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# The Ullmann Condensation Reaction of Haloanthraquinone Derivatives with Amines in Aprotic Solvents. III.
## The Formation and Role of Copper(II) Species in the Condensation with 2-Aminoethanol by Copper(I) Catalyst

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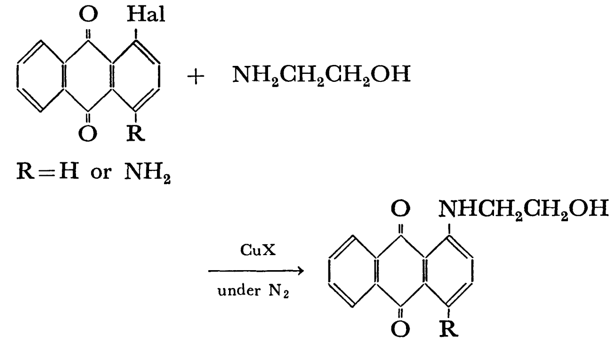
The ESR spectra of the Ullmann condensation reaction system of 1-bromoanthraquinone–2-aminoethanol–CuBr showed that copper(II) species and 1-bromoanthraquinone radical anion were formed by an electron transfer from copper(I) species to 1-bromoanthraquinone. Although copper(II) species alone had little catalytic activity, the resulting copper(II) species increased the catalytic activity of the copper(I) species, and a pseudo-first order rate constant could be expressed as follows: $k=k_1[\mathrm{Cu^I}]+k_2[\mathrm{Cu^I}][\mathrm{Cu^{II}}]$. According to the magnitude of $k_1$ and $k_2C_0$, where $C_0$ is the initial concentration of copper(I) catalyst, the reaction of haloanthraquinone with 2-aminoethanol by copper(I) catalyst can be classified into three modes. When $k_1<k_2C_0$, an induction period is present. The possible mechanisms of the cooperation between copper(I) and copper(II) species have been proposed. It has been also found that 1-bromoanthraquinone radical anion was responsible for the debromination.

In our preceding papers,[1,2] we reported that copper(II) species was formed in the Ullmann condensation reaction of haloanthraquinones with amines by using a copper(I) salt as a catalyst in aprotic solvents under a nitrogen atmosphere. The reaction rate did not remarkably decrease in spite of the formation of copper(II) species.[1] An induction period was observed in some reaction systems, such as 1-bromoanthraquinone (AQBr)–2-aminoethanol(AE)–CuBr or AQBr–AE–CuI. These results were explained by suggesting that the formation of the copper(II) species increased the catalytic activity of the copper(I) species, though the copper(II) species alone was found to have little catalytic activity for these reactions.[2] Therefore, the formation and catalytic action of the copper(II) species are considered to be a very interesting problem connected with the Ullmann condensation reaction of haloanthraquinones in aprotic media.

In this paper, the formation and role of copper(II) species will be described in more detail and we will propose the reaction mechanism of haloanthraquinones with 2-aminoethanol by copper(I) catalyst in aprotic media under a nitrogen atmosphere.



## Results and Discussion

*The Formation of Copper(II) Species.* Previously we described that copper(I) species was oxidized to copper(II) species during the progress of the Ullmann condensation reaction of haloanthraquinones with 2-aminoethanol(AE).[1] The ESR spectra showed that the formation of the copper(II) species was accompanied by an organic paramagnetic species (*g* value 2.003) (Fig. 1). The spectra seem to reveal that the copper(II) species is mostly present as copper(II) complex containing 2-aminoethanol in the coordination sphere, because the ESR spectra of the copper(II) species in the reaction system are very similar to that of copper(II) bromide in AE solution.

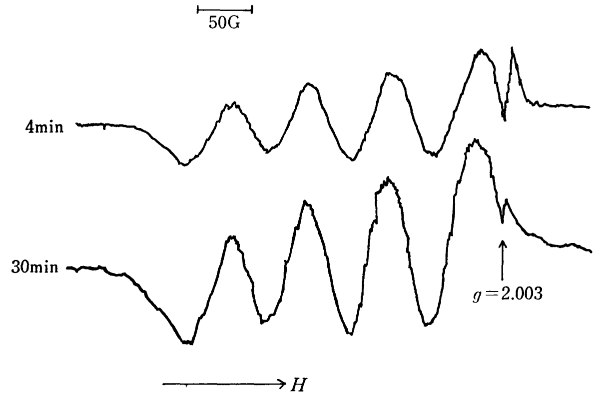


Fig. 1. ESR spectra of the reaction system of 1-bromoanthraquinone–2-aminoethanol–CuBr. $[\mathrm{AQBr}]_0=5.00\times10^{-3}$ mol/l, $[\mathrm{AE}]_0=0.50$ mol/l, $[\mathrm{CuBr}]_0=2.00\times10^{-3}$ mol/l, temp 70 °C, solvent 1,2-dimethoxyethane–methyl cellosolve 4 : 1.

