Photoamination of 1-hydroxyanthraquinone in a water-acetonitrile mixed solvent

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We investigated the photoamination kinetics of 1-hydroxyanthraquinones in a water-acetonitrile mixed solvent by stationary light irradiation. The progression of the reaction under an inert atmosphere demonstrated the existence of additional reaction pathways. The excited triplet state of the base form of the 1-hydroxyanthraquinones was found to be responsible for the additional pathways. On the other hand, the same reaction under air involved an attack of the amine-derived radical species (aminium and amino radicals) on the ground state of the 1-hydroxyanthraquinones. One of the pathways preferentially led to 2-amination, and the other led exclusively to 4-amination. Results also indicate the attainment of an equilibrium state between the aminium and amino radicals. Copyright © 2008 John Wiley & Sons, Ltd.
Supporting information may be found in the online version of this paper.

Keywords: photoamination; 1-hydroxyanthraquinone; 1-hydroxy-2-methylanthraquinone; aminium radical; amino radical; mechanism

INTRODUCTION

1-Aminohaloanthraquinones undergo photoamination in the presence of aliphatic amines and under visible-light irradiation.[1–7] The halogen atom at the 4-position of the anthraquinone nucleus is substituted with an amine, whereas the halogen atom at the 2-position is not substituted. Photoamination of the 1-aminoanthraquinones occurs through intramolecular CT states. The underlying mechanism for this reaction pathway has been investigated in detail.[3–6] Recently, we reported that the photoamination behaviors of 1-hydroxyanthraquinone (**1a-OH**) and 1-hydroxyhaloanthraquinones are different from those of haloaminoanthraquinones.[8,9] The 4-amination is known to occur effectively, even if no bromine atom exists at the 4-position of the anthraquinone nucleus. Similarly, 2-amination takes place in the absence of bromine at the 2-position.[8] The photoamination mechanism of **1a-OH** in acetonitrile under air has been previously reported.[9]

For **1a-OH** and 2-hydroxyanthraquinones, it has been reported[10] that the hydrogen at the peri-position is reactive in amination; that is, amination occurs at the 4-position in **1a-OH** and at the 1-position in 2-hydroxyanthraquinone. Although the contribution of an amine radical has been tentatively suggested, the mechanism is not clear. The reaction mechanism that we have reported entails the following processes: electron transfer from the amine to the triplet state of 9-hydroxy-1,10-anthraquinone, which is a tautomer of **1a-OH**, and attack of the radical species (aminium and amino radicals) derived from the amine on the ground state of **1a-OH**.[9] Proton dissociation of the aminium radical, which is produced as a result of the electron transfer, causes formation of the amino radical. Furthermore, it has also been demonstrated for the amination of **1a-OH** that the ratio of the quantum yield of 2-amination to that of 4-amination in acetonitrile under air is not significantly different from that under

an inert atmosphere. On the other hand, the ratio in the water-acetonitrile mixed solvent differs depending on the reaction atmosphere. In our previous study, the production ratio for amination in the water-acetonitrile mixed solvent under air was approximately the same as the ratio in acetonitrile, regardless of the water content, whereas the production ratio in the water-acetonitrile mixed solvent under an inert gas increased with the increase in the water content of the solvent. In addition, the production ratio for amination under an inert gas was greater than that under air. These reaction behaviors for amination in the water-acetonitrile mixed solvent are interesting from the viewpoints of regioselectivity and reaction mechanism.

In the present investigation, we report the photoamination mechanism of 1-hydroxyanthraquinones (**1a-OH** and **1b-OH**; as shown in Scheme 1) in a water-acetonitrile mixed solvent based on investigations using stationary light irradiation. Our results

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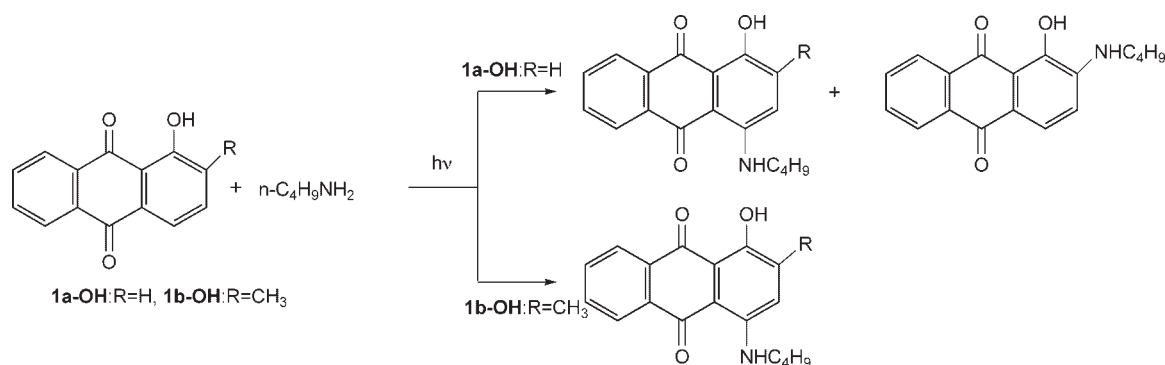
Scheme 1. Photoamination of 1-hydroxyanthraquinoines

reveal the existence of reaction pathways that were restricted to the reaction under an inert gas atmosphere, which differed from the reaction pathways operating under air. They also demonstrate the attainment of proton dissociation equilibrium by the radical species derived from the amine.

EXPERIMENTAL

Materials

1a-OH was synthesized using the method described in our previous paper.[8] 1-Hydroxy-2-methylanthraquinone (**1b-OH**) was prepared by the diazotization of 1-amino-2-methylanthraquinone (Tokyo Chemical Industry Co., Ltd., Japan), followed by decomposition in an aqueous sulfuric acid solution and purification by silica gel column chromatography using benzene as the eluent.[11] The 2-methyl-2-nitrosopropane dimer was obtained from Tokyo Chemical Industry and used without further purification. Zone refined anthracene was obtained from Tokyo Chemical Industry. Guaranteed reagent grade *n*-butylamine (Tokyo Chemical Industry) was used as obtained. Methylene Blue (**MB**) was a specially prepared analytical reagent (Tokyo Chemical Industry). The acetonitrile and water were UGR grade (Kanto Kagaku Co., Ltd.) and HPLC grade (Kanto Kagaku), respectively.

