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Formation of oxazine dye by photochemical reaction of *N*-acyl oxazine derivatives

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Abstract

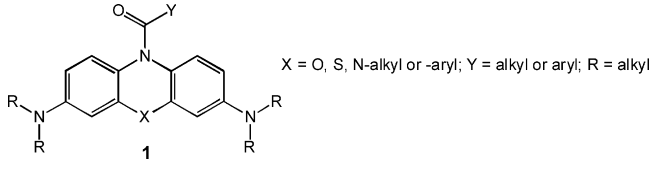
The synthesis and photochemical reaction mechanism of *N*-benzoyl oxazine derivatives have been investigated. The synthesized materials were found to be photosensitive and capable of generating oxazine dye upon light irradiation. The initial reactions were found to include homolytic bond cleavage between the oxazine nitrogen and benzoyl carbon atoms proceeding through the excited singlet state and the formation of oxazine and benzoyl radicals. Subsequent reaction steps include direct electron transfer between two oxazine radicals or disproportionation of the oxazine dimer species formed through the recombination of two oxazine radicals. These reactions lead to the formation of the oxazine dye cation and anion pair.

Keywords: Photochromism; Dye precursor; Fluorescing dyes

1. Introduction

Materials possessing functionality that can be activated by light-irradiation are of great importance because of their potential use in various applications such as drug delivery systems (DDS) [1,2], biological function imaging [3], printing [4], optical data storage [5–7], etc. Among the type of functionality, fluorescence switching is one of the most important functions for volumetric optical data storage. The access of the stored data is achieved by measuring the fluorescence emitted by the fluorescing form with the photochromic material [8–11].

N-Acetyl or *N*-benzoyl azine derivatives (**1**), which are known as leuco dyes, are used in many kinds of applications including pressure-sensitive carbonless paper [12], thermographic and photothermographic imaging [13].



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Using external stimuli, such as oxidation and γ-ray irradiation, the pale yellow derivatives release leuco dye and develop intense color. The color development process of the dye precursor includes removal of the acetyl or benzoyl protective group from the azine nitrogen atom and oxidation of the leuco azine dye generated after the removal of the protective group. For example the color development mechanism of *N*-benzoyl methylene blue (X=S) has been attributed to dye formation reaction which includes two steps: hydrolysis of the dye precursor in acidic environment and oxidation of leuco dye, generated by oxygen [14]. Not only the methylene blue dye precursor, but other types of dye precursor such as oxazine type (X=O) and phenazine type (X=*N*-alkyl of *N*-aryl) are also expected to follow this mechanism. In general, acid is required for the removal of the protective group to generate leuco dye and oxygen or transition metal ion species are necessary for the oxidation of the leuco dye.

Among these azine dye precursors, the oxazine type is the most important for applications based on fluorescence switching because its strong fluorescence could be generated by the direct electron transfer between the two oxazine radicals. It is interesting to note that although many patents referring to practical applications of oxazine dye precursor have been filed, few scientific papers have been published in the open literature. To the best of our knowledge, photochemical dye formation of *N*-benzoyl oxazines has not been reported. UV irradiation of

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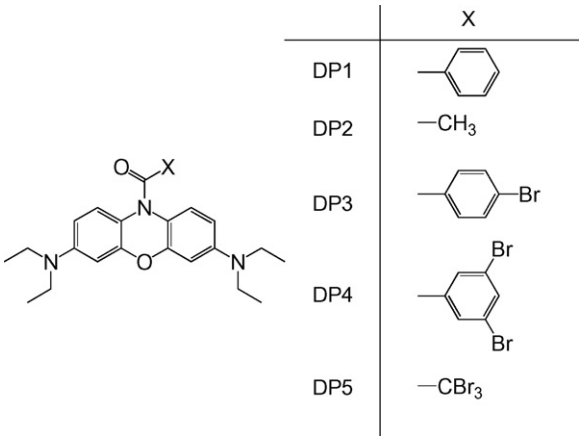


Fig. 1. Chemical structure of oxazine dye precursors.

N-benzoyl methylene blue, the sulfur counterpart of oxazine is known to induce dye formation [15], however, the mechanism of this photochemical reaction is not known. Only a few studies have reported dye formation from *N*-alkoxycarbonyl oxazine by γ-ray irradiation [16] and even in these cases, the reaction mechanism has not been described in detail. The γ-ray mechanism may be very different from that for UV light irradiation because the enormous energy of these γ-rays is expected to promote an electron to higher energy level above a bond dissociation level and most probably ionize the molecule and generate ion radicals.

In our study, *N*-benzoyl oxazine derivatives were found to be photosensitive and capable of generating oxazine dye upon UV light irradiation without the addition of acid or presence of oxygen. In this paper, we describe the spectroscopy and kinetics of the *N*-benzoyl oxazine photochemical reaction and, based on this data, we propose a reaction mechanism.