The copper(II) and organic paramagnetic species are considered to be formed by single electron transfer from copper(I) species to 1-bromoanthraquinone (AQBr) or its condensation product [1-(2-hydroxyethylamino)anthraquinone]. A mixture of the condensation product with CuBr–AE, however, gave scarcely any organic paramagnetic species and copper(II) species. The system of AQBr–CuBr–2-(dimethylamino)ethanol, which did not give any amination product, also gave copper(II) and organic paramagnetic species. These results seem to indicate that the organic paramagnetic species cannot be ascribed to a radical anion of the condensation product. Further, the organic paramagnetic species may be a 2-aminoethanol radical cation, formed by an electron transfer from AE to the resulting copper(II) species.[3] However, this possibility can be ruled out by the finding that the ESR spectra of the system of AQBr–AE–$CuBr_2$ showed only the copper(II) species. The copper(II) species may be possibly formed by the dismutation of the copper(I) species: 2Cu(I)→Cu(II)+Cu(0).[4] In the absence of 1-bromoanthraquinone, however, no copper(II) and organic paramagnetic species were observed.

Consequently, all of the experimental results indicate that the copper(II) species is not formed by the dismutation of the copper(I) species, but formed by an electron transfer from the copper(I) species to 1-bromoanthraquinone, and that the organic paramagnetic species is a 1-bromoanthraquinone radical anion ($AQBr^{\overline{\cdot}}$): $AQBr+Cu(I) \rightarrow AQBr^{\overline{\cdot}}+Cu(II)$. Single electron transfer from copper(I) species to aryl halides has been proposed in the halogen-exchange reaction between aryl halides and copper(I) salts[5] and in the Ullmann coupling reaction of *o*-bromonitrobenzene by copper(I) bromide,[6] even though the radical anions of aryl halides have not been directly detected.

In the reaction system of AQBr–AE–CuBr, anthraquinone was produced, along with the condensation product (Fig. 2). This result also seems to support the formation of $AQBr^{\overline{\cdot}}$ in the course of the reaction, since $AQBr^{\overline{\cdot}}$ can be considered to be debrominated in a similar manner to the dehalogenation of the radical anions of aryl halides: $AQBr^{\overline{\cdot}} \rightarrow AQ\cdot \rightarrow AQH$.[7] It is well known that the Ullmann condensation reaction of haloanthraquinones or aryl halides are accompanied by the dehalogenation reaction.[8–14] Although homolytic, heterolytic, or hydride transfer mechanisms have been proposed,[15] our results suggest that the radical anion, formed by an electron transfer from copper(I) species to AQBr, is mainly responsible for the dehalogenation.

After 120 min the yield of anthraquinone was only about 8%, whereas the yield of the copper(II) species was estimated as about 34% on the basis of the ESR signal height for the $CuBr_2$–AE solution. If the radical anion decays out only by its debromination, the yield of anthraquinone should be the same as that of the copper(II) species. Therefore, the 1-bromoanthraquinone radical anion should be considered to decay out only by the debromination, but by other faster decay processes,[16] such as an electron transfer to copper(II) species[17] and/or some other substance, and the dismutation,[18] although the rate of the debromination of the radical anion has remained unknown.

*The Role of Copper(II) Speceis.* In our preceding paper[2] we reported that the copper(II) species increased the catalytic activity of the copper(I) species, since the addition of copper(II) bromide($CuBr_2$) resulted in the vanishing of an induction period in the reaction system of AQBr–AE–CuBr. As is shown in Fig. 3, with the increase of $CuBr_2$ the pseudo-first order rate constant increases, passes through a maximum, and finally falls, when the total concentration of copper species is kept constant. Thus, the addition of copper(II) bromide increases the catalytic activity of the copper catalyst. From Fig. 3 the pseudo-first order rate constant($k_{app}$) may be simply expressed by Eq. 1.

$$k_{app} = k_a(1-\alpha) + k_b\alpha(1-\alpha), \qquad (1)$$

where $\alpha$ denotes the mole fraction of the copper(II) bromide. However, if $k_a$ and $k_b$ are assumed to be constant, Eq. 1 cannot reproduce the plot in Fig. 3. Because of the addition of copper(II) bromide as copper(II) species, the bromide ions were present in a larger amount than an equivalent to the copper concentration. Thus, the pseudo-first order rate constant seems likely to be affected by the presence of the excess bromide ions.

