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Triplet-sensitized deoxygenation reaction of 6-cyanophenanthridine 5-oxide in ethanol

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Abstract

Deoxygenation of 6-cyanophenanthridine 5-oxide (6CPNO) in the lowest triplet state was confirmed by triplet sensitization of proflavine with visible $S_1 \leftarrow S_0$ absorption band ($\lambda_{max} = 460$ nm) in ethanol. Absorption bands of 6-cyanophenanthridine (6CP) grew up at the expense of those of the *N*-oxide in a selective steady-light (>420 nm) irradiation of proflavine in the presence of the *N*-oxide. In the 460 nm laser pulse excitation of proflavine, furthermore, weak transient absorption due to sensitized triplet of the *N*-oxide was detected around 410 nm. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 6-Cyanophenanthridine 5-oxide; Proflavine; Deoxygenation; Triplet sensitization; The lowest triplet state; Transient absorption

1. Introduction

Photochemical deoxygenation or photoreduction of aromatic amine *N*-oxide to parent amine usually takes place as a minor process in addition to various photorearrangement reactions [1–5], as far as no strong oxygen-acceptors such as boron trifluoride [6], triphenylphosphine [7], aliphatic amines [8], and dienes [9] are present. In the photolysis of some aromatic amine *N*-oxides, however, deoxygenation may be the main photochemical process in appropriate solvents being oxidized [5]. When benzophenone was added as sensitizer to alcoholic solution of 2,4,6-triphenylpyridine *N*-oxide, dramatic increase and decrease in the formation of parent amine and rearrangement product were observed by Kumler and Buchardt [10]. They claimed that at least deoxygenation takes place in an excited state different from that leading to the rearrangement. Furthermore, deoxygenation is the only photochemical process of benzo[c]cinnoline *N*-oxide in degassed ethanol and 2-propanol [11]. When benzophenone was added as sensitizer, a dramatic increase was observed in the formation of parent amine. Molecular oxygen and 1-chloronaphthalene inhibited such a photoreduction. Consequently, Tanikaga proposed [11] that the formation of benzo[c]cinnoline proceeds via a triplet excited state of the *N*-oxide. On the basis of biacetyl-sensitization of quinoline- and isoquinoline *N*-oxides as well as eosine-sensitization of acridine *N*-oxide, Hata et al. [6] demonstrated that the lowest triplet state is regarded as a reactive intermediate. Based upon diacetyl-sensitization, Albini et al. [12] also proposed a triplet mechanism for deoxygenation of 4-benzoylpyridine *N*-oxide. However, it should be noted that parent amines produced in these sensitized experiments were just confirmed by TLC [6,10,11] or HPLC [12] in product analysis.

There has been no spectroscopic study combined with triplet sensitization. We undertook a triplet sensitization of 6-cyanophenanthridine 5-oxide (6CPNO) in a selective excitation of proflavine in ethanol. According to product analysis [13], *N*-ethoxyphenanthridone (*N*-EtO-phen) is major photoproduct upon direct excitation of 6CPNO in ethanol. Deoxygenation to form 6-cyanophenanthridine (6CP) takes place as a minor process. The present paper describes the proflavine-sensitized deoxygenation of 6CPNO, which is confirmed by growing absorption bands of 6CP at the expense of the absorption bands of 6CPNO in a selective steady-light illumination of proflavine. Occurrence of triplet energy transfer from proflavine to 6CPNO is directly evidenced by the transient absorption measurement, in which proflavine is selectively excited by a blue laser pulse (460 nm). As is distinct from direct excitation of 6CPNO, 6CP is predominantly formed in the proflavine sensitization of 6CPNO (Scheme 1).

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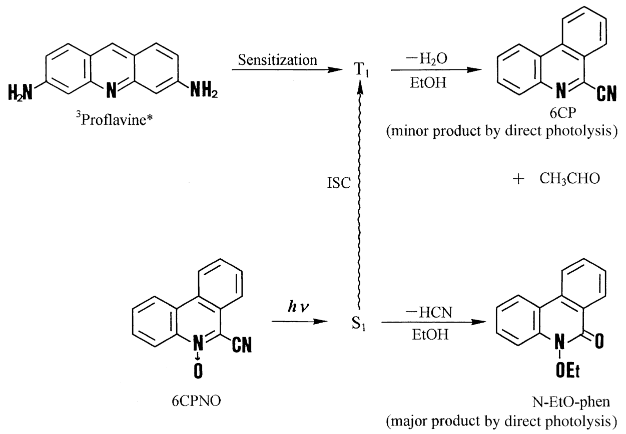


Scheme 1.

