October, 1989] Bull. Chem. Soc. Jpn., 62, 3143—3149 (1989)

The Ullmann Condensation Reaction of Haloanthraquinone Derivatives with Amines in Aprotic Solvents. VI.[1)] The Combination of Cu(I) and Hydroxo or Alkoxo Cu(II) as Effective Catalyst System

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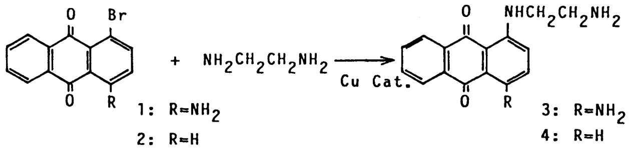
(Received April 14, 1989)

The reaction rate of the Ullmann condensation reaction of haloanthraquinone with ethylenediamine (EN) by copper(I) halide catalyst decreased along with the formation of inactive Cu(II) species $[Cu(EN)_2X_2]$ by one-electron transfer from Cu(I) to haloanthraquinone. However, the combination of Cu(I) and Cu(II) salts, having an OH, OCH_3, or OCOR group, enhanced the reaction rate in the following order: $CuCl < CuCl\text{-}CuCl(OCH_3) < CuCl\text{-}Cu(OCH_3)_2 < CuCl\text{-}Cu(OH)_2$. In condensation using $Cu(OR)_2$ or $CuCl(OCH_3)$ alone, the Cu(II) species was reduced to Cu(I) to form an active catalyst system [Cu(I)+Cu(II)]. On the other hand, $CuBr_2$ or $CuCl_2$ was not reduced and was ineffective for the reaction. These were confirmed by ESR measurements and the presence of a dehalogenation product. Mixed valence species bridged by the alkoxo or hydroxo group was proposed as an active species.

A wide variety of copper species, such as copper powder, copper(I) oxide, copper(I) halides, and copper(II) salts, has been used for the catalyst of nucleophilic substitution of aryl halides (the Ullmann condensation).[2,3)] The choice of the catalyst depends on the structure of aryl halides, nucleophiles, and solvents; however, it is often found that a catalyst that is effective for a certain reaction is ineffective for another reaction system.[3)] The mechanism of the Ullmann condensation is further complicated by the fact that a copper species changes its oxidation state during a reaction. For example, a Cu(0) catalyst was changed to the effective Cu(I) species by oxidation with molecular oxygen or some other oxidants.[4)] In the case of a Cu(II) catalyst, the reduction of Cu(II) to Cu(I) accelerated the reaction.[4,5)]

Although Cu(I) salts were more effective catalysts than Cu(II) salts in the homogeneous Ullmann condensation of haloanthraquinones with amines in aprotic solvents,[6)] Cu(II) species formed by a one-electron transfer from Cu(I) to haloanthraquinone under a nitrogen atmosphere played a very important role. The catalytic activity of Cu(I) was enhanced by Cu(II) species produced in condensation with 2-aminoethanol,[6–8)] whereas with ethylenediamine (EN)[9)] only Cu(I) was active and the reaction rate decreased along with the formation of an ineffective Cu(II) species. On the other hand, the alkoxocopper(II) species enhanced the rate of condensation with EN by a cooperative interaction with the Cu(I) species.[1)]

These results prompted us to study a combination of Cu(I) and Cu(II) species in order to explore the more active catalyst system in the Ullmann condensation reaction. In this paper we will report on the results for the catalytic behavior of alkoxo or hydroxo copper(II) as a promoter in the Ullmann condensation reaction of haloanthraquinones with ethylenediamine.



1: $R=NH_2$
2: R=H
3: $R=NH_2$
4: R=H

Experimental

Materials. 1-Amino-4-bromoanthraquinone (**1**) and 1-bromoanthraquinone (**2**) were prepared by desulfonation of sodium 1-amino-4-bromoanthraquinone-2-sulfonate with 80% sulfuric acid and by Sandmeyer's bromination of 1-aminoanthraquinone, respectively, as reported previously.[6)] Copper(I) bromide and copper(I) chloride were prepared and purified as described in the literature.[10)] Commercially available copper(II) bromide and copper(II) chloride (Kanto Chemical Co. Inc., GR grade) were purified according to methods described in the literature.[11)] Chloromethoxycopper(II)[12)] was prepared by the reaction of copper(I) chloride with molecular oxygen in methanol (Found: Cu. 49.0%). Dimethoxycopper(II)[13)] was obtained by the reaction of anhydrous copper(II) chloride with lithium methoxide in methanol (Found: Cu, 50.7%). All other copper salts were commercial materials (Kanto Chemical Co. Inc., GR grade) and used without further purification. All solvents and ethylenediamine were dried and purified by the standard procedure, and stored under a nitrogen atmosphere.

