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Solvent Effects on the Photoamination of 1-Amino-2,4-dibromoanthraquinone. II. Dual Mode of the Photoamination in Ethanol *via* the $S_1(^1CT)$ and $T_1(^3CT)$ States

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The photoamination of 1-amino-2,4-dibromoanthraquinone (**1**) by butylamine in ethanol was investigated. The reaction was accelerated under an air atmosphere ($\Phi_{air}=1.7\times10^{-3}$, $\Phi_{N_2}=2.3\times10^{-4}$, where [butylamine]$=5.00\times10^{-2}$ mol/dm^3). A detailed kinetic study indicated that, under nitrogen, the photoamination proceeded *via* the $T_1(^3CT)$ state populated by the intersystem crossing from the $S_1(^1CT)$ state, while under air it proceeded *via* both the $T_1(^3CT)$ and the $S_1(^1CT)$ states. The latter pathway under air included an interaction between the $S_1(^1CT)$ state and oxygen to form an exciplex or a collisional complex such as $[AQ^{\delta+}\cdots O_2^{\delta-}]$. The deactivation constant from the $T_1(^3CT)$ of **1** in ethanol was revealed to be one order of magnitude smaller than that in benzene and one order magnitude larger than that of 1-aminoanthraquinone in benzene. These results were discuessd in relation to the energy diagram in the excited state and the intramolecular heavy-atom effect of bromine in **1**.

It has long been emphasized that the excited triplet $n\pi^*$ state is reactive in almost all the photochemical reactions of anthraquinone derivatives, while the intramolecular CT state has little reactivity.[1] It has also been proved that the excited triplet $n\pi^*$ state is reactive even in the photoreduction of 2-piperidinoanthraquinone by an electron transfer from the hydroxide ion in aqueous 2-propanol,[2] which had been postulated to proceed *via* the intramolecular CT level.[3] However, we recently reported an interesting new photosubstitution reaction of aminoanthraquinones as the first example of a reaction actually demonstrated to proceed *via* the CT level.[4]

In the preceding paper we reported the striking solvent effects on the photoamination of 1-amino-2,4-dibromoanthraquinone (**1**) by butylamine.[5] In ethanol, 1) the dissolved oxygen promoted the photoamination of **1** and 2) the yield (%) of the aminated product (**2**) was not equivalent to the conversion (%) of **1** and the ratio (0.79) between them was unchanged during the photoreaction. The last result suggests that the photodecomposition of **1** and its photoamination took place simultaneously, as was previously observed in the photoamination of sodium 1-amino-4-bromoanthraquinone-2-sulfonate (**3**) in aqueous 2-propanol.[4] In benzene, 1) oxygen acted as a strong quencher to the reaction and 2) the yield of **2** was equal to the conversion of **1**, suggesting that the photoamination of **1** proceeded quantitatively.[5] On the basis of the postulated energy diagram of the excited **1** shown in Fig. 1, it was suggested that, in benzene, the photoamination proceeded through the $T_1(^3CT)$ level without the aid of oxygen because of a dominant population on the T_1 level by means of a close contiguity or an inversion in the disposition of $S_1(^1CT)$ and $T_2(^3n\pi^*)$ levels. In this paper we will report on our detailed kinetic analysis of the photoamination of **1** in ethanol and will propose a reaction mechanism with a dual mode from the $S_1(^1CT)$ and the $T_1(^3CT)$ levels of **1** in contrast with the single mode in benzene.

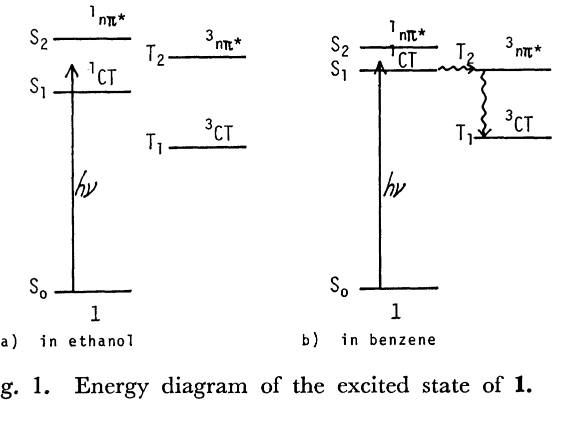
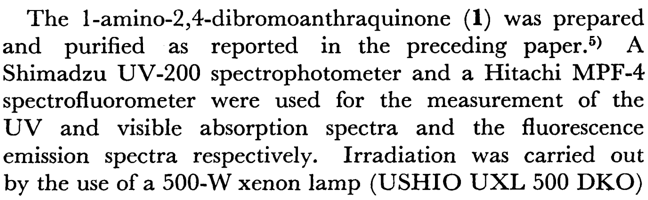


Fig. 1. Energy diagram of the excited state of **1**.