2. Experimental

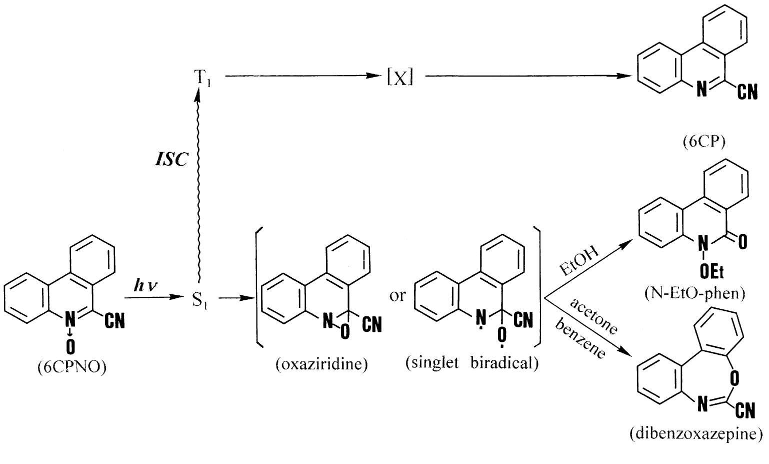
Both 6CPNO and 6CP were synthesized from phenanthridine by reported procedures [14]. Proflavine, selected as a triplet sensitizer, was prepared by neutralization of proflavine hemisulfate (Nakarai) with ammonia water, and then purified by recrystallization from ethanol. 9,10-Dibromoanthracene (DBrA) from Tokyo Kasei was purified by repeated vacuum sublimation. Spectrograde ethanol (99.5%) of Nacalai Tesque was used as received. As a sample solution of *N*-ethoxyphenanthridone (major photoproduct of 6CPNO), we employed photolysed ethanol solution of 6CPNO, the 394 nm absorption of which had disappeared. Sample solutions were degassed by repeated freeze–pump–thaw cycles. Absorption spectra were recorded on a Hitachi U-3200 spectrophotometer. A xenon arc lamp (Eagle LX 300F) was used as steady-light source. Steady-light (>360 nm) transmitted through a cutoff filter (Corning 0-51) was used for direct excitation of 6CPNO. Steady-light (>420 nm) transmitted through a cutoff filter (Toshiba Y-46) was used for selective excitation of proflavine in the presence of 6CPNO. Triplet sensitization was also examined by a transient absorption spectroscopy using pulsed Xe flash as monitoring beam. The 460 nm pulse from the dye laser (Coumarine 47/Lambda Physik FL3002), pumped by an excimer laser (Lambda Physik EMG53MSC or COMPex 102), was employed for the selective excitation of proflavine. The pulsed Xe flash beam crossed with the dye laser beam at the angle of ca. 20°.

Transient absorption spectra on direct photolysis of 6CPNO and proflavine were obtained by UV laser pulse excitations of them. The third harmonics (355 nm) of a YAG laser (Continuum Powerlite Precision 8000) and XeCl pulse (308 nm) of an excimer laser (Lambda Physik COMPex 102) were employed UV pulses. These UV pulse beams perpendicularly intersect with a pulsed Xe flash beam.

A digital delay generator (Stanford Research Systems DG535) was used for synchronization of laser pulse, pulsed Xe flash, and electromechanical shutter to prevent sample solution from photodegradation caused by monitoring Xe beam. Electric signals from a photomultiplier (Hamamatsu Photonics R928) were digitized by a storagescope (Iwatsu TS-8123). A personal computer (Fujitsu Micro 11BS) was used for the acquisition and analysis of the digitized data.