If $k_a$ is assumed to be unaffected by the presence of the excess bromide ions, it can be estimated from the intercept of the plot of the pseudo-first order rate constant($k_{app}$) against $\alpha$. Then $k_b$ can be given as a function of the concentration of the excess bromide ions by substituting the value of $k_a$ in Eq.1. The rate constant $k_b$ decreases linearly with increasing of the concen-

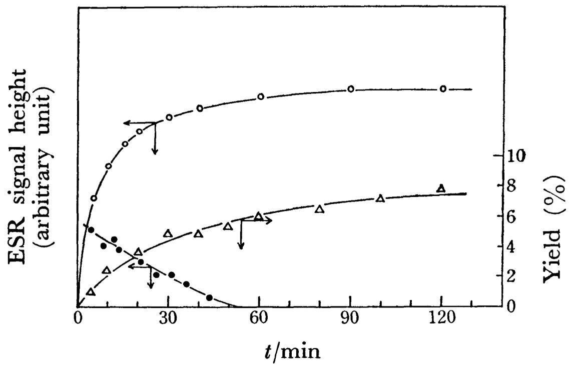


Fig. 2. The time dependence of ESR signal height and the yield of anthraquinone. $[AQBr]_0=5.00\times10^{-3}$ mol/l, $[AE]_0=0.50$ mol/l, $[CuBr]_0=2.00\times10^{-3}$ mol/l, temp 70 °C, solvent 1,2-dimethoxyethane–methyl cellosolve 4 : 1. ○: Cu(II) species, ●: $AQBr^{\overline{\cdot}}$., △: anthraquinone.

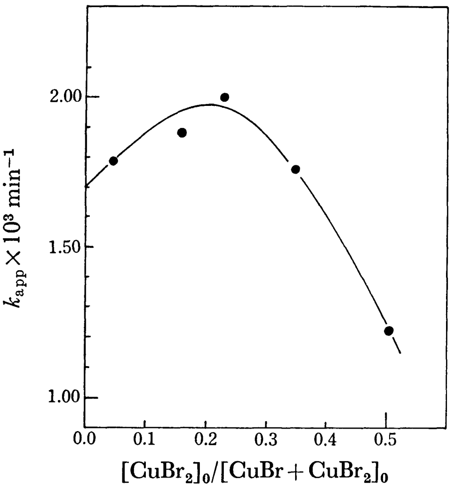


Fig. 3. The effect of the addition of $CuBr_2$ on pseudo-first order rate constant ($k_{app}$). $[AQBr]_0=5.00\times10^{-3}$ mol/l, $[AE]_0=0.50$ mol/l, $[CuBr+CuBr_2]_0=2.00\times10^{-3}$ mol/l, temp 70 °C, solvent 1,2-dimethoxyethane–methyl cellosolve 4 : 1. The full circles represent the experimental values. The solid line represents the curve calculated by Eq. 3.

tration of the excess bromide ions (Eq. 2).

$$k_b = k_{bo}(1-\beta), \qquad (2)$$

where $\beta$ is the excess of bromide ions. By combining Eq. 1 with Eq. 2 the pseudo-first order rate constant ($k_{app}$) is given by Eq. 3:

$$k_{app} = \{k_a + k_{bo}(1-\beta)\alpha\}(1-\alpha). \qquad (3)$$

The solid curve in Fig. 3 represents the result calculated according to Eq. 3 by assuming that $k_a$ and $k_b$ are $1.7\times10^{-3}$ and $3.9\times10^{-3}$ min$^{-1}$, respectively.

In order to confirm the effect of the excess bromide ions, tetraethylammonium bromide was added to the reaction mixture. As shown in Table 1, $k_{app}$ decreased clearly by the addition of tetraethylammonium bromide. The calculated values of $k_{app}$ by using Eq. 3 were close to the observed ones, though the reason for the effect of the excess bromide ions is not yet clearly understood.

