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Reductive photocyanation of 1,10-phenanthroline in aqueous media

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Abstract

Reductive photocyanation of 1,10-phenanthroline (phen) took place in an aqueous NaCN solution, yielding 5-cyano-5,6-dihydro-1,10-phenanthroline (Hphen-CN) with the reaction and quantum yields of 5–50% and 10^{-3} to 10^{-4}, respectively. The photoreaction in the presence of Mg^{2+} (aerated conditions) improved the reaction quantum yield by a factor of ∼7 as compared to that without Mg^{2+}, through coordination of Mg^{2+} with phen: phen:Mg^{2+} complex. The fluorescence lifetimes of phen and the phen:Mg^{2+} complex were ∼3 and ∼10 ns, respectively, and the fluorescence of the phen:Mg^{2+} complex was shown to be quenched more efficiently by a cyanide ion as compared to that of phen itself. The fluorescence quenching percents of phen by NaCN in the absence and presence of Mg^{2+} were 3 and 24%, respectively, and the eight-fold increase in the quenching percent in the presence of Mg^{2+} gave rise to the approximately seven-fold increase in the reaction quantum yield. On the basis of such results, we proposed that the present photocyanation reaction proceeded via electron transfer from a cyanide ion to the excited singlet-states of phen and/or the phen:Mg^{2+} complex as the primary step: anion radical ($S_{N\text{-}R}1Ar^*$) mechanism. The characteristic features of the present photoreaction of phen in the presence of Mg^{2+} and the possible reaction mechanisms are discussed in detail.

Keywords: Photocyanation; 1,10-Phenanthroline; Mg^{2+} effects; Fluorescence dynamics; Anion radical

1. Introduction

Aromatic nucleophilic photosubstitution reactions have been studied widely as one of the central research topics in organic photochemistry. Among various aromatic photosubstitution reactions, the study on the photocyanation of aromatic hydrocarbons (ArH) has a long research history since the first report for *p*-nitroanisole by Havinga and co workers [1] and, later, the work has been extended to various unsubstituted and substituted arenes: naphthalene, biphenyl, fluorene derivatives, and so forth [2]. Various attempts have been explored to improve the reaction yield by employing crown-ethers to dissolve an alkali cyanide in aprotic solvents [3] and phase transfer catalysts [4]. Analogous photocyanation reactions have been also reported for heteroaromatic compounds: furan [5], thiophene [6], imidazole [7], and indazole derivatives [8]. On the other hand, Mizuno et al. reported for the first time the cyanation of ArH (naphthalene derivatives, phenanthrene, anthracene, and pyrene) in the presence of an electron acceptor (A) via a photoinduced electron transfer (PET) mechanism in an aqueous acetonitrile solution (CH_3CN:H_2O = 9:1 vol%) [9]. Later, Yasuda et al. [10] and Bunce et al. [11] demonstrated that the cation radical of ArH was produced in the presence of A and subjected to nucleophilic attack with a cyanide ion, yielding the cyanated product of ArH. In practice, a flash photolysis study demonstrated certainly formation of the cation radical of ArH in such systems [12].

As an alternate approach to the study along the line as mentioned above, we reported recently that a photocyanation reaction of ArH proceeded very efficiently in an oil/water emulsion system via a PET mechanism [13–15]. In the case of pyrene (Py) in a benzonitrile/water emulsion in the presence of NaCN, as an example, PET between Py and A in oil droplets produces the cation radical of Py and the anion radical of A. The cation radical is then subjected to

