Photolysis of Perfluoroazooctane in Perfluorohexane upon 185 nm Irradiation

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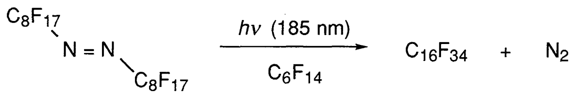
The photolysis of perfluoroazooctane in perfluorohexane upon 185 nm irradiation was investigated by means of quantum yield, light intensity dependence, and UV-vis spectra of the photolysis of perfluoroazooctane. Perfluoroazooctane (trans isomer) was photoisomerized by one photon absorption to cis isomer, followed by extrusion of nitrogen by another photon absorption.

The photochemistry of azo compounds has been extensively investigated to date in the field of organic chemistry.[1] It is well-known that azoalkanes are widely used as presursors of carbon-centered radicals which are generated upon UV irradiation.[2] Particularly perfluoroazoalkanes possess a potential utility for the photochemical preparation of perfluoroalkyl-substituted organic compounds which are attractive substances as medicines and functionalized materials.[3] However, the preparative generation of perfluoroethyl radicals from the corresponding azo compound upon a XeCl excimer laser (308 nm) required the remarkable high intensity (10 x 10^6 W cm^{-2}, 50 Hz, 3 h).[4] Adam et al. reported that cyclic azoalkanes decomposed to generate alkyl radicals upon 185 nm irradiation (π-π* excitation), whereas they were reluctant to extrusion of nitrogen upon >300 nm irradiation (n-π* excitation).[5] Recently we also found that perfluoroazooctane (**1**) was effectively photolyzed upon 185 nm irradiation in benzene by extrusion of nitrogen, and then resulting perfluorooctyl radicals were introduced into benzene.[6] However, since benzene absorbs most photons and the energy transfer process from the excited benzene to **1** was undeniable in this reaction system, the mechanism of the photolysis of **1** could not be clarified in detail. We now would like to report the mechanism of the photolysis of **1** in perfluorohexane which has no absorption of 185 nm light[7,8] and is relatively unreactive to resulting radicals.

Trans-**1**[9] exhibits its absorption maxima at 188 nm (π-π*, ε 23100) and 380 nm (n-π*, ε 30) in hexane.[6] A perfluorohexane solution of trans-**1** (1 x 10^{-3} mol dm^{-1}) was irradiated at >300 nm with a 500 W high pressure Hg lamp (Ushio USH-500D) through a filter (Toshiba UV-31) for 24 h under a nitrogen atomosphere, then analyzed by GC-MS with n-nonane as an internal standard. This analysis showed that the photolysis of **1** by extrusion of nitrogen was negligible and that mainly trans-cis isomerization of **1** occurred. On the other hand, the effective decomposition of trans-**1** was derived from the use of 185 nm light with a 60 W low pressure Hg lamp (Eikosha EL-S-SQ-60) through a 185 nm bandpass filter (185 nm transmission 17.2%, Acton Research Corp. 185-HR-25) for 7 h to give perfluorohexadecane (**2**) by recombination of perfluorooctyl radicals in a quantitative yield. These results show that 185 nm irradiation (π-π* excitation) is much more effective for the denitrogenation of trans-**1**, compared with >300 nm irradiation (n-π* excitation). This is the first example of photoreluctant azo compounds having n-alkyl substituent upon n-π* excitation.



trans-**1** **2**

In order to investigate the mechanism of the photolysis of trans-**1** upon 185 nm irradiation, the quantum yield and the light intensity dependence of the formation of **2** by the photolysis of trans-**1** were examined in perfluorohexane (1 x 10^{-3} mol dm^{-1}). The azo compound trans-**1** was photodenitrogenated upon 185 nm irradiation in a quantum yield ($\Phi_{\text{-azo}} = 0.15$)[10] based upon cis-trans isomerization of cis-cyclooctene ($\Phi_{\text{cis-trans}} = 0.32$) as an actinometer.[11] As shown in Figure 1, the formation of **2** was proportional to the square of 185 nm light intensity. These results suggest that trans-**1** was photolyzed upon 185 nm irradiation by two-photonic absorption in perfluorohexane.[12]

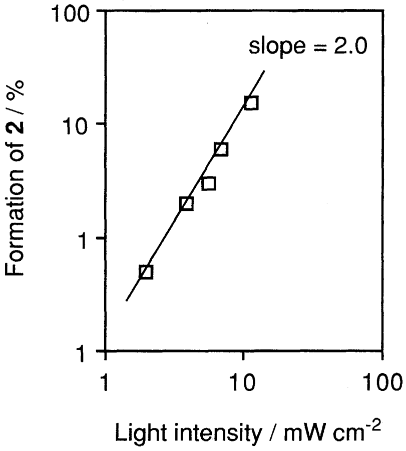


Figure 1. The light intensity dependence of the formation of **2** by the photolysis of trans-**1** upon 185 nm irradiation.

