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Photolysis mechanism of a squarylium dye

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ABSTRACT

The photodegradation mechanism of a squarylium dye was investigated by analyzing the photoproducts using a UV–Vis spectrometer, MALDI-TOF-MASS, HPLC and GC–MS. We found that a squarylium dye was likely decomposed into smaller species by way of an intermediate species which was an adduct of an original dye with a solvent molecule or solvent radical. The reaction mechanism was confirmed using the quantum chemical calculation by estimating the structure of the intermediate species. Since the solvent molecules are involved in the reaction, the reaction rate depended on the used solvent, and the photodegradation rate was much faster in a chloromethane than in an alcohol.

1. Introduction

The squarylium dye is one of the dye categories, and known as a functional dye used for the light absorbing material for solar cells [1,2], optical recording media [3,4], nonlinear optical material [5,6], bio-labeling [7], singlet oxygen generation [8], etc. Squarylium dyes, which are 1,3-disubstituted compounds were synthesized by condensation of one equivalent of squaric acid with two molar equivalents of electron rich aromatic or heterocyclic methylene bases [9,10], or by stepwisely the introduction to squaric acid skelton of aromatic or heterocyclic compounds via dialkyl squarate or squaryl dichloride. The feature of this dye category is that they have a sharp and intense absorption and fluorescence in the red to near-infrared region [11,12]. Furthermore, the absorption wavelength can be controlled by the functional group connected to each side of the squaric acid, and series of dyes have been investigated and synthesized [13,14].

In the practical applications used as functional dyes, we need to know the mechanism of the photodegradation and light resistance of the dye molecule, however there are only a few reports on the degradation of the squalyrium dyes; reports on a photodegradation process [11], a thermal decomposition process [15,16] and photocatalytic decomposition process [17] can be found. Here we investigated the mechanism of the photodegradation processes of a squarilium dye using various analytical methods and we found that characteristic intermediate species are involved in the photodegradation reaction and that the reaction rate is dependent on the solvent.

2. Experimental setup

The sample dye was one of the squalyrium dyes (SQ) ($C_{28}H_{26}ClN_3O_3$, MW: 487, λ_{max} 577.5 nm (CHCl3)) (Kyowa Hakko Chemicals, Co., Ltd.), and the structure is shown in Fig. 1. On each side of the squaric acid, it has indolenine and pirazole frameworks. The SQ was dissolved in a methanol, ethanol, propanol, chloroform, and dichloromethane. In the photodegradation monitoring by an absorption spectrum, the samples with a concentration of 0.05 mM were irradiated with a nanosecond pulse laser with a wavelength of 532 nm, a pulse energy of 3 mJ/pulse, a repetition rate of 20 Hz, a beam diameter of 8 mm (GAIA, Rayture systems). The sample was put in a 10 mm × 45 mm optical cell with a screw cap with a thickness of 1 mm, and the laser light was shone without focusing. The sample was kept moving during the irradiation. The absorption spectrum was measured by a spectrometer (V-650, JASCO) every time after the irradiation of time. The photodegradation speed was accelerated about 10 times using a nanosecond pulse laser instead of a continuous wave laser (532 nm, 100 mW, Photop). It was confirmed that the photoproduct species generated by both the lasers were similar, which was confirmed by MALDI-TOF-MASS measurements. It is considered that the photoproducts (intermediate species) are involved in the reaction and they are concentrated in case of a short optical pulse because the generated species cannot diffuse away from the irradiated area. However, it is supposed that the reaction mechanism is similar because the generated (intermediate) species are similar.

