

# Mechanism of the photoamination of 1-hydroxyanthraquinone reaction in acetonitrile under air

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## Abstract

It has been revealed by a kinetic study that the photoamination of 1-hydroxyanthraquinone (**1**) takes place through an attack by radical species derived from the amine to the ground state of **1** under air. Detection of the anion radical of **1** by measuring the visible absorption spectrum of irradiated solution under nitrogen indicates that an aminium radical is initially formed by electron transfer. From quenching and sensitization of the reaction, an electron should transfer from the amine to the triplet state of 9-hydroxy-1,10-anthraquinone, a tautomer of **1**. The mechanism involving the contribution of reversible proton dissociation of the aminium radical has been kinetically proposed.

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**Keywords:** Photoamination; 1-Hydroxyanthraquinone; Mechanism

## 1. Introduction

The photoreactivity of anthraquinones having electron-donating substituents has been considered very low because their lowest excited states are intramolecular CT states inactive for hydrogen abstraction [1–5]. This is caused by the fact that the photochemical behavior of anthraquinone derivatives has been studied for a long time with respect to the photofading of vat dyes and photosensitized oxidation [1–5]. The object of those studies was restricted to hydrogen abstraction by an excited carbonyl group and intense interest had been obtained concerning photoreduction via the lowest triplet  $n\pi^*$  state.

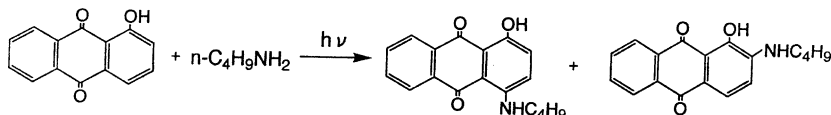
Several reactions, however, have been reported for the derivatives having electron-donating substituents [6–13] including our report on the photoamination of sodium 1-amino-4-bromoanthraquinone-2-sulfonate [14,15] in the area of photosubstitution. Some examples of photosubstitution have also been presented for the derivatives having electron-withdrawing substituents [16–27]. The functional group is substituted by a hydroxide ion [6] and an amine, and a hydrogen atom of the anthraquinone skeleton is also substituted by an amine [7–9] in methoxyanthraquinones. The radical arising from the hydroxide ion is considered

to participate in the substitution by the hydroxide ion [6]. The substitution by an amine is regarded as a nucleophilic reaction [7,8]. Sulfonation occurs at the 2-position of 1-aminoanthraquinone and at the 2- and 4-positions of 1-hydroxyanthraquinone [10–12]. These substitutions are anticipated to proceed via an attack of the sulfite radical on the quinones.

We have already clarified the mechanism of the photoamination of haloaminoanthraquinones including sodium 1-amino-4-bromoanthraquinone-2-sulfonate [28–31], where the halogen atom at the 4-position was substituted by amine. On the other hand, the photoamination of 1-hydroxyanthraquinone and 1-hydroxyhaloanthraquinones showed different behavior from that of the haloaminoanthraquinones as previously reported [32]. Amination at the 2-position was newly discovered in the case of 1-hydroxyanthraquinone. For example, the quantum yields of 4-butylamination and that of 2-butylamination were  $6.8 \times 10^{-3}$  and  $1.5 \times 10^{-3}$ , respectively, under the condition of  $[1\text{-hydroxyanthraquinone}] = 3.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{butylamine}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$  in acetonitrile under air [32]. For the 1- and 2-hydroxyanthraquinones, it has been reported that the hydrogen at the peri-position is reactive for amination, that is, the amination occurs at the 4-position in 1-hydroxyanthraquinone and at the 1-position in 2-hydroxyanthraquinone [13]. Although the probability of contribution by the amine radical has been tentatively

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suggested, the mechanism has been not clarified [13]. In this paper, we report the mechanism of the photoamination of 1-hydroxyanthraquinone in acetonitrile under an air atmosphere based on a kinetic study. The obtained results indicate the occurrence both of an electron transfer from an amine to the triplet state of 9-hydroxy-1,10-anthraquinone, a tautomer of 1-hydroxyanthraquinone, and of an attack of the radical species derived from the amine on the ground state of 1-hydroxyanthraquinone. A mechanism containing the contribution of reversible proton dissociation of the aminium radical has been proposed.



## 2. Experimental

### 2.1. Materials

1-Hydroxyanthraquinone (**1**) was obtained by the method described in our previous paper [32]. 2-Methyl-2-nitroso-propane dimer was purchased from Tokyo Kasei Co. and used without further purification. Butanethiol (Kanto Kagaku Co.), *n*-butylamine (Tokyo kasei Co.) and *n*-butylamine hydrochloride (Tokyo kasei Co.) were of guaranteed reagent grade and were used without further purification. The acetonitrile was of Kanto Kagaku's UGR grade.

