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Time-delayed, Two-color Excimer Laser Photolysis of 1,8-Bis(substituted-methyl)naphthalenes with Group 16 Atom Leaving Groups

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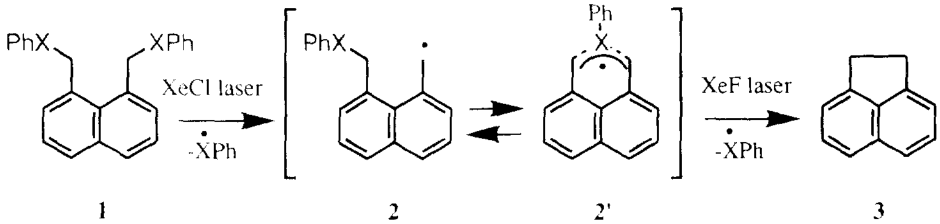
Abstract: Time-delayed, two-color photolysis of 1,8-bis(phenoxymethyl)-(**1a**), 1,8-bis(phenylthiomethyl)-(**1b**), and 1,8-bis(phenylselenomethyl)-naphthalene (**1c**) was conducted by successive irradiation of XeCl (308 nm) and XeF (351 nm) excimer lasers. The yield of the two-photon product, acenaphthene **3**, was strongly dependent on the delay time and showed two maxima at different delay times.

Two-color photolysis has been often used in spectroscopic studies of photochemically generated short-lived intermediates; however, only limited work has been performed on quantitative product analysis associated with the two-color photochemistry.[1] The advantage of using two wavelengths for such photolysis has been pointed out, in which the first wavelength is adjusted to match the absorption of the starting material and the second to that of the photochemically generated intermediate, thus increasing the efficiency of two-photon reactions and, consequently, the yield of the products. When the reaction is conducted with two pulsed lasers, however, consideration must be given to the time dependence of the concentration of the intermediates after the first laser pulse[1c] because the yield of the product formed by the photolysis of the intermediate by the second laser pulse should depend on the intermediate concentration. From this fact it is postulated that by measuring the delay time dependence on the yield of the product the time profile of the concentration of the intermediate in consideration can be obtained. Thus, this technique may provide a mean for obtaining information on the time profile of the intermediate when spectroscopic methods are not applicable because of the spectroscopic overlapping of several species.

We report here a time-delayed, two-color laser photolysis of 1,8-bis(phenoxymethyl)naphthalene (**1a**), 1,8-bis(phenylthiomethyl)naphthalene (**1b**), and 1,8-bis(phenylselenomethyl)naphthalene (**1c**) (Scheme 1);[2] this photolysis technique was applied in order to match the wavelength of the laser to both the starting material and the intermediate, and adjust the time for the efficient photolysis of the intermediate. The intermediate for the formation of the two-photon product, acenaphthene **3**, in these reactions is expected to be a monoradical, which has two plausible structures,[3] *i.e.*, the open-form **2** and the bridged-form **2'**.