For the structure analysis of the photoproduct species, MALDI-TOF-MS (AXIMA-CFR, SHIMADZU), GC–MS (6890N Network GC System, Agilent Technologies) were mainly used. For the MALDI-TOF-MS measurements, 1,8,9-trihydroxyanthracene was used as a matrix material. For these analyses, the sample solutions were

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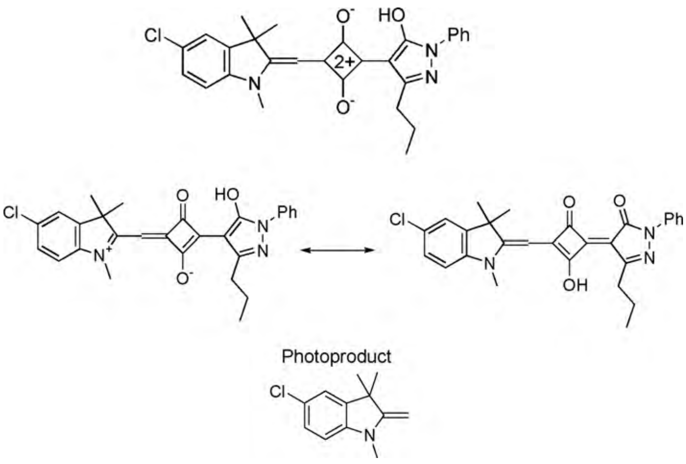

Fig. 1. The molecular structure of the used squalirium dye. The photoproduct species observed by GC–MS measurement was also shown.

irradiated by a nanosecond pulse laser for 120 min for alcohol solutions, and for 3 min for chloromethane solutions.

3. Results and discussion

The absorption spectra during the light irradiation are shown in Fig. 2 for methanol, ethanol, and chloroform solvents. In alcohol solutions, it took a few hours for the decay of the main peak, namely photodegradation, while it took only several minutes for chloromethane solvents. The degradation time until the original molecule was reduced to half was 120, 150, 150, 20, 4 min for methanol, ethanol, propanol, dichloromethane, chloroform, respectively. The insets in each figure show the normalized spectrum for various irradiation times at the intensities of the main peaks because it can be easily seen that the intensities of the shoulder peaks around 530 nm gradually increased relatively to the main peaks. At the same time, a small absorption profile gradually increased in the UV region.

The photodegradation rate was much faster in chloromethane solvents than in alcohol solvents, and it implies that solvent molecules are involved in the reaction mechanism, causing the difference in the reaction rate. Since the shoulder peak around 530 nm decreased with time but increased its ratio to the main peak intensity, it is considered that it corresponds to the peak for an intermediate species in the photodegradation process. It is assumed that the intermediate species remains its molecular structure similar to the original molecule because of the visible absorption close to the absorption for the original molecule. The monotonic increase in the UV absorption indicates photoproducts with a smaller molecular size were generated as final products.

To confirm the assumption that the shoulder peak corresponds to the intermediate speices, 3D-HPLC was measured for the ethanol solutions and the result was shown in Fig. 3. The eluent was THF/0.1% formic acid in water (50:50). The original molecule corresponds to the peak at 14.3 min, which was confirmed by the absorption spectrum shown in Fig. 3b. The other peaks except for the one at 9.7 min showed no absorption in the visible wavelength region. For the peak at 9.7 min, the absorption around 520 nm was confirmed. Since the absorption peak is close to the shoulder peak observed in Fig. 2, this corresponds to the main intermediate species.

MS spectra before and after irradiation of light were shown in Fig. 4 for methanol and chloroform solvents. Light was irradiated for 120 min for alcohol solvents and for 3 min for chloromethane solvents. The original molecular peak of SQ showed a typical peak profile including a chloride isotope. In alcohol solutions, besides