Table 1. Effect of the excess bromide ion on pseudo-first order rate constants($k_{app}$)[a)]

| $\frac{[CuBr_2]_0}{[CuBr]_0+[CuBr_2]_0}$ | $k_{app}$(min$^{-1}$) Controlled | Addition of $(C_2H_5)_4N^+Br^-$ [b)] Obsd | Calcd[c)] |
|---|---|---|---|
| 0.063 | $1.82\times10^{-3}$ | $1.71\times10^{-3}$ | $1.71\times10^{-3}$ |
| 0.158 | $1.88\times10^{-3}$ | $1.77\times10^{-3}$ | $1.70\times10^{-3}$ |

a) $[AQBr]_0=5.00\times10^{-3}$ mol/l; $[AE]_0=0.50$ mol/l; $[CuBr]_0+[CuBr_2]_0=2.00\times10^{-3}$ mol/l; temp 70°C; solvent 1,2-dimethoxyethane–methyl cellosolve 4 : 1. b) The excess of bromide is $1.0\times10^{-3}$ mol/l. c) The values calculated by Eq. 3.

These experimental results tell us that the kinetics of the Ullmann condensation reaction cannot be described in terms of the action of copper(I) catalyst alone. Thus, on the basis of the above considerations, the rate law is assumed to be expressable as follows:

$$-\frac{d[AQBr]}{dt} = k_1[Cu^I][AQBr] + k_2[Cu^I][Cu^{II}][AQBr] + k_3[Cu^{II}][AQBr] + k_0[AQBr]. \qquad (4)$$

Since $k_3$ and $k_0$ are very small compared to $k_1$ and $k_2$, both $k_3$ and $k_0$ may be neglected. Therefore, the pseudo-first order rate constant can be expressed by Eqs. 5 and 6.

$$k = k_1[Cu^I] + k_2[Cu^I][Cu^{II}], \qquad (5)$$

$$k = k_1C_0 + (k_2C_0-k_1)[Cu^{II}] - k_2[Cu^{II}]^2, \qquad (6)$$

where $C_0$ denotes the concentration of total copper or the initial concentration of copper(I) catalyst. Differentiating Eq. 6 by time $t$, Eq. 7 is derived.

$$\frac{dk}{dt} = (k_2C_0 - k_1 - 2k_2[Cu^{II}])\frac{d[Cu^{II}]}{dt} \qquad (7)$$

Since the rate constant has a maximum value, in such a case an induction period is observed:

$$k_2C_0 - k_1 - 2k_2[Cu^{II}] = 0. \qquad (8)$$

Thus,

$$[Cu^{II}]_{max} = (k_2C_0-k_1)/2k_2 \qquad (9)$$

where $[Cu^{II}]_{max}$ is the concentration of copper(II) species which gives the maximum rate constant($k_{max}$). When $k_1<k_2C_0$,

$$k_{max} = \left(C_0 - \frac{k_2C_0-k_1}{2k_2}\right)\left(k_1 + \frac{k_2C_0-k_1}{2}\right). \qquad (10)$$

Therefore,

$$\sqrt{k_{max}} = \frac{\sqrt{k_2}}{2}C_0 + \frac{k_1}{2\sqrt{k_2}}. \qquad (11)$$

Consequently, when $k_1<k_2C_0$, the induction period will be present and the rate constant will have a maximum value. If the above assumption is valid, a linear relationship between $\sqrt{k_{max}}$ and $C_0$ will be obtained. Figure 4 shows that the relationship indicates a good linearity, when $C_0$ is larger than $k_1/k_2$ obtained from the intercept on the abscissa axis. This result suggests that the above assumption is valid. The rate constants ($k_1$ and $k_2$) are determined from the slope and intercept of the line, as shown in Table 2. By comparing Eq. 3 with Eq. 6, it is obvious that $k_1C_0$ and $k_2C_0^2$ correspond to $k_a$ and $k_{bo}$ in Eq. 3, respectively. In the reaction system of AQBr–AE–CuBr, the rate constant $k_a(1.7\times10^{-3})$ is nearly equal to the value $k_1C_0$ $(1.778\times10^{-3})$, while $k_{ob}$ $(3.9\times10^{-3})$ is approximate to $k_2C_0^2$ $(3.088\times10^{-3})$.