3. Results and discussion

Photorearrangement reactions of 6CPNO have been studied [9,13,15,16]. According to product analysis, the rearrangement of 6CPNO is dependent on solvent, and 6-cyanodibenzo[d,f][1,3]oxazepine is the major photoproduct in aprotic solvents such as acetone [13] and benzene [9]. A possible oxaziridine [13,15,16] or a biradicaloid [9,17] is assumed as key intermediate generated from 6CPNO in the lowest excited singlet state (S_1). On the other hand, major photoproduct in alcohol is 5-alkoxyphenanthridone implying a reaction between the intermediate and alcohol (solvent molecule). In addition to these rearrangement reactions of *N*-oxide group in S_1, it has been assumed that simple deoxygenation of the *N*-oxide group takes place in the lowest triplet state (T_1) (Scheme 2).



Scheme 2.

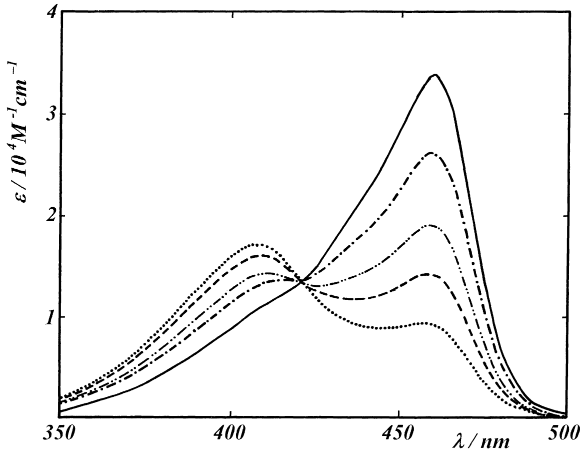


Fig. 1. Absorption spectra of various concentrations of proflavine in air-saturated ethanol at 293 K: 5.0×10^{-6} M (solid); 5.0×10^{-5} M (dot–dashed); 1.5×10^{-4} M (dot–dot–dashed); 5.0×10^{-4} M (dashed); 1.0×10^{-3} M (dotted).

Direct evidence for the deoxygenation in T_1 may be brought about by triplet sensitization. The choice of triplet sensitizer is not easy, because possible sensitizer at least must fill two necessary conditions such that it exhibits a visible absorption spectrum for selective excitation of it without exciting 6CPNO and that T_1 of sensitizer should not be sufficiently lower in energy than T_1 of 6CPNO. Assuming that the energetic condition is filled, we selected proflavine (3,6-diaminoacridine) as a triplet sensitizer of 6CPNO. Dilute ethanol solution of proflavine exhibits the visible absorption band (λ_{max} = 460 nm), which is well separated from the longest wavelength band (λ_{max} = 394 nm) of 6CPNO. However, aggregation of proflavine should be taken into account in ethanol, since dimerization of 2,8-diaminoacridine free base in ethanol has been reported by Mataga [18]. Fig. 1 shows the absorption spectra of various concentrations of proflavine in ethanol. While the long-wavelength band (λ_{max} = 460 nm) decreases in intensity with increasing concentration of proflavine, the short-wavelength band (λ_{max} = 407 nm) increases. An isosbestic point is seen at 418 nm. Aggregation number (n) was determined to be 1.9 from the slope of a log–log plot for concentration dependence. It is thus recognized that monomeric and dimeric species of proflavine are responsible for the long- and the short-wavelength bands, respectively. The monomer–dimer equilibrium constant was estimated to be $2.3 \times 10^3\ M^{-1}$, and the predominant species in dilute ($<10^{-4}$ M) solution is monomer.

As shown in Fig. 2a, proflavine monomer in ethanol exhibits a visible absorption band (λ_{max} = 460 nm) and an UV band (λ_{max} = 261 nm). A spectral window between these bands enables us to monitor the absorption spectrum of 6CPNO even in the presence of proflavine. Such a wide