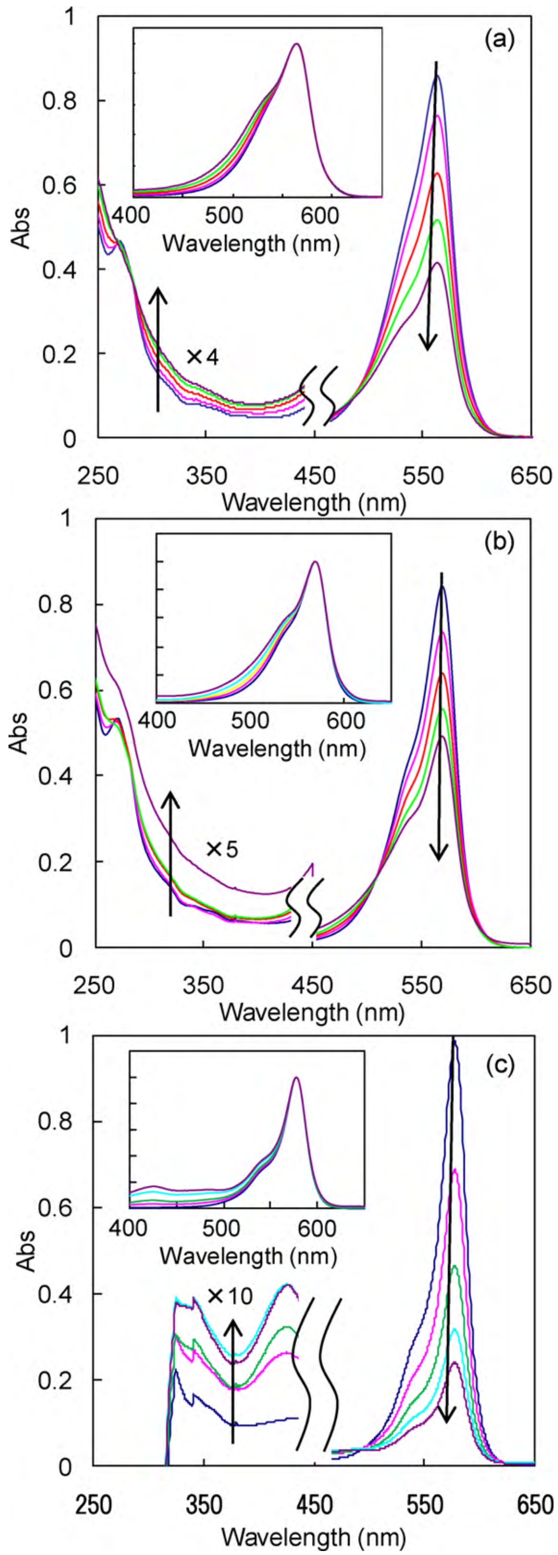

Fig. 2. Temporal change in the absorption spectra of the squalirium dye in (a) methanol, (b) ethanol, and (c) chloroform solvents by irradiation of a pulse laser (wavelength: 532 nm, pulse energy: 3 mJ/pulse, repetition rate: 20 Hz). In (a) and (b), spectra for every 30 min are shown, while those for every 1 min are shown in (c). In (c), absorption spectra for the wavelength less than 320 nm were not measured due to fluorescence. The insets show the spectra normalized by the intensity of the main absorption peak. The absorption profiles in the UV region were expanded for clarity.