### 2.2. Procedures

Light irradiation was carried out using a 500 W high-pressure mercury lamp through appropriate glass and interference filters. In the presence of an amine, **1** (acid form) can be in equilibrium with the phenoxide form (basic form). However, the equilibrium almost shifted to the acid form under the experimental condition of this study. Therefore, the acid form was excited. The amination products of **1** were assayed using a Shimadzu HPLC system. The quantum yield of the reaction was determined in comparison with the photoamination of 1-amino-2,4-dibromoanthraquinone [31] in aerated ethanol ( $\phi = 1.7 \times 10^{-3}$ , [butylamine] =  $5.0 \times 10^{-2}$  mol dm<sup>-3</sup>). The visible absorption spectra were recorded using a Shimadzu MPS-2000 spectrophotometer.

## 3. Results and discussion

### 3.1. Effect of triplet quencher on the photoamination

The photoamination of **1** was quenched by anthracene ( $E_T = 178$  kJ mol<sup>-1</sup>). Stern–Volmer plots were the same straight lines passing through the intercept of 1 in both the 2- and 4-aminations (Fig. 1). The slopes of the linear plots

depended on the amine concentration, and the reciprocals of the slopes and the amine concentration was linear as shown in Fig. 2. These results indicate that both the 2- and 4-aminations occur via the same excited triplet state and that anthracene quenches the excited state that the amine directly attacks. The lines in Fig. 1 express the following relation:

$$\frac{\phi^0}{\phi} = 1 + \frac{k_q[\text{Anthracene}]}{k_d + k_{qT}^{\text{O}_2}[\text{O}_2] + k_{\text{et}}[\text{BuNH}_2]} \quad (1)$$

where  $\phi$  represents the quantum yield of the amination and superscript 0 means the absence of a quencher. The  $k_q$ ,  $k_d$ ,  $k_{qT}^{\text{O}_2}$  and  $k_{\text{et}}$  are the rate constants of the triplet quenching by anthracene, of the radiationless deactivation of the triplet state, of the triplet quenching by oxygen, and of the reaction of the triplet state with the amine, respectively. Therefore, the quantum yield of the amination is expressed as

$$\phi_i = \phi_T \left( \frac{k_{\text{et}}[\text{BuNH}_2]}{k_d + k_{qT}^{\text{O}_2}[\text{O}_2] + k_{\text{et}}[\text{BuNH}_2]} \right) \gamma_i \quad (2)$$

where  $\phi_T$  and  $\gamma_i$  ( $i = 2$ : 2-amination;  $i = 4$ : 4-amination) are the quantum yield of the triplet state formation and the efficiency of the amination after the attack of the amine on the triplet state, respectively.

The photoamination was not quenched by both 1-bromonaphthalene ( $E_T = 247$  kJ mol<sup>-1</sup>) and *trans*-stilbene ( $E_T = 206$  kJ mol<sup>-1</sup>), and sensitized by 1-bromonaphthalene. The <sup>3</sup>nπ\* level of anthraquinone is situated at the energy of ca. 260 kJ mol<sup>-1</sup> and is considered not to change its energy regardless of the substituents introduced on the quinone nucleus [2]. The reactive triplet excited state, therefore, is not the <sup>3</sup>nπ\* level, but is a triplet state situated under the <sup>3</sup>nπ\* level. Photoamination of 1-acylaminoanthraquinone having a similar energy diagram as **1** occurs at the <sup>3</sup>CT level through the pass <sup>1</sup>CT(S<sub>1</sub>) → <sup>3</sup>nπ\*(T<sub>2</sub>) → <sup>3</sup>CT(T<sub>1</sub>) [33]. An electron transfer from the amine to <sup>3</sup>nπ\*(T<sub>2</sub>) has been confirmed in the case of 1-acetylamino-4-bromoanthraquinone [30]. If the photoamination of **1** take places at the <sup>3</sup>CT level through the pass <sup>1</sup>CT(S<sub>1</sub>) → <sup>3</sup>nπ\*(T<sub>2</sub>) → <sup>3</sup>CT(T<sub>1</sub>), the reaction would be quenched by both 1-bromonaphthalene and *trans*-stilbene.

The intramolecular proton transfer of 1,5-dihydroxyanthraquinone in its excited singlet state has been reported [34,35] and the experimental evidence that suggest the occurrence of an intramolecular proton transfer has been obtained for **1** [36]. It has been suggested by a semi-empirical molecular orbital calculation that <sup>1</sup>CT(S<sub>1</sub>) of 9-hydroxy-1,10-anthraquinone (**2**) is close to that of 1-aminoanthraquinone, which possesses a longer λ<sub>max</sub> than