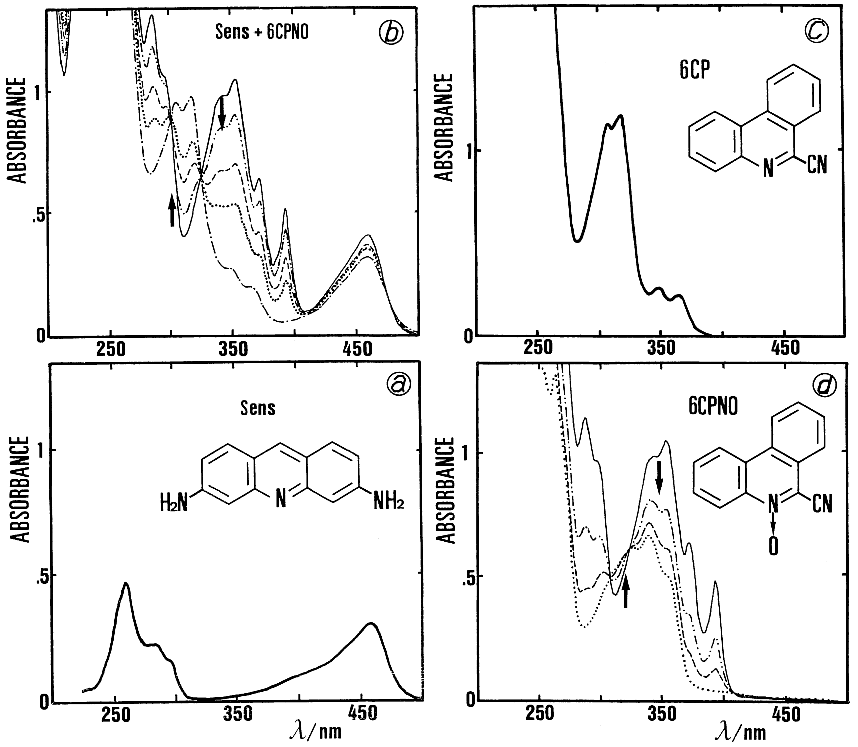


Fig. 2. Absorption spectra of (a) proflavine (0.01 mM) and (c) 6CP in ethanol, progressive absorption spectral changes caused by selective excitation of proflavine monomer in the presence of 0.13 mM 6CPNO in degassed ethanol (b), and those by direct excitation of 6CPNO in air-saturated ethanol (d). Irradiation times of >420 nm steady-light for (b) are 0 (solid), 3 (dot–dot–dashed), 8 (dashed), 12 (dotted), and 21 min (dot–dashed). Irradiation times of >360 nm steady-light for (d) are 0 (solid), 30 (dot–dot–dashed), 60 (dashed), and 240 s (dotted).

optical window is not provided by proflavine in aprotic solvents such as hexane, benzene, and acetonitrile.

Fig. 2b shows the absorption spectral changes caused by a selective excitation of proflavine (0.014 mM) in the presence of 6CPNO (0.13 mM) in degassed ethanol at room temperature. The absorption bands (λ_{max} = 288, 354, 373, and 394 nm) due to 6CPNO decrease and finally disappear. On the other hand, new absorption bands grow up and finally exhibit peaks at 307, 318, 349, and 422 nm. Such peaks are characteristic of 6CP, whose absorption spectrum is shown in Fig. 2c. Proflavine-sensitized photodeoxygenation of 6CPNO was clearly confirmed by a spectroscopic manner. Unfortunately, photodegradation of proflavine (sensitizer) in ethanol cannot be neglected. The 460 nm absorption band due to proflavine is reduced by ca. 20% at perfect disappearance of the 394 nm peak due to 6CPNO.

Fig. 2d shows the absorption spectral change with isosbestic points at 307 and 326 nm induced by direct photolysis of 6CPNO in ethanol at room temperature. The absorption spectrum (λ_{max} = 324, 339 nm), remained after the complete disappearance of the absorption bands (λ_{max} = 355, 372, and 394 nm) due to 6CPNO, may be ascribed to *N*-ethoxyphenanthridone (*N*-EtO-phen) in ethanol. Such spectral changes reflecting the formation of *N*-EtO-phen is clearly different from the spectral changes reflecting the formation of 6CP with proflavine-sensitization of 6CPNO. Alternation of major photoproduct on going from direct photolysis to proflavine-sensitization indicates that different reactive excited states are involved in these photolytic processes. It has been reported that *N*-EtO-phen is generated from S_1, and a poor $S_1 \rightarrow T_1$ intersystem crossing probability has been assumed for 6CPNO. For proflavine-sensitization, therefore, it is strongly implied that a triplet-sensitized deoxygenation of 6CPNO.

