Effects of Proton Beam Irradiation on Spirophenanthrooxazine Dissolved in Chloroform

In-Ja Lee,* Tae-Wook Kang, and Tong-Eun Kim
Department of Chemistry, Dongguk University, 707 Suckjang-dong, Gyeongju-Si, Gyeongbuk 780-714, Korea

(Received July 29, 2008; CL-080738; E-mail: lij@dongguk.ac.kr)

The proton-beam-induced reaction of spirophenanthrooxazine (SPO) is investigated as a function of fluence by UV–vis absorption spectroscopy, color measurement, and GC/MS. The reaction is a decomposition reaction of SPO with a rate constant of 0.275 min^{-1} and proceeds in a different way from its photochromic reaction.

Photochromic spiropyrans (SP) and spirooxazines (SO) have been the subject of extensive study due to their potential applications in optical memory storage, optical switching, and displays.[1–3] Upon exposure to a non-ionizing UV radiation, spirocompounds exhibit color change, which relies on the photoinduced heterolytic cleavage of C–O spirobond to generate their colored photomerocyanine (PMC) (Scheme 1).[4–6] PMC form tends to revert back to the spiro form photochemically[7] as well as thermally.[8]

On the contrary, there are very few papers regarding how ionizing radiation such as proton beams affect the nature of spirocompounds. Moscovitch et al. showed both theoretically and experimentally that ionizing radiation in the form of heavy charged-particles (HCP) is capable of changing the information originally stored on three-dimensional optical random access memory materials.[9,10] And they also proposed the use of SP for real-time dosimetry of neutrons or HCPs.[11,12] However, the nature of the radiation-induced chemical changes of SP is not discussed in the papers. Recently, Irie et al. observed diarylethene exhibits color change under γ-irradiation in a similar way to its photochromic reaction.[13]

Here, we studied the effects of the proton beam on spirophenanthrooxazine (SPO; 1,3-dihydro-1,3,3-trimethylspiro[2*H*-indol-2,3′-[3*H*]-phenanthro[9,10*b*][1,4]oxazine]) dissolved in chloroform.

25 MeV proton beams from a MC-50 cyclotron were utilized to irradiate 4×10^{-4} M SPO solution. The beam current was 10 nA and the fluence was adjusted to the range of 1.0×10^{10}–2.0×10^{12} ions/cm^2. The UV–vis spectra of solutions were measured 1 day after terminating the irradiation.

Figure 1 shows that the color of SPO solution significantly depends on the applied proton fluence. Because of the equilibrium between the closed and the open form, the un-irradiated solution appeared as blue. As the irradiation proceeds, its color gradually turns to pale black, dark green, greenish brown, and then finally to bright brown. This indicates the composition of the solution continuously varies with increasing fluence. Because the UV–vis spectra of solvent itself show no noticeable difference between before and after the proton irradiation, every change observed in the spectra of SPO solution is entirely attributed to the chemical change of SPO. The proton beam also conspicuously modifies neither NMR nor IR spectra of the solvent. However, this does not mean nothing happened in chloroform. Rather it is thought that the fraction of solvent which experiences some sort of reaction during the irradiation is too small to be detected by the traditional spectroscopic methods.

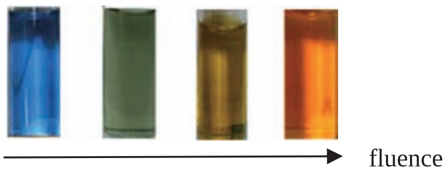


Figure 1. Changes in the color of SPO solution with the proton fluence.

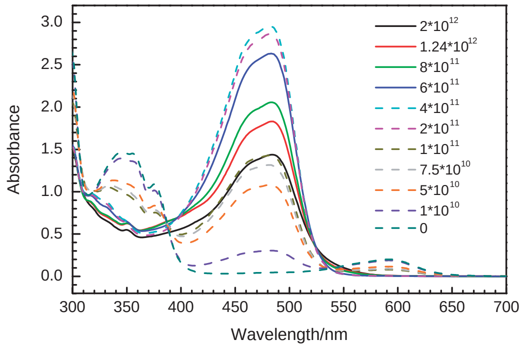
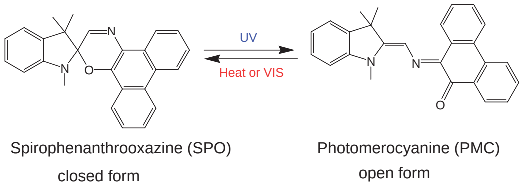


Figure 2. Effects of proton fluence on the spectra of SPO solutions. The proton energy was 25 MeV and the numbers in the figure indicate ion fluence. Each spectrum was measured using a cell with suitable path length and then its difference was corrected.



Scheme 1. Photochromism of SPO.

Figure 2 represents the absorption spectra of SPO solution as a function of proton fluence. Depending on absorbance of the solutions, one of three cells having different path lengths (2, 5, and 10 mm) was utilized for the spectral measurements and then its difference was corrected to give Figure 2. It is clear that the shapes and the absorbance of the spectra depend to a great extent on the fluence. The dashed lines correspond to the fluence up to 4.0×10^{11} ions/cm^2 and the solid lines correspond to the fluence greater than that. The un-irradiated SPO solution shows an absorption band at 350 nm and a smaller one at 590 nm. As the fluence increases (dashed lines), both bands decrease and at the same time a new band appears at 480 nm. This is somewhat surprising because UV irradiation to spirocom-

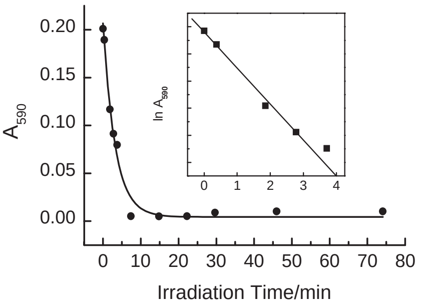


Figure 3. The dependence of the absorbance at 590 nm on proton irradiation time. The inset represents the first-order plot. The solid lines are fits to the experimental data.

pounds generates PMC resulting in absorption increase at typically between 550 and 610 nm.[14,15] The presence of the isosbestic points at 388 and 535 nm in the dashed lines implies SPO stoichiometrically changes into the species absorbing at 480 nm. We will refer the species as "B." The fact that the absorption band of B is located at 480 nm indicates it possesses conjugated double bonds.