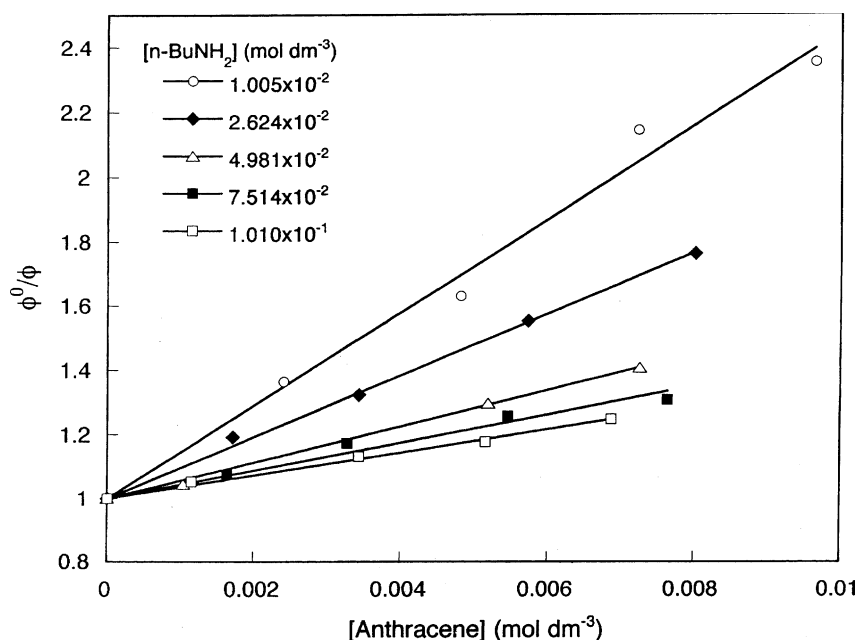


Fig. 1. Stern–Volmer plots for quenching of the photoamination by anthracene.

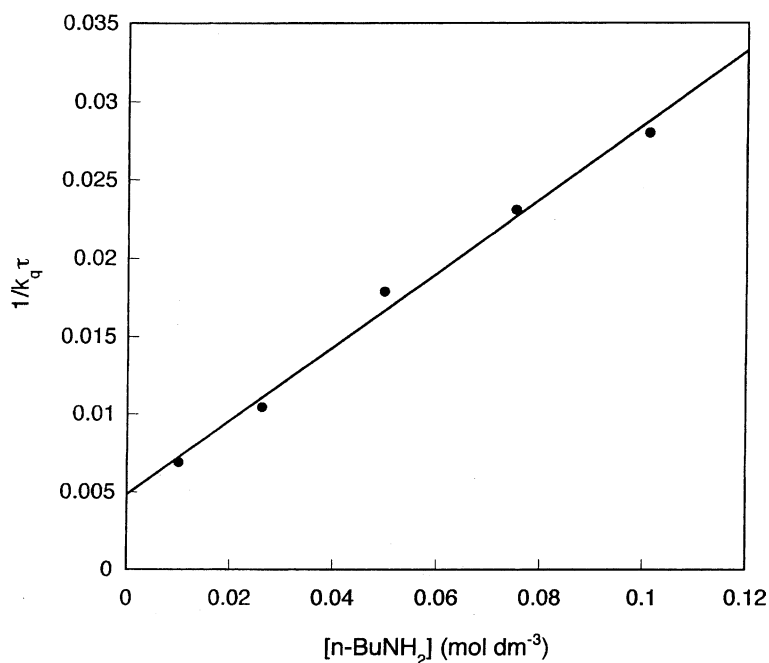


Fig. 2. Plot of  $1/k_q\tau$  vs. the concentration of *n*-butylamine.

that of 1-acetylaminoanthraquinone, and that the state is located below the lowest  $^3n\pi^*$  state.<sup>1</sup> Therefore, the effects of the quencher mentioned above should indicate that the  $^3CT(T_1)$  of **2**, which is produced by the tautomerization of

<sup>1</sup> CI calculation containing five HOMOs and two LUMOs was carried out using the PM3 method in MOPAC93. Calculated energies of excited states are as follows: 9-hydroxy-1,10-anthraquinone the lowest excited singlet  $\pi\pi^*$  state: 3.17 eV, the lowest excited triplet  $n\pi^*$  state: 4.01 eV; 1-aminoanthraquinone the lowest excited singlet  $\pi\pi^*$  state: 3.35 eV, the lowest excited triplet  $n\pi^*$  state: 4.03 eV.

**1** in its excited state, is the active excited triplet state for the amination.

### 3.2. Concentration effect of 1-hydroxyanthraquinone on the photoamination

The higher the concentration of **1**, the higher the quantum yield of the amination. This means the participation of the ground state of **1** in the reaction. The D–D mechanism, which is well known for the photodegradation of xanthene

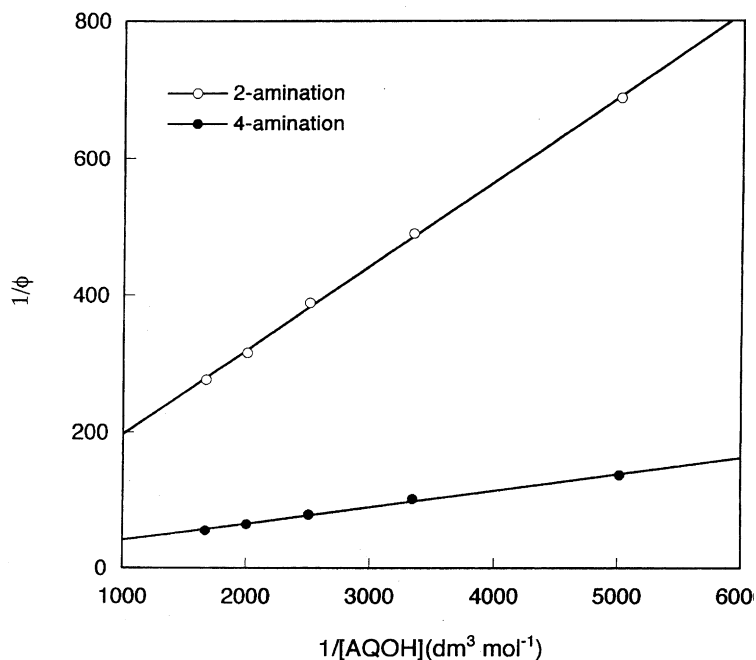


Fig. 3. Effect of the concentration of **1** on the photoamination ( $[n\text{-Butylamine}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ).