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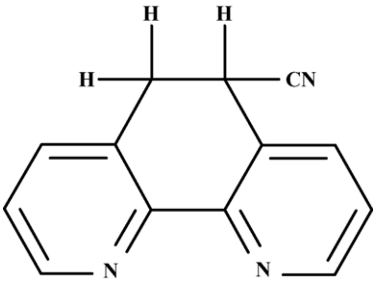
nucleophilic attack by a cyanide ion at the droplet/water interface or in the water phase, and subsequent oxidation of the cyanated pyrenyl radical by O_2 or O_2^{-} yields 1-cyanopyrene with the isolated and quantum yields of 78 and 0.17%, respectively [14]. It is worth noting that the reaction yield is higher in the emulsion system as compared to that in a homogeneous acetonitrile/water mixture, owing to PET between Py and A in small oil droplets and subsequent quick distribution of the cation radical to the surrounding NaCN/water phase as discussed in detail elsewhere [14]. For further advances in the photocyanation reaction in emulsion systems, those of heteroaromatic compounds are very interesting. In practice, we confirmed that the photocyanation of *N*-ethylcarbazole and 1,10-phenanthroline (phen) in the presence of A proceeded in oil/water emulsion systems [16]. In the case of *N*-ethylcarbazole, the photoreaction gave 3-cyano-, 3,7-dicyano-, and 3,8-dicyano-*N*-ethylcarbazole (total yield of ~78%), while that of phen yielded 5-cyano-5,6-dihydro-1,10-phenanthroline as a sole product (Hphen-CN in Scheme 1, yield ~56%). The results are very important as the photochemistry of heteroaromatic compounds. However, the number of the report on the photocyanation of heteroaromatics via a PET mechanism is still limited; tertially amines [17], catharanthine, and rindoline [18] where cyanotrimethylsilane and an organic dye (9,10-dicyanoanthracene as an example) are employed as A and a photosensitizer, respectively.

Among various heteroaromatics, the photocyantion of phen is quite interesting, since phen and its derivatives are very important as a ligand for various metal ions and, their one-step photocyanation reactions will be very meaningful in the fields of both photochemistry and coordination chemistry. In the course of studying the photocyanation reaction of phen via a PET mechanism in an oil/water emulsion, we found that the reaction of phen proceeded in an aqueous solution even in the absence of an electron acceptor, suggesting that the reaction mechanism was totally different from that of pyrene or other ArHs via a PET mechanism. As characteristics of the photocyanation reaction of phen in water, furthermore, we also found that the reaction yield was dependent on the concentration of an added Mg^{2+} ion. The photocyanation reaction of phen is thus very unique and worth studying in detail. In this paper, we report the photocyanation of phen in aqueous solutions under several conditions and, discuss possible reaction mechanisms on the basis of the spectroscopic and excited-state properties of phen in the absence and presence of a cyanide ion and/or an Mg^{2+} ion.



Scheme 1. Structure of 5-cyano-5,6-dihydro-1,10-phenathroline (Hphen-CN).

2. Experimental

2.1. Chemicals

1,10-Phenanthroline monohydrate (phen, Wako Pure Chemicals Ind. Ltd., GR grade) was purified by repeated recrystallizations from an ethyl acetate/*n*-hexane mixture. Sodium cyanide, magnesium sulfate (both GR grade), and chloroform (HPLC grade) purchased from Wako Pure Chemicals Ind. Ltd. were used without further purification. Magnesium chloride hexahydrate (Kanto Kagaku Co. Ltd.) was used as supplied. Chemicals used for ferrioxalate actinometry were the highest grade available from Japanese suppliers.

2.2. Photochemical experiments and product analysis

2.2.1. Large-scale experiments

An aqueous solution (300 mL) containing phen (1.1×10^{-3} M (=mol/dm^3)), NaCN (1.0 M), and $MgCl_2$ (1.0 M) under stirring was irradiated internally by a 300 W high-pressure Hg lamp through a $CuSO_4$ solution filter (1.0 M, wavelength, $\lambda > 330$ nm) under an O_2 gas stream for 1.5 h. After the photoreaction, the mixture was extracted with chloroform and the products were analyzed by column chromatography (alumina/chloroform). The main product isolated was purified further by recrystallizations from a chloroform/*n*-hexane mixture. ^{1}H NMR (300 MHz, Varian Gemini-2000), GC-MS (Shimadzu QP-5050A), and elemental analyses demonstrated that the product was 5-cyano-5,6-dihydro-1,10-phenanthroline (Hphen-CN): isolated yield = 50%. ^{1}H NMR ($CDCl_3$); $\delta = 3.4$ (t, $J = 6.0$ Hz, 2H), 4.3 (dd, $J = 6.9$ Hz, 10.2 Hz 1H), 7.3–8.8 (m, 6H). FD-MS: $m/z = 207$. mp: 158–160 °C. anal., $C_{13}H_9N_3$, found (calc.): C, 75.32 (75.34); H, 4.59 (4.38); N, 20.39 (20.28).