Reaction Procedure. The condensation was initiated by the addition of a solution of copper salt and ethylenediamine in ethanol to the haloanthraquinone solution in THF–ethanol at a regulated temperature. The reaction was carried out under a dry, oxygen-free nitrogen atmosphere. The yield was determined spectrophotometrically as described in our previous papers.[1,6)] The debromination product was analyzed by the use of a Shimadzu LC-3A HPLC (column: Unisil C18; mobile phase: methanol-water 4:1) with 1-amino-2-bromoanthraquinone as an internal standard.

Instruments. UV and visible spectra were measured with a Shimadzu UV-210 spectrometer. ESR spectra were obtained by the use of a JEOL-PE-3X spectrometer, equipped with a 100-kHz field modulation unit.

Results and Discussion

The reaction rate of the condensation of 1-amino-4-bromoanthraquinone (**1**) or 1-bromoanthraquinone (**2**) with ethylenediamine (EN) catalyzed by Cu(I) salt (CuCl or CuBr) decreases along with the formation of an inactive Cu(II) species [$Cu(EN)_2X_2$] by a one-electron transfer from Cu(I) to haloanthraquinone.[9] However, upon the addition of hydroxo or alkoxo Cu(II) salt the condensation catalyzed by Cu(I) salt was accelerated. As a typical example, Fig. 1 indicates the results of the condensation of **1** with EN using a CuCl-$Cu(OH)_2$ catalyst system. The yield of 1-amino-4-(2-aminoethylamino)anthraquinone (**3**) depended on the molar fraction of $Cu(OH)_2$ to the total copper ([CuCl]+[$Cu(OH)_2$]). An induction period was observed when the copper species was $Cu(OH)_2$ alone.

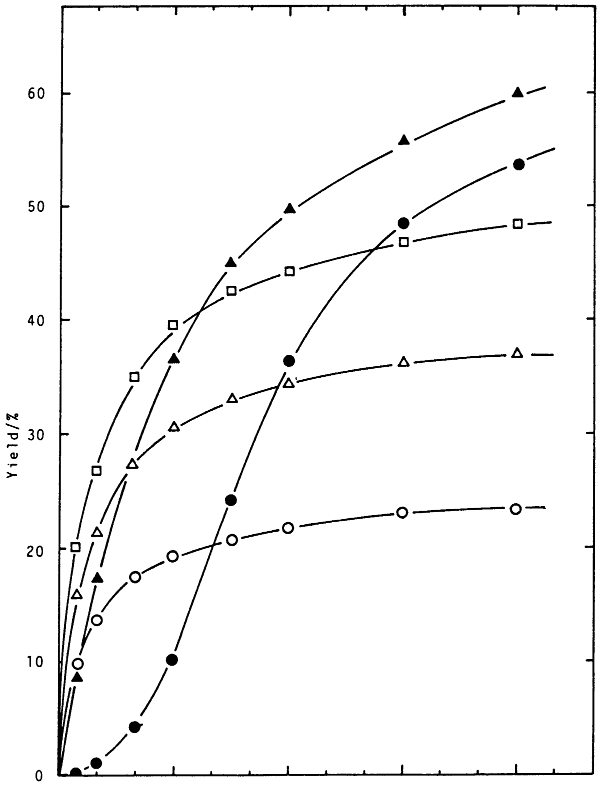


Fig. 1. Time course of the reaction of **1** with EN by CuCl-$Cu(OH)_2$ catalyst system.
$[\mathbf{1}]_0=5.0\times10^{-3}$ mol dm^{-3}, $[EN]_0=0.5$ mol dm^{-3}, $[CuCl+Cu(OH)_2]_0=2.1\times10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF-EtOH 1 : 1.
○: r ($[Cu(OH)_2]_0/[CuCl+Cu(OH)_2]_0$)=0, △: r=0.164, □: r=0.288, ▲: r=0.755, ●: r=1.0.