Amination of **1a-OH** yielded two products (2- and 4-amination products), and these products have been characterized elsewhere.[8] Only the 4-amination product was obtained in the case of **1b-OH**.

1-Hydroxy-2-methyl-4-butylaminoanthraquinone: mp 142.9-143.7 °C (decomp). Anal Calcd for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53; found: C, 74.11; H, 6.15; N, 4.44. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.01 (t, 3H, $J = 7.32$ Hz, NH(CH$_2$)$_3$CH$_3$), 1.53 (qd, 2H, $J = 7.32$, 7.32 Hz, NH(CH$_2$)$_2$ CH$_2$CH$_3$), 1.74 (tt, 2H, $J = 7.32$, 7.32 Hz, NHCH$_2$CH$_2$CH$_2$CH$_3$), 2.34 (d, 3H, $J = 0.84$ Hz, ArCH$_3$), 3.35 (td, $J = 7.32$, 6.56 Hz, NHCH$_2$CH$_2$CH$_2$CH$_3$), 7.01 (br s, 1H, H-arom), 7.67–7.78 (m, 2H, H-arom), 8.29–8.33 (m, 2H, H-arom), 10.33 (br s, 1H, NH), 14.25 (s, 1H, OH).

Procedures

Light irradiation was carried out using the light from a 500-W high-pressure mercury lamp and passing it through glass filters (Toshiba IRA-25S and L390) and an interference filter (Toshiba KL-40). Toshiba interference filter KL-42 was used instead of KL-40 in the quenching experiment using anthracene. All irradiation operations were carried out under air and/or under an argon atmosphere. In the presence of an amine, **1a-OH** and **1b-OH** (acid forms) were in equilibrium with the phenoxide forms (base forms). The equilibrium between the acid and base forms shifted to the base forms as the water content of the solvent increased. The water content of the solvent in this study was fixed at 10 and 15 vol% to avoid the co-excitation of the base forms upon excitation of the acid forms. Analysis of the amination products was carried out using a Shimadzu HPLC system for **1a-OH**, and by direct absorption spectrum measurement of the irradiated solution for **1b-OH**. The quantum yield of the reaction was determined in comparison with the photoamination of 1-amino-2,4-dibromoanthraquinone[5] in aerated ethanol ($\phi = 1.7 \times 10^{-3}$, [butylamine] $= 5.0 \times 10^{-2}$ mol dm^{-3}). The visible absorption spectra were recorded using a Shimadzu MPS-2000 spectrophotometer.

COMPUTATIONAL DETAILS

HF/6-31G(d,p) and B3LYP/6-31G(d,p) level calculations were carried out with the Gaussian 03 program package.[12] The geometry of the base form of **1a-OH** was fully optimized at each level of the calculation. The spin densities of the triplet state of the base form were obtained using an unrestricted calculation with a spin multiplicity of 3. The CIS method was also adopted for the calculation of the atomic charges of the excited triplet state of the base form, although this was limited to HF calculation. Natural population analysis was performed in addition to Mulliken population analysis.

RESULTS

Concentration effect of 1b-OH on the photoamination of 1b-OH

The photoamination of **1b-OH** in acetonitrile containing 10 vol% water (Ac10H$_2$O) under air was affected by the concentration of **1b-OH**. The plots of the reciprocal quantum yield (ϕ_b) *versus* the concentration of **1b-OH** were linear (Fig. 1). This result was similar to the result for **1a-OH** in acetonitrile under air. The values for the slope/intercept of the linear lines in Fig. 1 were constant, regardless of the amine concentration, whereas those in the case of **1a-OH** in acetonitrile under air were dependent on the amine concentration.[9]
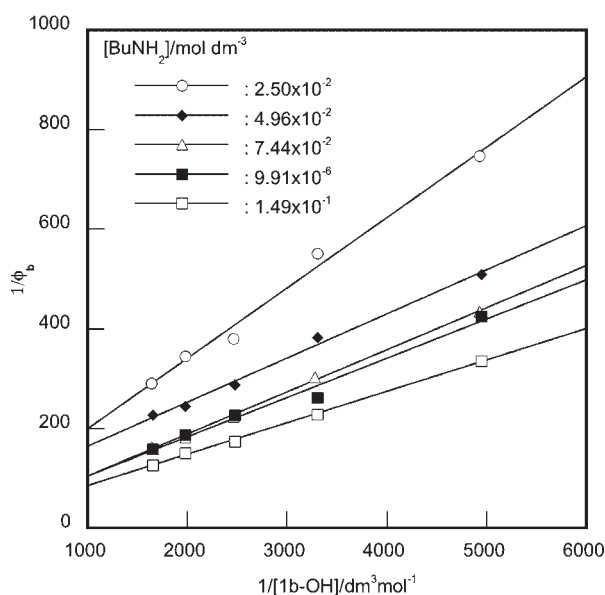
Figure 1. Effect of concentration of **1b-OH** on photoamination under air in Ac10H$_2$O. ϕ_b: quantum yield of photoamination of **1b-OH**