dyes, is ruled out as a mechanism of the reaction, because the Stern–Volmer constants obtained by the quenching experiment were dependent on the amine concentration as mentioned above. Plots of the reciprocal of  $\phi_i$  versus the concentration of **1** were linear in both the 2- and 4-amination cases as shown in Fig. 3. This indicates that some chemical species attack the ground state of **1**. Furthermore, the value of the slope/intercept of the linear relation for the 2-amination case was almost the same as that in the case of the 4-amination and increased linearly with the amine concentration (Fig. 4,  $[\text{BuNH}_2 \cdot \text{HCl}] = 0.0 \text{ mol dm}^{-3}$ ). From these results, the following relation is derived:

$$\frac{1}{\phi_i} = \frac{1}{\phi_T \delta_i} \left( a + \frac{b + c[\text{BuNH}_2]}{[\text{AQOH}]} \right) \quad (3)$$

where  $\delta_i$  is the efficiency being independent of the concentration of **1**, and  $a$ ,  $b$  and  $c$  are constants.

### 3.3. Effect of radical scavenger on the photoamination

Radical scavengers inhibited the photoamination of **1** as shown in Fig. 5. This means the participation of radical species during the reaction. A new absorption that was not observed with the irradiation under air appeared in the region of longer than 700 nm during irradiation under nitrogen. This new absorption is characteristic of the anthraquinone anion radical [37] and disappeared with the introduction of air. These results indicate the occurrence of an electron transfer from the amine to the excited triplet state of anthraquinone. Considering the participation of the ground state of **1** to the reaction as mentioned above, radical species derived from

the amine by the electron transfer would attack the ground state of **1**.

The Stern–Volmer type plot to determine the effect of the radical scavenger on the photoamination was the same straight line passing through an intercept of 1 in the both 2- and 4-aminations (Fig. 6). The slope of the line was dependent on the concentration of **1** and a plot of the reciprocal of

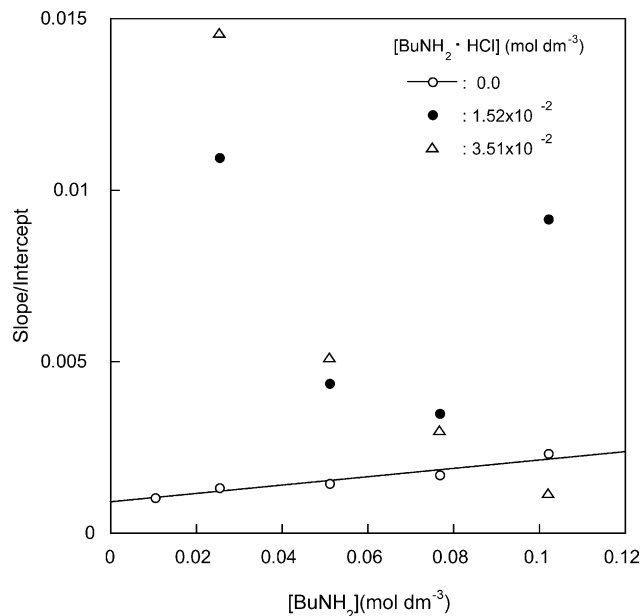


Fig. 4. Effect of the butylamine concentration on the values of the slope/intercept for the linear relation between the reciprocal of the quantum yield and the concentration of **1**.

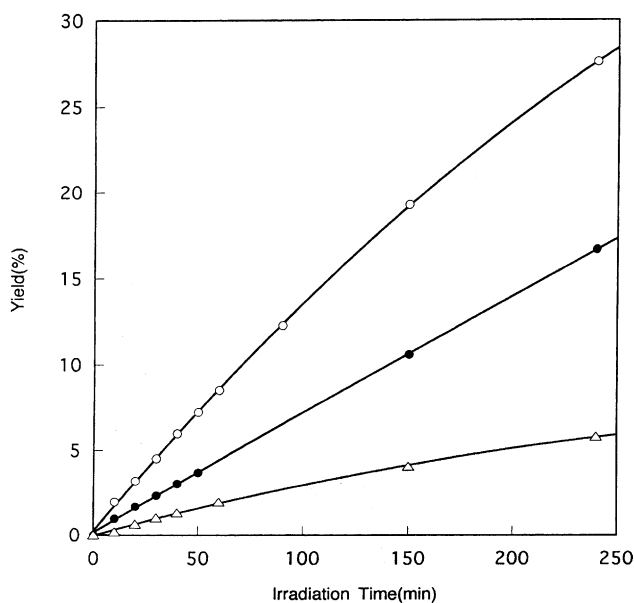


Fig. 5. Effect of radical scavenger on the photoamination. Yield (%) as ordinate means the total yield of the amination. Excitation wavelength: 400 nm; (○) no radical scavenger; (●) [butanethiol] =  $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ; (△) [2-methyl-2-nitrosopropane] =  $1.5 \times 10^{-2} \text{ mol dm}^{-3}$ .