Triplet-sensitization of 6CPNO by proflavine was examined by transient absorption spectroscopy. Transient absorption on direct excitation of 6CPNO should be mentioned a prior to that on proflavine-sensitization. In the previous study, it has been reported [15] that a transient absorption band (λ_{max} = 470 nm) increases in intensity with 2 Hz consecutive N_2-laser pulse excitations of 6CPNO in aerated ethanol. The 470 nm transient absorption spectrum was not ascribed to 6CPNO but to *N*-EtO-phen (major photoproduct of 6CPNO in ethanol). In the 308 nm XeCl laser pulse excitation of *N*-EtO-phen in the presence of 0.043 mM DBrA in degassed ethanol, we observed that the 420 nm $T_n \leftarrow T_1$ absorption band of DBrA grows with the time constant of 1.1 μs at the expense of a band (λ_{max} = 475 nm). It is thus reasonable that the 475 nm band is assigned to the $T_n \leftarrow T_1$ absorption spectrum of *N*-EtO-phen. In order to measure weak transient absorption of 6CPNO itself with an intense laser pulse, photodegradation to generate *N*-EtO-phen should be minimized as possible as one can. For this reason, fresh air-saturated solution was exposed for each laser shot. Transient absorption spectra with the lifetime of 230 ns were obtained in such a way. They consist of a sharp band (λ_{max} = 425 nm) and a broad band in the 450–750 nm region. For isoquinoline *N*-oxide in EPA glass at 77 K, Ono and Hata [19] reported the long-lived (τ = 60 ms) $T_n \leftarrow T_1$ absorption spectrum, in which a sharp and intense band (λ_{max} = 400 nm) is accompanied by a broad and weak band (λ_{max} = 480 nm). The transient absorption spectrum of 6CPNO is similar to the reported $T_n \leftarrow T_1$ absorption spectrum of isoquinoline *N*-oxide. Therefore, it is reason-

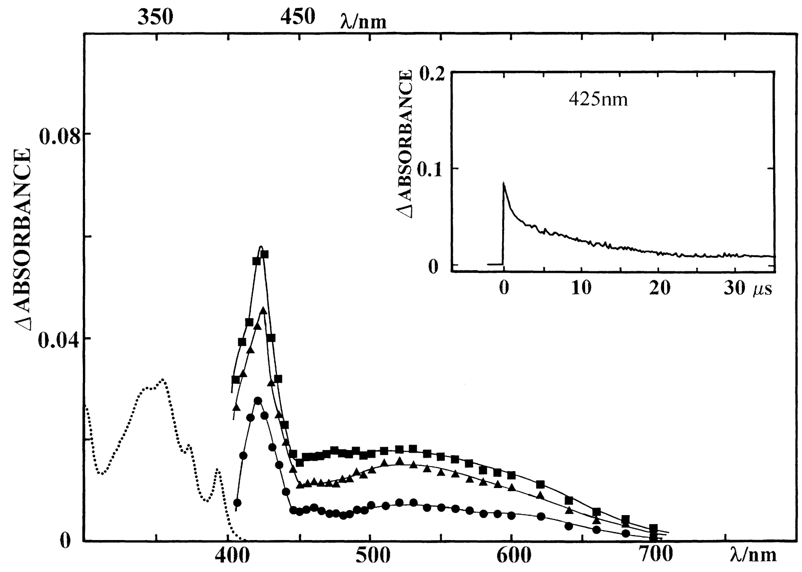


Fig. 3. Time-resolved transient absorption spectra observed in a 355 nm YAG laser pulse excitation of 6CPNO (0.23 mM) at room temperature. Times after laser pulse excitation are 0.50 (■), 1.0 (▲), and 4.0 μs (●). Dotted curve represents the $S_n \leftarrow S_0$ absorption spectrum of 6CPNO. Inset shows the 425 nm transient absorption signal obtained in the experimental setup being different from that for spectral measurement.

able to assign the observed transient absorption spectrum to the $T_n \leftarrow T_1$ absorption spectrum of 6CPNO. On the other hand, a large volume (50 ml) of degassed ethanol solution was exposed after shaking for each laser shot. Extent in the photodegradation of 6CPNO was ca. 10% after 32 laser shots. Time-resolved absorption spectra of 6CPNO obtained in such a way are shown in Fig. 3. As the 425 nm transient absorption signal clearly reveals, it consists of short- (1.2 μs) and long-lived (16 μs) decay components. Although weak $T_n \leftarrow T_1$ absorption spectrum of *N*-EtO-phen seems to be superimposed in the 450–500 nm region, the short-lived absorption band (λ_{max} = 425 nm) is almost the same as the $T_n \leftarrow T_1$ absorption spectrum of 6CPNO in air-saturated ethanol. It should be noticed that the short-lived absorption band (λ_{max} = 425 nm) is replaced by the long-lived ones (λ_{max} = 420 nm), though they are similar with each other. The long-lived transient absorption spectrum may be ascribed to a reactive intermediate generated from T_1.