Effect of the amine concentration on photoamination of 1a-OH and 1b-OH

Photoamination of **1a-OH** and **1b-OH** in Ac10H$_2$O under both air and an inert gas was dependent upon the amine concentration. The Stern–Volmer-type plots were linear for the reaction under air, whereas the plots for the reaction under an inert gas were not linear (Fig. 2). In the reaction of **1a-OH**, the plot for 2-amination was similar to that for 4-amination (the plot for 2-amination is not shown in Fig. 2). The ratio of the quantum yield of 2-amination to that of 4-amination was found to depend on the amine
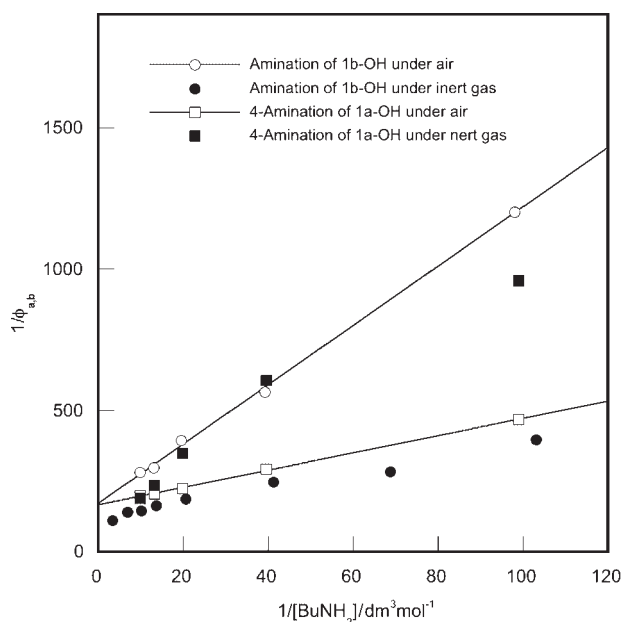

Figure 2. Effect of the butylamine concentration on photoamination of **1a-OH** and **1b-OH** in Ac10H$_2$O([**1a-OH**] $= 2.9 \times 10^{-4}$ mol dm^{-3}; [**1b-OH**] $= 3.0 \times 10^{-4}$ mol dm^{-3}). $\phi_{a,b}$: quantum yield of photoamination of **1a-OH**(ϕ_a) or that of **1b-OH** (ϕ_b)
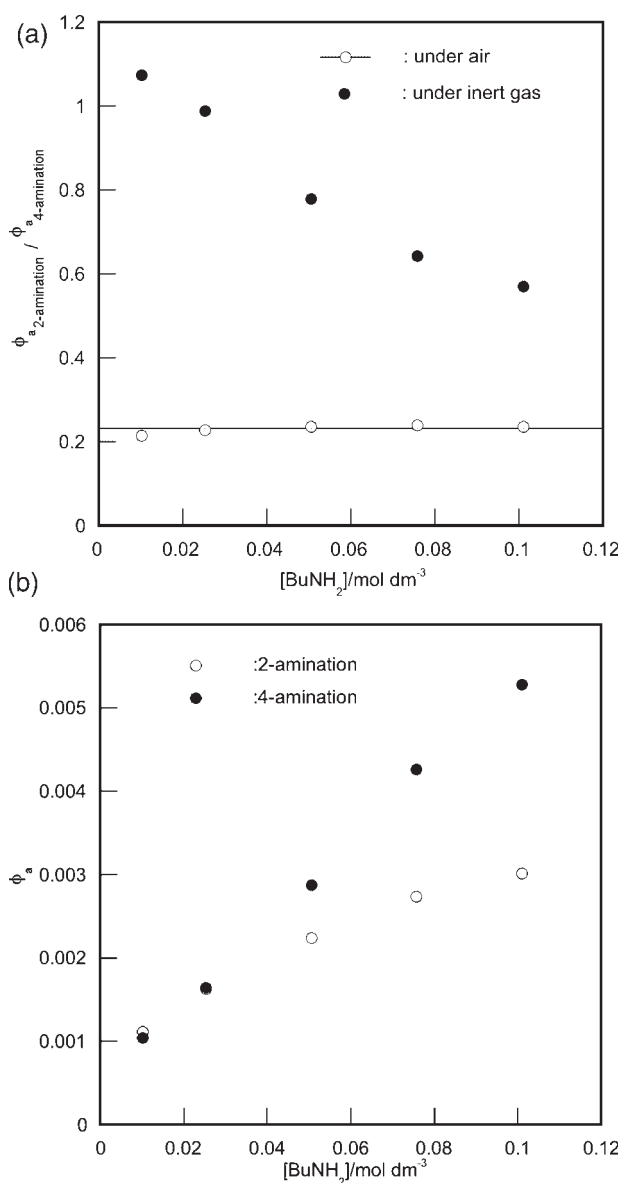

Figure 3. (a) Dependence of the production ratio ($\phi a_{2\text{-amination}}/\phi a_{4\text{-amination}}$) of photoamination of **1a-OH** on butylamine concentration in Ac10H$_2$O ([**1a-OH**] $= 2.9 \times 10^{-4}$ mol dm^{-3}). $\phi a_{2\text{-amination}}$: quantum yield of photoamination 2-amination of **1a-OH**. $\phi a_{4\text{-amination}}$: quantum yield of photoamination 4-amination of **1a-OH**. (b) Dependence of quantum yields of the amination of **1a-OH** on butylamine concentration in Ac10H$_2$O under inert gas ([**1a-OH**] $= 2.9 \times 10^{-4}$ mol dm^{-3}). ϕ_a: quantum yield of photoamination of **1a-OH**

concentration in Ac10H$_2$O under inert gas. On the other hand, the ratio under air is constant (approximately 0.2), regardless of the amine concentration (Fig. 3(a)). The dependency under the inert gas is due to the fact that the rate of increase in the quantum yield of 4-amination with increasing amine concentration was greater than that of 2-amination, as shown in Fig. 3(b).

Quenching of the photoamination of 1a-OH and *1b-OH* by anthracene

The photoamination of **1b-OH** in Ac10H$_2$O under air was quenched by anthracene. The Stern–Volmer plots for the reaction
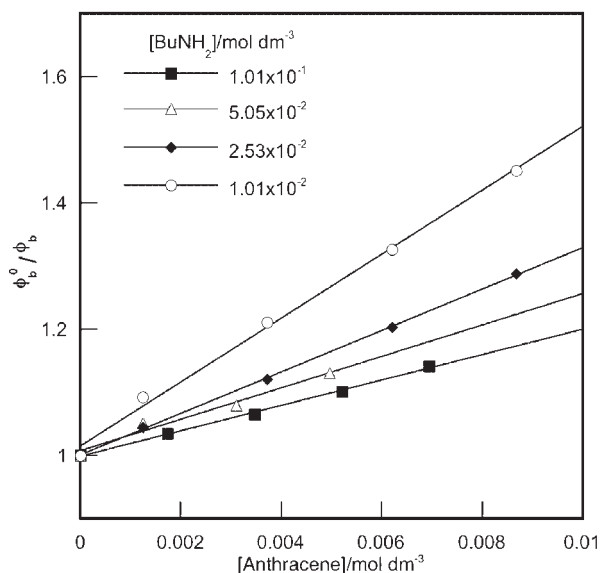
Figure 4. Stern–Volmer plots for quenching of photoamination of **1b-OH** by anthracene in Ac10H$_2$O under air atmosphere ([**1b-OH**] $= 3.0 \times 10^{-4}$ mol dm^{-3}). ϕ_b: quantum yield of photoamination of **1b-OH**; superscript 0 indicates the absence of quencher