the slope versus the concentration of **1** was linear (Fig. 7). Therefore, the following relation is valid regardless of the position of the substitution:

$$\frac{\phi}{\phi_{\text{RSC}}} = 1 + \frac{d[\text{RSC}]}{e[\text{AQOH}] + f} \quad (\text{RSC : radical scavenger}) \quad (4)$$

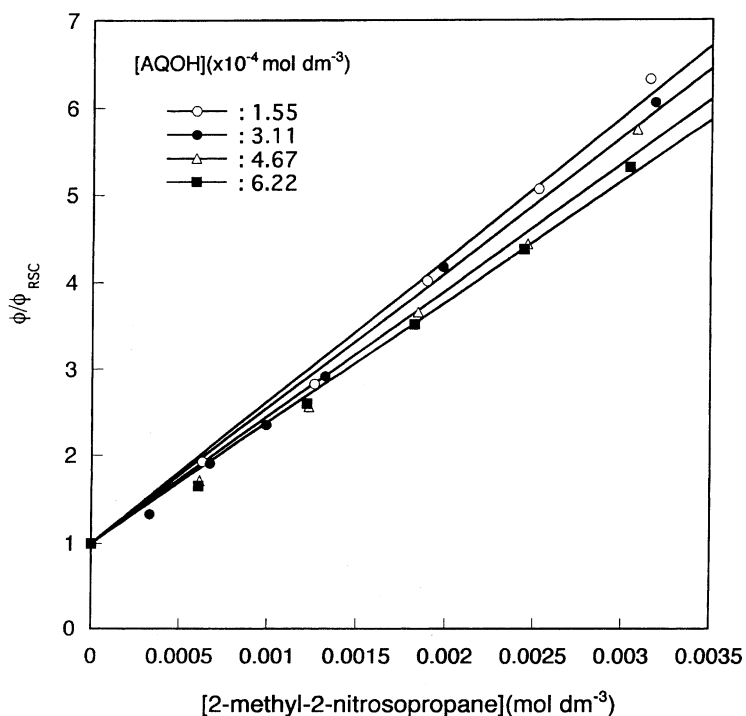


Fig. 6. Stern–Volmer type plot for the suppression by 2-methyl-2-nitrosopropane.

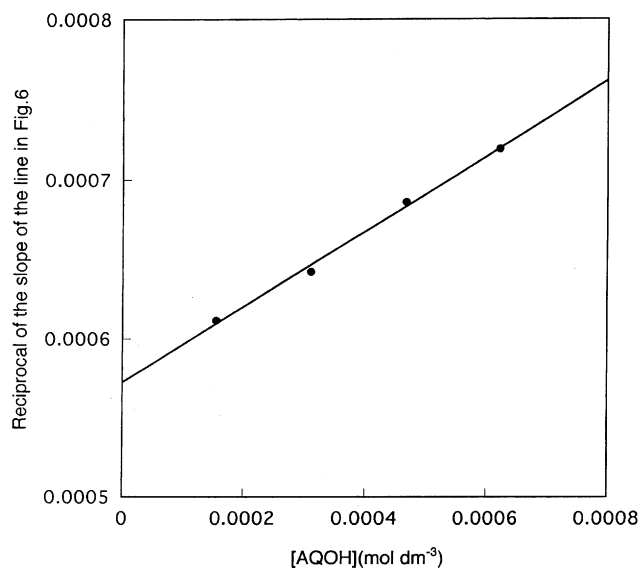


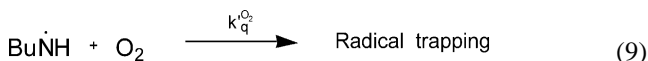
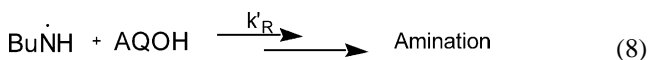
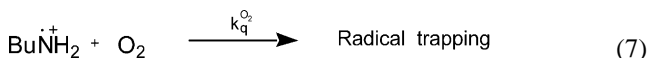
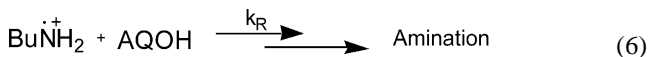
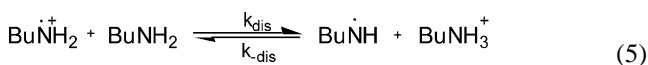
Fig. 7. Plot of  $1/\text{slope}$  of the line in Fig. 6 vs. the concentration of **1**.

where  $\phi$  and  $\phi_{\text{RSC}}$  are the quantum yield of amination in the absence of a radical scavenger and that in the presence of a radical scavenger, respectively, and  $d$ ,  $e$  and  $f$  are constants.