In order to confirm the triplet sensitization of 6CPNO by proflavine, selective excitation of proflavine in the presence of 6CPNO (0.13 mM) was undertaken by the use of a 460 nm dye laser pulse. Time-resolved transient absorption spectra are shown in Fig. 4. Transient absorption signals observed at 435 and 525 nm are shown in the inset of Fig. 4, and that at 410 nm is shown in Fig. 5. The $T_n \leftarrow T_1$ absorption spectra of both 6CPNO and proflavine are essential for interpreting the time-resolved spectra. As has been mentioned, the $T_n \leftarrow T_1$ absorption spectrum of 6CPNO exhibits the transient absorption spectrum (λ_{max} = 425 and 540 nm) in ethanol. It is depicted again in lower inset of Fig. 5. Shown in higher inset is the $T_n \leftarrow T_1$ absorption spectrum of proflavine in ethanol, which is similar to reported spectrum (λ_{max} = 520 nm) in benzene [20]. The $T_n \leftarrow T_1$ absorption spectra of 6CPNO and proflavine are similar with each other in the 480–700 nm region. Owing to the $S_1 \leftarrow S_0$ absorption band (λ_{max} = 460 nm) of proflavine, the $T_n \leftarrow T_1$ absorption band (λ_{max} = 420 nm) of 6CPNO is not clearly seen in Fig. 4.

Depletion and recovery of the $S_1 \leftarrow S_0$ absorption band may be responsible for negative transient absorption spectra

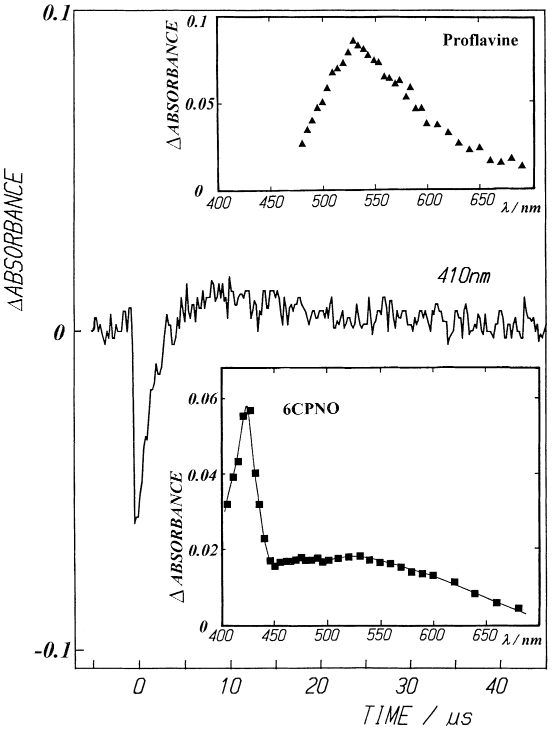


Fig. 5. The 410 nm transient absorption signal observed in a selective excitation of proflavine in the presence of 6CPNO (0.13 mM) in degassed ethanol at room temperature. Insets show the $T_n \leftarrow T_1$ absorption spectra of 6CPNO (■) and proflavine (▲).