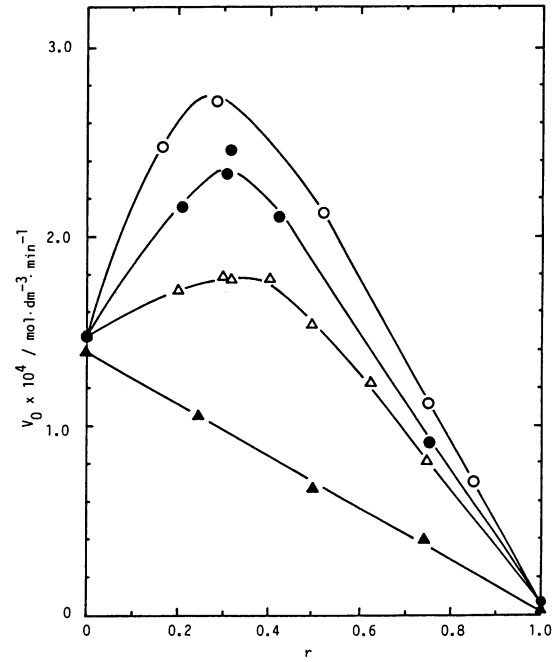


Fig. 2. The dependence of the initial rates, (V_0) on the ratio r ($[Cu(II)]_0/[Cu(I)+Cu(II)]_0$) in the reaction of **1** with EN.
$[\mathbf{1}]_0=5.0\times10^{-3}$ mol dm^{-3}, $[EN]_0=0.5$ mol dm^{-3}, $[Cu(I)+Cu(II)]_0=2.1\times10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF-EtOH 1 : 1.
○: CuCl-$Cu(OH)_2$, ●: CuCl-$Cu(OMe)_2$, △: CuCl-CuCl(OMe), ▲: CuBr-$CuBr_2$.

Copper(II) Species as a Promoter. Figure 2 illustrates plots of the initial rate (V_0) vs. the fraction of Cu(II) to the total copper. In condensation using a CuBr-$CuBr_2$ catalyst system, the initial rate decreased linearly with an increase in the fraction.[1] On the other hand, in catalyst systems containing alkoxo or hydroxo Cu(II) species, the maximum initial rate was observed at a fraction of around 0.3 and the catalytic activity increased in the following order: CuCl-CuCl(OCH_3)<CuCl-$Cu(OCH_3)_2$<CuCl-$Cu(OH)_2$. These results clearly show that in condensation using a CuBr-$CuBr_2$ catalyst system, only Cu(I) is effective and the Cu(II) species containing two halide ligands is ineffective. This contrasts to other catalyst systems where the Cu(II) species acts as a promoter.

The initial rates of the condensation by various kinds of Cu(II) species were compared at a molar ratio of about 0.3 (Table 1). Cu(II) species having an OH, OCH_3, or OCOR group increased the catalytic activity of Cu(I), whereas a Cu(II) species having NO_3, ClO_4, or S, deactivated the condensation. The hyperfine coupling constants (A)[13] of $CuBr_2$ or $CuCl_2$ in a THF-EtOH (1 : 1) solution containing EN were around 80 G, whereas those of the Cu(II) species coordinated by an OY-type ligand (Y=H, R, COR) were around 70 G.

Consequently, the initial rate (V_0) can be expressed as

$$V_0 = k_1[Cu(I)] + k_2[Cu(I)]^m[Cu(II)]^n. \quad (1)$$

Table 1. Initial Rates (V_0)[a] for the Condensation of **1** with EN by Cu catalyst and the Coupling Constants (A) of Cu(II) Species

Catalyst system			V_0	A
Cu(II)	+	Cu(I)	mol·dm^{-3}·min^{-1}	G
$Cu(OH)_2$		CuCl	2.70	69.6
$Cu(OMe)_2$		CuCl	2.33	70.5
CuCl(OMe)		CuCl	1.72	70.4
$Cu(CO_3)\cdot Cu(OH)_2\cdot H_2O$		CuCl	1.69	—
$CuSO_4\cdot 5H_2O$		CuCl	1.33	—
$Cu(AcO)_2\cdot CuO\cdot 6H_2O$		CuCl	1.19	—
$Cu(HCOO)_2\cdot 4H_2O$		CuCl	1.08	70.8
$CuCl_2$		CuCl	1.00	79.7
$CuBr_2$		CuBr	0.92	79.5
$Cu(NO_3)_2\cdot 3H_2O$		CuCl	0.71	69.4
$Cu(ClO_4)_2\cdot 6H_2O$		CuCl	0.55	69.8
CuS		CuCl	0.057	—

a) $[\mathbf{1}]_0=5.0\times10^{-3}$ mol·dm^{-3}, $[\mathrm{EN}]_0=0.5$ mol·dm^{-3}, $[\mathrm{Cu(I)}+\mathrm{Cu(II)}]_0=2.1\times10^{-3}$ mol·dm^{-3}, $[\mathrm{Cu(II)}]_0/[\mathrm{Cu(I)}+\mathrm{Cu(II)}]_0=0.3$, temp 50 °C, solvent THF-EtOH 1 : 1.