2. Experimental

2.1. Synthesis

All chemicals were purchased from Aldrich, TCI and Wako. Basic Blue 3, which is the starting material, had about 30% dye content, and was used without further purification. 4-Bromobenzoylchloride and 3,5-dibromobenzoyl chloride were prepared from the reaction of benzoic acid with thionyl chloride.

The structures of the oxazine precursors that we studied are shown in Fig. 1.The syntheses of the oxazine dye precursors were carried out using the modified literature procedures [13]. The general method for the synthesis of these precursors is described below in Scheme 1. Basic Blue 3 was dissolved in a mixture of distilled water and toluene, then sodium dithionite was added followed by vigorous stirring. After the water and the toluene layers were separated the water layer was removed and discarded, then sodium dithionite was added to the toluene solution. The reaction mixture was refluxed with a Dean-Stark trap in order to remove the remaining water, azeotropically. Subsequently, acid chloride was added to the toluene solution, followed by triethylamine and then refluxed. The products were purified by silica gel column chromatography using ethyl acetate–hexane as the eluent.

Leuco oxazine, which was obtained from the reduction of Basic Blue 3 by sodium dithionite, is quite unstable in the presence of oxygen and can be easily re-oxidized by it. Therefore, it was used without any further separation or purification. The synthesized compounds were characterized by ^{1}H NMR in deuterated chloroform.

2.1.1. 3,7-Bis(diethylamino)-10-benzoylphenoxazine (DP1)

^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm) 1.17 (t, 12H, amino-CH_3), 3.32 (q, 8H, amino-CH_2), 6.21 (d, 2H, oxazine-2, 8H), 6.43 (s, 2H, oxazine-4, 6H), 7.13 (d, 2H, oxazine-1, 9H), 7.30 (t, 2H, benzoyl-3, 5H), 7.34 (t, 1H, benzoyl-4H), 7.44 (d, 2H, benzoyl-2, 6H). EIMS (*m*/*z*): calcd. for $C_{27}H_{32}N_3O_2$, 430, 431; found, 430, 431 ($[M+H]^+$).

2.1.2. 3,7-Bis(diethylamino)-10-acetylphenoxazine (DP2)

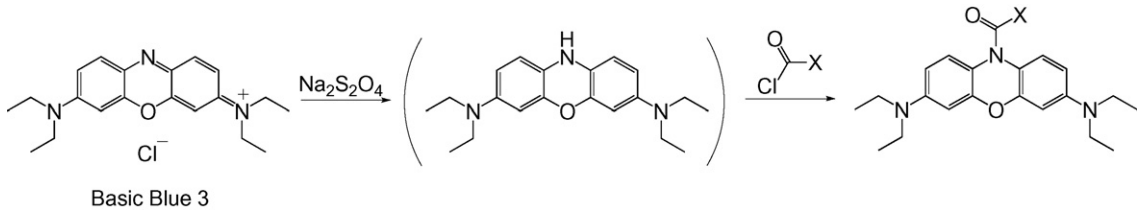
^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm) 1.18 (t, 12H, amino-CH_3), 2.29 (s, 3H, acetyl-CH_3), 3.33 (q, 8H, amino-CH_2), 6.39 (m, 4H, oxazine-2, 4, 6, 8H), ∼7.3 (b, 2H, oxazine-1,9H). EIMS (*m*/*z*): calcd. for $C_{22}H_{30}N_3O_2$, 368, 369; found, 368, 369 ($[M+H]^+$).

2.1.3. 3,7-Bis(diethylamino)-10-(4-bromobenzoyl) phenoxazine (DP3)

^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm) 1.15 (t, 12H, amino-CH_3), 3.32 (q, 8H, amino-CH_2), 6.23 (d, 2H, oxazine-2, 8H), 6.42 (s, 2H, oxazine-4, 6H), 7.12 (b, 2H, oxazine-1, 9H), 7.32 (d, 2H, benzoyl), 7.41 (d, 2H, benzoyl). EIMS (*m*/*z*): calcd. for $C_{27}H_{31}BrN_3O_2$, 510, 508, 509, 511; found, 510, 508, 509, 511 ($[M+H]^+$).

2.1.4. 3,7-Bis(diethylamino)-10-(3,5-dibromobenzoyl) phenoxazine (DP4)

^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm) 1.17 (t, 12H, amino-CH_3), 3.33 (q, 8H, amino-CH_2), 6.25 (d, 2H, oxazine-2, 8H), 6.44 (s, 2H, oxazine-4, 6H), ∼7.1 (b, 2H, oxazine-1, 9H), 7.46 (s, 2H, benzoyl-2, 6H), 7.62 (s, 2H, benzoyl-4H). EIMS



Scheme 1.

(*m*/*z*): calcd. for $C_{27}H_{30}Br_2N_3O_2$, 588, 590, 586, 589, 587, 591; found, 588, 590, 586, 589, 587, 591 ($[M+H]^+$).

