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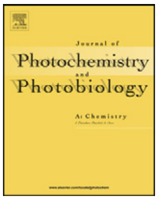

Photochromic behavior of spironaphthoxazine in metal ion-containing solutions

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ABSTRACT

The isomerization and metal chelation of spironaphthoxazine (SNO) in ethanol solutions have been investigated by measuring the UV–vis absorption spectra as a function of time. The protonated species of merocyanine (MC), an isomer of SNO, was gradually formed in the solutions containing SNO and aluminum ions in the dark. The proton was provided by the reaction of the aluminum ions with a slight amount of water contained in the ethanol solvent. The protonated species was slowly transformed into the aluminum chelate complex of MC by ligand exchange of the ethanol-solvated aluminum for MC in the dark. UV irradiation promoted the isomerization and chelation without forming the protonated species. The spectroscopic analysis with various compositional ratios of SNO and aluminum ions revealed that one aluminum ion was coordinated to three bidentate MC ligands in the ethanol solution.

1. Introduction

Many photochromic organic compounds have been found and widely investigated in various fields [1]. The color reaction of colorless molecules during UV irradiation can be applicable to light control glasses or materials. Photochromism is also an important phenomenon to provide a photochemical technique for development of electronic devices such as photo-quantum switching and memory [1–6]. The photochromic phenomena are caused not only by the photo-isomerization of molecules, but also by the photoinduced metal chelation of organic ligands [7–13]. One needs to control the photoreaction and photochemical properties of the molecules in order to perform a fast and effective photochromism. Therefore, it is important to study the reaction mechanism and kinetics of such organic molecules in various solutions.

Spirooxazines exhibit the well-known photochromic reaction of photo-induced interconversion between the original colorless form and the colored merocyanine (MC) form [3,6]. The MC easily coordinates to specific metal ions (e.g., Zn^{2+}) in solution and forms fluorescent and non-fluorescent MC-M^{n+} complexes; the former is stable to heat and visible light while the latter is unstable [7,8].

We previously reported the details of the fluorescence and excitation spectra of spironaphthoxazine (SNO) in various solvents [14]. Two types of fluorescent intermediate species (X_s and X_h) intervened between SNO and MC by cleavage of the spiro C–O bond, as shown in Scheme 1 [15–17]. In low-polar solvents such as benzene, upon the excitation of SNO (E_1), the 390-nm fluorescence (F_1) was normally emitted from its excited state (SNO*). In aprotic polar solvents such as acetonitrile, some of the SNO molecules were transformed into a non-planar, strongly solvated species (X_s). The transition from species X_s to X_s^* (E_2) is followed by the 450-nm fluorescent emission (F_2). In protic polar solvents such as ethanol and water, some of the SNO molecules are normally excited to SNO* (E_1) to produce the hydrogen-bonded species (X_h^*) by the C–O bond breakage in the excited states, followed by the 430-nm fluorescent transition to X_h (F_3). The species X_h was immediately transformed into SNO or MC in the ground state. The fluorescence of the MC-Zn^{2+} complex is observed at around 540 nm by UV irradiation of SNO and Zn^{2+} in aprotic polar solvents such as acetone and acetonitrile [7,8,18,19].

In this study, we observed the isomerization and metal interaction of SNO in an ethanol solution containing SNO and certain types of metal ions in the dark and during UV irradiation. The dark and photochemical reaction processes and kinetics were investigated by measuring the UV–vis absorption spectra as a function of time.

2. Experimental

SNO was synthesized and purified according to a procedure described elsewhere [20]. Ethanol (99.5%, S grade), aluminum chloride (S grade), magnesium chloride (S grade), zinc chloride (S grade), and 5.0 mol dm^{-3} hydrochloric acid (for volumetric analysis) were purchased from Wako Pure Chemicals and used without further purification.