Experimental

The 1-amino-2,4-dibromoanthraquinone (**1**) was prepared and purified as reported in the preceding paper.[5] A Shimadzu UV-200 spectrophotometer and a Hitachi MPF-4 spectrofluorometer were used for the measurement of the UV and visible absorption spectra and the fluorescence emission spectra respectively. Irradiation was carried out by the use of a 500-W xenon lamp (USHIO UXL 500 DKO) through the following filter system: a soda glass for the irradiation of $\lambda>300$ nm, a Toshiba interference filter KL-40 for the monochromatic irradiation of $\lambda=400$ nm, a Toshida glass filter VY-42 for $\lambda>420$ nm, and VY-45 and KL-47 filters for the light of $\lambda=470$ nm. The amount of the aminated product (**2**) generated in the irradiated reaction mixture was determined by colorimetric analysis of the first absorption band of **2** ($\lambda_{max}=625$ nm, $\varepsilon=1.40\times10^5$ dm^2/mol). The number of photons absorbed by the reaction mixture was determined by the use of the chemical actinometer of potassium tris(oxalato)ferrate(III). The amount of hydrogen peroxide in the irradiated reaction mixture was determined by colorimetric analysis of the absorption intensity at 357 nm, which is characteristic of the I_3^- generated by the addition of an aqueous solution of potassium iodide to an acidified reaction mixture.

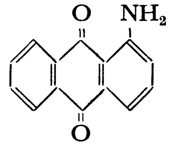
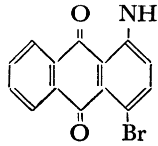
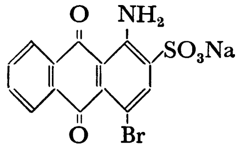
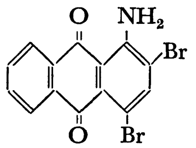
Results and Discussion

*The Photoamination of **1** in Ethanol under a Nitrogen Atmosphere.* The photoamination of **3** in a 2-propanol–water (4 : 1 v/v) mixture proceeded through an exciplex formation between the excited **3** in its ^{1}CT state and the ground state oxygen; the reaction was hardly observed at all under a nitrogen atmosphere.4) On the other hand, the photoamination of **1** in ethanol does proceed even under nitrogen, though the reactivity is about one-seventh of that under air ($\Phi_{air}=1.7\times10^{-3}$, $\Phi_{N_2}=2.3\times10^{-4}$, where [butylamine]$=5.00\times10^{-2}$ mol/dm^3). The previous study of the photoamination of **1** in benzene revealed that the ^{3}CT level of **1** is also responsible for the photoamination. Hence, the photoamination of **1** in ethanol under nitrogen may be explained by either of the following suggestions: 1) a direct photoamination proceeds *via* the ^{1}CT level of **1** without the aid of oxygen, or 2) the ^{3}CT level of **1** is responsible for the reaction.

In Table 1 the 0-0 level of the $S_1(^1CT)$ state and the relative fluorescence intensity of **1** in ethanol are compared with those of other aminoanthraquinones. Since the $S_1(^1CT)$ states of aminoanthraquinones (**3**—**5**) have much the same energy as that of **1**, and since the nπ^* levels of anthraquinones have been thought to be hardly affected by the introduction of substituents,1) it may be accepted that the excited states of **3**—**5** have energy diagrams similar to that of **1**. On the other hand, the relative intensity of the fluorescence decreased with the increase in $\sum\zeta^2$, the sum of the squares of the spin-orbit coupling factors over all the atoms in the corresponding molecule. These results suggest that the intersystem crossing between the $S_1(^1CT)$ and the $T_1(^3CT)$ levels in **1** might be enhanced by the spin-orbit interaction promoted by the heavy-atom effect of the two bromine atoms as compared with those of other aminoanthraquinones. In order to make clear the multiplicity of the reactive excited state of **1** in the photoamination in ethanol under a nitrogen atmosphere, the effect of a triplet quencher, cyclooctatetraene (COT)($E_T=163$ kJ/mol), was investigated. As is shown in Fig. 2, a good linear Stern-Volmer plot was obtained with a slope of 54.0 dm^3/mol. This clearly indicated that the photoamination of **1** under nitrogen proceeded *via* only one pathway. Since COT was confirmed to act as a triplet quencher by the fact that the fluorescence intensity of **1** in ethanol was hardly affected at all by the presence of COT (5.0×10^{-2} mol/dm^3), it seems that the photoamination proceeded through the triplet ^{3}CT level of **1**.