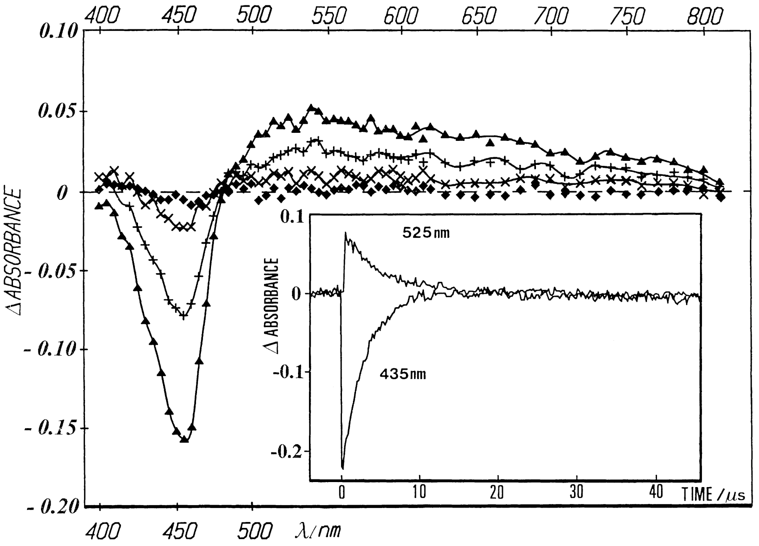
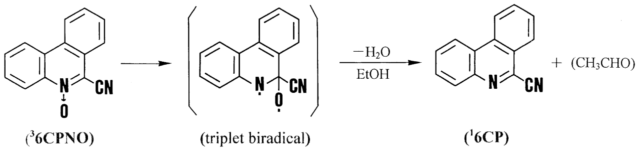


Fig. 4. Time-resolved transient absorption spectra observed in the 460 nm pulse excitation of proflavine in the presence of 0.13 mM 6CPNO in degassed ethanol at room temperature. Times after laser pulse excitation are 2.5 (▲), 4.9 (+), 9.6 (×), and 20 μs (◆).

in the 420–480 nm region. Growing $T_n \leftarrow T_1$ absorption spectrum of 6CPNO at the expense of the $T_n \leftarrow T_1$ absorption spectrum of proflavine is expected to confirm the triplet sensitization by proflavine. As the 410 nm transient absorption signal reveals in Fig. 5, positive transient absorption is generated after the recovery of the depleted $S_1 \leftarrow S_0$ absorption due to proflavine. Weak positive absorption in the 400–420 nm region may be ascribed to sensitized 6CPNO triplet, since the $T_n \leftarrow T_1$ absorption band of 6CPNO exhibits a sharp peak at 425 nm. Growing $T_n \leftarrow T_1$ absorption is followed by an exponential decay of 16 μs, which is ascribable to a reactive intermediate generated quickly from T_1.

Transient absorption signals at the wavelengths longer than 420 nm exhibit a double exponential decay ($\tau = 3.2$ and 16 μs). Assuming that molar extinction coefficient of proflavine triplet is larger than that of 6CPNO triplet in the >420 nm region, it is recognized that the short lifetime reflects the triplet energy transfer from proflavine to 6CPNO. From the decay time of 3.2 μs in the presence of 0.13 mM 6CPNO, triplet energy transfer rate constant is roughly estimated to be $1.9 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$, which is less than $9.2 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ (diffusion-controlled rate constant). Triplet energy of proflavine is reported to be $214\ \mathrm{kJ\,mol}^{-1}$ [21]. The fact implies an endothermic triplet energy transfer. Consequently, triplet sensitization of 6CPNO by proflavine was evidenced by transient absorption spectroscopy.

Photodeoxygenation of 6CPNO in T_1 was evidenced by selective excitations of proflavine with steady-light and laser pulse excitation. It is probable that the deoxygenation of *N*-oxide function in T_1 may be general for most aromatic amine *N*-oxides. Parent amine is formed as a by-product. This is presumably due to low probability of the $S_1 \rightarrow T_1$ intersystem crossing, which competes with rapid rearrangement reactions. In the laser photolysis of pyridine *N*-oxide, Buchner and Scaiano [22] observed the transient absorption of CH_3CNO generated by the oxidation of solvent CH_3CN molecule by atomic oxygen (^3O). Rapid liberation of ^3O from *N*-oxide functional group in the lowest excited singlet state (S_1) is assumed for pyridine *N*-oxide. In contrast to this, a long-lived (16 μs) reactive intermediate is generated from T_1 of 6CPNO in ethanol. A possible candidate for the reactive intermediate is a triplet biradical. It is also probable that ethanol molecule is oxidized to yield acetaldehyde. Further experiments to elucidate the triplet mechanism of oxygen transfer from *N*-oxide group to solvent molecule are required (Scheme 3).



Scheme 3.

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