An SNO ethanol solution and metal chloride ethanol solutions were prepared and adjusted to 5.0×10^{-5} and 5.0×10^{-4} mol dm^{-3}

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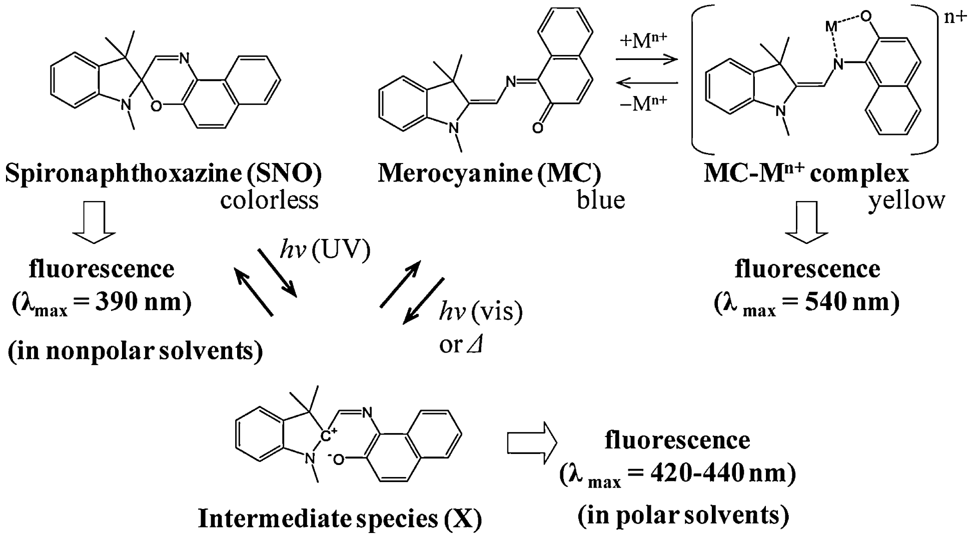

Scheme 1. Isomerization and metal chelation of SNO.

concentrations, respectively. The UV–vis absorption spectra were measured as a function of time in the dark at 293, 303, 313, and 323 K and during UV irradiation at 293 K using a Shimadzu UV-2500PC spectrophotometer. UV (350 ± 10 nm) irradiation was conducted using a fluorescence spectrophotometer (Shimazdu RF-5000) with a 150-W Xe short arc lamp (Ushio UXL-155) in order to study the photochromic behavior.

3. Results and discussion

3.1. Reaction in the dark

Changes in the UV–vis absorption spectra in the dark were investigated in order to examine the thermal influence on the SNO behavior in the ethanol solutions containing Al^{3+}, Mg^{2+}, and Zn^{2+}. No spectral change was observed in the solution containing Mg^{2+} or Zn^{2+}. In the ethanol solution, hydrogen bonding induced the isomerization from SNO to MC in the ground state via the unstable X_h [14]. The species X_h was immediately transformed into SNO or MC. However, the equilibrium constant of the reaction from SNO to MC is low at around room temperature. The concentration of MC was very low under the present condition. Fig. 1 shows the change in the UV–vis absorption spectrum of the SNO solution with Al^{3+} in the dark at 323 K. The time course of the absorbance values for the main peaks is plotted in Fig. 2. The spectral band having peaks at around 300, 320 and 350 nm and a shoulder at around 370 nm originates from the naphthoxazine ring moiety of SNO [21–23]. In addition, the spectrum observed just after the preparation (at 0) exhibited a band at 530 nm assigned to the species protonated at the naphtholate part of the MC (MCH^+) [24,25]. This assignment was confirmed by the spectral change in the SNO ethanol solution containing hydrochloric acid (1.0×10^{-3} mol dm^{-3}) as shown in Fig. 3. An isosbestic point was observed at 325 nm in Fig. 3, indicating the acid–base equilibrium between SNO and MCH^+. The proton assisted in the C–O bond cleavage and ring opening of SNO. There is the possibility of formation of the protonated SNO ($SNOH^+$) and its fast thermal isomerization to MCH^+.

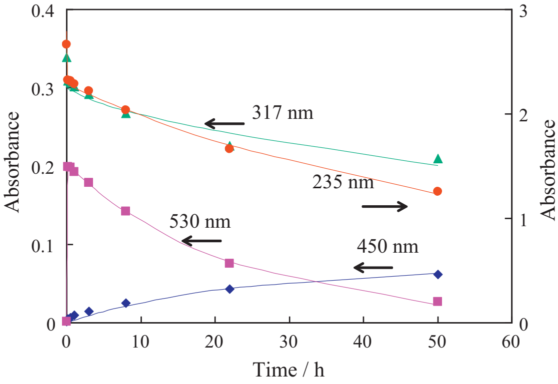

Fig. 2. Time course of absorbance value at each wavelength for the ethanol solution containing SNO and $AlCl_3$ in the dark at 323 K.