2.1.5. 3,7-Bis(diethylamino)-10-tribromoacetylphenoxazine (DP5)

^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm) 1.99 (t, 12H, amino-methyl), 3.35 (q, 8H, amino-ethylene), 6.42 (m, 4H, oxazine-2,4,6,8-H), ~7.2 (b, 1H, oxazine-1, 9-H), ~7.6 (b, 1H, oxazine-1, 9H). EIMS (*m*/*z*): calcd. for $C_{22}H_{26}Br_3N_3O_2Na$, 628, 626, 630, 624, 627, 629, found 628, 626, 630, 624, 627, 629 ($[M+Na]^+$).

2.2. Measurements

Absorption spectra were measured by a Shimazu UV-1601 UV–visible spectrophotometer. A SureLite II (Continuum) laser that generates 355 nm (THG) and 266 nm (FHG) light pulses was used for excitation of the dye precursors and for the determination of the photochemical reaction quantum yield. A 150 W Xe Arc lamp with the appropriate filters was also used to study the photolysis and reaction mechanism.

3. Results and discussion

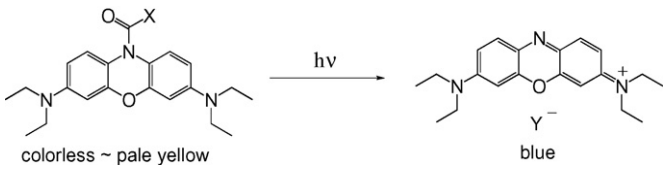
3.1. Photochemical reaction

All of the dye precursors in this study were found to undergo photochemical reaction upon irradiation with UV light that resulted in the generation of oxazine dye derivatives (Scheme 2), which exhibit a blue color with a strong absorption band in the 645 nm region.

Dye precursors do not fluoresce, while photogenerated oxazine dyes emit strong fluorescence.

The changes in the absorption spectra of air-saturated acetonitrile solution of DP1 as a function of time after irradiation with UV light are shown in Fig. 2. Three isosbestic points at 248, 265 and 355 nm were observed in the absorption spectra after UV irradiation. The intensity of the absorption band at 645, 450 and 260 nm were found to increase as a function of time after light irradiation, whereas the absorption intensities at 227 and 281 nm decreased. The absorption band formed at 645 nm is typical of an oxazine dye absorption including its maximum wavelength and spectral shape. Therefore, it is evident, from these kinetic data that the photoreaction of DP1 leads to the formation of its respective oxazine dye.

Although the dye precursors employed in this study are all neutral compounds, the photochemically generated oxazine dyes are cationic molecules, which suggests that an oxidation reaction step must be involved in the formation of the dye.



Scheme 2.

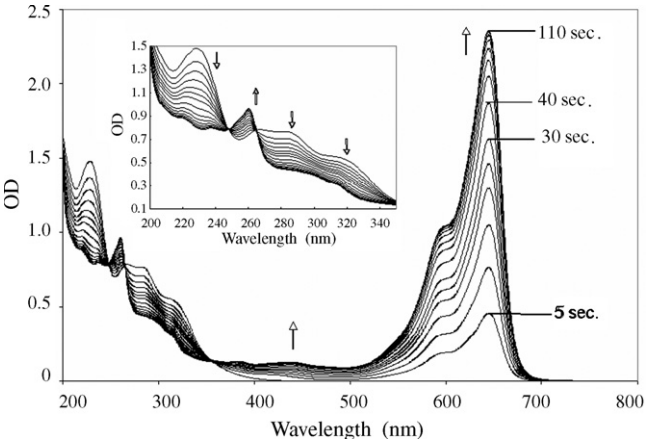


Fig. 2. Absorption spectra changes of DP1 in air-saturated acetonitrile solution as a function of time after excitation with UV light.

A possible oxidizing agent is the dissolved oxygen contained in the air-saturated solution. To ascertain the effect and need of oxygen for the oxidation of the dye, we measured the quantum yield of the products in the presence and absence of oxygen.

Fig. 3 shows the absorption spectral changes upon light irradiation of deoxygenated acetonitrile solution having the same concentration dye precursor as that of the air-saturated solution. The air-dissolved oxygen was removed by three freeze–pump–thaw cycles before any measurements were made.

Three isosbestic points were observed at 242, 270 and 350 nm with increase in absorbance at 645, 420 and 260 nm and decreases at 227 and 281 nm. Fig. 4 shows the change in absorbance at 645 nm as a function of UV irradiation time. Increase in absorption intensity at 645 nm, which corresponds to the formation of oxazine dye, was also observed in air-saturated solution and found to be twice as large as that without air.