#### 3.4. Mechanism for the photoamination of 1-hydroxyanthraquinone

As mentioned in the previous sections, the amination would proceed through the attack of radical species derived from the amine by electron transfer to the ground

state of **1**. The butylamine cation radical ( $\text{Bu}\dot{\text{N}}\text{H}_2^+$ ) produced by the electron transfer is a candidate for reactive species. Aminium radicals are known to release an amino proton and the  $pK_a$  values have been evaluated for [38]. Furthermore, the aminium radicals are also known to release an  $\alpha$ -proton in an alkyl group [38]. Candidates for the radical species are, therefore, the butylamine cation radical ( $\text{Bu}\dot{\text{N}}\text{H}_2^+$ ), a radical produced by an elimination of an amino proton in  $\text{Bu}\dot{\text{N}}\text{H}_2^+$  ( $\text{Bu}\dot{\text{N}}\text{H}$ ) and a radical produced by elimination of an  $\alpha$ -proton in the alkyl group ( $\text{BuNH}_2\dot{\text{C}}$ ). Since no attack of the third radical on the ground state of **1** lead to the amination, this radical is ruled out as a candidate. Consequently, the following reaction mechanism containing a reversible proton dissociation in the radical  $\text{Bu}\dot{\text{N}}\text{H}_2^+$  (Eqs. (5)–(9)) can be postulated.



$$k_{\text{R}} = k_{\text{r}2} + k_{\text{r}4}, \quad k'_{\text{R}} = k'_{\text{r}2} + k'_{\text{r}4},$$

r2, 2-amination, r4, 4-amination

By applying the steady-state approximation to the radicals,  $\text{Bu}\dot{\text{N}}\text{H}_2^+$ ,  $\text{Bu}\dot{\text{N}}\text{H}$  and the excited species arising from **1**, we obtained the quantum yield of the amination

$$\phi(i) = \phi_{\text{T}} \left( \frac{k_{\text{et}}[\text{BuNH}_2]}{k_{\text{d}} + k_{\text{qT}}^{\text{O}_2}[\text{O}_2] + k_{\text{et}}[\text{BuNH}_2]} \right) \frac{U}{W} [\text{AQOH}] \quad (10)$$

where  $U$  and  $W$  are

$$U = (k'_{\text{R}}[\text{AQOH}] + k_{\text{q}}^{\text{O}_2}[\text{O}_2] + k_{\text{dis}}[\text{BuNH}_3^+])k_{\text{ri}}\beta_i + k_{\text{dis}}k'_{\text{ri}}[\text{BuNH}_2]\beta'_i,$$

$$W = (k_{\text{R}}[\text{AQOH}] + k_{\text{q}}^{\text{O}_2}[\text{O}_2] + k_{\text{dis}}[\text{BuNH}_2])(k'_{\text{R}}[\text{AQOH}] + k_{\text{q}}^{\text{O}_2}[\text{O}_2] + k_{\text{dis}}[\text{BuNH}_3^+]) - k_{\text{dis}}k_{\text{dis}}[\text{BuNH}_2][\text{BuNH}_3^+]$$

where  $\beta(i)$ ,  $\beta'(i)$  are efficiencies of the amination after the attack of the two radicals ( $\text{Bu}\dot{\text{N}}\text{H}_2^+$  and  $\text{Bu}\dot{\text{N}}\text{H}$ ) on the ground state of **1**. When the ratio of the rates in the reversible reaction (Eq. (5)) is expressed as

$$\alpha = \frac{k_{\text{dis}}[\text{Bu}\dot{\text{N}}\text{H}][\text{BuNH}_3^+]}{k_{\text{dis}}[\text{Bu}\dot{\text{N}}\text{H}_2^+][\text{BuNH}_2]} \quad (11)$$

the concentration of  $\text{Bu}\dot{\text{N}}\text{H}$  is

$$[\text{Bu}\dot{\text{N}}\text{H}] = \frac{\alpha k_{\text{dis}}[\text{Bu}\dot{\text{N}}\text{H}_2^+][\text{BuNH}_2]}{k_{\text{dis}}[\text{BuNH}_3^+]} \quad (12)$$

On the other hand, since the concentrations of  $\text{Bu}\dot{\text{N}}\text{H}$  is given as Eq. (13) by applying the steady-state approximation

$$[\text{Bu}\dot{\text{N}}\text{H}] = \frac{k_{\text{dis}}[\text{BuNH}_2][\text{Bu}\dot{\text{N}}\text{H}_2^+]}{k'_{\text{R}}[\text{AQOH}] + k_{\text{q}}^{\text{O}_2}[\text{O}_2] + k_{\text{dis}}[\text{BuNH}_3^+]} \quad (13)$$

We have the following relation comparing Eqs. (12) and (13)

$$k'_{\text{R}}[\text{AQOH}] + k_{\text{q}}^{\text{O}_2}[\text{O}_2] + k_{\text{dis}}[\text{BuNH}_3^+] = \frac{k_{\text{dis}}[\text{BuNH}_3^+]}{\alpha}$$