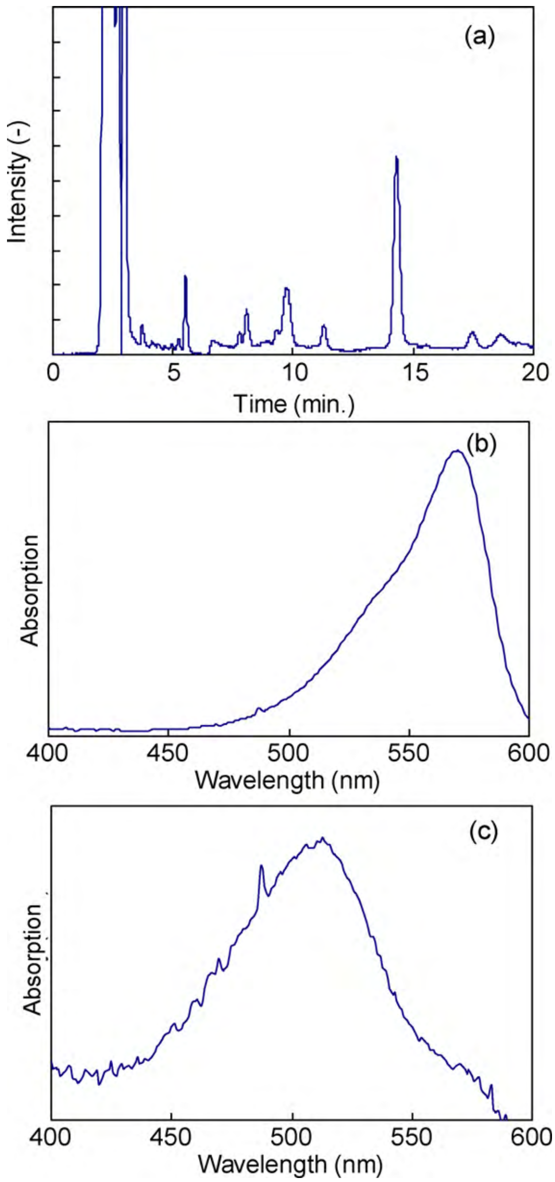

Fig. 3. A 3D-HPLC result for a sample after 4 h irradiation of light in 0.05 mM EtOH solution; the LC chart (a) and absorption spectra for the retention time 14.3 min (b) and 9.7 min (c), respectively.

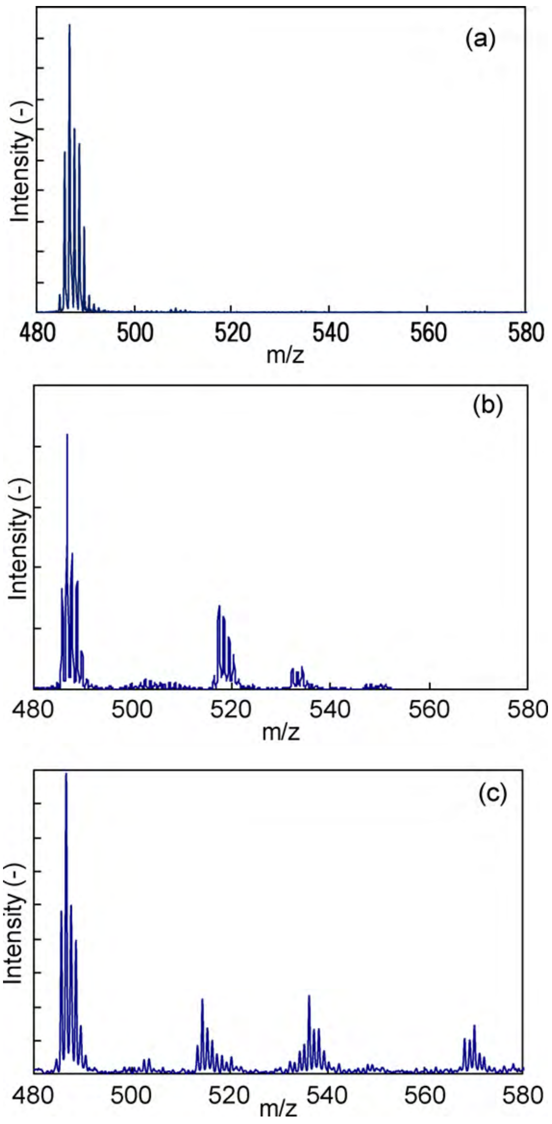

Fig. 4. Mass spectra (MS) for the squalirium dye before and after the irradiation of the pulse laser. The MS spectrum for the original molecule is shown in (a), and the followings correspond to those after irradiation in (b) methanol for 120 min and in (c) chloroform for 3 min.