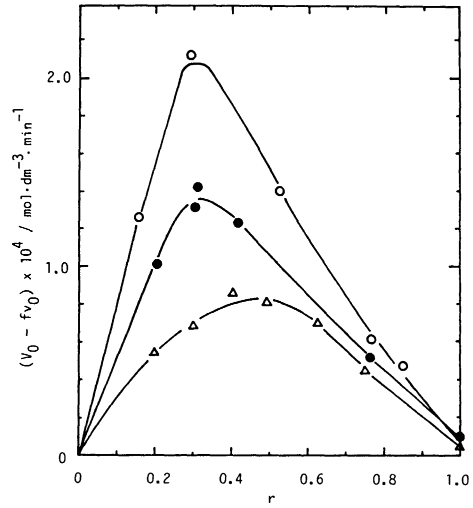


Fig. 3. The dependence of the rate catalyzed by the cooperative Cu(I) and Cu(II) combination on the ratio r ($[\mathrm{Cu(II)}]_0/[\mathrm{Cu(I)}+\mathrm{Cu(II)}]_0$) in the reaction of **1** with EN.
$[\mathbf{1}]_0=5.0\times10^{-3}$ mol dm^{-3}, $[\mathrm{EN}]_0=0.5$ mol dm^{-3}, $[\mathrm{Cu(I)}+\mathrm{Cu(II)}]_0=2.1\times10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF-EtOH 1 : 1.
○: CuCl-$Cu(OH)_2$, ●: CuCl-$Cu(OMe)_2$, △: CuCl-CuCl(OMe).

If f and v_0 denote the fraction of Cu(I) to the total copper ($[\mathrm{Cu(I)}]+[\mathrm{Cu(II)}]$) and the initial rate catalyzed by Cu(I) alone, respectively, Eq. 1 becomes

$$V_0 - fv_0 = k_2[\mathrm{Cu(I)}]^m[\mathrm{Cu(II)}]^n. \qquad (2)$$

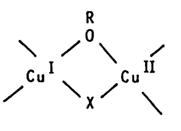
Figure 3 shows a plot of V_0-fv_0, which indicates the rate catalyzed by a Cu(I) and Cu(II) couple, against fraction (r) of Cu(II) to total copper. In the CuCl-CuCl(OMe) system, the maximum rate was observed at r=0.5, whereas in the CuCl-$Cu(OMe)_2$ and CuCl-$Cu(OH)_2$ systems it appeared at r=0.3. Therefore, in a CuCl-CuCl(OMe) catalyst system the ratio of m to n is 1 : 1, whereas in CuCl-$Cu(OH)_2$ and CuCl-$Cu(OMe)_2$ catalyst systems the ratio is 2 : 1. These results suggest that the active species (alkoxo or hydroxo Cu(I)) is formed by the following ligand-exchange reactions:

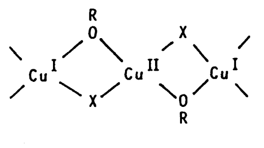
$$\mathrm{CuCl} + \mathrm{CuCl(OMe)} \rightarrow \mathrm{CuOMe} + \mathrm{CuCl_2}$$

and

$$2\mathrm{CuCl} + \mathrm{Cu(OR)_2} \rightarrow 2\mathrm{CuOR} + \mathrm{CuCl_2}.$$

However, the coupling constant (A) of CuCl-$Cu(OH)_2$ (2 : 1) in a THF-EtOH (1 : 1) solution was not 80 G but, rather, 70 G and the ESR spectrum of this system was the same as that of $Cu(OH)_2$-EN. These results exclude the possibility of alkoxo or hydroxo Cu(I) formation by a ligand-exchange reaction. The above results can be explained in terms of the idea that a Cu(II) species having OH or OCH_3 interact with the Cu(I) species to form an oxygen-bridged multi copper species as follows:





Although we failed to detect the presence of these oxygen-bridged species by ESR measurement, many examples of alkoxo- or hydroxo-bridged copper species have been reported.[14)] On the other hand $CuBr_2$ or $CuCl_2$, which does not form an oxygen-bridged species, is ineffective as a promoter. No reasonable explanation is possible for the deactivation by $Cu(NO_3)_2$, $Cu(ClO_4)_2$.