2.2.2. Small-scale experiments

As controlled experiments for the photoreaction, the following small-scale experiments were conducted by using a glass cylindrical cell (inner diameter = 3 cm). An aqueous solution containing phen (2×10^{-3} M) and NaCN (1.0×10^{-2} M) in the absence or presence of Mg^{2+} ($MgSO_4$ or $MgCl_2$, 1.0×10^{-2} M) was irradiated externally by the Hg lamp ($\lambda > 330$ nm) under stirring. The distance between the Hg lamp and the glass cell was set 8 cm throughout the experiments and, the photoreactions were conducted under an aerated, O_2-, or N_2-gas atmosphere. After the photoreaction, the mixture was extracted with chloroform (10 mL) and the products were analyzed by HPLC (Shimadzu Co. Ltd.): HRC-ODS column with a 4:1 (vol%) methanol:phosphate buffer (pH ~ 7) solution as an eluent. The yield of Hphen-CN was determined on the basis of the HPLC analysis and the calibration curve for Hphen-CN prepared by separate experiments. No other major product other than Hphen-CN was observed under the present HPLC conditions.

The quantum yield of the photocyanation reaction of phen (Φ) was determined on the basis of a ferrioxalate chemical actinometer [19]. Although the experimental conditions were similar to those mentioned above, a 334 nm line from the Hg lamp was isolated to determine Φ by using $CuSO_4$ (1.0 M) and $NiSO_4$ (2.0 M) solution filters combined with a UV-D33S glass filter (Toshiba Co. Ltd.) [20]. By assuming the quantum yield of the photoreduction of ferrioxalate at 334 nm to be 1.23 [20], the photon number absorbed by phen at 334 nm was evaluated as $I = 5.5 \times 10^{18}$ quanta/min. The absolute Φ values, under given conditions, were then calculated on the basis of the I value and the mole number of Hphen-CN produced during the initial stage of the photoreaction.

2.3. Spectroscopic measurements

Steady-state absorption and fluorescence spectroscopies were conducted by using a Hitachi UV-3300 spectrophotometer and a Hitachi F-4500 spectrofluorometer, respectively. Time-resolved fluorescence spectroscopy was conducted by using a time-correlated single photon counting method reported previously [21].

3. Results and discussion

3.1. General features of photocyanation reaction of 1,10-phenanthroline

Direct photoirradiation of phen ($\lambda > 330$ nm) in an aqueous NaCN and $MgCl_2$ (both 1.0 M) solution for 1.5 h under an O_2-gas atmosphere gave 5-cyano-5,6-dihydro-1,10-phenanthroline (Hphen-CN) in 50% yield as described in Section 2.2.1: large-scale experiments. In the case of the photocyanation of phenanthrene in an CH_3CN:H_2O mixture under an N_2-gas atmosphere, Yasuda et al. reported that 9-cyano-9,10-dihydrophenanthrene and 9-cyanophenanthrene were obtained in 55 and 16% yields, respectively, while that under aerated conditions afforded 9-cyanophenanthrene in 78% yield [10]. In the present case, however, Hphen-CN was the sole product of the photoreaction and, 5-cyano-1,10-phenanthroline as a substitution product was not obtained under the present experimental conditions studied: an aerated, O_2-, or N_2-gas atmosphere. Analogous photoreaction of phen in D_2O to that mentioned above afforded deuteration of the cyanated-product (i.e., Dphen-CN) as confirmed by EI-MS: $m/z = 208$. Therefore, we concluded that the hydrogen source for the present reductive photocyanation of phen was water as a medium.

We evaluated the photocyanation quantum yield (Φ) under several reaction conditions as the data were summarized in Table 1. The Φ value under aerated conditions in the absence or presence of $MgSO_4$ (1.0×10^{-2} M) was 2.5×10^{-4} (reaction yield = 5%, Run 1 in Table 1) or 1.7×10^{-3} (54%, Run 4), respectively. Such a trend of the Mg^{2+} effects on Φ was observed irrespective of an atmosphere and, the Φ value in the presence of Mg^{2+} was always higher by a factor of 5–7 as compared to the relevant value in the absence of Mg^{2+}. Furthermore, Table 1 demonstrated that the photoreaction proceeded more efficiently under an N_2-gas stream as compared to those in the presence of O_2. It is worth pointing out that the photoreaction proceeds in the absence of an electron acceptor toward the excited-state of phen. An addition of an inorganic salt such as NaBr or Na_2SO_4 (1.0×10^{-2} M) instead of adding $MgSO_4$ or $MgCl_2$ did not influence the reaction yield. These results demonstrate that the photocyanation reaction of phen does not proceed via a simple PET mechanism reported for those of ArH by Mizuno et al. [9] and Yasuda et al. [10] This also indicates that the present Mg^{2+} effects on Φ cannot be explained by the salt effects reported for various PET reactions: increase in the charge separation yield of an ion radical pair [22–24].