the peak for SQ molecule (m/z = 488 as $[M+H]^+$), another peak at m/z = 519 for methanol, at m/z = 533 for ethanol was observed. The molecular weights for the newly observed peaks correspond to those for SQ + CH_3O (or CH_3OH) and CH_3CH_2O (or CH_3CH_2OH), respectively. In chloromethane solvents, the peak for SQ molecule decreased again by light irradiation, and a few other peaks were observed. For a chloroform solvent, peaks at m/z = 516, 536, and 571 were found. They correspond to the molecular weights for SQ + CH_2CH_2, CHCl and CCl_2, respectively. We could not find new peaks in the region of the smaller molecular number than 487, possibly because they were not ionized or buried in the matrix spectra. To confirm the above results, a sample after 4 h irradiation of the light in 0.05 mM EtOH solution was also analyzed by LC–ESI-MS. In the LC–ESI-MS measurement, a component corresponding to SQ + CH_3CH_2O (CH_3CH_2OH) was found from the observed peaks at m/z 534 (ESI^+) and m/z 532 (ESI^-).

From the above results, it is considered that addition of solvents or their radicals to a SQ molecule is the initial step for the photodegradation process. In alcohol solvents, it is supposed that an adduct of the SQ molecule with a solvent molecule is formed. In chloromethane solvents, it is considered that the excited state of a SQ dye was interacted with a solvent molecule, which induces the dissociation of C–H or C–Cl bonds, causing formation of solvent radicals. A hydrogen position was assumed to be substituted by the radicals. Radical formation is supported by the fact that the photodegradation rate of SQ is much faster in chloromethane solvents and that various adduct species (CH_2CH_2, CHCl and CCl_2, etc.) were observed in the MS spectra. Since it is considered that the addition of such solvents or solvent radicals does not cause the total disappearance of the absorption in the visible wavelength region, it is safely concluded that the adduct species are the intermediate species corresponding to the shoulder peak in Fig. 2 and the peak at 9.7 min in Fig. 3.

The subsequent process of the photodegradation should be considered because the solution color was finally lost in the process. Since the final photoproducts corresponding to the UV absorption observed in Fig. 2 could not be detected by MALDI-TOF-MS, the photoproducts were analyzed by GC–MS, expecting the detection of smaller photoproducts, although SQ itself cannot be detected