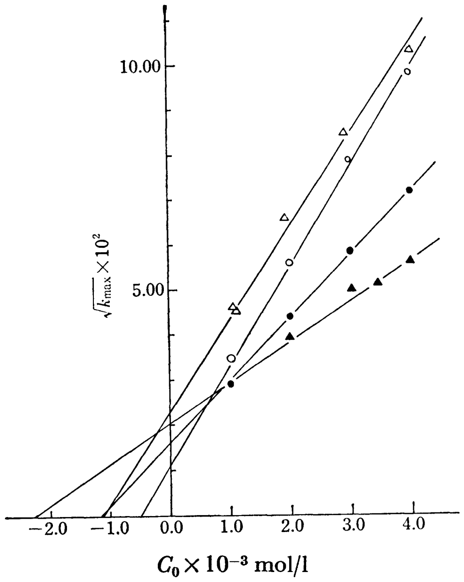


Fig. 4. The relation between $\sqrt{k_{max}}$ and $C_0$. [haloanthraquinone]$_0=5.00\times10^{-3}$ mol/l, $[AE]_0=0.50$ mol/l, temp 70 °C, solvent 1,2-dimethoxyethane–methyl cellosolve 4 : 1.
△: 1-Amino-4-bromoanthraquinone–AE–CuI,
○: 1-amino-4-bromoanthraquinone–AE–CuBr,
▲: AQBr–AE–CuI, ●: AQBr–AE–CuBr.

Table 2. Rate constants($k_1$ and $k_2$)

| Rate constant | AQBr CuBr | AQBr CuI | 1-NH$_2$-4-BrAQ CuBr | 1-NH$_2$-4-BrAQ CuI |
|---|---|---|---|---|
| $k_1$(l·mol$^{-1}$·min$^{-1}$) | 0.889 | 0.737 | 1.009 | 1.911 |
| $k_2$(l$^2$·mol$^{-2}$·min$^{-1}$) | 772 | 332 | 2015 | 1685 |

Temp 70°C; solvent 1,2-dimethoxyethane–methyl cellosolve 4 : 1.

The time dependence of the copper(II) species concentration can be well expressed by Eq. 12, if the intensity of ESR signal is proportional to the copper(II) species concentration.

$$[\mathrm{Cu^{II}}] = a(1-\mathrm{e}^{-\gamma t}) \qquad (12)$$

By combining Eq. 6 with Eq. 12 and integrating, Eq. 13 can be derived, if the amount of the debrominated product can be assumed to be negligible.

$$-\ln(1-x) = \mathrm{A}(1-\mathrm{e}^{-2\gamma t}) + \mathrm{B}(1-\mathrm{e}^{-\gamma t}) + \mathrm{C}t \qquad (13)$$

where $x$ denotes the yield of the aminated product, and where A, B, and C are $-a^2k_2/2\gamma$, $(a/\gamma)\{k_1+k_2\cdot(2a-C_0)\}$, and $(k_1+ak_2)(C_0-a)$, respectively. At the amine concentration of 0.5 mol·l$^{-1}$ in the reaction system of AQBr–AE–CuBr, $k_1$, $k_2$, $a$, and $\gamma$ are given as follows: 0.889, 772, $6.8\times10^{-4}$, and 0.082. Figure 5 shows that the calculated values are in good agreement with the experimental data.

As shown in Table 3, $k_1$ increases with the increase in the concentration of 2-aminoethanol, but the reverse is found in the value of $k_2$. When the initial concentration of copper(I) catalyst was kept constant, the induction period was shortened with the increase in the concentration of amine and it was absent at high concentrations of amine, as reported previously.[2] In the reaction system of 1-iodoanthraquinone–AE–copper(I) salt and AQBr–AE–[Cu(CH$_3$CN)$_4$]ClO$_4$, the induction period was absent.[2] The presence of the induction period would be ascribed to the catalytic activity of copper(I) species, the reactivities of haloanthraquinones, and the degree of contribution of copper(II) species as a promoter. According to the magnitude of $k_1$ and $k_2C_0$, the reaction between haloanthraquinone and 2-aminoethanol by copper(I) catalyst can be classified into three modes, as illustrated in Fig. 6. That is to say, when $k_1<k_2C_0$, an induction period will be present, but when $k_1>k_2C_0$, the reaction rate decreases with the formation of copper(II) species. In the case of the constant concentration of amine, the induction period was shortened with the increase in the concentration of copper(I) catalyst. This result also supports the classification of the reaction mentioned above.