Table 1
Reductive photocyanation of phen (2.0×10^{-2} M) in aqueous NaCN (1.0×10^{-2} M) solutions

Run	$[MgSO_4]$/M	Atmosphere	$\Phi \times 10^3$
1	0	Air	0.25
2	0	O_2	0.21
3	0	N_2	0.46
4	1.0×10^{-2}	Air	1.7
5	1.0×10^{-2}	O_2	1.1
6	1.0×10^{-2}	N_2	2.2

So far, it has been reported that various ArH including heteroaromatic compounds are cyanated photochemically by NaCN or KCN even in the absence of an electron acceptor as described briefly in section 1 [1–8]. For the photocyanation of heteroaromatic compounds, however, the presence of a nitro group(s) in the compound seems to be required with a typical example being 2-nitrofuran [5], 2-nitrothiophene [6], or 5-nitroimidazole [7], and these compounds undergo *photosubstitution* reactions giving the relevant 2-cyano or 5-cyano derivative. To the best of our knowledge, the reductive photocyanation of an unsubstituted heteroaromatic compound has not been reported. The present photocyanation reaction mechanisms of phen are thus worth elucidating in detail for further advances in the relevant researches.

3.2. A spectroscopic study

In order to reveal the roles of Mg^{2+} in the photocyanation reaction, we studied effects of Mg^{2+} on spectroscopic and excited-state properties of phen in aqueous solutions. As shown in Fig. 1, phen in an aqueous solution showed weak fluorescence in $\lambda = 340$–450 nm with the maximum wavelength of ∼360 nm. The fluorescence maximum wavelength observed in the present study agreed very well with the reported value [25]. In the presence of Mg^{2+}, on the other hand, the fluorescence intensity of phen increased with an increase

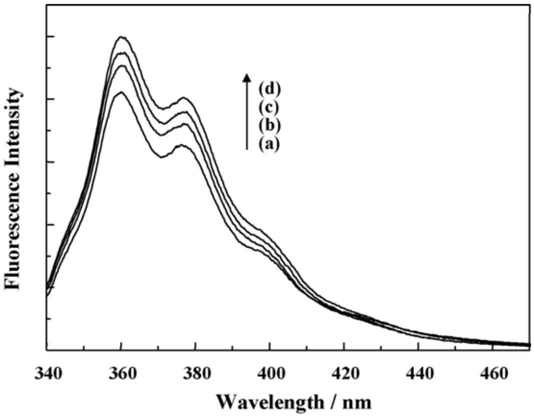


Fig. 1. Fluorescence spectra of phen (1.0×10^{-4} M) in the absence and presence of $MgSO_4$ in water. [Mg^{2+}]: 0 (a), 5.0×10^{-4} (b), 1.0×10^{-3} (c), and 2.0×10^{-3} M (d). Excitation wavelength was 320 nm.

in the Mg^{2+} concentration ([Mg^{2+}]) without any change in the spectral band shape, while the absorbance of phen in $\lambda = 300$–350 nm increased slightly with [Mg^{2+}] (data are not shown here). Since phen is a typical ligand for various metal ions, it is easily expected that phen is coordinated with Mg^{2+}, producing the phen:Mg^{2+} complex in the ground-state. Although the binding constant of the phen:Mg^{2+} complex (K_a) can be determined by ^{1}H-NMR titration, we evaluated the K_a value on the basis of the [Mg^{2+}] dependence of the fluorescence intensity of phen. In practice, we obtained a linear Benesi-Hildebrand plot for the data in Fig. 1, proving 1:1 complexation between Mg^{2+} and phen. The K_a value of the phen:Mg^{2+} complex was then estimated to be 240 M^{-1} [26].