Hence,  $U$  and  $W$  are reduced to

$$U = \frac{k_{\text{dis}}}{\alpha} \left( [\text{BuNH}_3^+]k_{\text{ri}}\beta_i + \frac{k_{\text{dis}}}{k_{\text{dis}}} \alpha [\text{BuNH}_2]k'_{\text{ri}}\beta'_i \right),$$

$$W = \frac{k_{\text{dis}}[\text{BuNH}_3^+]}{\alpha} \{ k_{\text{R}}[\text{AQOH}] + k_{\text{q}}^{\text{O}_2}[\text{O}_2] + k_{\text{dis}}(1 - \alpha)[\text{BuNH}_2] \}$$

and Eq. (10) becomes

$$\phi(i) = \frac{\phi_{\text{T}}}{k_{\text{dis}}[\text{BuNH}_3^+]} \left( \frac{k_{\text{et}}[\text{BuNH}_2]}{k_{\text{et}}[\text{BuNH}_2] + k_{\text{qT}}^{\text{O}_2}[\text{O}_2] + k_{\text{d}}} \right) \times \left\{ \frac{k_{\text{dis}}k_{\text{ri}}\beta_i[\text{BuNH}_3^+] + \alpha k_{\text{dis}}k'_{\text{ri}}\beta'_i[\text{BuNH}_2]}{k_{\text{R}}[\text{AQOH}] + k_{\text{q}}^{\text{O}_2}[\text{O}_2] + k_{\text{dis}}(1 - \alpha)[\text{BuNH}_2]} \right\} \times [\text{AQOH}] \quad (14)$$

The reciprocal of the quantum yield of the photoamination is

$$\frac{1}{\phi(i)} = \frac{k_{\text{dis}}[\text{BuNH}_3^+]}{\phi_{\text{T}}} \left( 1 + \frac{k_{\text{qT}}^{\text{O}_2}[\text{O}_2] + k_{\text{d}}}{k_{\text{et}}[\text{BuNH}_2]} \right) \times \left( \frac{1}{k_{\text{dis}}k_{\text{ri}}\beta_i[\text{BuNH}_3^+] + \alpha k_{\text{dis}}k'_{\text{ri}}\beta'_i[\text{BuNH}_2]} \right) \times \left( k_{\text{R}} + \frac{k_{\text{q}}^{\text{O}_2}[\text{O}_2] + k_{\text{dis}}(1 - \alpha)[\text{BuNH}_2]}{[\text{AQOH}]} \right) \quad (15)$$

If the value  $\alpha$  and  $[\text{BuNH}_3^+]$  are considered constant regardless of the amine concentration, the experimental results shown in Figs. 3 and 4 ( $[\text{BuNH}_2 \cdot \text{HCl}] = 0.0 \text{ mol dm}^{-3}$ ) are explained by Eq. (15). Since a certain amount of  $\text{BuNH}_3^+$  will exist in the system during the stage of sample preparation under the influence of atmospheric carbon dioxide, the assumption that  $[\text{BuNH}_3^+]$  is constant should be not inappropriate. In the presence of butylamine hydrochloride as a source of  $\text{BuNH}_3^+$ , the plots of the reciprocal of the quantum yields versus the concentration of **1** were linear

and the values of the slope/intercept of the linear relations for the 2-amination were almost the same as those for the 4-amination similar to the case in the absence of butylamine hydrochloride. However, the values of the slope/intercept did not linearly increase with the amine concentration (Fig. 4,  $[\text{BuNH}_2 \cdot \text{HCl}] = 1.52 \times 10^{-2}$ ,  $3.51 \times 10^{-2} \text{ mol dm}^{-3}$ ) in contrast to the case of  $[\text{BuNH}_2 \cdot \text{HCl}] = 0.0 \text{ mol dm}^{-3}$ . This value nonlinearly decreased with the amine concentration at  $[\text{BuNH}_2 \cdot \text{HCl}] = 3.51 \times 10^{-2} \text{ mol dm}^{-3}$ , which can be construed as that of  $\alpha$  in Eq. (15) is more than unity and decreases with the amine concentration. The change in the values seem to correspond to the change of  $\alpha$  in Eq. (15) from more than unity to less than unity in the case of  $[\text{BuNH}_2 \cdot \text{HCl}] = 1.52 \times 10^{-2} \text{ mol dm}^{-3}$ . These results strongly suggest that the  $\alpha$  changes with both the concentrations of butylamine and butylamine hydrochloride. The linear relation in the absence of butylamine hydrochloride should be explained by considering that  $\alpha$  is less than unity and is constant regardless of the amine concentration. A kinetic consideration of the reaction based on the reaction scheme (Eqs. (5)–(9)) indicates that a consistent explanation of the results shown in Figs. 3 and 4 is impossible unless the reverse process denoted by Eq. (5) is considered.