Change of Oxidation States of Copper Species during the Condensation. Figure 4 shows the results of an ESR measurement of the condensation system (**1**-EN-CuCl). The Cu(II) signal height[15)] increased as the condensation proceeded and the coupling constant A remained unchanged at 80 G during the condensation. The ESR spectra of this condensation system were the same as that of a violet solution[16)] of $CuBr_2$-EN or $CuCl_2$-EN in THF-EtOH (1 : 1) (A=80 G; Table 1). Therefore, the ineffective Cu(II) species formed during the condensation is considered to be a mononuclear Cu(II) complex: $Cu(EN)_2X_2$.

On the other hand, in the case of CuCl-$Cu(OH)_2$ (2 : 1) catalyst system, which is the most effective one, the formation of the Cu(II) species was much depressed compared to that using the CuCl catalyst system (Fig. 4). However, the coupling constant (70 G) was gradually increased and went up to 77 G after 90 min. This would be due to the coordination of bromide ions accumulated in the solution. These results suggest that a Cu(I)-Cu(II) couple containing an OH group was relatively stable or that a concurrent reduction of Cu(II) to Cu(I) occurred with the oxidation of Cu(I).

In condensation using CuCl-$Cu(OCH_3)_2$ (2 : 1) and CuCl-CuCl(OCH_3) (2 : 1) catalyst systems the time

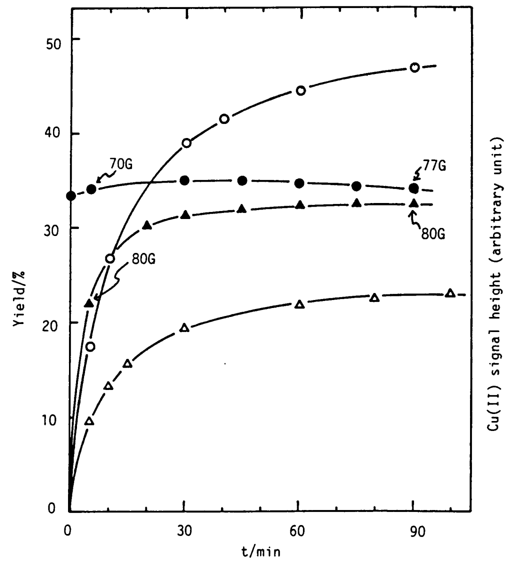


Fig. 4. Time course of the reaction of **1** with EN by Cu catalyst.
$[\mathbf{1}]_0=5.0\times10^{-3}$ mol dm^{-3}, $[\mathrm{EN}]_0=0.5$ mol dm^{-3}, $[\mathrm{Cu}]_0=2.1\times10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF-EtOH 1 : 1.
△: Yield of **3** by CuCl catalyst, ○: yield of **3** by CuCl-Cu(OH)$_2$ catalyst (r=0.288), ▲: Cu(II) signal height of the reaction system by CuCl catalyst, ●: Cu(II) signal height of the reaction system by CuCl-Cu(OH)$_2$ catalyst (r=0.288).

