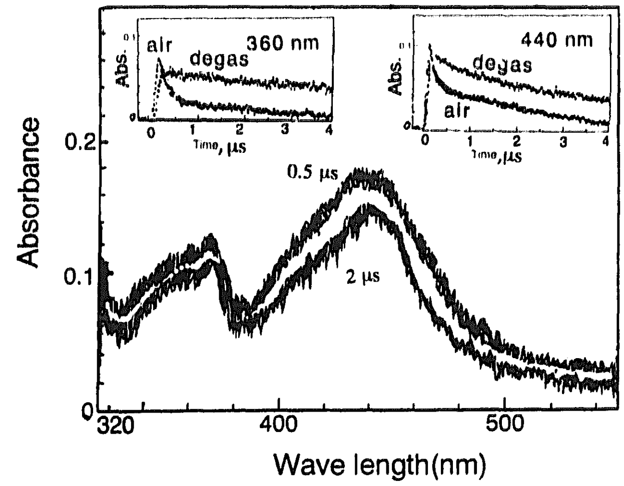

Fig. 4. Transient absorption spectra observed after laser photolysis of mono-BrMN (1 mM) with 266 nm light in degassed cyclohexane. Decay profiles at 360 and 440 nm in the absence and presence of O_2 (2.1 mM) are also shown.

On the addition of triplet quenchers such as ferrocene and *trans*-piperylene, acceleration of the decay rate was observed for the rapidly decaying parts of the 440 nm band. In Fig. 5, absorption of the rapidly decaying part is shown in spectrum a, which was evaluated by subtracting spectrum b obtained in O_2-saturated solution from the spectrum obtained in degassed solution (Fig. 4). Although both bands of spectrum

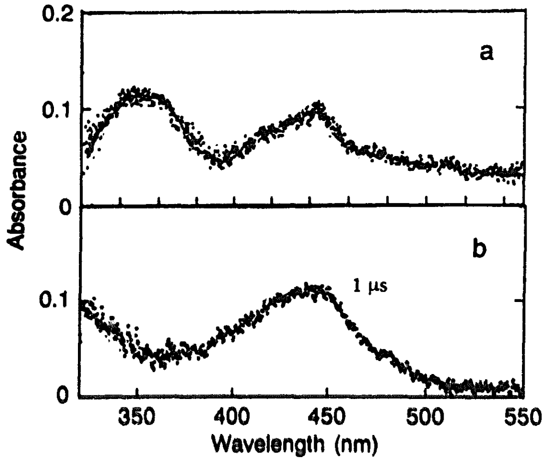

Fig. 5. Transient spectrum of the fast decay species of mono-BrMN (spectrum a) obtained by subtracting the transient spectrum of mono-BrMN obtained in O_2-saturated solution (at 1 μs after laser pulse) (spectrum b) from the total spectrum in Fig. 4 (at 0.5 μs after laser pulse).

a were O_2 sensitive, only the band at 440 nm is quenched by a triplet quencher such as 1,3-cyclohexadiene, whose E_{T1} is 49 kcal mol^{-1} [29]. Thus, this band is attributed to the triplet state of mono-BrMN. The transient band at 360 nm can be ascribed to the carbon-centred radical (NM radical) because it was reactive only to O_2. These assignments are consistent with that of mono-ClMN; the band shape of Fig. 4 at 360 nm is also similar to that of Fig. 1. Compared with mono-ClMN, an increase in the ratio of the triplet state to the radical of mono-BrMN is due to the acceleration of intersystem crossing by a heavy atom effect.

In spectrum b in Fig. 5, the band at 440 nm is broader than that of the rapidly decaying part, although the absorption peak is, by accident, similar. The slowly decaying part can be attributed neither to the usual carbon-centred radical nor to the triplet state, because of the low reactivity to O_2. One possible assignment of spectrum b is to Br_2, which has absorption maximum at 420 nm ($\epsilon = 200$ M^{-1} cm^{-1} [33]); since Br_2 is stable in solution, the observed slow decay may be attributed to the reaction of Br_2 with radical species such as the carbon-centred radical. Another possible assignment of spectrum b is to a charge transfer band between a Br atom and starting mono-BrMN [34,35].

In the case of di-BrMN, similar transient absorption spectra to those of mono-BrMN were observed as shown in Fig. 6, although the band at 435 nm became broader than that from mono-BrMN. A weak absorption band also appeared at 350 nm, which is attributed to the carbon-centred radical (BrM–NM radical) from the similarity of the absorption peak to that of the NM radical. Because of the low reactivity to O_2 as shown in Table 1, approach of O_2 to the carbon-radical centre may be sterically hindered by neighbouring Br atom.