Mg^{2+} effects on the fluorescence characteristics analogous to the results in Fig. 1 have been reported for aromatic carbonyl compounds possessing the lowest excited π–π* singlet-state (S_1) and n–π* triplet-state (T_1) [27,28]. In such compounds, very fast S_1–T_1 intersystem crossing (ISC) takes place as predicted by the El-Sayed rule [27], and the compounds are essentially non-fluorescent. In the presence of Mg^{2+}, however, since the carbonyl oxygen in such a compound interacts with Mg^{2+}, the excited n–π* state energy increases. Therefore, S_1–T_1 ISC of the compound is impeded considerably in the presence of Mg^{2+}, giving rise to a very large enhancement of the fluorescence intensity as compared to that without Mg^{2+}. Besides the changes in the fluorescence characteristics, furthermore, it has been reported that the photochemical reactivity of an aromatic carbonyl compound also varies in the presence of Mg^{2+} or other Lewis acids [28]. In the case of phen, nonetheless, since both S_1 and T_1 states are in a π–π* character [29,30], the fluorescence intensity response upon an addition of Mg^{2+} in Fig. 1 cannot be explained along the same context with those mentioned above for aromatic carbonyl compounds.

On the other hand, it has been reported that phen is easily protonated in acidic media ($pK_a = 4.96$) [25] and the monoprotonated form of phen shows the fluorescence maximum at around 410 nm [30]. Armaroli et al. also reported that an addition of trifluoroacetic acid to a dichloromethane solution of phen or its derivative brought about red shifts of both absorption and fluorescence spectra owing to protonation of phen [31]. Since the acidity of Mg^{2+} as a Lewis acid is much weaker than that of trifluoroacetic acid and the present solution pH is ∼7, red-shifted fluorescence (∼410 nm) of phen is not observed. However, the present results in Fig. 1 (K_a (phen:Mg^{2+}) = 240 M^{-1}) and the discussions described above indicate that the spectral changes in Fig. 1 are due to coordination of Mg^{2+} with phen, but not to the change in the ISC rate and yield of phen by Mg^{2+}.

Complex formation between phen and Mg^{2+} was also confirmed by fluorescence lifetime measurements. Since the fluorescence intensity of phen was almost unchanged for both aerated and deaerated samples, fluorescence lifetime measurements were conducted under aerated conditions. In the absence of Mg^{2+} as shown in Fig. 2, the fluorescence of phen (2.0×10^{-3} M) in water decayed single exponentially with the lifetime (τ_0) of 3.0 ns, while that in the presence of Mg^{2+} (1.0×10^{-2} M) showed a double exponential decay with the time constants of 2.9 and 10.5 ns. The K_a value (∼240 M^{-1}) described above indicates that the most of the phen molecules coordinate with Mg^{2+} at [Mg^{2+}] = 1.0×10^{-2} M [32]. Therefore, the results demonstrated that the ∼3 and ∼10 ns components observed were assigned to the excited-state lifetimes of phen and the phen:Mg^{2+} complex, respectively. Although an obvious change in the spectral band shape was not discernible in Fig. 1, time-resolved fluorescence spectroscopy discriminated the excited-state species involved in the system. Furthermore, it is worth emphasizing that the longer fluorescence lifetime of the phen:Mg^{2+} complex as compared to that of phen itself agrees well with the increase in the fluorescence intensity of phen in the presence of Mg^{2+}. The longer fluorescence lifetime of the phen:Mg^{2+} complex as compared to that of phen should be the favorable conditions for the photocyanation reaction of phen.

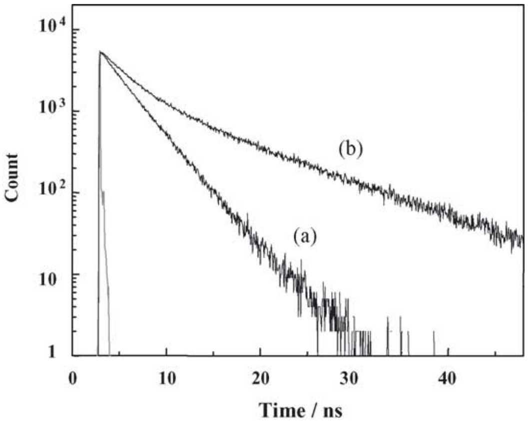


Fig. 2. Fluorescence decay profiles of phen (2.0×10^{-3} M) in the absence (a) and presence of $MgSO_4$ (1.0×10^{-2} M) (b), in water under aerated conditions. Excitation and fluorescence monitoring wavelengths were 300 and 380 nm, respectively.