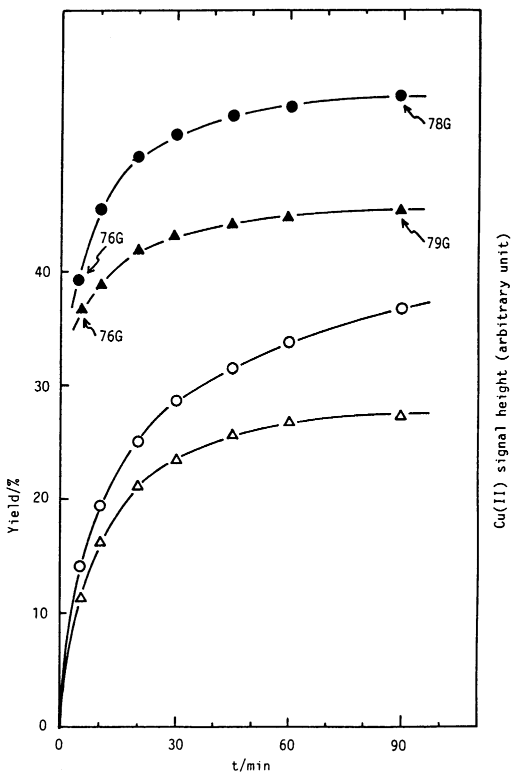


Fig. 5. Time course of the reaction of **1** with EN by Cu catalyst.
$[\mathbf{1}]_0=5.0\times10^{-3}$ mol dm^{-3}, $[\mathrm{EN}]_0=0.5$ mol dm^{-3}, $[\mathrm{Cu}]_0=2.1\times10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF-EtOH 1 : 1.
△: Yield of **3** by CuCl-CuCl(OMe) catalyst (r=0.309), ○: yield of **3** by CuCl-Cu(OMe)$_2$ catalyst (r=0.306), ▲: Cu(II) signal height of the reaction system by CuCl-CuCl(OMe) catalyst (r=0.309), ●: Cu(II) signal height of the reaction system by CuCl-Cu(OMe)$_2$ catalyst (r=0.306).

course of the yield of **3** and the coupling constant of Cu(II) (see Fig. 5) lies between those of the CuCl system and CuCl-Cu(OH)$_2$ system.

In condensation using Cu(OH)$_2$, Cu(OMe)$_2$, or CuCl(OMe) alone, which has an induction period, the Cu(II) signal height decreased and then slightly increased as the condensation proceeded (Figs. 6 and 7). It was also observed that the reaction rate tended to decrease along with an increase in the coupling constant. These results show that a part of the Cu(II) species was reduced to the Cu(I) species to form an active catalyst system [Cu(I) + Cu(II)]; then, Cu(I) was oxidized to ineffective Cu(II) by one-electron transfer from Cu(I) to haloanthraquinone and the coupling constant (A) of Cu(II) increased from 70 G to 80 G along with an increase of halide ions in the solution.

The reduction of Cu(II) to the Cu(I) species was also supported by the debromination of **1**. We previously reported that the debromination was caused through a radical anion intermediate, as follows:[8]

$$\mathrm{AQBr} + \mathrm{Cu(I)} \rightarrow \mathrm{AQBr}^{\overline{\cdot}} + \mathrm{Cu(II)}$$

$$\mathrm{AQBr}^{\overline{\cdot}} \rightarrow \mathrm{AQH}.$$

In fact, Fig. 6 shows that in the case of the **1**-EN-Cu(OH)$_2$ system 1-aminoanthraquinone was formed with an decrease in the Cu(II) signal height. The yields of the aminated product, [1-(2-aminoethylamino)anthraquinone: **4**], and the debrominated product, (anthraquinone) in **2**-EN-Cu(OH)$_2$, were larger than those in **1**-EN-Cu(OH)$_2$. This result corresponds to the fact that the decrease in the Cu(II) signal height was larger in the system of **2**-EN-Cu(OH)$_2$ than in that of **1**-EN-Cu(OH)$_2$ (Fig. 7).

Reduction of Cu(II) to the Cu(I) Species. As described above, the reduction of Cu(II) to the Cu(I) species was clearly observed in a condensation system using Cu(OH)$_2$, Cu(OMe)$_2$, or CuCl(OMe). Figure 6 also shows that in the absence of haloanthraquinone, the Cu(II) signal height was slightly decreased. The catalyst solution [Cu(OH)$_2$-EN] was heated at 50 °C for 110 min and then added to a solution of **1**. In this case the induction period was slightly shortened. These results also indicated that Cu(OH)$_2$ was slightly reduced to the Cu(I) species, even in the absence of haloanthraquinone. Contrary to haloanthraquinones, 1-aminoanthraquinone or anthraquinone did not facilitate a reduction of the Cu(II) species in the system of Cu(OH)$_2$-EN. These results suggest that the Cu(II) species is coordinated by the halogen moiety of haloanthraquinone, and reduced to Cu(I) by a one-electron transfer from EN. This was also sup-