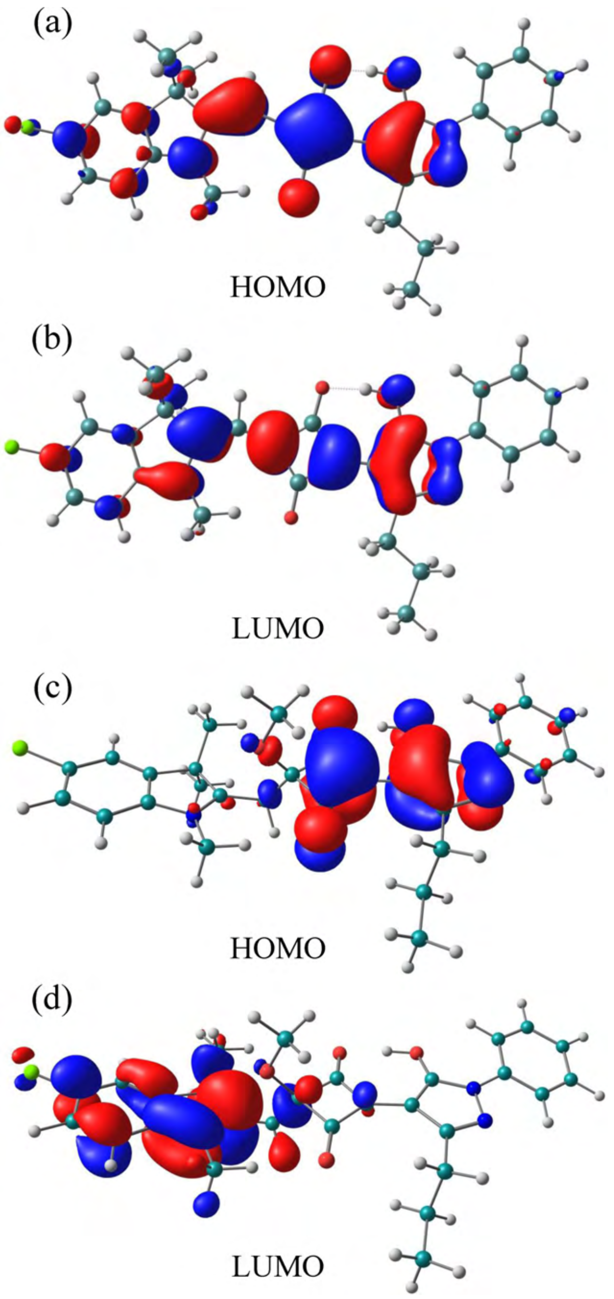

Fig. 5. Highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) for the squarylium dye (a, b) and its adduct (c, d) with a methanol molecule at the equilibrium structure in the electronic ground state.

by GC–MS due to high evaporation temperature. The indolenine framework was found only for the samples after light irradiation, and the molecular structure is shown in Fig. 1. This result strongly suggests that the single bond connecting the indoleneine framework and the squarine ring was dissociated in the photodegradation process.

In order to obtain the detailed understanding of the reaction mechanism involving the intermediate states, we have performed quantum chemical calculations for the original SQ dye and its adduct species with solvent molecules. The geometry optimization in the electronic ground state (S_0) is carried out using density functional theory (DFT) with the B3LYP combination of exchange and correlation functionals and a 6-31G(d,p) basis set. Subsequently, the time-dependent (TD) DFT calculations [18,19] are performed for calculating the vertical excitation energy at the equilibrium structure using the BLYP functionals with the long-range correction (LC) [20] and a 6-31G(d,p) basis set. All calculations are performed using the GAMESS package [21].

The $S_0 \rightarrow S_1$ transition in the SQ dye is viewed as HOMO → LUMO transition, and as seen in Fig. 5a and b, it involves a charge-transfer from the oxygen atoms at the both sides of the squaric ring to the carbon atoms in the ring. The excitation energy obtained by TD-DFT calculation was calculated to be 2.46 eV (504 nm), which is about 0.3 eV more than the experimental value. This discrepancy is mainly due to the neglect of solvent molecules.

Considering the final photoproduct of indolenine framework and the observation that the electronic excitation energy is localized around the squaric ring, we speculate that a solvent molecule attack on the left side of the squaric ring. Thus, the following adduct, where CH3O– add on the left carbon atom in the squaric ring (Fig. 5c and d), was examined in the calculation. After the geometry optimization, the electronic excitation energy was calculated to be 2.61 eV (475 nm), which is about 30 nm blue-shifted from the original SQ molecule. This excitation is also HOMO → LUMO transition and it involves a charge transfer from the central squaric ring to the left indolenine framework. The oscillation strength for this transition was given as 0.2, which is relatively small due to the nature of long-range charge-transfer transition. The observed blue-shift is in agreement with the experimental findings and it is partly due to the breaking of the electronic conjugation between the two moieties attached to the squaric ring. It is assumed that the addition of solvent molecules weaken the bond strength between the indolenine and squaric ring part, leading to the dissociation. Furthermore, it was predicted from the NMR spectrum of the intermediate species that the double bond peak corresponding to the indolenine and squaric ring bond was weakend.

Finally, it is commented that the above reaction is not a thermally induced reaction. It was checked by the change in the absorption spectrum of SQ solutions at 323 K, but no change was observed for hours. Since the temperature rise due to light irradiation is only a few degrees in our experiment, the degradation observed is due to light irradiation.

4. Conclusion

The photodegradation process of a squarilium dye was investigated by several analytical methods. It was clarified that the processes depended on the solvent and the solvent molecules were involved in the reaction mechanism. Since there have been only a few reports on the molecular mechanism of the photodegradation of squarilium dyes, the mechanism would be informative for those who design the molecular structure or utilize squarilium dyes as photosensitizer, recording media, etc.

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