For air-saturated samples of DP1 the absorbance at 645 nm increased with an initial slope of 1.4 and reached an intensity of 2.4 A, while the equivalent deoxygenated solution slope was 0.57 and the maximum absorption intensity was 0.96. The initial slope of the air-saturated solution is 2.5 times that of the deoxygenated samples, therefore 2.5 times more dye molecules were

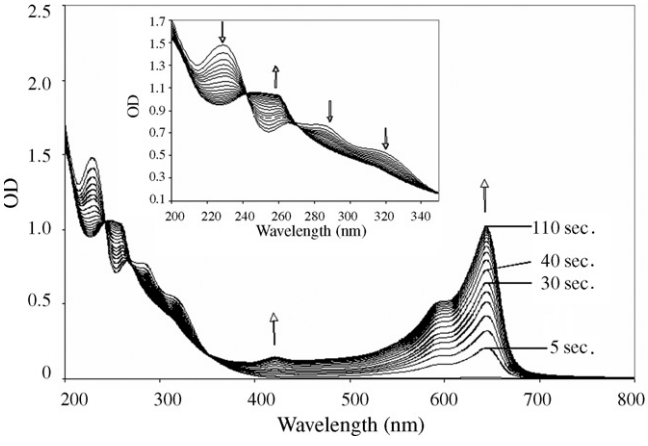


Fig. 3. Absorption spectral changes of DP1 in deoxygenated acetonitrile solution as a function of time(s).

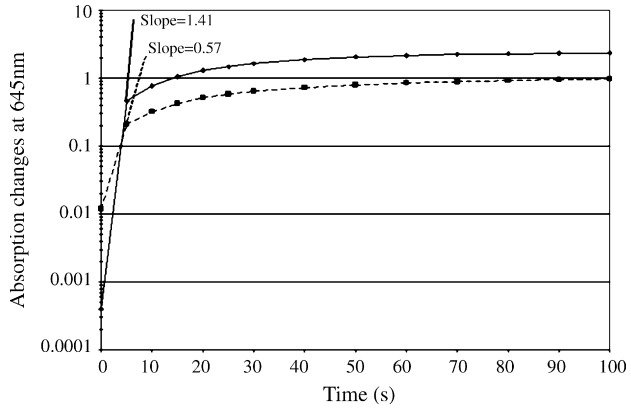


Fig. 4. Absorption changes of DP1 at 645 nm vs. UV irradiation time (s) in the presence of oxygen (solid line) and the absence of oxygen (dashed line). The absorbance experimental error was measured to be 15%.

generated in the presence of oxygen compared to those in the absence of oxygen.

A similar oxidation effect was also observed for DP2 and DP4. These data are listed in Table 1 where the effect of oxygen on the photochemical reaction of oxazine dye formation rate and converged absorbance with and without oxygen are summarized.

The oxazine dye formation data show that oxygen increases the dye formation reaction rate by a factor of 2.5 over the rate without oxygen and consequently yields 2.5 times more dye molecules compared to the samples without oxygen.

3.2. Quantum yield

Quantum yields of oxazine dye formation are summarized in Table 2. The acetyl-type dye precursors (DP2 and DP5) were found to be more sensitive to light than the benzoyl-type derivatives (DP1, DP3 and DP4). For acetonitrile solution excited at 266 nm, the quantum yield of DP1 was measured to be 2.3×10^{-2} and that for DP2 was 0.11, which is about 5 times higher than that for DP1. Moreover, DP5, in which three hydrogen atoms on the acetyl carbon of DP2 are substituted with bromine atoms, showed a quantum yield of 0.24 for oxazine dye formation. The quantum yields of DP1 excited at 355 nm in several solvents were also measured. No relationship was observed between quantum yield and solvent properties, such as polarity or protic/aprotic character, however large enhancement of the quantum yield in bromoform, which was measured to be 0.17, was observed. Although this result seems to imply external heavy atom effect, this mechanism does not agree with other data. Further details of the solvent effect on quantum yield are under investigation.

Table 1
Ratio of the dye formation rates and convergent absorbance plateau with and without oxygen

Dye precursor	Ratio of the dye formation rates	Ratio of the absorbance plateau
DP1	2.5	2.5
DP2	1.6	2.4
DP4	2.4	2.7

Table 2
Quantum yields of dye formation in the presence of oxygen, $\lambda_{exc} = 355$ nm

Dye precursor	Solvent	Quantum yield
DP1	Acetonitrile	4.9×10^{-3}
	Methanol	2.7×10^{-3}
	Propanol	2.8×10^{-3}
	THF	1.5×10^{-3}
	Dichloroethane	5.8×10^{-3}
	Toluene	2.3×10^{-3}
	Ethyl acetate	5.7×10^{-3}
	Chloroform	6.7×10^{-3}
	Bromoform	0.17
DP2	Acetonitrile	$\sim 2.5 \times 10^{-2}$
DP3	Acetonitrile	1.7×10^{-3}
DP4	Acetonitrile	3.7×10^{-4}
DP5	Acetonitrile	0.24

The oxygen effect on the quantum yield of dye formation was also measured at 266 and 355 nm excitation wavelengths, these results are summarized in Table 3. Oxygen was found to affect the quantum yields of dye formation. In the presence of oxygen, for DP1 excited at 355 nm, the quantum yield was measured to be 4.9×10^{-3}, which is 1.9 times larger than the 2.6×10^{-3} quantum yield for samples without oxygen. In the case where DP1 was excited with 266 nm light, the quantum yield in the presence of oxygen was 1.8 times larger than that without oxygen. For DP2 excited at 266 nm, the dye formation reaction was slightly smaller than that measured for DP1.