a: X=O ; b: X=S; c: X=Se

Scheme 1

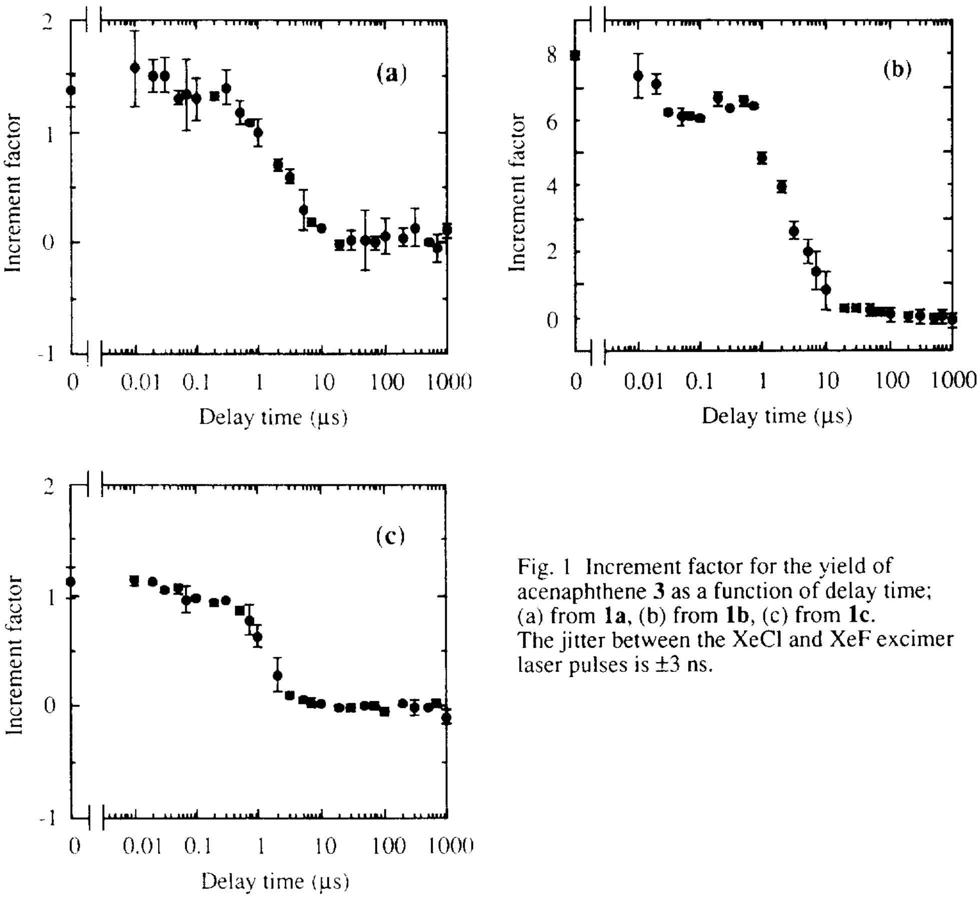


Fig. 1 Increment factor for the yield of acenaphthene **3** as a function of delay time; (a) from **1a**, (b) from **1b**, (c) from **1c**. The jitter between the XeCl and XeF excimer laser pulses is ±3 ns.

The compounds **1a-c** have considerable absorption at 308 nm (ε for **1a**: 890, for **1b**: 8040, for **1c**: 11550 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$) but *no* absorption at 351nm for **1a,b** and a weak absorption for **1c** (ε : 150 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$). On the other hand, the intermediate radicals **2a-c** are expected to have strong absorption at 351 nm because the parent 1-naphthylmethyl radical (**I**), which has the same conjugate π-electron system as that of **2**, has strong absorption bands at ca. 340 nm and 365 nm,[4] and the red shift of the absorption bands by the additional alkyl substitution is estimated to be ca. 10 nm;[5] the absorption of the radicals **2'a-c** is expected to appear at longer wavelength because of the extended conjugation of the π-electron system. The intermediates **2a-c** and/or **2'a-c** are generated from **1a-c** by photolysis with a XeCl excimer laser[6] (308 nm, 6.2 x 10^{20} $photons \cdot m^{-2} \cdot pulse^{-1}$) and further excited with a XeF excimer laser (351 nm, 9.4 x 10^{20} $photons \cdot m^{-2} \cdot pulse^{-1}$) to give the two-photon product acenaphthene **3**. The photolyses of **1a-c** were conducted in cyclohexane (10^{-5} $mol^{-1} \cdot dm^{-3}$) by irradiation of three sets of laser pulses; a set of the laser pulses consisted of one pulse of XeCl excimer laser and one subsequent pulse of XeF excimer laser with varied delay times in the nanosecond to millisecond region.[7]

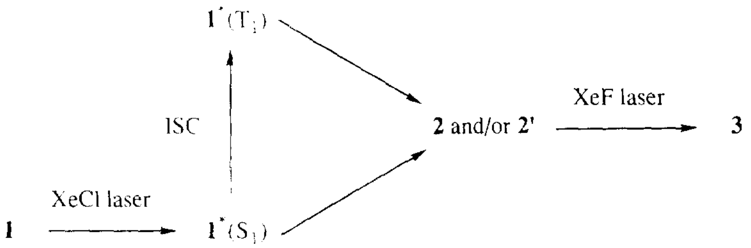
Control experiments showed *no* disappearance of the starting materials **1a,b** and only 4% consumption of **1c** by *one-color* photolysis by XeF laser.[8] Moreover, consumption of **1a-b** in the two-color photolysis was independent of the delay times and almost the same as that in one-color photolysis by XeCl laser;[9] the consumption of the starting materials was selectively induced by the XeCl laser. It was confirmed that *no* decomposition of the two-photon product acenaphthene **3** occurred by XeCl or XeF excimer laser irradiation.

The effect of the delay time on the formation of **3** is shown in Figs. 1a-c using the increment factor 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* photolysis by the XeCl laser.[9] The increment factor of zero in these figures indicates that **3** was formed only by the first XeCl laser pulse and no additional formation of **3** occurred by the subsequent XeF laser pulse.[6] Thus, the increment factor over zero shows additional formation of **3** by the second XeF laser pulse by the photolysis of the intermediate **2** and/or **2'**. As seen in the figures, the increment factor, *i.e.*, the additional formation of **3**, strongly depends on the delay time; the highest increment factor was 1.5 for **1a**, 8.0 for **1b**, and 1.1 for **1c**.