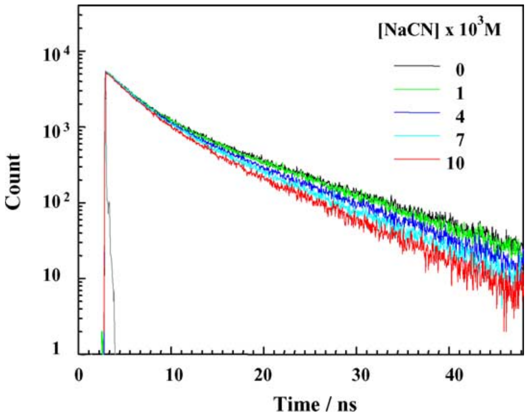


Fig. 3. Fluorescence quenching of phen (2.0×10^{-3} M) by NaCN in the presence of $MgSO_4$ (1.0×10^{-2} M) in water under aerated conditions. Excitation and fluorescence monitoring wavelengths were 300 and 380 nm, respectively.

The excited-states of both phen and the phen:Mg^{2+} complex are quenched by a cyanide ion. As a typical example, the fluorescence decay curves of the phen:Mg^{2+} complex ([phen] = 2.0×10^{-3} M and [Mg^{2+}] = 1.0×10^{-2} M, aerated conditions) in the absence and presence of NaCN are shown in Fig. 3. Detailed analysis of the data demonstrated that the long lifetime component in the absence of NaCN (10.5 ns) became shorter with the increase in [NaCN] (8.5 ns at 1.0×10^{-2} M as an example), while the fluorescence lifetime of phen showed a slight decrease with [NaCN]: 2.85–2.79 ns. Although the change in the decay profile with [NaCN] in Fig. 3 was not necessarily clear enough, the Stern–Volmer plots for fluorescence quenching of the phen:Mg^{2+} complex and phen by NaCN were linear as shown in Fig. 4. The quenching rate constants (k_q) of the complex and phen by a cyanide ion were thus determined to be 3.0×10^9 and 1.2×10^9 M^{-1} s^{-1}, respectively.

These k_q values indicate that the quenching percent (Q) of the fluorescence of phen or phen:Mg^{2+} complex ([Mg^{2+}] = 1.0×10^{-2} M) by NaCN (1.0×10^{-2} M), defined by $Q = k_q\tau_0[\mathrm{NaCN}]/(1 + k_q\tau_0[\mathrm{NaCN}])$, is calculated to be 3 or 24%, respectively. The Q values of 3 and 24% brought about Φ to be 2.5×10^{-4} (Run 1 in Table 1) and 1.7×10^{-3} (Run 4), respectively. Therefore, the increase in Q by a factor of 8 in the presence of Mg^{2+} as compared to that without Mg^{2+} gives rise to approximately seven-fold increase in Φ. In the absence of Mg^{2+}, there is no direct evidence that the excited-state responsible for the photoreaction is the singlet-state. Nevertheless, since the change in the fluorescence quenching percent with [Mg^{2+}] corresponds very well to that in Φ, we conclude that a magnesium ion facilitates the photocyanation reaction of phen in the excited singlet-state. Excited singlet-state quenching of the phen:Mg^{2+} complex and, probably, phen by NaCN should be thus the primary step for the present photocyanation reaction.

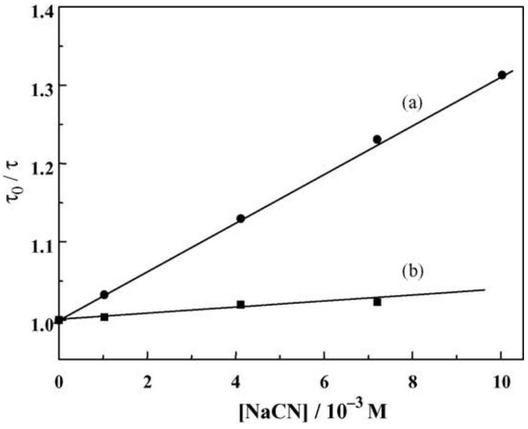


Fig. 4. Stern–Volmer plots for fluorescence quenching of phen (a)) and the phen:Mg^{2+} complex in water (b)).