The dependence of the quantum yields of dye formation, on excitation wavelength, was also determined in the presence and absence of oxygen. The dye formation quantum yield at 266 nm excitation was found to be ~5.0 times larger than the quantum yield measured with 355 nm wavelength excitation. This result suggests that a more efficient pathway to the product may open up at the higher, 266 nm, excited state than at the 355 nm lowest excited state.

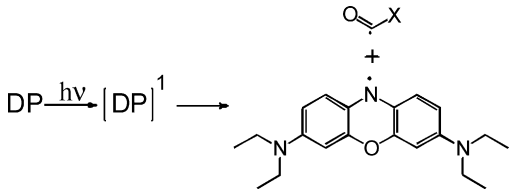
3.3. Photoreaction mechanism

It is probable that the dye formation reaction proceeds through a singlet excited state of the dye precursor. This mechanism is based on the following observations: oxygen is known to quench triplet excited states, which should lead to a decrease in the quantum yield of dye formation reaction in the presence of oxygen. However, the opposite dependence on oxygen is observed in our experiments. We find that the quantum yield

Table 3
Effect of oxygen and excitation wavelength on dye formation quantum yield in acetonitrile

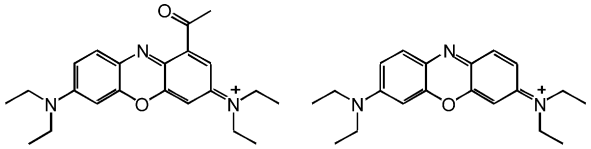
Dye precursor	λ_{exc} 266 nm		λ_{exc} 355 nm	
	$+O_2$	$-O_2$	$+O_2$	$-O_2$
DP1	2.3×10^{-2}	1.3×10^{-2}	4.9×10^{-3}	2.6×10^{-3}
DP2	0.11	7.2×10^{-2}	$\sim 2.5 \times 10^{-2}$	

increases in the presence of oxygen rather than decrease. If the triplet state lifetime is shorter than 10^{-6} s then oxygen at 10^{-3} M concentration will not completely quench the triplet state, but neither enhance the triplet state reaction. However, we find that if one assumes only a singlet state mechanism it does not explain the increase in quantum yield observed in Bromoform solution. The involvement of triplet state in the photoreaction mechanism cannot be completely excluded.



Higher light sensititvity of acetyl type dye precursors DP2 and DP5 may be due to the stability of acyl radicals, which are usually less stable than benzoyl radicals. Therefore, less stable acetyl radicals could decrease the possibility of the back reaction that leads the starting material and increase the quantum yield of the photoreaction. Furthermore, acetyl radicals would, inherently, conduct decarbonylation reactions, in which the acetyl radicals decompose into the highly reactive methyl radical and carbon monoxide [17]. This decarbonylation would also prevent the acetyl radicals from generating the starting material through the reverse reaction. Other factors may also contribute to the sensitivity of DP2 and DP5. The photochemical reaction products were analyzed by several methods including UV, NMR and mass spectroscopy. For DP2 in the absence of oxygen, a signal at $m/z = 366.5$ was observed in positive mass spectra, which is two mass units smaller than the m/z of the starting DP2 material. The $m/z = 366.5$ corresponds to a structure that involves the oxazine chromophore with an acetyl group that has migrated from the original nitrogen atom to a carbon atom (**2**). This migration is well known as Fries rearrangement [18,19], in which the acetyl group migrates from the nitrogen atom to the carbon atom via a radical mechanism involving homolytic cleavage of the N–C bond [20,21]. The mass spectra data, therefore, strongly suggest that an early step of the photochemical reaction of the oxazine dye precursors involves radical formation by homolytic cleavage of the C–N bond originating from a singlet excited state.

We also observed $m/z = 324.5$, which corresponds to the oxazine dye (**3**), and no other signals of reasonable intensity were detected in the presence of oxygen. In addition negative mass spectra of DP1 reveal an $m/z = 121$ peak in the presence of oxygen and not in its absence. This signal may be due to benzoate anion.



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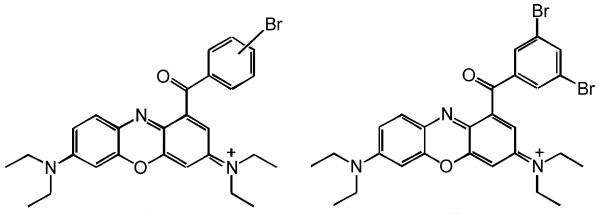
When oxygen is present it is expected to react with the radicals generated via singlet excited state C–N bond dissociation to generate benzoate anion. In the absence of oxygen, the singlet excited state was found to generate a radical mix, that rearrange and react with each other, because of the lack any of the other reactant, such as oxygen, to yield a Fries rearrangement product. Even in the absence of oxygen, oxazine dye was still generated even though there is absence of an obvious oxidation reagent. This observation suggests that the oxazine radical, which is generated by homolytic bond cleavage through the singlet excited state, must be oxidized by a compound, which is generated during the reaction (Scheme 3).