Within the pulsewidth of the first XeCl laser (<14 ns) the increment factor indicates the degree of enhancement in the second step of the reaction, namely, **2** and/or **2'** → **3**. However, in the time domain of >14 ns delay time, the increment factor is expected to reflect the concentration of the intermediate **2** and/or **2'** at each delay time since, in this time domain, **3** is only formed by the second XeF laser from the intermediate **2** and/or **2'**;[6] this is clear from the control experiments. It is significant to note that the increment factor has two maxima[10] for all **1a-c**, the first maximum at 0-40 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** and/or **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 $\mathbf{1} \rightarrow \mathbf{1}^*(S_1) \rightarrow \mathbf{1}^*(T_1) \rightarrow \mathbf{2}$ and/or $\mathbf{2'} \rightarrow \mathbf{3}$ 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.[11] The first maximum indicates the existence of another path for the fast generation of the intermediate radical **2** and/or **2'**. This very fast process can be rationalized by a direct formation of **2** and/or **2'** 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, especially since the existence of such a pathway has been reported for 1-(halomethyl)naphthalenes (**II**),[12] whose reactivity is expected to be similar to the first-step reactivity of **1**. Acenaphthene **3** obtained by the *one-color* photolysis by the XeCl laser must have been formed through this reaction path because the shortness of the pulsewidth of the laser makes it improbable that successive photolysis of the intermediate **2** and/or **2'** which is generated through the long-lived T_1 state can be conducted within a pulse.

Scheme 2



In the case of **1c**, acenaphthene **3** was formed not only by the excitation of the naphthalene ring but also by the direct excitation of the phenylselenyl leaving groups. It was reported that an increase of the two-photon product **3** was observed when the reaction was conducted by the direct excitation of the leaving groups.[13b] Therefore, the small increment factor for **1c** is due to the higher yield of **3** obtained by the one-color photolysis by the XeCl laser, which consequently decreased the value of the increment factor.

The yield of **3** after the second maximum followed a second-order decay. The result implies decrease in the concentration of **2** and/or **2'** by dimerization, analogous to the related naphthylmethyl radical (**I**), for which a second-order decay (dimerization) has been reported.[4a]

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2. Formation of **3** from **1a-c** by *single-beam* laser jet photolysis[13a] and by *one-color* photolysis by KrF excimer laser[13b] has been reported.
3. The heat of formation was calculated to be 62.5 and 87.8 kcal·mol^{-1} for **2a** and **2'a**, 103.7 and 90.8 kcal·mol^{-1} for **2b** and **2'b**, and 81.8 and 57.0 kcal·mol^{-1} for **2c** and **2'c**. Calculations were conducted by PM3 method (RHF, CI) in MOPAC Version 6.0; *cf.* Stewart, J. J. P. *MOPAC Version 6.0, QCPE Bull.* **1989**, 9, 10.
4. (a) Tokumura, K.; Udagawa, M.; Itoh, M. *J. Phys. Chem.*, **1985**, 89, 5147-5149; (b) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.*, **1985**, 107, 6368-6372; (c) Slocum, G. H.; Schuster, G. B. *J. Org. Chem.*, **1984**, 49, 2177-2185.
5. Absorption maximum which corresponds to the $S_1(\pi,\pi^*)$ excitation band of the naphthalene ring in cyclohexane is 271 nm for 1-(phenoxymethyl)naphthalene *vs.* 278 nm for **1a**, 285 nm for 1-(phenylthiomethyl)naphthalene *vs.* 295 nm for **1b**, and 290 nm for 1-(phenylselenomethyl)naphthalene *vs.* 302 nm for **1c**.
6. In the case of **1c**, a small amount of the intermediate **2c** (and/or **2'c**) is also generated by XeF laser; however, the effect of the first photolysis by XeF laser is almost negligible:[8] the consumption was 4.2±0.9% and the yield of **3** was 0.19±0.07%.
7. The excimer lasers used were Lambda Physik EMG 201 MSC, fwhm: 26 ns (XeF); and Lambda Physik EMG 102 MSC, fwhm: 14 ns (XeCl). Delay time, which represents the time between two peaks of the XeCl and XeF laser pulses, was generated by a four-channel digital delay/pulse generator, Stanford Research Systems, Inc., Model DG535. The products were identified by comparison of HPLC retention times with authentic samples. The consumption of **1a-c** and the yields of **3** were obtained from four independent runs.
8. The photolysis was conducted with three pulses of XeF excimer laser. The consumption of **1c** and the yield of **3** were obtained from the average of two independent runs.
9. The photolysis was conducted with three pulses of XeCl excimer laser and the results were obtained from the average of six independent runs: the consumption of **1** and the formation of **3** was 36.4(+0.5, -0.2)% and 0.41(+0.05, -0.08)% for **1a**, 74.8(+1.5, -1.4)% and 0.67(+0.07, -0.12)% for **1b**, and 83.1(+0.5, -0.6)% and 7.74(+0.68, -0.50)% for **1c**.
10. The minimum between the two maxima, however, may be due to the filter effect of **1**$^*(T_1)$ for the second XeF laser because a considerable decrease of **2** and/or **2'** could not be expected in this time domain.
11. 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.[14] The lifetimes of the S_1 and T_1 states of **II** were reported to be <1 ns [15] and 0.5 - 0.7 µs,[4] which are expected to be comparable to those of **1a-c**. Additional alkyl substitution in **II** might cause a slight decrease in the T_1 lifetime of **1a-c**;[16] therefore, the rise time of **2** from **1** should be in the order of sub-microsecond.
12. The formation of 1-naphthylmethyl radical (**I**) from the short-lived S_1 state[15] of 1-(halomethyl)naphthalenes (**II**) has been reported.[4c]
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