Figure 5. Stern–Volmer plots for quenching of photoamination of **1a-OH** by anthracene in Ac10H$_2$O ([**1a-OH**] $= 3.1 \times 10^{-4}$ mol dm^{-3}, [BuNH$_2$] $= 5.0 \times 10^{-2}$ mol dm^{-3}). ϕ_a: quantum yield of photoamination of **1a-OH**; superscript 0 indicates the absence of quencher

were straight lines that passed through the intercept of 1 (Fig. 4). The slopes of the plots ($k_q\tau$ values) are dependent upon the amine concentration, and the plots of the reciprocal of the slope *versus* the amine concentration showed a linear relationship with a positive slope. This suggests that anthracene quenched the excited state that was attacked directly by the amine. These results were similar to those obtained for **1a-OH** in acetonitrile under air.[9] The ratio of the slope to the intercept in the linear plot was 15 dm^3 mol^{-1}.

The Stern–Volmer plot for the reaction of **1a-OH** in Ac10H$_2$O under air, which was the same for both 2-amination and 4-amination, was also a straight line that passed through the intercept of 1, similar to the case for **1b-OH** (Fig. 5). However, the plots for the reaction under an inert gas displayed an upward convex, and were located lower than the plot for the reaction under air (Fig. 5). This difference indicates that another reaction pathway not affected by anthracene plays a part in the reaction under inert gas.

Effect of radical scavenger on the photoamination of 1a-OH

A radical scavenger inhibited the photoamination of **1a-OH** in Ac10H$_2$O. The Stern–Volmer plot for the effect of the radical scavenger on photoamination was the same straight line that passed through the intercept of 1 in both 2-amination and 4-amination in Ac10H$_2$O under air (Fig. 6). The linear relation is explained by Eqn. (1) (as shown below), where **[1b-OH]** and some of the rate constants must be replaced with [**1a-OH**], and the corresponding rate constants. Similar results were obtained for the reaction in acetonitrile containing 15 vol% water (Ac15H$_2$O). The ratio of the quantum yield for 2-amination to that for 4-amination was approximately 0.2, regardless of the radical scavenger concentration (Fig. 7). These results were similar to those obtained for the reaction in acetonitrile under air.[9]
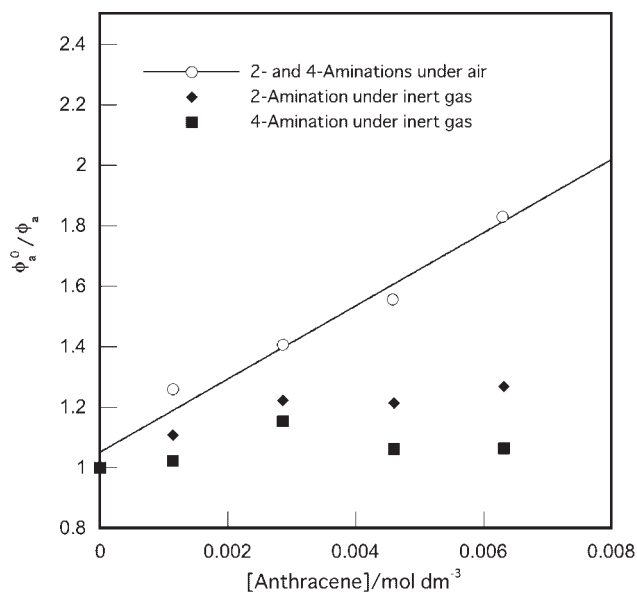
In the reaction under an inert gas, the Stern–Volmer plots are not linear, and the plot for 2-amination is situated above that for 4-amination (Fig. 6). This result indicates that 2-amination was more highly suppressed by the radical scavenger than 4-amination. The downward-convex plots in Fig. 6 may indicate that the radical scavenger traps more than two kinds of radicals responsible for amination. Similar plots were obtained for the reaction in Ac15H$_2$O under inert gas. Under an inert gas, the ratio
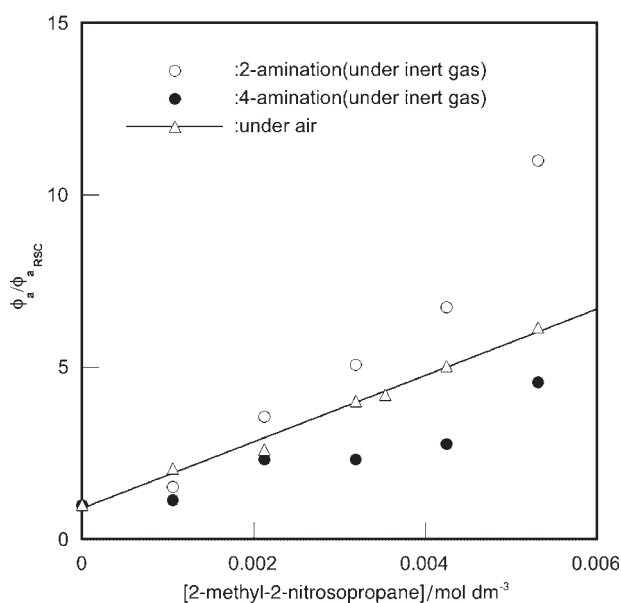