To clarify the photochemical reaction mechanism of the oxazine dye precursor, further mass spectroscopic analyses were conducted with DP4 that possesses two bromine atoms added to its molecular structure. Bromine makes the mass spectra signals of the products much more distinguishable owing to the highly distinctive isotope pattern of the bromine atoms. The positive mass spectroscopy of such DP4 molecules shows three signals at $m/z = 324$, 506 and 586 both in the presence and absence of oxygen. The most intense signal was observed at $m/z = 324$ without the bromine isotope pattern, which corresponds to the oxazine dye (**3**) cation mentioned above. The rest of the weak signals at $m/z = 506$ and 586 are assigned to the one-bromine and two-bromine isotope pattern, respectively. These signals can be attributed to the oxazine dye cation with the mono-bromobenzoyl (**4**) and di-bromobenzoyl (**5**) moiety migrated from N atom to C atom, respectively.



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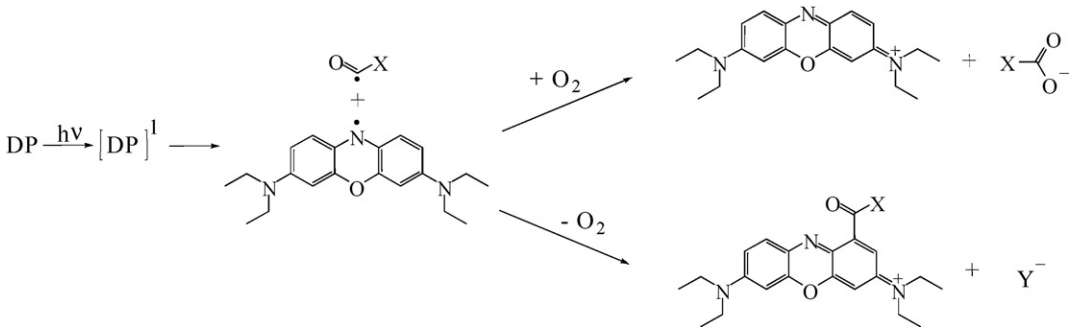
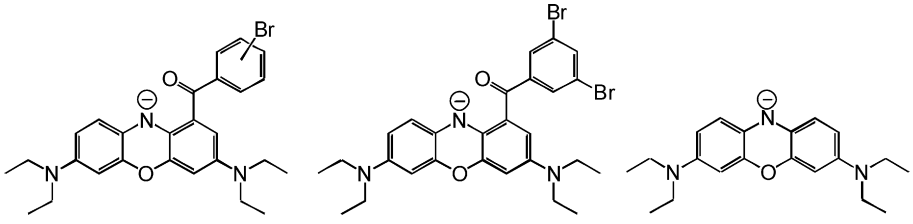
It is not accurate to calculate the concentration of each material in the sample, from intensities of signals observed in mass spectrum, because signal intensities depend on the charge, type of the atom holding the charge and ionization efficiency of species. However, the three cations have the same positive charge, +1 and the same π-conjugated electron system in which the formal charge mainly resides on the quaternary nitrogen atom. Therefore we estimated the ratios of quantity of the cations from the mass spectra signal intensities. The ratio of mono-bromo (**4**; $m/z = 506$) and di-bromo oxazine dye cation (**5**; $m/z = 586$) to the non-bromo (**3**; $m/z = 324$) is 0.13 and 0.21 in the absence of oxygen and 0.03 and 0.22 in the presence of oxygen, respectively.

In the negative mass spectrum of DP4, a rich mass spectrum was observed in the presence of oxygen. Some of the signals, may be due to contaminants from the mass spectrometer apparatus that cannot be avoided yet make the spectrum analysis difficult. Two signals were observed with bromine isotope patterns in the absence of oxygen. One at $m/z = 547$ had a clear one bromine isotope pattern and another at $m/z = 627$ with the two bromine isotope pattern. Interestingly, both signals are 41 mass units larger than those at $m/z = 506$ and 586, which are derived from the oxazine dye cation with mono-bromo and di-bromo benzoyl substituent in the positive mass spectrum.



Scheme 3.

Since the photochemical reaction was conducted in acetonitrile solution, it is quite reasonable to attribute the 41 mass units to acetonitrile. However, the signals at $m/z = 506$ and 586 cannot be attributed to the oxazine dye cation because these cations should not be detected under negative mass spectroscopy conditions. Therefore, they might belong to species possessing the same composition formula as those of the oxazine dye cations, but of the opposite charge namely: mono-bromo oxzaine anion (**6**), di-bromo oxazine anion (**7**) and oxazine anion (**8**).