In addition, UV-vis spectral analysis of this photoreaction at 5 min intervals indicated that the intensity of the absorption band of azo group at 380 nm decreased with increase of irradiation time and that a broad absorption band which appeared at longer wavelength decreased gradually (Figure 2). The azo group of trans-**1** has an absorption band at λ_{max} 380 nm, whereas that of cis-**1** absorbs at λ_{max} 435 nm.[4] Therefore, these spectral changes indicate that trans-cis isomerization of **1** and the subsequent denitrogenation of resulting cis-**1** took place during the irradiation.

As described above, it was found that this photolysis of trans-**1** took place via two-photonic process and trans-cis isomerization. In order to confirm the mechanism of this photolysis it is necessary to investigate the light intensity dependence of the photolysis of pure cis-**1** upon 185 nm irradiation. However, as it was difficult to obtain pure cis-**1** from the direct preparation and isomerization of trans-**1**, cis-rich

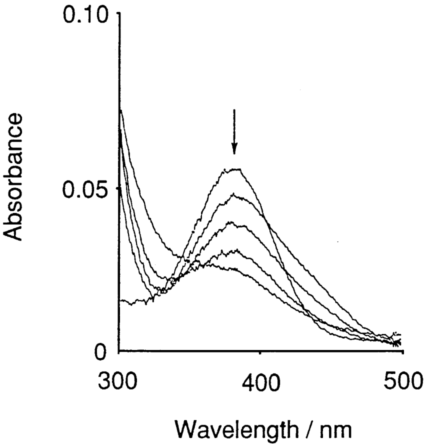


Figure 2. The UV-vis spectra were recorded after 0, 5, 10, 15, and 20 min 185 nm irradiation of trans-**1**.

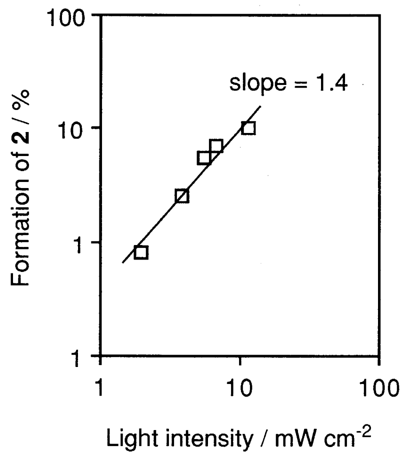
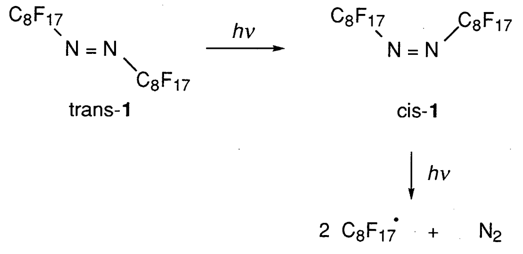


Figure 3. The light intensity dependence of the formation of **2** by the photolysis of cis-rich **1** upon 185 nm irradiation.

1 was used (trans : cis = 1.00 : 1.46),[13] which was obtained from photoisomerization of trans-**1** in cyclohexane (5 x 10^{-3} mol dm^{-1}) upon 370 nm irradiation with a 500 W Xe lamp (Ushio UI-501C) through filters (Toshiba UV-35 and UV-D33S filter) for 2 h at room temperature.[4] As shown in Figure 3, the slope of the formation of **2** against various light intensity was 1.4, showing that this photolysis of cis-rich **1** consisted of the mixture of one- and two-photonic processes. These results suggest that trans-**1** was photoisomerized to cis-**1** by one photon absorption,[11] followed by photodecomposition of cis-**1** to perfluorooctyl radicals by another photon absorption (Scheme 1).

In conclusion, the photoreluctant azo compound trans-**1** upon >300 nm irradiation was effectively photolyzed by two-photonic 185 nm light absorption via the following pathway: (a) one photon is utilized trans-cis isomerization of trans-**1**; (b) resulting cis-**1** is photodenitrogenated by another photon absorption to form perfluorooctyl radicals. In the case of such a multiphotonic process, the irradiation with an ArF excimer laser (193 nm) will be accessible for the photolysis of trans-**1**. Furthermore, it was proved that 185 nm irradiation led the preparative and feasible generation of perfluorooctyl radicals from trans-**1** compared with n-π* excitation (>300 nm) according to Kaupp's method.[4] Application of this method for the generation of perfluoroalkyl radicals to the introduction of these radicals into alkanes is under investigation.



Scheme 1.

References and Notes

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