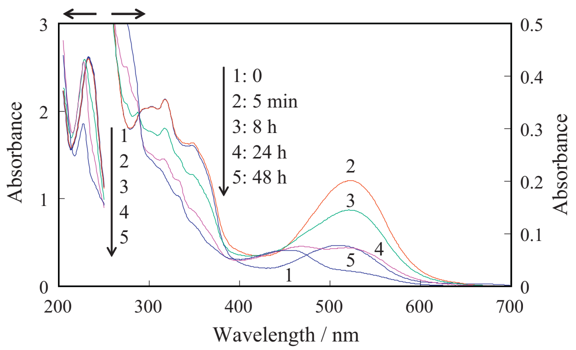

Fig. 1. Change in UV–vis absorption spectrum of the ethanol solution containing SNO and $AlCl_3$ in the dark at 323 K.

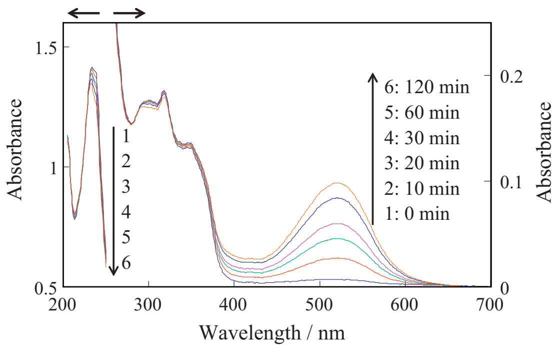

Fig. 3. Change in UV–vis absorption spectrum of the ethanol solution containing SNO and HCl in the dark at 293 K.

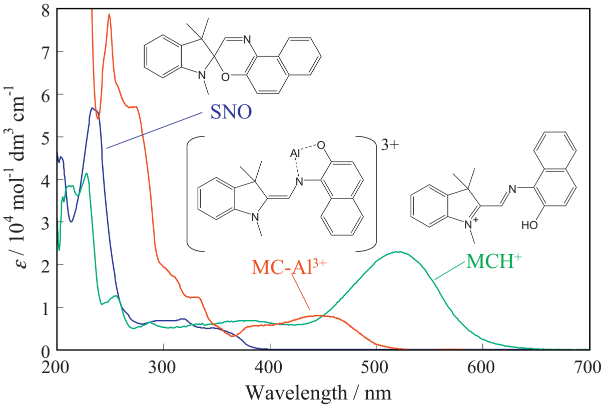

Fig. 4. The UV–vis absorption spectra of SNO, MCH^+, and MC-Al^{3+} species obtained from the kinetic analysis of the UV–vis absorption spectra of the ethanol solution containing SNO and $AlCl_3$ in the dark at 323 K.

The band intensity at 530 nm increased and then decreased in the presence of Al^{3+}. With this decrease, a band at 450 nm became evident due to the aluminum-chelation of MC. Most of the aluminum ions are expected to be solvated in the ethanol solution and form hydrogen-bonded complexes such as $[Al(EtOH)_4]^{3+}$ [26]. The proton was provided by the reaction of Al^{3+} with a slight amount of water contained in the ethanol solvent, and then some aluminum ions formed $[Al(OH)(EtOH)_3]^{2+}$ [27]. The possibility of such a reaction is lower in the solutions containing Mg^{2+} and Zn^{2+} because the ionization energy values to produce them, i.e., their electron affinity, 15.0 and 18.0 eV, respectively, are lower than that to produce Al^{3+}, i.e., its electron affinity, 28.4 eV [28]. The protonated species was slowly transformed into the aluminum chelate complex of MC (MC-Al^{3+}) by the ligand exchange of $[Al(EtOH)_4]^{3+}$ for MC. These reactions are expressed by the following consecutive reactions:

$$\mathrm{SNO} + \mathrm{H}^+ \rightarrow \mathrm{MCH}^+ \quad (1)$$

$$\mathrm{MCH}^+ + \mathrm{Al}^{3+} \rightarrow \mathrm{MC\text{-}Al}^{3+} + \mathrm{H}^+ \quad (2)$$

in which the solvent molecules are omitted. The reaction rate constants of these reactions, k_1 and k_2, were estimated to be 1.52×10^{-2} and $1.21 \times 10^{-5}\,\mathrm{s}^{-1}$, respectively, by the first order analysis of the time course of the absorbance values at the main peaks, i.e., 235, 317, 450, and 530 nm. Here the concentrations of H^+ and Al^{3+} are regarded as much higher than that of SNO. The analysis determined the molar extinction coefficient values at the main peaks. Consequently, the spectra of the individual species were separated from the total absorption spectra. Fig. 4. shows the spectra of SNO, MCH^+, and MC-Al^{3+}. The spectrum of SNO was observed in ethanol without H^+ and Al^{3+}. The spectrum of MCH^+ was obtained by subtracting the SNO spectrum from the spectrum observed in the ethanol solution containing hydrochloric acid, taking into account the molar extinction coefficients of SNO and MCH^+ at the main peaks and their amounts. Finally, the spectrum of MC-Al^{3+} was obtained by subtracting the spectra corresponding to the amounts of SNO and MCH^+ from the spectrum observed in the Al^{3+}-containing ethanol solution after a 48-h reaction.

The reaction constants at different temperatures were also obtained and the Arrhenius parameters for these reactions were estimated from the related plots as shown in Fig. 5. The values of the activation energy and frequency factor were 79 kJ mol^{-1} and $1.3 \times 10^{11}\,\mathrm{s}^{-1}$ for the first reaction, and 62 kJ mol^{-1} and $1.4 \times 10^5\,\mathrm{s}^{-1}$ for the second reaction. These activation energy values are lower than those of the forward and backward reactions from SNO to MC, which were reported to be 100–102 and 81 – 83 kJ mol^{-1}, respectively [21,22]. The protonation and aluminum chelation of SNO easily proceeded under the present conditions. The chelation was assisted by the addition reaction of protons and subsequent ring-opening.

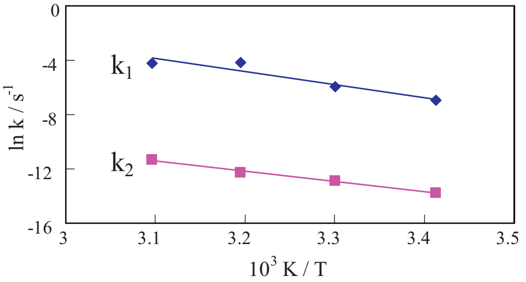

Fig. 5. The Arrhenius plots for protonation and metal chelation of SNO.

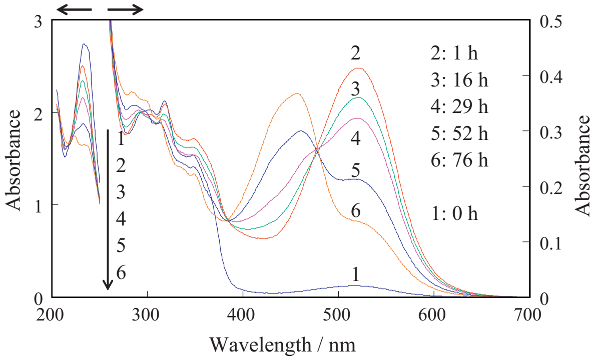

Fig. 6. Change in UV–vis absorption spectrum of the ethanol solution containing SNO and $AlCl_3$ during 350-nm light irradiation at 293 K.