6 **7** **8**

Pulse radiolysis studies on methylene blue in aqueous solution have found that two methylene blue radicals are generated from reduction of methylene blue by the hydrated disproportionation reaction electron that undergo further disproportionation reaction to form methylene blue (MB^+), leuco methylene blue (MBH) and hydroxide ion [22,23].

$$2MB^{\cdot} + H_2O \rightarrow MB^+ + MBH + OH^-$$

It seems reasonable therefore to assume that the methylene blue anion generated from the disproportionation reaction would easily remove a proton from water to generate leuco methylene blue, because the reaction takes place in aqueous solution. Assuming this reaction occurs, it is expected that the two oxazine radicals resulting from UV homolytic bond cleavage will also undergo the same type of disproportionation reaction even in non-aqueous solution, such as acetonitrile, to generate oxazine dye and oxazine anion pair. The details of this reaction mechanism are not completely known at the present time.

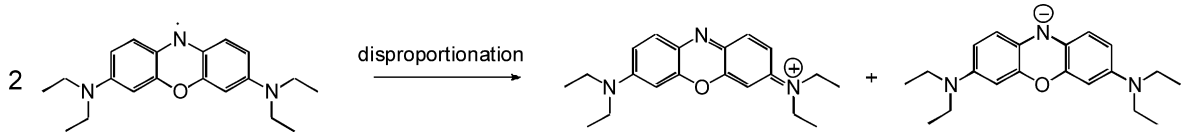
Two mechanisms are possible in terms of the disproportionation reaction between two oxazine radicals in the absence of oxygen: dimer formation and direct electron transfer. The disproportionation reaction via dimer formation between two oxazine radicals is shown in Scheme 4.

Our results do not exclude that the reaction may be, such as direct electron transfer between two oxazine radicals as a possible means for the generation of the "oxazine anion".

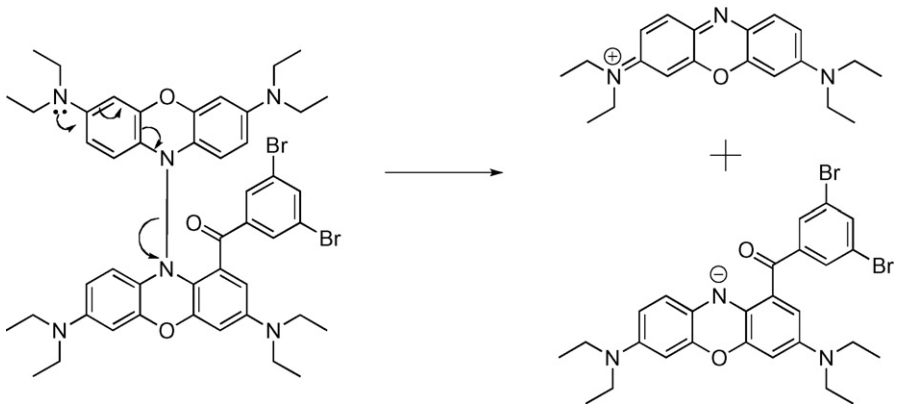
In the presence of oxygen, we find that the "oxazine anion" species disappeared from negative mass spectra. This fact may suggest another reaction pathway to generate the products, in which oxygen oxidizes directly to the oxazine radical.

In addition to the "oxazine anion" signals described above, a signal at $m/z = 365$ was observed in the negative mass spectra of DP4 regardless of the presence or absence of oxygen. This signal may be attributed to acetonitrile ($m/z = 41$) plus the simple "oxazine anion" without a benzoyl migration group (**8**, $m/z = 324$). Such assignment is ambiguous because no bromine isotope pattern was observed.

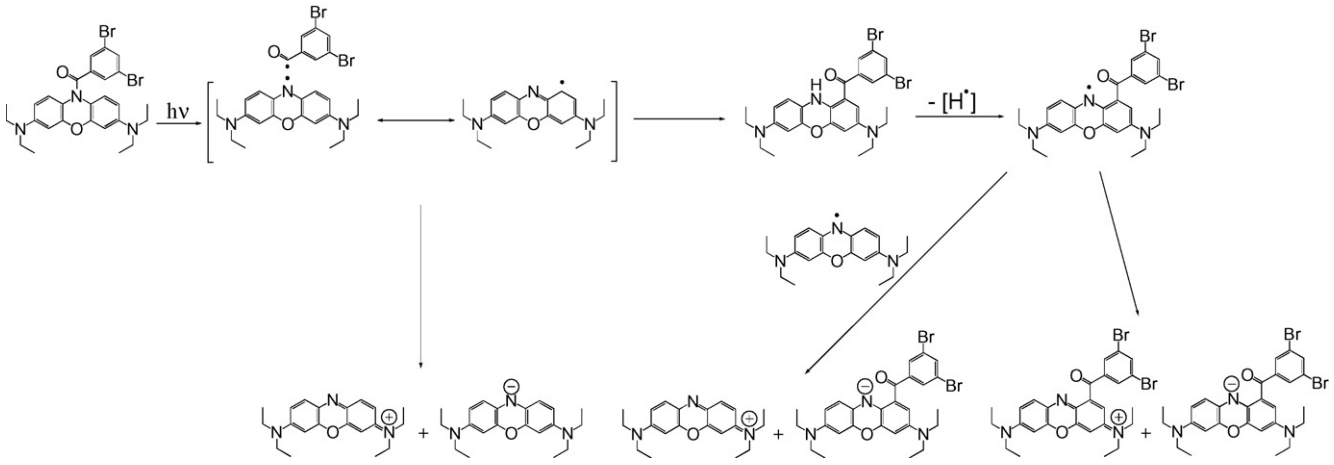
Possible photochemical reaction mechanisms in the absence of oxygen are summarized in Scheme 5. As mentioned above, the early steps of the reaction involve homolytic bond cleavage and subsequent generation of benzoyl oxazine radicals. Consequently, several intermediates are possible as a result of radical recombination. It is obvious that the recombination of benzoyl and oxazine radicals could produce the starting material. It is also possible that the rearranged molecule is formed by the resonance structures of the oxazine radical (Fries rearrangement) in addition.