Figure 6. Stern–Volmer plots for suppression of photoamination of **1a-OH** by 2-methyl-2-nitrosopropane in Ac10H$_2$O([**1a-OH**] $= 3.1 \times 10^{-4}$ mol dm^{-3}, [BuNH$_2$] $= 5.0 \times 10^{-2}$ mol dm^{-3}). ϕ_a: quantum yield of photoamination of **1a-OH**; subscript **RSC** indicates the presence of radical scavenger
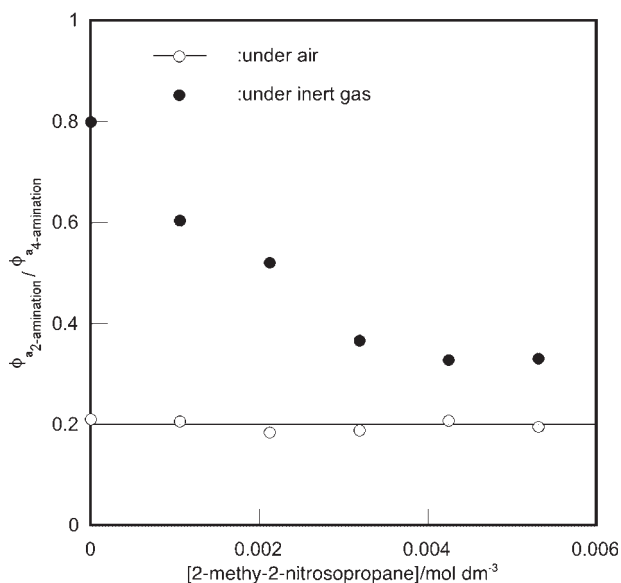
Figure 7. Dependence of production ratio ($\phi a_{2\text{-amination}}/\phi a_{4\text{-amination}}$) in photoamination of **1a-OH** on concentration of 2-methyl-2-nitrosopropane in Ac10H$_2$O([**1a-OH**] $= 3.1 \times 10^{-4}$ mol dm^{-3}, [BuNH$_2$] $= 5.0 \times 10^{-2}$ mol dm^{-3}). $\phi a_{2\text{-amination}}$: quantum yield of photoamination 2-amination of **1a-OH** $\phi a_{4\text{-amination}}$: quantum yield of photoamination 4-amination of **1a-OH**

Figure 8. Effect of **MB** on photoamination of **1a-OH** in Ac10H$_2$O([**1a-OH**] $= 3.1 \times 10^{-4}$ mol dm^{-3}, [BuNH$_2$] $= 4.9 \times 10^{-2}$ mol dm^{-3}). ϕ_a: quantum yield of photoamination of **1a-OH** [**MB**] in the abscissa expresses the initial concentration of **MB**. The decrease in the absorption of **MB** was observed in the reaction under inert gas. The absorption was restored by introduction of air into irradiated solution

of the quantum yield for 2-amination to that for 4-amination was dependent upon the scavenger concentration (Fig. 7). Furthermore, the value of the ratio under inert gas was greater than that under air. These results suggest that a reaction pathway in which radical species participate exists, and that 2-amination occurs over 4-amination under an inert gas.

Effect of MB on the photoamination of 1a-OH

The effect of **MB** on the photoamination of **1a-OH** in Ac10H$_2$O was investigated. The quantum yield of 2-amination under an inert gas decreased with the addition of **MB**, and had a tendency to increase as the amount added increased. On the other hand, the quantum yield of 4-amination under an inert gas and the quantum yields of both aminations under air increased (Fig. 8). The ratio of the quantum yield of 2-amination to that of 4-amination under inert gas was reduced by the addition of **MB** from ~0.8 ([**MB**] $= 0.0$ mol dm^{-3}) to ~0.2 ([**MB**]$> \sim 3 \times 10^{-5}$ mol dm^{-3})), whereas that under air was not affected (~0.2). These results indicate that a reaction path where **MB** effectively affects 2-amination exists in the reaction under inert gas. Since the E_T of the base form is estimated to be more than that of **MB**,[†] the quenching by **MB** would be based on the energy

[†]*The energy of the 0–0 transition of the base form of **1a-OH** was estimated to be about 211 kJ mol^{-1} from the intersection of the normalized fluorescence and the absorption spectra of the base form. The energy of 1-aminoanthraquinone has been reported to be 218 kJ mol^{-1}.[13] Since the T_1 level of 1-aminoanthraquinone has been reported to lie in the range of 176–197 kJ mol^{-1},[14] if the S–T splitting of the base form of **1a-OH** is approximately the same as that of 1-aminoanthraquinone, the E_T of the base form lies in the range of 169–190 kJ mol^{-1} and is higher than the E_T of **MB**, 138 kJ mol^{-1}.[15] This assumption is reasonable, considering the fact that the first absorption bands of both anthraquinones are CT absorptions and are situated in approximately the same wavelength region; hence, the amino and deprotonated hydroxyl groups are considered to have similar electron-donating properties.*
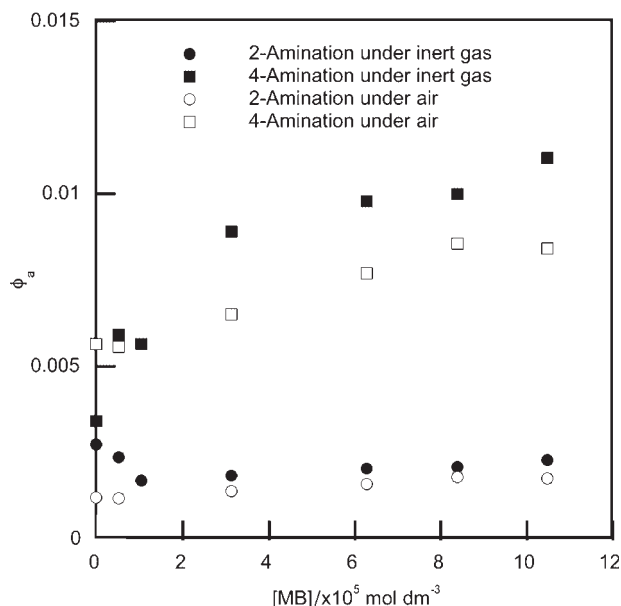
transfer from the excited triplet state of the base form of **1a-OH** to **MB** (Scheme 3, as shown below). The quenching of the excited triplet state of the base form of **1a-OH** by **MB** would cause a decrease in the quantum yield of 2-amination under inert gas.