A plot of the reciprocal of the quantum yield of the photoamination of **1** versus the reciprocal of the concentration of butylamine gave a fairly straight line (Fig. 3), indicating the presence of a collisional process between the excited **1** and butylamine in the photoamination in ethanol under a nitrogen atmosphere. The ratio of the slope to the intercept in Fig. 3 was 3.7×10^{-3} mol/dm^3. When the photoamination reac-

TABLE 1. 0-0 LEVELS OF THE 1ST ABSORPTION BANDS[a] AND RELATIVE FLUORESCENCE INTENSITIES OF AMINOANTHRAQUINONES IN ETHANOL

Aminoanthraquinones		0-0 level / kJ/mol	Relative fluorescence intensity	$\sum\zeta^2$ / cm^{-1}
	(**4**)	218	100	6.21×10^3
	(**5**)	216	49	6.11×10^6
	(**3**)	216	36	6.33×10^6
	(**1**)	218	18	1.22×10^7

a) The 0-0 levels of aminoanthraquinones were estimated from the intersections of the corresponding absorption and fluorescence spectra in a mirror image.

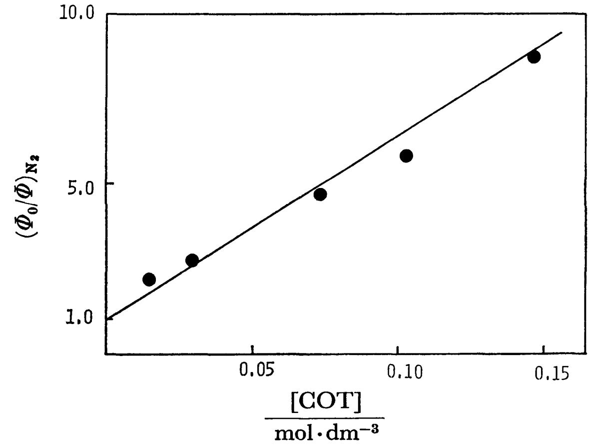


Fig. 2. Stern-Volmer plot for the quenching effect of cyclooctatetraene on the photoamination of **1** (1.00 $\times 10^{-4}$ mol/dm^3) by butylamine (5.00$\times 10^{-2}$ mol/dm^3) in ethanol under nitrogen atmosphere by the irradiation of the light of λ=470 nm.

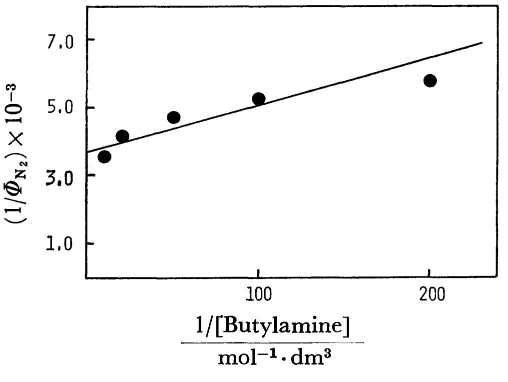


Fig. 3. Effect of the concentration of butylamine on the photoamination of **1** (1.00$\times 10^{-4}$ mol/dm^3) in ethanol under nitrogen atmosphere by the irradiation of the light of λ=470 nm.