The disproportionation reaction between two identical or different oxazine radicals could lead to the formation of oxazine



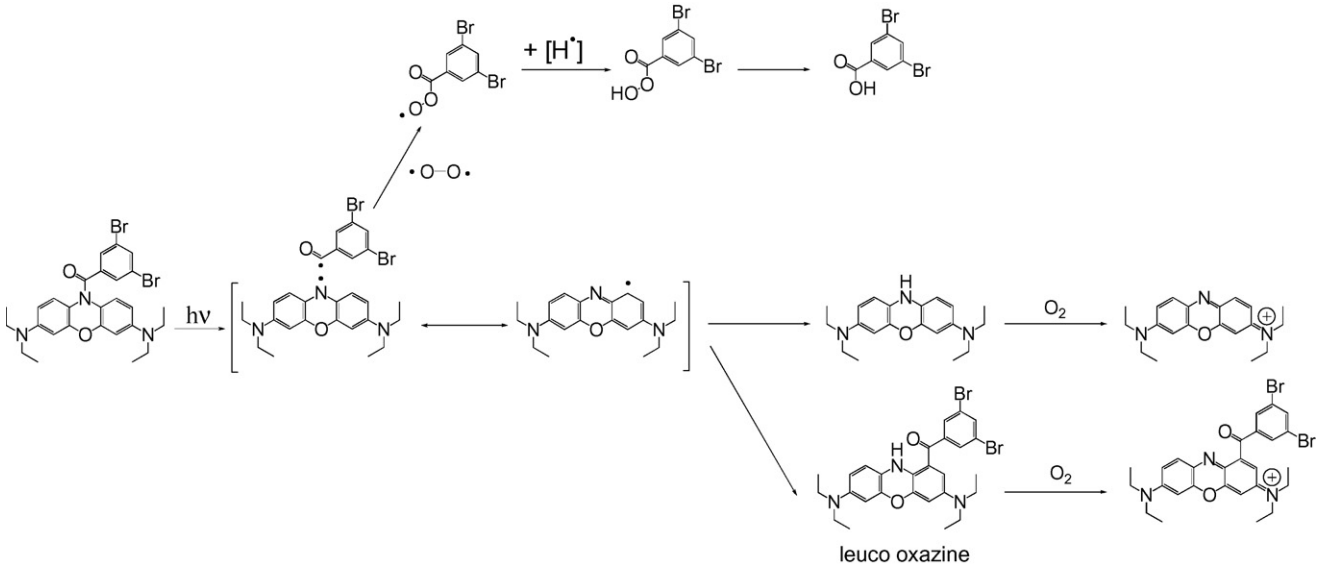
Scheme 4.



Scheme 5.

dye cation and "oxazine anion" pairs. In the case where the reaction is between two oxazine radicals with or without a benzoyl group, the benzoyl substituted oxazine moiety might accommodate the anion charge more easily than the normal oxzaine moiety because of the electron withdrawing stabilization effect of benzoyl group.

The reaction mechanisms in the presence of oxygen are summarized in Scheme 6. It is all probable that the benzoyl radical



Scheme 6.

may react with oxygen to generate perbenzoic radical [24], which may extract hydrogen to generate perbenzoic acid. This peroxyacid subsequently reacts with other species in turn such as the dye precursor, leuco oxazines, or other reaction intermediates to generate benzoic acid [25,26]. On the other hand, the oxazine radical may extract hydrogen to form leuco oxazines [20,26], which are rapidly oxidized by oxygen [14] resulting in the generation of oxazine dye cations and anions. At the present time, the exact structures of the intermediate species cannot be determined accurately. These reactions are expected to be competitive and solvent dependent.

4. Conclusion

The synthesis, spectra and mechanism of the photoreaction of a dye precursor to generate a fluorescing dye have been described. The change in the absorption spectra as a function of time and wavelength have been measured and the quantum yields of the photoreaction that generates the dye have been measured as a function of wavelength in both the presence and absence of oxygen. Based on the data a mechanism of the photochemical reaction has been proposed.

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