Photoamination occurred under both air and inert gas, with only excitation of **MB**. It is well known that electron transfer to the excited triplet state of **MB** from electron donors occurs.[16–19] The amine-derived radicals resulting from the electron transfer from butylamine to the excited triplet state of **MB** would induce amination in these cases.

Charge and spin density of the excited triplet state of the base form of 1a-OH

The results of the calculation are shown in Table 1. The charge on the carbon at the 4-position had a tendency to be less negative than that on other carbons that carried a substitutable hydrogen atom, although the values varied slightly depending on the method of calculation employed. The difference in the charge indicates the possibility of a nucleophilic attack at the 4-position. The spin densities of the carbon atoms at the 2- and 4-positions had a tendency to be greater than those of other carbon atoms with a substitutable hydrogen atom, and the spin density of the carbon atom at the 2-position was slightly larger than that at the 4-position. This suggests that a radical species can easily attack the 2- and 4-positions, especially the 2-position.

DISCUSSION

In the amination under air, the concentration effect of **1b-OH** (Fig. 1), the quenching behavior of anthracene (Figs 4 and 5) and the effect of the radical scavenger (Figs 6 and 7) were similar to

Table 1. Charge and spin densities of the triplet state of the base form of **1a-OH** calculated using the 6-31G(d,p) basis set
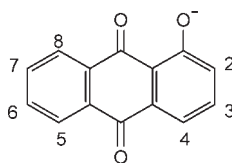
Position	Charge						Spin density			
	UHF		UB3LYP		CIS		UHF		UB3LYP	
	Mulliken	Natural	Mulliken	Natural	Mulliken	Natural	Mulliken	Natural	Mulliken	Natural
2	−0.1782	−0.2375	−0.1180	−0.2528	−0.1786	−0.1895	0.9072	0.6918	0.4511	0.3954
3	−0.1501	−0.2609	−0.0943	−0.2915	−0.1760	−0.3458	−0.7697	−0.5355	−0.1528	−0.1007
4	−0.1163	−0.1533	−0.1011	−0.1427	−0.0563	−0.0279	0.8889	0.6688	0.4193	0.3674
5	−0.1218	−0.1973	−0.1179	−0.2111	−0.1237	−0.2004	0.7110	0.5175	0.0227	0.0178
6	−0.1538	−0.2389	−0.0989	−0.2577	−0.1605	−0.2453	−0.6877	−0.4890	−0.0003	0.0061
7	−0.1647	−0.2528	−0.1010	−0.2685	−0.1601	−0.2476	0.7217	0.5208	0.0601	0.0504
8	−0.1222	−0.1909	−0.1180	−0.2039	−0.1252	−0.1966	−0.7339	−0.5288	−0.0326	−0.0211

Mulliken: Mulliken population analysis. Natural: natural population analysis.

those for the amination of **1a-OH** in acetonitrile under air. From these results, we conclude that the amination of both **1a-OH** and **1b-OH** in a water-acetonitrile mixed solvent under air proceeds through the same mechanism as that of the amination of **1a-OH** in acetonitrile under air.

As previously reported,[9] the results of a kinetic study on the amination of **1a-OH** in acetonitrile under air substantiate the following mechanism (Scheme 2):

$k_R = k_{r2} + k_{r4}$, $k'_R = k'_{r2} + k'_{r4}$; r2: 2-amination , r4: 4-amination

RSC: radical scavenger
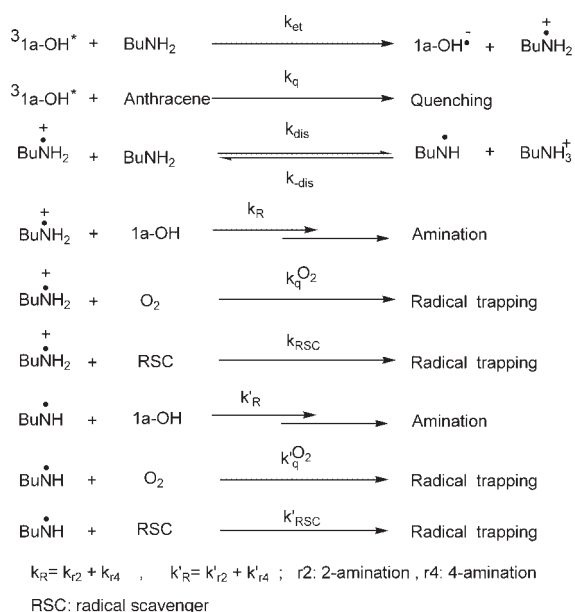
Scheme 2. Mechanism of the photoamination of **1a-OH** in acetonitrile under air

In the amination under an inert gas, the oxidation by oxygen introduced upon exposure to air results in the formation of the final amination products. Based on this mechanism, the quantum yield of the reaction of **1b-OH** (ϕ_b) is expressed by Eqn (1) by replacing [**1a-OH**], k_R and k'_R in Scheme 2 with [**1b-OH**], k_{r4} and k'_{r4}, respectively.

$$\phi_b = \frac{\phi_T}{k_{-dis}[BuNH_3^+]}\left(\frac{k_{et}[BuNH_2]}{k_{et}[BuNH_2] + k_{qT}^{O_2}[O_2] + k_q[\text{Anthracene}] + k_d}\right)$$
$$\times \left\{\frac{k_{-dis}k_{r4}\beta_4[BuNH_3^+] + \alpha k_{dis}k'_{r4}\beta'_4[BuNH_2]}{k_{r4}[\mathbf{1b-OH}] + k_q^{O_2}[O_2] + k_{dis}(1-\alpha)[BuNH_2] + k_{RSC}[RSC]}\right\}$$
$$\times [\mathbf{1b-OH}]$$