*Reaction Mechanism.* As described in Table 3, the rate constant $k_1$ increased with the increase in the concentration of amine. The plot of $1/k_1$ against $1/$[AE] gave a good straight line(Fig.7). On the other hand, the rate constant $k_2$ decreased with the increase in the concentration of amine. The plot of $1/k_2$ against [AE] gave a good straight line (Fig. 8).

All of the results mentioned above can be reasonably explained by assuming the following mechanism.

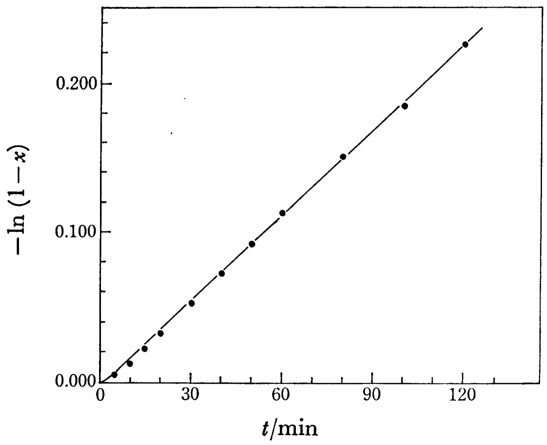


Fig. 5. Pseudo-first order plots for the reaction of 1-bromoanthraquinone with 2-aminoethanol by CuBr catalyst.
[AQBr]$_0$=$5.00\times10^{-3}$ mol/l, [AE]$_0$=0.50 mol/l, [CuBr]$_0$=$2.00\times10^{-3}$ mol/l, temp 70 °C, solvent 1,2-dimethoxyethane–methyl cellosolve 4 : 1. The full circles represent the experimetal values. The solid line represents the curve calculated by Eq. 13.

TABLE 3. AMINE CONCENTRATION DEPENDENCE OF $k_1$ AND $k_2$ FOR THE REACTION OF 1-BROMOANTHRAQUINONE WITH 2-AMINOETHANOL BY CuBr CATALYST

| [AE]$_0$ mol·l$^{-1}$ | 0.25 | 0.33 | 0.50 | 0.76 |
|---|---|---|---|---|
| $k_1$(l·mol$^{-1}$·min$^{-1}$) | 0.576 | 0.691 | 0.889 | 1.059 |
| $k_2$(l$^2$·mol$^{-2}$·min$^{-1}$) | 953 | 880 | 772 | 596 |

Temp 70 °C; solvent 1,2-dimethoxyethane-methyl cellosolve 4 : 1.

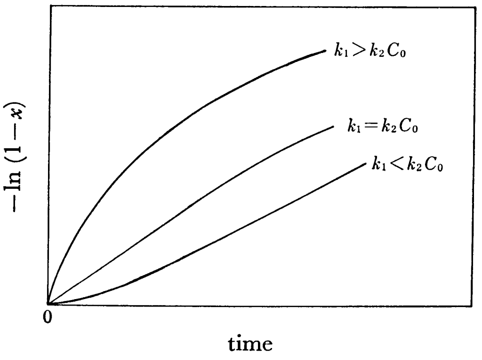


Fig. 6. The modes of pseudo-first order plots for the reaction between haloanthraquinone and 2-aminoethanol by copper(I) catalyst.

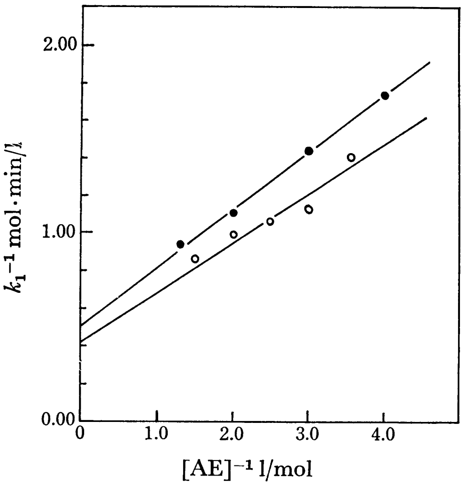


Fig. 7. Plots of $1/k_1$ against 1/[AE]. Temp 70 °C, solvent 1,2-dimethoxyethane–methyl cellosolve 4 : 1. ●: AQBr–AE–CuBr, ○: 1-amino-4-bromoanthraquinone–AE–CuBr.