3.2. Reaction during UV irradiation

No spectral change was observed in the SNO solutions containing Mg^{2+} or Zn^{2+} even during UV irradiation, although metal chelation was observed in the aprotic polar solvents [7,8,18,19]. This is because the hydrogen bonding to ethanol molecules prevents the chelation. In addition, the interaction of MC with Mg^{2+} and Zn^{2+} is weaker than with Al^{3+} due to their lower electron affinity. Fig. 6 shows the change in the UV–vis absorption spectrum of the solution with Al^{3+} during UV irradiation at 293 K. The time course of the absorbance values at the main peaks is plotted in Fig. 7. Under this condition, the reaction rates were faster and the amounts of products were greater than in the dark although the spectral peak positions and the patterns of increase and decrease in their intensities were similar to those in the dark. However, the changes in the

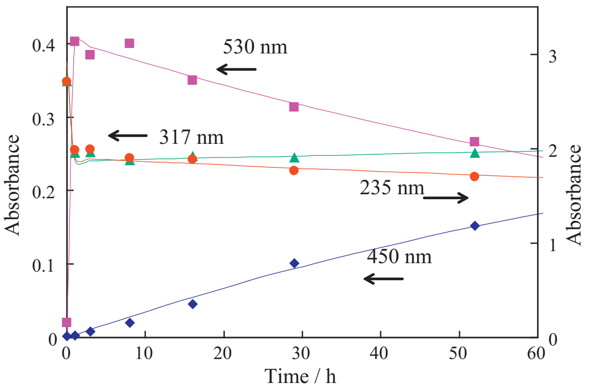

Fig. 7. Time course of absorbance value at each wavelength for the ethanol solution containing SNO and $AlCl_3$ during 350-nm light irradiation at 293 K.

Table 1
Reaction constants of protonation and aluminum chelation of SNO.

Temperature (K)	k_1 (s^{-1})	k_2 (s^{-1})	k_3 (s^{-1})
Dark			
293	9.59×10^{-4}	1.03×10^{-6}	–
303	2.60×10^{-3}	2.58×10^{-6}	–
313	1.49×10^{-2}	4.53×10^{-6}	–
323	1.52×10^{-2}	1.21×10^{-5}	–
UV irradiation			
293	1.49×10^{-2}	2.31×10^{-6}	2.93×10^{-6}

absorbance values were not fitted to the above consecutive reaction model (1) and (2). The following reaction in which SNO forms the MC-Al^{3+} complex was suggested in order to analyze the reactions:

$$\text{SNO} + Al^{3+} \rightarrow \text{MC-}Al^{3+} \qquad (3)$$

This process can be regarded as a first-order reaction because the rate of the aluminum chelation is much faster than that of the ring-opening isomerization to form MC [7,18]. Consequently, the reaction rate constants of the reactions (1)–(3), k_1, k_2, and k_3, were estimated to be 1.49×10^{-2}, 2.31×10^{-6}, and 2.93×10^{-6} s^{-1} by the first order analysis of the time course of the absorbance values at the main peaks. All the reaction rates in this study are summarized in Table 1. The photoreaction process of the aluminum chelation of SNO (3) was confirmed by this spectroscopy during UV irradiation. The constants, k_1, and k_2, were higher than those observed at the same temperature in the dark. With respect to reaction (1), the photoisomerization from SNO to MC induced forming MCH^+ because the quantum yield of the photoisomerization is reported to be a certain value, 0.2–0.4 [29,30]. With respect to reaction (2), MCH^+ somewhat absorbs UV light, which can thermally induce the aluminum chelation to some extent after the internal conversion because the chelation is suggested to be a ground state process. The constant for the photoinduced chelation process, k_3, was not significantly higher than that of the chelation process of MCH^+, k_2. This is because the steady state UV irradiation partly promoted the dissociation of MC-Al^{3+} to form MCH^+ and consequently decreased the apparent reaction constant of the chelation of MCH^+.