3.3. Proposed reaction mechanisms

The present photocyanation reaction of phen proceeds in the absence of an electron acceptor as described above. Furthermore, since we could not confirm an excitation intensity dependence of the reaction rate, two-photon or multi-photon ionization of phen producing the cation radical did not participate under the present experimental conditions. Therefore, the cation radical of phen is excluded as the intermediate of the photoreaction.

According to the reported mechanisms for photochemical nucleophilic aromatic substitution reactions [33], a possible mechanism will be either the S_N2Ar^*- or $S_{R\text{-}N}1Ar^*$-type mechanism. In the S_N2Ar^* mechanism, the excited-state of phen is subjected to nucleophilic attack by a cyanide ion and the subsequent reaction proceeds via a σ-bonded intermediate: σ-complex. By neglecting complexation of Mg^{2+} with phen for simplicity, the primary steps for the present photocyanation reaction are expressed as in Eqs. (1a) and (1b),

$$^1\mathrm{phen}^* + \mathrm{CN}^- \rightarrow \ \mathrm{phen\text{-}CN}^-(\sigma\text{-complex}) \qquad (1a)$$

$$\mathrm{phen\text{-}CN}^- + \mathrm{H}^+ \rightarrow \ \mathrm{Hphen\text{-}CN} \qquad (1b)$$

where ^{1}phen* represents the excited singlet-state of phen. It has been reported that photocyanation reactions of methoxynitroarenes proceed via the S_N2Ar^* mechanism [33]. However, the photocyanation of an unsubstituted arene via this mechanism has not been reported, suggesting important roles of a substituent(s) in the charge distribution in the excited-state and subsequent stabilization of the σ-bonded intermediate. In the present case, complexation of Mg^{2+} with phen would vary the charge distribution in the excited-state and complex formation might stabilize the σ-bonded complex. Therefore, the present photoreaction of phen might proceed via the S_N2Ar^* mechanism. It is worth noting, however, that since the pH of the reaction mixture is ∼10 (i.e., in the presence of NaCN), protonation to the σ-bonded intermediate will be unfavorable: Eq. (1b). As seen in Table 1, furthermore, the photoreaction proceeds more efficiently under deaerated conditions. Since the fluorescence lifetime of phen is almost independent of the absence and presence of O_2, suppression of the photoreaction of phen in the presence of O_2 will not be explained directly by the S_N2Ar^* mechanism.

In the case of the $S_{R\text{-}N}1Ar^*$ mechanism, on the other hand, the excited-state of phen undergoes electron transfer with a cyanide ion and the resulting cyan radical participates as in Eq. (2):

$$^1\text{phen}^* + \text{CN}^- \rightarrow \text{phen}^{-\bullet} + \text{CN}^\bullet \tag{2a}$$

$$\text{phen}^{-\bullet} + \text{H}^+ \rightarrow \text{Hphen}^\bullet \tag{2b}$$

$$\text{Hphen}^\bullet + \text{CN}^\bullet \rightarrow \text{Hphen-CN} \tag{2c}$$

In acetonitrile, the redox potentials of phen and a cyanide ion have been reported to be −2.18 and +1.3 V (versus SCE), respectively [34]. Knowing the excited singlet-state energy of phen to be 3.45 V, the Gibbs free energy change for PET between phen and NaCN is calculated to be $\Delta G \sim 0$ eV [35]. Although PET quenching of the excited singlet-state of phen by a cyanide ion is not necessary favorable, it is thermodynamically possible. As an important observation in the present study, furthermore, we found that the reduction potential of phen in acetonitrile shifted to the positive direction by ~200 mV in the presence of Mg^{2+} as compared to that without Mg^{2+}, indicating that the PET reaction in Eq. (2a) was more likely in the presence of Mg^{2+}. It is worth noting that fluorescence quenching of the phen:Mg^{2+} complex proceeds more efficiently as compared to that of phen itself as described before. These results agree very well with the Mg^{2+} effects on Φ. Furthermore, the O_2 effects on Φ will be explained by assuming Eq. (2a). In the presence of O_2, namely, the anion radical of phen will be likely to be oxidized by O_2 and this should suppress the photocyanation reaction. Therefore, we think that the present photocyanation reaction of phen will be explained more plausibly by the anion radical ($S_{R\text{-}N}1Ar^*$) mechanism rather than by the S_N2Ar^* mechanism.