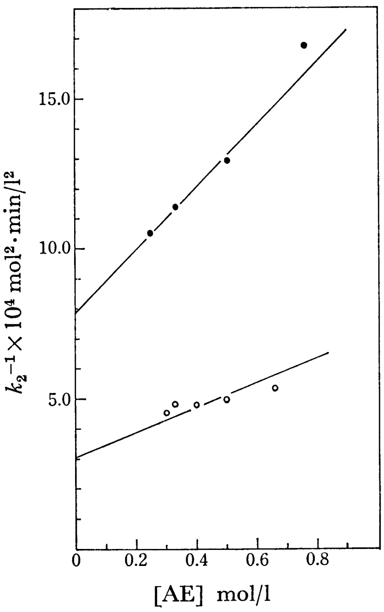


Fig. 8. Plots of $1/k_2$ against [AE]. Temp 70 °C, solvent 1,2-dimethoxyethane–methyl cellosove 4 : 1.
●: AQBr–AE–CuBr, ○: 1-amino-4-bromoanthraquinone–AE–CuBr.

Thus, copper(I) species is supposed to be in equilibrium among $Cu^I$, $Cu^I(AE)$, and $Cu^I(AQBr)$. The reaction of $Cu^I(AQBr)$ and AE gives an amination product. On the other hand, the copper(II) species formed in the course of the reaction is in equilibrium between $Cu^{II}$ and $Cu^{II}(AE)$. $Cu^I(AQBr)$ reacts with $Cu^{II}(AE)$ to give the product.

$$\left.\begin{array}{l} Cu^I + AE \xrightleftharpoons{K_1} Cu^I(AE) \\ Cu^I + AQBr \xrightleftharpoons{K_2} Cu^I(AQBr) \xrightarrow[k_r]{AE} \text{Product} \\ Cu^{II} + AE \xrightleftharpoons{K_1'} Cu^{II}(AE) \\ Cu^I(AQBr) + Cu^{II}(AE) \xrightarrow[k_r']{} \text{Product} \end{array}\right\} \quad (14)$$

On the basis of this reaction scheme (Eq. 14) the rate constant $k_1$ is expressed by Eq. 15, while $k_2$ is expressed by Eq. 16.

$$k_1 = \frac{k_rK_2[AE]}{1+K_1[AE]+K_2[AQBr]} \quad (15)$$

$$k_2 = \frac{k_r'K_2}{1+K_1[AE]+K_2[AQBr]}\cdot\frac{K_1'[AE]}{1+K_1'[AE]} \quad (16)$$

Previously we reported that the pseudo-first order plots were independent of the initial concentration of haloanthraquinone.[2)] Therefore, $K_2[AQBr]$ can be supposed to be much smaller than unity: $K_2[AQBr] \ll 1$. In addition, Fig. 9 shows that $k_1/k_2$ is proportional to the concentration of 2-aminoethanol. This result indicates that $K_1'[AE]$ is much larger than unity: $K_1'[AE] \gg 1$. Thus, Eqs. 15 and 16 can be rewritten as follows:

$$k_1 = \frac{k_rK_2[AE]}{1+K_1[AE]} \quad (17) \quad \text{or } k_1^{-1} = \frac{1}{k_rK_2}\left(\frac{1}{[AE]}+K_1\right), \quad (18)$$

$$k_2 = \frac{k_r'K_2}{1+K_1[AE]} \quad (19) \quad \text{or } k_2^{-1} = \frac{1}{k_r'K_2}(1+K_1[AE]). \quad (20)$$

Therefore,

$$(k_1/k_2) = (k_r/k_r')[AE] \quad (21)$$

Both $k_rK_2$ and $K_1$ can be evaluated by the slope and the intercept of the straight line in the plot of $1/k_1$ against $1/[AE]$ (Fig. 7), and $k_r'K_2$ and $K_1$ from the straight line in the plot of $1/k_2$ against [AE] (Fig. 8). The values of $K_1$ evaluated independently from Eqs. 18 and 20 are nearly equal (Table 4). Since the equilibrium between $Cu^I$ and AE does not include haloanthraquinone, there should not be any difference in the magnitude of $K_1$ between haloanthraquinones (1-bromoanthraquinone and 1-amino-4-bromoanthraquinone). Table 4 shows that this is the case.