tion of **1** (1.00$\times 10^{-4}$ mol/dm^3) was carried out in the presence of fluorenone (E_T=226 kJ/mol) (1$\times 10^{-2}$ mol/dm^3) as a triplet sensitizer under the irradiation of a light of λ>300 nm,[6] a good linear relationship was also found between the reciprocals of the quantum yield and the concentration of butylamine, with the value of the ratio of the slope to the intercept being 4.3$\times 10^{-3}$ mol/dm^3. The good agreement between these values obtained from the direct-irradiation experiment and the triplet-sensitizing experiment also strongly suggested that the photoamination proceeded through the $T_1(^3CT)$ level of **1** under a nitrogen atmosphere. When the fluorenone-sensitizing photoamination was carried out under air-saturated conditions, the reciprocals of the quantum yield and the concentration of amine also gave a good linear relationship. However, the ratio of the slope to the intercept, determined to be 39.1$\times 10^{-3}$ mol/dm^3, was much larger than that determined under a nitrogen atmosphere. Since the ratio of the slope to the intercept of the plot corresponds to the ratio of the rate constant of the deactivation to the reaction of the excited **1**, which is reactive to amine, the larger value of the ratio in the plot implies a larger deactivation from the excited **1** (^{3}CT) under air. This is in accord with the fact that the $T_1(^3CT)$ level of **1** was efficently quenched by the dissolved oxygen in benzene.[5]

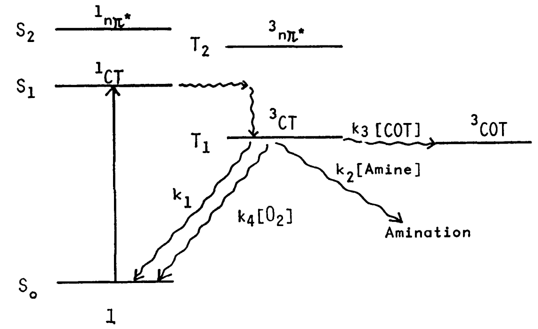


Fig. 4. Reaction scheme of the photoamination of **1** by butylamine under nitrogen atmosphere in ethanol.

*The Reaction Mechanism of the Photoamination of **1** in Ethanol under a Nitrogen Atmosphere.* On the basis of the above experimental results, the reaction scheme of the photoamination of **1** in ethanol under a nitrogen atmosphere may be depicted as in Fig. 4. The excited **1** in its $T_1(^3CT)$ state, populated by the intersystem crossing from the $S_1(^1CT)$ state, interacts directly with the amine to produce the aminated product, **2** (k_2). The $T_1(^3CT)$ state decays with the rate constant of k_1 and is quenched by COT (k_3). The reciprocal of the quantum yield of the photoamination under nitrogen *via* the $T_1(^3CT)$ level of **1**, $\Phi_{N_2}(^3CT)$, can be written as

$$1/\Phi_{N_2}(^3CT) = \frac{1}{\Phi_{isc}} \cdot \left(1+\frac{k_1}{k_2[A]}\right) \cdot \frac{1}{\alpha}, \tag{1}$$

where Φ_{isc}=the efficiency of the intersystem crossing of $S_1(^1CT) \rightarrow T_1(^3CT)$, α=the yield of the aminated product, **2**, for every collision between the amine and **1** in its $T_1(^3CT)$ level.

The Stern-Volmer plot with COT present under a nitrogen atmosphere is expressed by

$$(\Phi_0/\Phi)_{N_2} = 1 + \frac{k_3[COT]}{k_1+k_2[A]}. \tag{2}$$

Moreover, the reciprocal of the quantum yield, $\Phi^s_{N_2}$ (^{3}CT), of the photoamination in the fluorenone-sensitizing experiment under a nitrogen atmosphere can be written as

$$1/\Phi^s_{N_2}(^3CT) = \frac{1}{\Phi_{ET}} \cdot \left(1+\frac{k_1}{k_2[A]}\right) \cdot \frac{1}{\alpha}, \tag{3}$$

where Φ_{ET}=the triplet yield of **1** in the fluorenone-sensitizing experiment under a nitrogen atmosphere and under these conditions.

When the fluorenone-sensitizing experiment is carried out under air-saturated conditions, Eq. 3 is modified to Eq. 4 because of the quenching effect of oxygen on the $T_1(^3CT)$ level of **1**:

$$1/\Phi^s_{air}(^3CT) = \frac{1}{\Phi'_{ET}} \cdot \left(1+\frac{k_1+k_4[O_2]}{k_2[A]}\right) \cdot \frac{1}{\alpha}, \tag{4}$$

where Φ'_{ET}=the triplet yield of **1** in the fluorenone-sensitizing experiment under air-saturated conditions.

