Time-delayed, Two-color Excimer Laser Photolysis of 1,8-Bis(halomethyl)naphthalenes[1]

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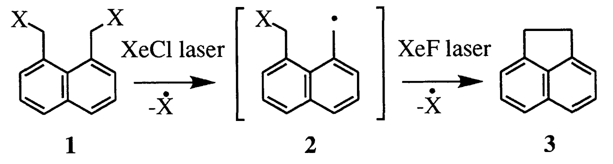
Time-delayed two-color photolysis of 1,8-bis(bromomethyl)naphthalene and 1,8-bis(chloromethyl)naphthalene was conducted by successive irradiation of XeCl (308 nm) and XeF (351 nm) excimer lasers. Increase in the yield of the two-photon product, acenaphthene, strongly depended on the delay time of the two lasers and showed two maxima at the delay times of 0-30 ns and 0.2-0.5 μs.

Stepwise multiphoton reactions often have a large drawback in the matching of the laser wavelength because the large shifts in the absorptions are often observed between starting material and its intermediates. When the laser wavelength is matched with the starting material the intermediates suffer from insufficient absorption of the laser light and *vice versa*. In order to solve such disadvantage, two-color irradiations were tentatively applied to the organic photochemistry;[2] the first wavelength is adjusted to match the absorption of the starting material and the second to that of the photochemically generated intermediate, thus optimizing the wavelength both to the starting material and its intermediates and increasing the efficiency of the two-photon reactions. However, not only the adjustment of the laser wavelength to the absorptions of the substrates and intermediates but also consideration on the time dependence of the concentration of such photochemical intermediates is important because maximum efficiency for the second photon absorption will be achieved if the second laser flashes at the time when the concentration of the intermediate is at its maximum.[3] Such applications in two-photon chemistry appear not to have been thoroughly studied so far.

We present here our results on the time dependence of the intermediate concentration in two-photon reactions conducted by time-delayed, two-color laser photolysis. Compounds 1,8-bis(bromomethyl)naphthalene (**1a**) and 1,8-bis(chloromethyl)naphthalene (**1b**)[4] have considerable absorption at 308 nm (ε for **1a**: 9500, for **1b**: 4800 dm^3·mol^{-1}·cm^{-1}), which corresponds to the excitation to the $S_1(\pi, \pi^*)$ state, but no absorption at 351nm. On the other hand, the intermediate naphthylmethyl radicals **2a**,**b** are expected to have strong absorption at 351 nm because the parent 1-naphthylmethyl radical (**I**), which has same conjugated π-electron system as that of **2**, have strong absorption bands at ca. 340 nm and 365 nm;[5] the red shift of the absorption bands by the additional alkyl substitution is estimated to be ca. 10 nm.[6] Thus, the intermediates **2a**,**b** are generated from **1a**,**b** by photolysis with the XeCl excimer laser (308 nm, 6.2 x 10^{20} photons·m^{-2}·pulse^{-1}, fwhm: 14 ns) and further excited with the XeF excimer laser (351 nm, 9.4 x 10^{20} photons·m^{-2}·pulse^{-1}, fwhm: 26 ns) to give the two-photon product acenaphthene (**3**) (Scheme 1). The photolyses of **1a**,**b** were conducted in cyclohexane (10^{-5} mol·dm^{-3}) by irradiation of three sets of laser pulses; a set of the laser pulses consisted of one pulse of XeCl laser and one subsequent pulse of XeF laser with varied delay times in the nanosecond to millisecond region.[7]



Scheme 1. **a**: X=Br ; **b**: X=Cl

Control experiment showed *no* disappearance of the starting materials **1a**,**b** by *one-color* photolysis by XeF laser. Moreover, consumption of **1a**,**b** in the two-color photolysis was independent of the delay times; the average consumption was 29% for **1a** and 91% for **1b**, which were the same as those of one-color laser photolysis by XeCl laser.[8] The results indicate that the extent of disappearance of starting material **1a**,**b** depends only on the XeCl laser irradiation and is not affected by the

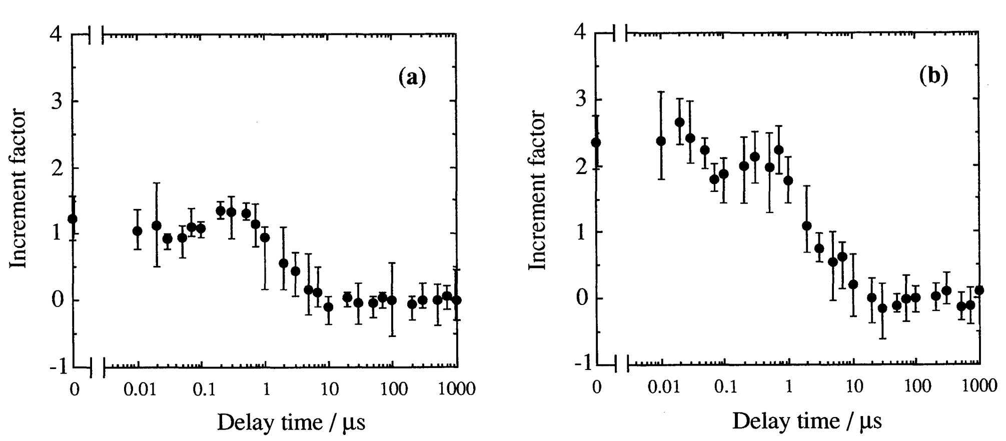


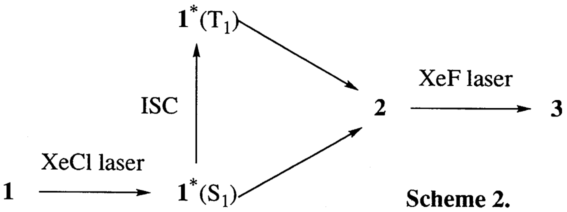
Figure 1. Increment factor for the yield of acenaphthene **3** as a function of delay time. (a) from **1a**, (b) from **1b**. The jitter between the two laser pulses is ±3 ns.

succeeding XeF laser irradiation. Another control experiment showed *no* decomposition of the two-photon product **3** by *one-color* irradiations of XeCl or XeF lasers.