The value of $k_r/k_r'$ given by the ratio between $k_rK_2$ and $k_r'K_2$ agrees with the slops of the linear plot of $k_1/k_2$ against the concentration of 2-aminoethanol. This result also supports the above mechanism. Table 4 also tells us that both values of $k_rK_2$ and $k_r'K_2$ of 1-amino-4-bromoanthraquinone are greater than those of 1-bromoanthraquinone. We reported previously that the latter was more reactive toward 2-aminoethanol in

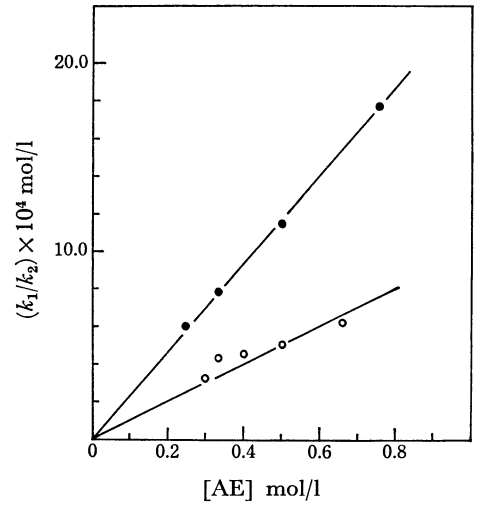


Fig. 9. Plots of $k_1/k_2$ against [AE]. Temp 70 °C, solvent 1,2-dimethoxyethane–methyl cellosolve 4 : 1.
●: AQBr–AE–CuBr, ○: 1-amino-4-bromoanthraquinone–AE–CuBr.

TABLE 4. RATE PARAMETERS FOR THE REACTION WITH 1-BROMOANTHRAQUINONE OR 1-AMINO-4-BROMOANTHRAQUINONE

| Rate parameter | | AQBr | 1-NH$_2$-4-BrAQ |
|---|---|---|---|
| $K_1$(l·mol$^{-1}$) | (from Fig. 7) | 1.67 | 1.67 |
| | (from Fig. 8) | 1.32 | 1.32 |
| $k_rK_2$(l$^2$·mol$^{-2}$·min$^{-1}$) | | 3.24 | 3.85 |
| $k_r'K_2$(l$^2$·mol$^{-2}$·min$^{-1}$) | | 0.127×10$^4$ | 0.326×10$^4$ |
| $k_r/k_r'$ | (from Figs. 7 and 8) | 2.55×10$^{-3}$ | 1.18×10$^{-3}$ |
| | (from Fig. 9) | 2.33×10$^{-3}$ | 1.00×10$^{-3}$ |

Temp 70 °C; solvent 1,2-dimethoxyethane-methyl cellosolve 4 : 1.

the absence of copper(I) than the former was, while the reverse was found in the presence of the catalyst.1) This is mainly caused by the fact that 1-amino-4-bromoanthraquinone possesses larger values of $k_r'K_2$ than 1-bromoanthraquinone does.

Another possible mechanism for the cooperation between copper(I) and copper(II) species can be a complex formation between them. Even if this is the case, however, $k_1$ can be expressed by Eq. 17, and $k_2$ by Eq. 19 rewritten by replacing $k_r'$ with $k_r'K_c$, where $K_c$ is the formation constant of the assumed complex between copper(I) and copper(II).

Several variations of the mechanism which satisfy the experimental results could be considered. However, it is difficult to decide which of these mechanisms is valid.

## Experimental

The 1-bromoanthraquinone, 1-amino-4-bromoanthraquinone, 1-(2-hydroxyethylamino)anthraquinone, and copper(I) halides were prepared by the methods described in the previous paper.1) The copper(II) bromide, 2-aminoethanol, and tetraethylammonium bromide were purified according to the usual methods. Commercial guaranteed reagent grade 2-(dimethylamino)ethanol was distilled, and stored under a nitrogen atmosphere. Solvents were dried in the usual manner, distilled, and stored under a nitrogen atmosphere.

The kinetic measurements were the same as those given previously.1) The anthraquinone formed in the course of the reaction was analyzed by the use of a Shimadzu Du Pont LC-1 high speed liquid chromatograph(column: Zorbax ODS; mobile phase: methanol-water 67 : 33) with 1-methylaminoanthraquinone as the internal standard.

The ESR spectra were measured at 70 °C under a nitrogen atmosphere by the use of a JEOL-PE-3X ESR spectrometer, and the *g* value was calculated by comparison with a $Mn^{2+}$ marker. Field and modulation width were 3360±500 and 6.3 G, respectively.

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