The value of the ratio of the slope to the intercept in Fig. 3 and Eq. 1, and the slope in Fig. 2 and Eq. 2 indicate the following relations:

$$k_1/k_2 = 3.7 \times 10^{-3}\ \text{mol/dm}^3,$$

$$k_3/(k_1+k_2[\text{A}]) = 54.0\ \text{dm}^3/\text{mol}.$$

The results of the fluorenone-sensitizing experiment under air-saturated conditions and Eq. 4 may also indicate that:

$$(k_1+k_4[\text{O}_2]_{\text{air}})/k_2 = 39.1 \times 10^{-3}\ \text{mol/dm}^3.$$

The concentration of the dissolved oxygen in air-saturated ethanol, $[\text{O}_2]_{\text{air}}$, was taken to be 2.07×10^{-3} mol/dm^3,[7] and $[\text{A}]=5.0\times10^{-2}$ mol/dm^3. If the quenching rate constant of the $\text{T}_1(^3\text{CT})$ state by the dissolved oxygen is assumed to be $k_4=9.2\times10^9$ dm^3 mol^{-1} s^{-1} (a diffusion-controlled one), the rate constants may be calculated as $k_1=2.0\times10^6$ s^{-1}, $k_2=5.4\times10^8$ dm^3 mol^{-1} s^{-1}, and $k_3=1.6\times10^9$ dm^3 mol^{-1} s^{-1}. The value of the quenching rate constant (k_3) of the $\text{T}_1(^3\text{CT})$ state by COT coincides well with that obtained in a benzene solution (1.6×10^9 dm^3 mol^{-1} s^{-1}).[5]

*The Photoamination of **1** under an Air Atmosphere.* As has been stated before, the photoamination reaction in ethanol was remarkably accelerated under an air atmosphere. By comparison with the photoamination of **3** in a 2-propanol–water (4 : 1 v/v) mixture,[4] it might be immediately concluded that the reaction in ethanol proceeded through the interaction between **1** in its ^{1}CT state and the ground-state oxygen. However, our observation of the photoamination under a nitrogen atmosphere implies that the photoamination of **1** under air has a dual reaction mode: the reaction without the aid of oxygen through the $\text{T}_1(^3\text{CT})$ level of **1**, and the reaction *via* its $\text{S}_1(^1\text{CT})$ level with the aid of oxygen. Hence, the following kinetic treatment of the photoamination *via* the $\text{S}_1(^1\text{CT})$ level of **1** under an air atmosphere was developed for the quantum yield, $\Phi_{\text{air}}(^1\text{CT})$, calculated by Eq. 5:

$$\Phi_{\text{air}}(^1\text{CT}) = \Phi_{\text{air}} - \Phi_{\text{air}}(^3\text{CT}), \qquad (5)$$

where Φ_{air} denotes the observed quantum yield of the photoamination under air, and $\Phi_{\text{air}}(^3\text{CT})$, the quantum yield of the reaction *via* the $\text{T}_1(^3\text{CT})$ level of **1** under air, which can be calculated by means of Eq. 6:[8]

$$\Phi_{\text{air}}(^3\text{CT}) = \Phi_{\text{isc}}\left(\frac{k_2[\text{A}]}{k_1+k_4[\text{O}_2]+k_2[\text{A}]}\right)\alpha. \qquad (6)$$

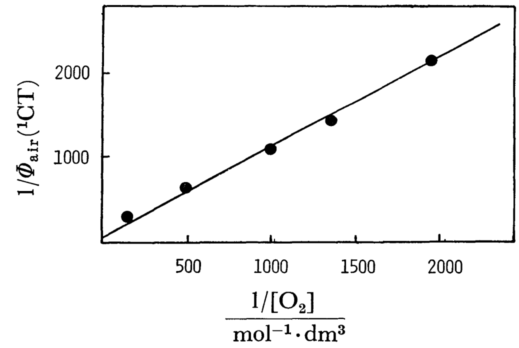


Fig. 5. Effect of the concentration of oxygen on the quantum yield $\Phi_{\text{air}}(^1\text{CT})$ calculated by Eq. 5; [**1**]: 1.00×10^{-4} mol/dm^3, [butylamine]: 5.00×10^{-2} mol/dm^3 in ethanol; irradiation light: $\lambda=470$ nm.