The quantum yield in the presence of a radical scavenger ( $\phi_{\text{RSC}}$ ) is derived in the same manner as the derivation of Eq. (14) on the assumption that a radical scavenger traps only the radicals,  $\text{Bu}\overset{+}{\text{N}}\text{H}_2$  and  $\text{Bu}\overset{\cdot}{\text{N}}\text{H}$ . The ratio of the quantum yield in the absence of a radical scavenger ( $\phi$ ) to that in the presence of a radical scavenger ( $\phi_{\text{RSC}}$ ) can be expressed for the both 2- and 4-aminations:

$$\frac{\phi}{\phi_{\text{RSC}}} = 1 + \frac{k_{\text{RSC}}[\text{RSC}]}{k_{\text{R}}[\text{AQOH}] + k_{\text{q}}^{\text{O}_2}[\text{O}_2] + k_{\text{dis}}(1 - \alpha)[\text{BuNH}_2]} \quad (16)$$

where  $k_{\text{RSC}}$  is the  $\text{Bu}\overset{+}{\text{N}}\text{H}_2$  radical trapping rate constant of the radical scavenger. Eq. (16) shows that a plot of  $\phi/\phi_{\text{RSC}}$  versus concentration of the radical scavenger is the same straight line passing through the intercept of 1 for both the 2- and 4-aminations and that the plot of the reciprocal of the slope versus the concentration of **1** is linear. These expectations agreed with the experimental results mentioned in Section 3.3. The ratio of the intercept to the slope in the linear plot of Fig. 7,  $2.42 \times 10^{-3} \text{ mol dm}^{-3}$ , corresponds to the value of  $(k_{\text{q}}^{\text{O}_2}[\text{O}_2] + k_{\text{dis}}(1 - \alpha)[\text{BuNH}_2])/k_{\text{R}}$ . The value of  $(k_{\text{q}}^{\text{O}_2}[\text{O}_2] + k_{\text{dis}}(1 - \alpha)[\text{BuNH}_2])/k_{\text{R}}$  is also obtained from the concentration effect of **1** (Fig. 3, Eq. (15)) and is  $1.47 \times 10^{-3} \text{ mol dm}^{-3}$ . These two values are in approximate agreement with each other. These results also strongly supported the fact that the mechanism mentioned above (Eqs. (5)–(9)) is reasonable.

In general, it is known that the acidity of aromatic compounds containing hydroxyl group is higher in an excited singlet state than in the ground state and that this tendency

is recognized in the excited triplet state although the difference in acidity is small [39]. The  $\text{pK}_{\text{a}}$  values of 9.3( $\text{S}_0$ ) [40], 1.2( $\text{S}_1$ ) [40] and 8.8( $\text{T}_1$ ) [41] have been reported for **1** in 33% dioxane–water. Although these values cannot directly apply to the case of acetonitrile, it is considered reasonable in acetonitrile to presume that the acidity of **1** in the excited singlet state is considerably higher than that in the ground state, and that the acidity of **1** in the excited triplet state is almost the same as that in the ground state. Considering the possibility of a dissociation of the hydroxyl group in the excited singlet state, the existence of the basic form of **1** in the excited states would be needed to take into account, even if the basic form of **1** rarely exists in the ground state and is not directly excited. Fluorescence emitted upon the excitation of **1** was quenched by *n*-butylamine. A dissociation of the hydroxyl group in the excited singlet state should be regarded as a reason of the quenching because high acidity of **1** in the excited singlet state is predicted as mentioned above. Therefore, a reaction path via the excited basic form of **1** cannot be ruled out. The basic form of **1** and that of **2** are considered iso-electronic in the CT excited states, which was supported by MO calculation [42]. Since the acidity of the excited triplet state should be expected lower than that of the excited singlet state, the reactive  $^3\text{CT}(\text{T}_1)$  of **2** (acid form) should be produced from the triplet basic form. The production of the  $^3\text{CT}(\text{T}_1)$  of **2** (acid form) not through the basic form, that is, directly from the excited acid form is also conceivable.

The Stern–Volmer plot for the amination during the quenching by anthracene under nitrogen was seemingly linear and the slope was smaller than the  $k_{\text{q}}\tau$  value under air atmosphere. This fact means the existence of another reaction path that is not affected by anthracene. Considering that the mechanism mentioned above (Eqs. (5)–(9)) is reasonable for the photoamination of **1** under air, a reaction via the excited basic form can be the other route to explain the quenching behavior by anthracene under nitrogen. Since the maximum absorption wavelength of the basic form of **1** in acetonitrile is ca. 500 nm and is inclined to be longer than that of 1-aminoanthraquinone in acetonitrile, ca. 470 nm, the  $E_{\text{T}_1}$  of the basic form is likely less than that of 1-aminoanthraquinone. It has been clarified in the photoamination of 1-amino-2,4-dibromoanthraquinone that a reaction via the lowest excited triplet state exists and that the reaction is not quenched by anthracene [29]. Although it is not clear whether the reaction from the triplet state of the basic form proceeds via a nucleophilic attack of the amine or via an attack of the radical species derived from the amine, the quenching behavior by anthracene under nitrogen may be qualitatively explained based on the assumption that the reaction path through the triplet state of the basic form exists as follows: a contribution of the reaction path through the triplet state of the basic form is essentially low and the reaction via this route is effectively quenched by the oxygen under air.

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