(1)

where ϕ_T is the quantum yield of the triplet state formation, k_{et}, $k_{qT}^{O_2}$, k_{RSC}, and k_d are the rate constant of the electron transfer from the amine to the triplet state of **1b-OH**, that of triplet quenching by the dissolved oxygen in solution, that of the Bu $\overset{\bullet}{N}$H$_2$ radical trapping rate of the radical scavenger, and that of the radiationless deactivation of the triplet state, respectively. β_4 and β'_4 represent the efficiency of amination after attack of the two radicals (Bu $\overset{\bullet}{N}$H$_2$ and Bu $\overset{\bullet}{N}$H) on the ground state of **1b-OH**, respectively, and α is the ratio of the rates for the reversible reaction between Bu $\overset{\bullet}{N}$H$_2$ and Bu $\overset{\bullet}{N}$H (Scheme 2):

$$\alpha = \frac{k_{-dis}[Bu\overset{\bullet}{N}H][BuNH_3^+]}{k_{dis}[Bu\overset{\bullet}{N}H_2][BuNH_2]}$$

(2)

When anthracene and the radical scavenger are absent, the reciprocal of the quantum yield of the photoamination (ϕ_b) of

1b-OH is expressed as follows:

$$\frac{1}{\phi_b} = \frac{k_{-dis}[BuNH_3^+]}{\phi_T}\left(1 + \frac{k_{qT}^{O_2}[O_2] + k_d}{k_{et}[BuNH_2]}\right)$$

$$\times \left(\frac{1}{k_{-dis}k_{r4}\beta_4[BuNH_3^+] + \alpha k_{dis}k_{r4}'\beta_4'[BuNH_2]}\right)$$

$$\times \left(k_{r4} + \frac{k_q^{o_2}[O_2] + k_{dis}(1-\alpha)[BuNH_2]}{[\mathbf{1b-OH}]}\right) \quad (3)$$

The results shown in Fig. 1 are in agreement with the relationship between $1/\phi_b$ and $1/\mathbf{1b-OH}$ shown in Eqn (3). The value of the slope/intercept of the linear relationship between the plot of $1/\phi_b$ and the concentration of **1b-OH** ([**1b-OH**]) is expressed as follows based on Eqn (3):

$$\frac{Slope}{Intercept} = \frac{k_q^{o_2}[O_2]}{k_{r4}} + \frac{k_{dis}(1-\alpha)[BuNH_2]}{k_{r4}} \quad (4)$$

Since the slope/intercept of the linear line in Fig. 1 was constant regardless of the amine concentration, α in Eqn (4) must be equal to 1. This means that the reversible reaction between Bu$\overset{\bullet+}{N}H_2$ and Bu$\overset{\bullet}{N}H$ (Scheme 2) is in equilibrium in Ac10H$_2$O. It has been shown for the amination of **1a-OH** in acetonitrile that this value depends on the amine concentration; therefore, the reversible reaction (Scheme 2) does not attain equilibrium in acetonitrile.[9] The addition of water would contribute to an increase in the reversible reaction rates (Scheme 2) relative to the rates of the other processes.

Since the value of α was equal to 1 in Ac10H$_2$O, as described above, Eqn (3) can be reduced to the following:

$$\frac{1}{\phi_b} = \left(\frac{1}{\phi_T(k_{r4}\beta_4 + \gamma k_{r4}'\beta_4')}\right)\left(1 + \frac{k_{qT}^{O_2}[O_2] + k_d}{k_{et}[BuNH_2]}\right)$$

$$\times \left(k_{r4} + \frac{k_q^{o_2}[O_2]}{[\mathbf{1b-OH}]}\right) \quad (5)$$

where $\gamma = [Bu\overset{\bullet}{N}H]/[Bu\overset{\bullet+}{N}H_2]$. The plot of $1/\phi_b$ versus 1/[butylamine] was linear, as shown in Fig. 2. The ratio of the intercept to the slope of the straight line was 16 dm^3 mol^{-1}. If $\phi_T(k_{r4}\beta_4 + \gamma k_{r4}'\beta_4')$ is independent of the butylamine concentration, the value corresponds to $k_{et}/(k_{qT}^{O_2}[O_2] + k_d)$, and it is suggested that the curved plot for the reaction under an inert gas is caused by an additional reaction pathway. The constancy of $\phi_T(k_{r4}\beta_4 + \gamma k_{r4}'\beta_4')$ is justified, as discussed below.

Since anthracene quenched the excited state that was attacked directly by the amine, the lines in Fig. 4 express the following relationship:

$$\frac{\phi_b^0}{\phi_b} = 1 + \frac{k_q[Anthracene]}{k_d + k_{qT}^{O_2}[O_2] + k_{et}[BuNH_2]} \quad (6)$$

where the superscript 0 indicates the absence of a quencher, and k_q is the rate constant of triplet quenching by anthracene. The dependence of the $k_q\tau$ values on the amine concentration can be derived from Eqn (6) as follows:

$$\frac{1}{k_q\tau} = \frac{k_{qT}^{O_2}[O_2] + k_d}{k_q} + \frac{k_{et}[BuNH_2]}{k_q} \quad (7)$$

Therefore, the value of 15 dm^3 mol^{-1} corresponds to $k_{et}/(k_{qT}^{O_2}[O_2] + k_d)$, and is consistent with the value of 16 dm^3 mol^{-1} obtained from the dependence of the amination on the amine concentration, assuming that $\phi_T(k_{r4}\beta_4 + \gamma k_{r4}'\beta_4')$ is independent of the amine concentration. This should corroborate the fact that $\phi_T(k_{r4}\beta_4 + \gamma k_{r4}'\beta_4')$ is constant regardless of the amine concentration. The existence of an additional reaction pathway under an inert gas is strongly suggested, as described above.

Herein, we describe the reversible reaction between Bu$\overset{\bullet+}{N}H_2$ and Bu$\overset{\bullet}{N}H$ (Scheme 2) and the existence of an additional reaction pathway under inert gas in the amination of **1b-OH**. This was attainable because of the ease of product analysis. The same discussion would hold true for **1a-OH**, because similar results were obtained for **1a-OH** (Fig. 2 and the linear plot in Fig. 5). The ratio of 2-amination and 4-amination in the reaction of **1a-OH** was found to depend on the amine and radical scavenger concentrations under inert gas. This finding is expected to be related to the existence of an additional reaction pathway under inert gas. Accordingly, we further discuss the additional reaction pathway in the amination of **1a-OH**.