As is shown in Fig. 5, a plot of the reciprocal of the quantum yield $\Phi_{\text{air}}(^1\text{CT})$ versus the reciprocal of the concentration of the dissolved oxygen gave a good straight line. This clearly indicated the presence of a collisional process between the excited **1** and the dissolved oxygen, leading to the aminated product, **2**. This is contrary to the case of the reaction *via* the $\text{T}_1(^3\text{CT})$ level of **1**, in which the dissolved oxygen acts as a strong quencher to the reaction. With respect to the fate of the oxygen, it was revealed that hydrogen peroxide was produced during the photoamination.[9] These results strongly suggested that the photoamination under air *via* the $\text{S}_1(^1\text{CT})$ proceeded through an exciplex or a collisional complex formation between the excited **1** in its ^{1}CT state and the ground-state oxygen, designated $[\text{AQ}^{\delta+}\cdots\text{O}_2{}^{\delta-}]$. However, the intercept in Fig. 5 has a very small value, suggesting that the low quantum yield of the photoamination (in the order of 10^{-3}) is mainly due to the low efficiency of the reaction process between the excited **1** in its ^{1}CT state and oxygen. This is in accord with the fact that the fluorescence of **1** is not affected by the dissolved oxygen.

A double reciprocal plot between the quantum yield of the photoamination, $\Phi_{\text{air}}(^1\text{CT})$, and the concentration of butylamine also gave a good straight line, with the ratio of the slope to the intercept of 2.5×10^{-2} mol/dm^3 (Fig. 6), suggesting that, on the reaction pathway, butylamine collided with an intermediate which could be treated with the steady-state approximation. When COT was added to the reaction system, the photoamination was retarded and the Stern-Volmer plot gave a good straight line with a slope of 41 dm^3/mol (Fig. 7), indicating that COT also acted as a quencher molecule to the photoamination *via* the $\text{S}_1(^1\text{CT})$ level of **1** under air. Moreover, 1,3-cyclohexadiene (CHD), which has a higher triplet level ($E_\text{T}=226$ kJ/mol) than the $\text{T}_1(^3\text{CT})$ level of **1** ($E_\text{T}=163$—176 kJ/mol in benzene), also quenched the photoamination of **1** under air. Since COT and CHD hardly quenched the fluorescence of **1** at all, it appears that such olefins as COT and CHD did not interact with the excited **1** in its $\text{S}_1(^1\text{CT})$ state, but interacted

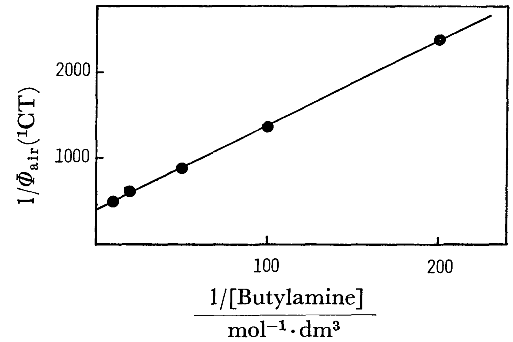


Fig. 6. Effect of the concentration of butylamine on the quantum yield $\Phi_{\text{air}}(^1\text{CT})$ calculated by Eq. 5; [**1**]: 1.00×10^{-4} mol/dm^3 in air-saturated ethanol; irradiation light: $\lambda=470$ nm.

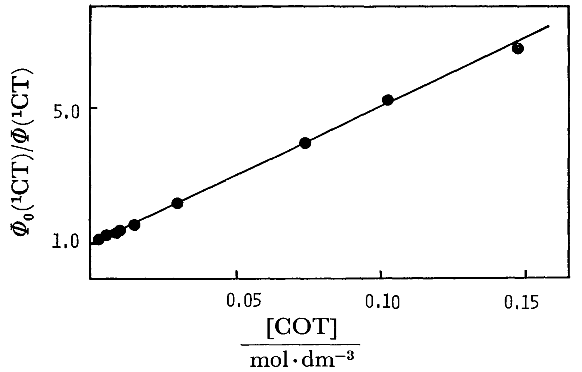


Fig. 7. Stern-Volmer plot for the quenching effect of cyclooctatetraene on the quantum yield of the photoamination under air; $\Phi_{air}(^1CT)$ was calculated by $\Phi_{air}(^1CT)$

$$=\Phi_{air}-\Phi_{isc}\cdot\left(\frac{k_2[A]}{k_1+k_3[COT]+k_4[O_2]+k_2[A]}\right)\cdot\alpha$$