The species responsible for the main band at 435 nm was not sensitive to O_2, suggesting that most of the absorptions could not be ascribed to either the triplet state or the normal carbon-centred radical. Triplet quenchers such as ferrocene, piperylene and 1,3-cyclohexadiene also did not affect the decay curve at the 435 nm band. A possibility for the assignment of the peak is a Br-bridged radical (in Scheme 2). If the distribution of the unpaired electron is different from that of the carbon-centred radicals such as the NM radical, it is conceivable that radicals exist with low reactivity to O_2. As another possible assignment, subsequent rearrangement may occur from the bridged radical. In the broad absorption in the region 350–500 nm, Br_2 may also be involved similarly to mono-BrMN.

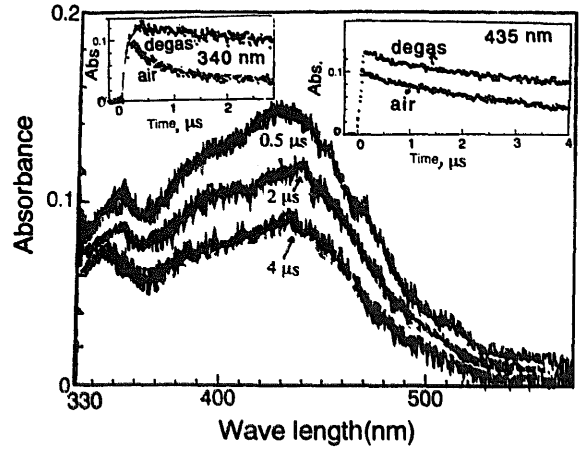

Fig. 6. Transient absorption spectra observed after laser photolysis of di-BrMN (1 mM) with 266 nm light in degassed cyclohexane. Decay profiles at 350 and 435 nm in the absence and presence of O_2 (2.1 mM) are also shown.

3.2. Molecular orbital calculation

In order to confirm the assignments of the transient absorption bands of the XM–NM radical described above, MO calculations were performed. The distribution of the unpaired electron densities of SOMO is illustrated in Fig. 7 with the heat of formation. When the geometry optimization was started from the non-bridged radicals, they converged to non-interacting radicals, in which the unpaired electron was mainly localized on the p_y orbital of the 1-methyl carbon atom, which is perpendicular to the naphthalene ring P_z plane. Such rotation had steric causes only, not electronic.

On the contrary, when we started from the symmetric bridged radicals, the optimized geometry converged to interacting open radicals, in which the halogen atom approached the 1-methyl carbon atom some electronic reasons, when the MNDO method was employed. For the ClM–NM radical, the interacting open structure is slightly more stable than the non-interacting open structure. On the contrary, the opposite tendency was found for BrM–NM radical; the probability of formation of a Br-bridged radical becomes low.

Halogen-substituted acenaphthene radicals were suggested by the PM3 method. In the case of the Cl-substituted acenapththene radical, the unpaired electron delocalizes on the π orbitals of the naphthalene skeleton. In the case of the Br derivative, the unpaired π electron localizes much on the Br

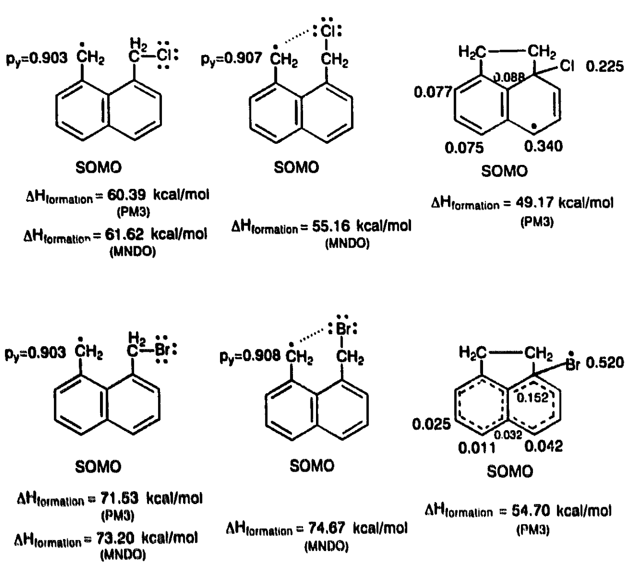

Fig. 7. Unpaired π electron density of SOMO and heat of formation for ClM–NM and BrM–NM radicals which are optimized by MO methods; p_y is in plane.

atom. Such a BrM–NM radical would be reasonably expected to be less reactive to O_2. In the rearranged radical, the calculated bond order of C–Br was 0.65, indicating that the C–Br bond is not weak, not like the normal charge transfer complex (π complex). This is in accord with our previous experimental results which showed clearly that the reaction producing acenaphthene proceeded by the two-photon-process.

4. Summary

Carbon-centred radicals, which exhibited O_2-sensitive absorption bands in the region 330–370 nm, were produced by the photolysis of four halomethylnaphthalenes examined in this study. In the case of the carbon-centred radicals from 1,8-bis(halomethyl)naphthalenes, the structure and reactivity were different for Cl and Br atoms. For the BrM–NM radical, the neighbouring Br atom may hinder the reactivity of the carbon-centred radical. The O_2-insensitive transient species produced from di-BrMN was attributed to rearranged radicals.

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