Figure 3 and its inset show that the proton-beam-induced reaction is first-order with a rate constant of 0.275 min^{-1}. The fact that photochemical reaction rates depend only on the light absorption rate implies that the reaction proceeds thermally. The proton-beam-induced thermal reaction can be explained by noting that the proton beam dissipates its energy mainly as heat when passing through the medium.[9] Because its energy release is localized in the medium,[16] it is not so difficult to imagine the medium temperature along the beam path will be considerably high.

Figure 4 represents gas chromatograms of SPO solution obtained before and after proton irradiation. Before the proton irradiation, only one peak is observed at 23.620 min. Its mass is estimated to be 378.40 u from the mass spectrum and it is attributed to SPO. As the beam fluence increases, two peaks at 10.173 and 18.538 min are evolved at the expense of the peak at 23.620 min. Their corresponding molecular masses are 175 u and 219 u, respectively, and the respective peaks are attributed to 1,3,3-trimethyl-2-oxyindole and phenanthro[9,10-*d*]-oxazole.[17] This result indicates that under the proton beam SPO mainly decomposes into 2 species and also that the proton-beam-induced reaction proceeds in a different way from the UV-induced photochromic reaction. This is somewhat different from the results obtained for diarylethene under γ-irradiation,[13] in which it exhibited a similar trend to the photochromic reaction. The nature of the colored species B is still unknown. Because dilution does not affect the spectral shape of the irradiated solution and because the absorption band at 590 nm is not restored upon the addition of ammonia,[17] it is unlikely that B is either an aggregate form or an acid form of SPO. The facts we observed for B are it absorbs at 480 nm and is a minor product obtained under the proton irradiation. Research to identify the structure of B is under way.

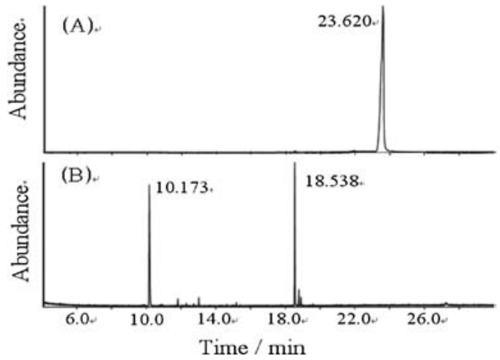


Figure 4. Gas chromatograms of SPO. (A) Before and (B) after the proton irradiation. The ion fluence of (B) is 1.0×10^{11} ions/cm^2.

In conclusion, under the proton-beam irradiation, SPO decomposes into two main products with a rate constant of 0.275 min^{-1}. The reaction proceeds in a different way from its photochromic reaction.

This work was supported by Proton Engineering Frontier Project.

References and Notes

1 R. Guglielmetti, in *Photochromism: Molecules and Systems*, ed. by H. Dürr, H. Bouas-Laurent, Elsevier, New York, **1990**.
2 R. C. Berthelson, in *Techniques of Chemistry: Photochromism*, ed. by C. H. Brown, Wiley-Interscience, New York, **1971**, Vol. 3.
3 N. Y. C. Chu, in *Photochromism: Molecules and Systems*, ed. by H. Dürr, H. Bouas-Laurent, Elsevier, New York, **1990**.
4 C. Lenoble, R. S. Becker, *J. Photochem.* **1986**, *34*, 83.
5 N. P. Ernsting, T. Arthen-Engeland, *J. Phys. Chem.* **1991**, *95*, 5502.
6 N. Tamai, H. Masuhara, *Chem. Phys. Lett.* **1992**, *191*, 189.
7 C. Lenoble, R. S. Becker, *J. Phys. Chem.* **1986**, *90*, 62.
8 E. Pottier, R. Dubest, R. Guglielmetti, P. Pardieu, A. Kelmann, F. Tfibel, P. Levoir, J. Aubard, *Helv. Chim. Acta* **1990**, *73*, 303.
9 M. Moscovitch, D. Emfietzoglou, *J. Appl. Phys.* **1997**, *81*, 58.
10 M. Moscovitch, G. W. Phillips, *Nucl. Instrum. Methods Phys. Res., Sect. B* **2001**, *184*, 207.
11 M. Moscovitch, U.S. Patent 5319210, **1994**.
12 M. Moscovitch, U.S. Patent 5498876, **1996**.
13 S. Irie, M.-S. Kim, T. Kawai, M. Irie, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1037.
14 A. Kellmann, F. Tfibel, R. Dubest, P. Levoir, J. Aubard, E. Pottier, R. Guglielmetti, *J. Photochem. Photobiol., A* **1989**, *49*, 63.
15 Y. S. Lee, J. G. Kim, Y. D. Huh, M. K. Kim, *J. Korean Chem. Soc.* **1994**, *38*, 864.
16 Y. Eyal, K. Gassan, *Nucl. Instrum. Methods Phys. Res., Sect. B* **1999**, *156*, 183.
17 I.-J. Lee, to be published.