[**1**]: 1.00×10^{-4} mol/dm^3, [butylamine]: 5.00×10^{-2} mol/dm^3 in air-saturated ethanol; irradiation light $\lambda=470$ nm.

with another intermediate on the reaction pathway of the photoamination *via* the $S_1(^1CT)$ level of **1** under air. Recently it has been reported that some exciplexes happen to be quenched by a third molecule (exciplex quenching).[10] The quenching effects of COT and CHD on the photoamination under air might be reasonably explained by assuming that these olefins interacted with the exciplex $[AQ^{\delta+}\cdots O_2^{\delta-}]$ to result in the quenching of the photoamination of **1** under air.

*The Reaction Mechanism of the Photoamination of **1** in Ethanol under Air.* The reaction scheme of the photoamination of **1** in ethanol under air may be depicted as in Fig. 8. The photoamination of **1** in ethanol has two possible reaction pathways. One is *via* the $S_1(^1CT)$ level of **1**. After being excited by the irradiation to the 1st absorption band of **1** ($\lambda_{max}=473$ nm), **1** in its $S_1(^1CT)$ state interacts with the ground-state oxygen (k_5) to form an exciplex or a collisional complex, $[AQ^{\delta+}\cdots O_2^{\delta-}]$. The exciplex decays with the rate constant k_6 and is attacked by butylamine to produce the aminated product, **2** (k_7). The exciplex also interacts with such olefins as COT or CHD to be quenched (k_8; exciplex quenching). The quantum yield of the photoamination *via* the $S_1(^1CT)$, $\Phi_{air}(^1CT)$, can be written as Eq. 7:

$$\Phi_{air}(^1CT)=\left(\frac{k_5[O_2]}{1/\tau_s+k_5[O_2]}\right)\left(\frac{k_7[A]}{k_6+k_7[A]}\right)\beta, \tag{7}$$

where A=butylamine, τ_s=the lifetime of the $S_1(^1CT)$ state, and β=the yield of the aminated product, **2**, for every collision between the exciplex and the amine. The reciprocal of the quantum yield is thus expressed by

$$1/\Phi_{air}(^1CT)=\left(1+\frac{1}{\tau_s\cdot k_5[O_2]}\right)\left(1+\frac{k_6}{k_7[A]}\right)\frac{1}{\beta}. \tag{8}$$

When COT is present, the Stern-Volmer equation may be expressed by

$$\Phi_0(^1CT)/\Phi(^1CT)=1+\frac{k_8[COT]}{k_6+k_7[A]}. \tag{9}$$

Hence, the following values are estimated from the ratio of the slope to the intercept in the linear plot of Fig. 6 and Eq. 8, and from the slope in the Stern-Volmer plot of Fig. 7 and Eq. 9:

$$k_6/k_7=2.5\times10^{-2}\ \text{mol/dm}^3,\ k_8/(k_6+k_7[A])=41\ \text{dm}^3/\text{mol},$$

where $A=5.0\times10^{-2}$ mol/dm^3.

Assuming the exciplex quenching rate constant, k_8, to be diffusion-controlled (9.2×10^9 dm^3 mol^{-1} s^{-1}), k_6 and k_7 may be calculated to be 7.5×10^7 s^{-1} and 3.0×10^9 dm^3 mol^{-1} s^{-1} respectively. Thus, the lifetime of the exciplex $[AQ^{\delta+}\cdots O_2^{\delta-}]$ was estimated to be about 13 ns. It may be significant that the lifetime of an exciplex such as $[AQ^{\delta+}\cdots O_2^{\delta-}]$ could be successfully estimated by means of this kinetic treatment, though in most cases the exsistence of a 'non-emmisive exciplex' on the reaction pathway is difficult to verify and its lifetime can hardly be estimated at all. The other reaction pathway is the photoamination *via* the $T_1(^3CT)$ level of **1**.[12] The quantum yield can be expressed by Eq. 6.