On the basis of these experimental results and discussions, we propose the following anion radical mechanisms: Eq. (2). Photoirradiation of the system induces PET between phen and a cyanide ion, producing the anion radical of phen and a cyan radical. It has been reported that the pK_a value of the anion radical of phen is >14 [36]. Therefore, the anion radical is very likely to be protonated in an aqueous medium even for the solution pH of ~10, producing a 5,6-dihydro-1,10-phenanthroline radical: Eq. (2b). In the presence of Mg^{2+}, the reactivity of the anion radical of phen toward the protonation reaction in Eq. (2b) might become lower than that of the anion radical of phen itself, owing to coordination of Mg^{2+} to phen. Nevertheless, we suppose that the very high pK_a value of the anion radical of phen as mentioned above would be still favorable conditions for the protonation reaction even in the presence of Mg^{2+}. The radical would be then reacted with a cyan radical, giving Hphen-CN. Although there is no direct evidence for participation of a cyan radical in the present system, it is worth pointing out that an electron donor such as triethanolamine or *p*-phenylenediamine quenches the fluorescence of phen in water, so that the anion radial of phen should be produced under such conditions. Nonetheless, the photoreaction of phen in the presence of both NaCN and the amine suppressed the reaction yield, indicating that formation of the anion radical of phen was not necessary enough for the photocyanation reaction. Therefore, we suppose that PET between phen and a cyanide ion, producing both the anion radical of phen and a cyan radical, will be the primary step for the present photocyanation reaction. In the $S_{R\text{-}N}1Ar^*$ mechanism, formation of 5,6-dihydro-1,10-phenanthroline and/or the coupling dimer of the Hphen radical would be expected in addition to that of Hphen-CN. As long as the present experiments are concerned, however, we could not confirm formation of such side products. Since there is no reason for inhibition of such reactions of the Hphen radical, further careful product analysis would reveal formaton of such species as minor products. It is important to note, furthermore that Konstantinov and Bunce have reported that the oxidation potential of a cyanide ion is strongly dependent on a medium: +1.3 V in acetonitrile, +1.95 V in methanol, and +1.7–2.26 V in water. Owing to such a high oxidation potential of a cyanide ion and its solvent dependence, they have concluded that the $S_{R\text{-}N}1Ar^*$ mechanism is not appropriate for a photocyanation reaction of ArH [33]. However, it is also true that the fluorescence of phen is quenched certainly by a cyanide ion and the S_N2Ar^* mechanism mentioned above does not explain well the present results. It is clear that further mechanistic studies including laser photolysis and radical trapping experiments are absolutely necessary to elucidate the reaction mechanism. Nonetheless, we suppose that the present experimental observations are explained more appropriately by the $S_{R\text{-}N}1Ar^\bullet$ mechanism rather than by the S_N2Ar^* mechanism.

4. Conclusions

The reductive photocyanation of 1,10-phenanthroline by a cyanide ion in aqueous solutions has been demonstrated for the first time. Although the product and quantum yields of Hphen-CN (54% and $\Phi = 1.7 \times 10^{-3}$) were not necessarily high enough, the photocyanation mechanism of phen was quite uncommon. The photocyantion of aromatic hydrocarbons and heteroaromatics so far reported proceeds via a PET (in the presence of A) or S_N2Ar^* mechanism, while the present photocyantion reaction of phen was suggested to undergo through an anion radical ($S_{N\text{-}R}1Ar^*$) mechanism. Furthermore, we found that the reaction yield was improved by a factor of ~7 in the presence of Mg^{2+} through coordination of Mg^{2+} with phen in the ground-state. Such characteristics of the present photocyanation reaction will be responsible for the coordinating ability of phen and the pK_a value of the anion radical (>14) [34]. Therefore, we suppose that the anion radical mechanism of the photocyanation reaction will not be common to other *N*-heteroaromatics and will be specific to phen. Despite this, one-step photocyanation of phen and its derivatives will be meaningful in the fields of both photochemistry and coordination chemistry. Further studies on photocyanation reactions of ArH are now underwent in our research laboratory, which will be reported in separate publications.

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