3.3. *Coordination number of aluminum*

A single coordination complex was expected under the above conditions of the aluminum-chelation because the concentrations of Al^{3+} were regarded as much higher than that of SNO. The aluminum ion possibly forms a multi-coordination complex, depending on the ligand concentration. As is well-known, the aluminum ion reacts with 8-hydroxyquinoline to form a Tris complex (Alq_3) through hexa-coordination [31–33]. The ligand/metal ratio can be estimated by a spectroscopic analysis of the "continuous variation method" [34–36]. The concentration of the MC-Al^{3+} complex was estimated by measuring the absorption spectra of the SNO ethanol solutions with Al^{3+} in different compositions of SNO and Al^{3+} during the UV irradiation at 293 K. Fig. 8 shows the time course of the absorbance at 450 nm assigned to the aluminum complexes of MC. The highest absorbance value was obtained in the solution in which the molar ratio of SNO to Al^{3+} was three after sufficient irradiation for the reaction. Fig. 9 shows the plot of the maximum absorbance values versus the SNO molar fraction. The highest absorbance value was obtained in the solution in which the molar fraction of SNO was 0.75. This value indicates that the ratio of the ligand to all the complex components is 3/4, i.e., the ligand/metal ratio is 3/1 [36]. These results concluded that the three coordination complex is the most stable in the ethanol solution. This is reasonable because one aluminum ion can coordinate to three MC's through the oxygen and nitrogen atoms bonded to the naphthalene ring to form a hexa-coordination complex similar to Alq_3.

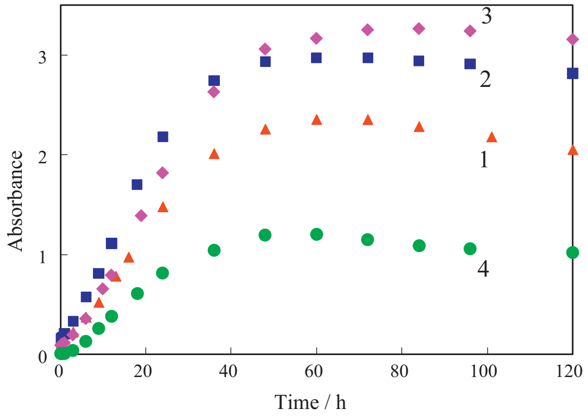

Fig. 8. Time course of absorbance values at 450 nm assigned to the aluminum complexes of MC for the ethanol solutions containing SNO and $AlCl_3$ during 350-nm light irradiation at 293 K. The molar ratios of SNO to Al^{3+} are (1) 1, (2) 2, (3) 3, and (4) 4.

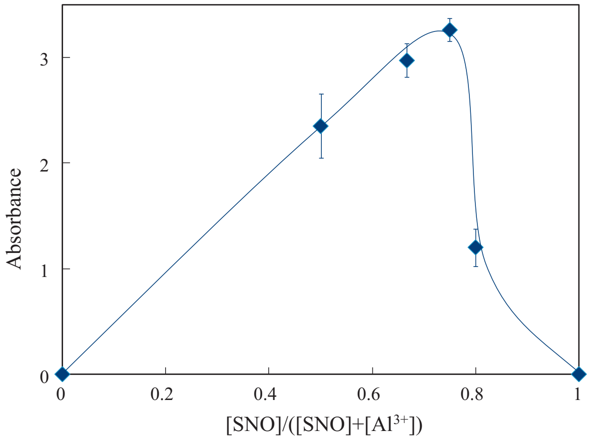

Fig. 9. The plot of the maximum absorbance values vs. SNO molar fraction for the ethanol solutions containing SNO and $AlCl^3$ after 350-nm light irradiation at 293 K.

4. Conclusions

The isomerization and metal chelation of SNO were observed in an ethanol solution containing SNO and some kinds of metal ions in the dark and during UV irradiation. The dark and photochemical reaction kinetics were investigated by measuring the UV–vis absorption spectra as a function of time. SNO was gradually protonated and isomerized to form MCH^+ in the solutions containing SNO and Al^{3+} in the dark. The proton was provided by the reaction of Al^{3+} with a slight amount of water contained in the ethanol solution. The protonated species was slowly transformed into the aluminum chelate complex of the MC by the ligand exchange of the solvated Al^{3+} such as $[Al(EtOH)_4]^{3+}$ for MC in the dark. The aluminum chelation was assisted by the addition reaction of protons and subsequent ring-opening in the dark. Furthermore, the UV irradiation promoted the isomerization, followed by fast chelation without forming MCH^+. On the other hand, SNO did not react with Mg^{2+} or Zn^{2+} to form any protonated species or metal complexes in the dark and during UV irradiation due to their low electron affinity. The spectroscopic analysis of various molar ratios of Al^{3+} to SNO revealed that one aluminum ion can coordinate to three MC's through the oxygen and nitrogen atoms bonded to the naphthalene ring to form a hexa-coordination complex.

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