In Table 2 the rate constants obtained in this study are compared with those obtained in benzene, together with the rate constants in the case of 1-amino-4-bromo-

TABLE 2. RATE CONSTANTS IN THE PHOTOAMINATION OF **1** AND **5** BY BUTYLAMINE

Anthraquinones		k_1 / s^{-1}	k_2 / dm^3/mol s	k_6 / s^{-1}	k_7 / dm^3/mol s
1	in ethanol	2.0×10^3	5.4×10^8	7.5×10^7	3.0×10^9
	in benzene	2.8×10^7	5.7×10^7	——	——
5	in ethanol	——	——	1.8×10^8	9.0×10^9
	in benzene	2.1×10^7	2.1×10^8	——	——

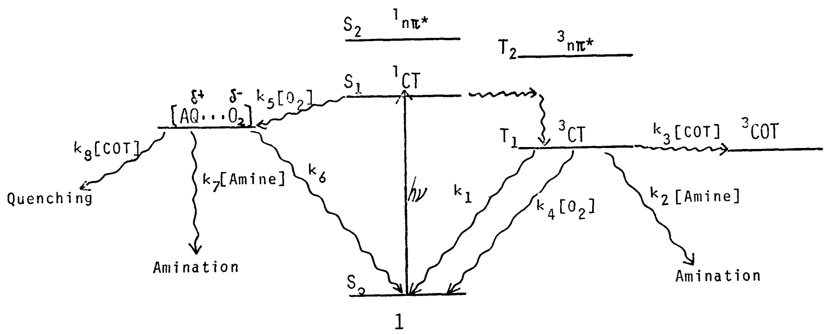


Fig. 8. Reaction scheme of the photoamiantion of **1** by butylamine under air atmosphere in ethanol.

anthraquinone (**5**) estimated by a similar kinetic treatment.

Contrary to the usual solvent effect, the deactivation constant, k_1, from the $T_1(^3CT)$ level is revealed to be one order of magnitude smaller in ethanol than that in benzene. This may be well correlated with the energy diagram of the excited state of **1** in ethanol and benzene shown in Fig. 1. In benzene, the $S_1(^1CT)$ state is supposed to interact more strongly with the $T_2(^3n\pi^*)$ state than in ethanol because of a close contiguity or a reversal of the disposition of $S_1(^1CT)$ and $T_2(^3n\pi^*)$, as is depicted in Fig. 1b). Hence, the $S_1(^1CT)$ state may interact more strongly with the $T_1(^3CT)$ state in benzene than in ethanol through the interaction among $S_1(^1CT)$, $T_2(^3n\pi^*)$, and $T_1(^3CT)$ states. The deactivation process (k_1) from the $T_1(^3CT)$ to the ground state, S_0, may borrow a part of the transition moment between the S_0 and the $S_1(^1CT)$ as a result of the mixing of the $S_1(^1CT)$ and $T_1(^3CT)$ states. Therefore, a larger deactivation from the $T_1(^3CT)$ may occur in benzene than in ethanol. It may also be noted that the deactivation constants, k_1, from the $T_1(^3CT)$ state of **1** and **5** in both ethanol and benzene are one or two orders of magnitude larger than that of 1-aminoanthraquinone (**4**) ($k_1=2\times10^5\ s^{-1}$),[11] which has no bromine atom in the molecule. These results clearly support the postulate that the heavy-atom effect on the spin-orbit interaction may be enhanced in **1**, which bears two bromine atoms. As has been reported in an earlier paper, the fluorescence intensity of **1** in benzene decreased by a factor of one-tenth as compared with that in ethanol.[6] This could also be successfully explained by the difference in the energy diagram with the alteration in the nature of the solvent (Fig. 1). On the other hand, the fluorescence intensity of **4** in benzene increased by a factor of 1.5 as compared with that in ethanol, in accordance with the usual solvent effect. Since **4** is supposed to have much the same energy diagram as that of **1** as has been stated before, this contradicting solvent effect on the fluorescence intensity may indicate that the close contiguity of the disposition of $S_1(^1CT)$ and $T_2(^3n\pi^*)$ and the spin-orbit interaction promoted by the intramolecular heavy-atom effect both play significant roles in the enhanced intersystem crossing between the $S_1(^1CT)$ and the $T_2(^3n\pi^*)$ of **1** in benzene.

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9) When **1** (1.00×10^{-4} mol/dm^3) and butylamine (5.00×10^{-2} mol/dm^3) in aerated ethanol were irradiated by light of $\lambda=470$ nm for 13 minutes, hydrogen peroxide was produced in an amount (0.6×10^{-4} mol/dm^3) equimolar with that of the aminated product, **2** (0.5×10^{-4} mol/dm^3).

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