Figures 1a,b show the increment factor on the formation of **3**, which is defined as (A-B)/B, where A is the yield of **3** obtained in the *two-color* photolysis and B is the yield of **3** obtained in the *one-color* XeCl laser photolysis. In these figures, the increment factor of zero means that **3** was formed only by the first XeCl laser pulse and no additional formation of **3** occurred by the subsequent XeF laser pulse; this is clear from the control experiments. Therefore, the increment factor over zero indicates additional formation of **3** by the photolysis of the intermediate **2** by the second XeF laser pulse. As seen in the figures, the increment factor, namely, the formation of **3**, strongly depends on the delay time and the highest factor obtained was 1.5 for **1a** and 2.7 for **1b**.

In the time domain of <14 ns delay time, which is within the pulsewidth of the first XeCl laser, the increment factor indicates the degree of enhancement in the second step of the reaction, *i.e.*, **2** → **3**. However, in the region of >14 ns delay time, the increment factor reflects the concentration of the intermediate **2** at each delay time since, in this time domain, **3** is only formed by the second XeF laser from the intermediate **2**. It is significant to note that the increment factor has two maxima for both **1a** and **1b**, the first maximum at 0-30 ns and the second at 0.2-0.5 μs. The existence of two maxima suggests the presence of at least two photochemical paths for the formation of **2**.

The second maximum can be explained in terms of the path through the long-lived T_1 state of **1**, *i.e.*, the path $\mathbf{1} \rightarrow \mathbf{1}^*(S_1) \rightarrow \mathbf{1}^*(T_1) \rightarrow \mathbf{2} \rightarrow \mathbf{3}$ in Scheme 2, since the delay time at the maximum is in good accord with the expected rise time of **2** through the T_1 state.[9] The occurrence of this reaction path is also supported by the fact that the second maximum is higher than the first for **1a**, whereas it is *vice versa* for **1b**. This is rationalized by the larger contribution of the T_1 state in the case of **1a** because of the higher efficiency in the intersystem crossing (ISC) $S_1 \rightarrow T_1$ promoted by the heavy atom effect of bromine.



Scheme 2.

In regard to the first maximum of the increment factor, which indicates that another path operates for the generation of the intermediate radical **2**. Figure 1 shows positive increment factors even at the delay time of *ca.* 0 ns. This implies very fast formation of **2**, most likely directly from the S_1 state of **1**, *i.e.*, the path $\mathbf{1} \rightarrow \mathbf{1}^*(S_1) \rightarrow \mathbf{2} \rightarrow \mathbf{3}$ in Scheme 2; the existence of such pathway has been proposed for 1-(halomethyl)naphthalenes (**II**),[5c] whose reactivity is expected to be similar to the initial reactivity of **1**. The minimum between the two maxima, however, might be due to the filter effect of $\mathbf{1}^*(T_1)$ for the second XeF laser because considerable decrease of **2** should not be expected in this time region.

The yield of **3** between 1 and 10 μs delay time followed a second-order decay. The result implies the decrease in the concentration of **2** by dimerization, analogous to the related naphthylmethyl radical (**I**), for which a second-order decay (dimerization) was reported.[5a] After a delay time of *ca.* 10 μs the increment factor dropped to zero, which is rationalized in terms of complete absence of the intermediate **2** in this time domain.

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References and Notes

1 Presented at the a) 67th Spring Annual Meeting of the Chemical Society of Japan, Tokyo, March 29 - April 1, 1994; b) XVth IUPAC Symposium on Photochemistry, Prague, Czech Republic, July 17 - 22, 1994.

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6 Absorption maximum which corresponds to the $S_1(\pi,\pi^*)$ excitation was measured in cyclohexane solutions, 1-(bromomethyl)naphthalene: 291 nm; **2a**: 302 nm; 1-(chloromethyl)naphthalene: 284 nm; **2b**: 294 nm.

7 The products were identified by comparison of HPLC retention times with authentic samples. The conversion of **1a,b** and the yield of **3** were obtained from the average of four independent runs.

8 The photolysis was conducted with three pulses of XeCl excimer laser. The consumption of **1a,b** and the yield of **3** were obtained from the average of six independent runs.

9 The parent 1-naphthylmethyl radical (**I**) was formed from 1-(halomethyl)naphthalenes (**II**) through the T_1 state when **II** was excited to the S_1 state.[11] The lifetimes of the S_1 and T_1 states of **II** were reported to be < 1 ns [12] and 0.5 - 0.7 μs,[5] respectively, which are expected to be comparable to those of **1a,b**. Additional alkyl substitution in **II** might cause a slight decrease in the T_1 lifetime of **1a,b**,[13] therefore, the rise time of **2** from **1** should be in the order of sub-microsecond.

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