Quenching of the excited triplet state of the base form of **1a-OH** by **MB** makes it possible to interpret the increase in quantum yields of the 2- and 4-aminations under air. In addition, this quenching enables interpretation of the increase in the quantum yield of 4-amination under inert gas as the result of the increase in steady concentrations of the radical species (Bu$\overset{\bullet+}{N}H_2$ and Bu$\overset{\bullet}{N}H$) caused by the electron transfer from butylamine to the excited triplet state of **MB**. The increase in the quantum yield of 2-amination under inert gas above an **MB** concentration of 3×10^{-5} mol dm^{-3} may be understood by considering that the increase in the steady concentrations of radical species was superior to quenching of the excited triplet state of the base form of **1a-OH**. The ratio of the quantum yield of 2-amination to that of 4-amination under inert gas became constant, ~0.2 (the same value as in the case of the reaction under air) above an **MB** concentration of about 3×10^{-5} mol dm^{-3}. This result may be interpreted as follows: the reaction mechanism begins to resemble that of a reaction under air above this concentration, even under an inert gas. The upward-convex Stern–Volmer plots for the reaction of **1a-OH** (Fig. 5) show that an additional reaction pathway, not affected by anthracene, exists under inert gas. The effect of the radical scavenger (Figs 6 and 7) suggests the existence of a reaction path under inert gas. In this pathway, radical species participate more preferentially in 2-amination than in the 4-amination. Considering the acidity of **1a-OH** in the excited state is higher than that of the compound in the ground state,[20,21] we conclude that the additional reaction path in question proceeded through the excited triplet state of the base form of **1a-OH**. Results of the spin density calculation (Table 1) support the existence of this reaction pathway.

The increase in the quantum yield of 4-amination surpassed that of 2-amination with increasing amine concentration, as shown in Fig. 3(b). The higher the amine concentration, the greater the ease with which **1a-OH** dissociates. The equilibrium between the aminium and the amino radicals shifts toward the amino radical with increasing amine concentration. Therefore, the difference in the rate increase between 2- and 4-amination is related to the contribution of the excited triplet state of the base form of **1a-OH** to the reaction, as well as that of the concentrations of the radicals. In the amination of 1-aminoanthraquinones, butylamine acts as a nucleophile to attack the 4-position of the anthraquinone nucleus when the quinones were in the excited triplet state.[4] Furthermore, the charges on the carbon atoms (Table 1) indicate the possibility of a nucleophilic

attack of the butylamine at the four-position. We deduce that the 4-amination resulting from the nucleophilic attack is one of the reasons for the difference in the rate increase. It has been reported that the production of an amino radical may be one of the reasons for the termination of the radical chain chlorination of decanoic acid by *N*-chlorinated secondary alkylamine, which is propagated by aminium radicals, due to the fast self-reaction of the amino radical.[22] The difference may also be attributed to the rate increase due to the relatively low potency of the amino radical in an attack on the anthraquinone nucleus.

A 3-amination product was not detected, regardless of the reaction atmosphere and solvent conditions. Aromatic substitution by aminium radicals naturally results in adoption of the orientation of the substituent that has already been introduced in the aromatic nucleus.[23] However, our inability to detect 3-amination is unlikely to be indicative of the real situation as long as radical substitution is considered to be responsible for the amination. Therefore, specific interactions between the radicals and **1a-OH** (the ground state and/or its base form in the excited triplet state) may be responsible for the regioselectivity of the amination. Since Bu$\overset{\bullet}{N}$H is less electrophilic than Bu$\overset{\bullet+}{N}$H$_2$, attack by this radical may be less regioselective. The following interactions are conceivable regardless of the target attacked by the radical Bu$\overset{\bullet+}{N}$H$_2$: (1) interaction between the hydrogen atom bonded to the nitrogen in Bu$\overset{\bullet+}{N}$H$_2$ and the carbonyl oxygen at the 10-position in the anthraquinone nucleus (for 4-amination) and (2) interaction between the hydrogen of Bu$\overset{\bullet+}{N}$H$_2$ and the oxygen of the hydroxyl group at the 1-position on the anthraquinone nucleus (for 2-amination). The lack of detection of a 3-amination product in this study presumably reflects the relatively low potency of the amino radical in an attack on the anthraquinone nucleus.

No direct evidence has been obtained to rule out the 4-amination of **1a-OH** through the excited triplet state of the base form with the amine-derived radical species and to indicate the 4-amination of **1a-OH** resulting from a direct attack of the amine on the excited triplet state of the base form. However, we propose the existence of additional reaction pathways that act under inert gas in acetonitrile containing water (Scheme 3). Effective quenching of the excited triplet state of the base form by oxygen is thought to cause the disappearance of this pathway in the reaction under air.
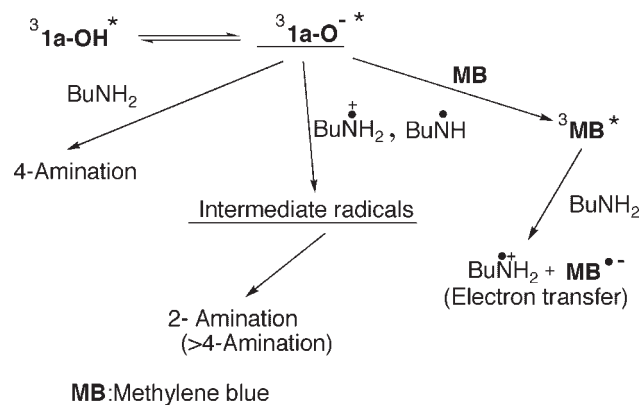
The absorption of the anthraquinone anion radical, which appeared in the region of $>700\,nm$[24] for the reaction under an inert gas atmosphere, did not disappear unless air was introduced. Although the possibility of change, such as disproportionation and proton transfer from the aminium radical, cannot be completely ruled out, the anthraquinone anion radical would be able to propagate without any chemical change, at least under the experimental conditions in the current investigation.

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Scheme 3. Amination pathway through excited triplet state of base form