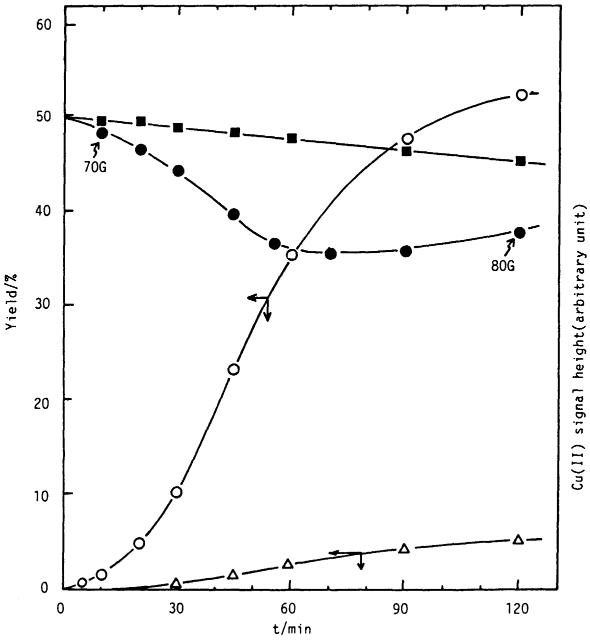


Fig. 6. Time course of the reaction of **1** with EN by $Cu(OH)_2$ catalyst.
$[\mathbf{1}]_0=5.0\times10^{-3}$ mol dm^{-3}, $[EN]_0=0.5$ mol dm^{-3}, $[Cu(OH)_2]_0=2.1\times10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF-EtOH 1 : 1.
○: **3**, △: 1-aminoanthraquinone, ●: Cu(II) signal height of the reaction system, ■: Cu(II) signal height in the absence of **1**.

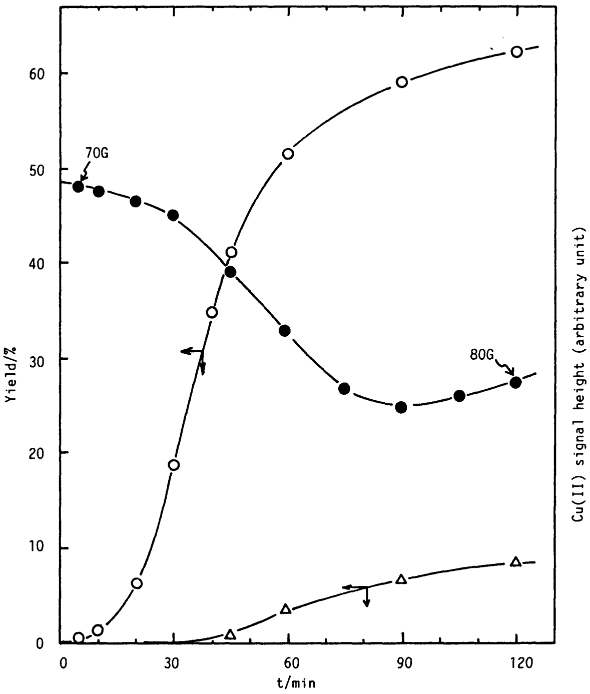


Fig. 7. Time course of the reaction of **2** with EN by $Cu(OH)_2$ catalyst.
$[\mathbf{2}]_0=5.0\times10^{-3}$ mol dm^{-3}, $[EN]_0=0.5$ mol dm^{-3}, $[Cu(OH)_2]_0=2.1\times10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF-EtOH 1 : 1.
○: **4**, △: anthraquinone, ●: Cu(II) signal height of the reaction system.

ported by the fact that the addition of 1-aminoanthraquinone equimolar to **2** little affected Cu(II) reduction in the system of **2**-EN-$Cu(OH)_2$.

The coupling constants of the catalyst systems containing alkoxo or hydroxo Cu(II) were smaller than that of the $CuCl$-$CuCl_2$ or $CuBr$-$CuBr_2$ system (Table 1). This suggests that the former Cu(II) species has a stronger covalent bond character than that of the latter.[17] On the basis of the reduction potentials of various Cu(II) complexes obtained by polarography, Patterson and Holm[18] reported that mononuclear Cu(II) complexes with a nonplanar structure (e.g., distorted tetrahedron and trigonal bipyramid) were readily reduced to Cu(I), compared with their planar analogs. It has also been reported that binuclear Cu(II) complexes with a planar structure and Cu(II) complexes with a distorted tetrahedral structure were readily reduced to Cu(I) by ascorbic acid, while planar mononuclear Cu(II) complexes were not reduced.[19] Consequently, copper(II) species having a promoter-character in our case has an alkoxo- or hydroxo-bridged structure and would be reduced to Cu(I) by EN. On the other hand, no reduction of Cu(II) to

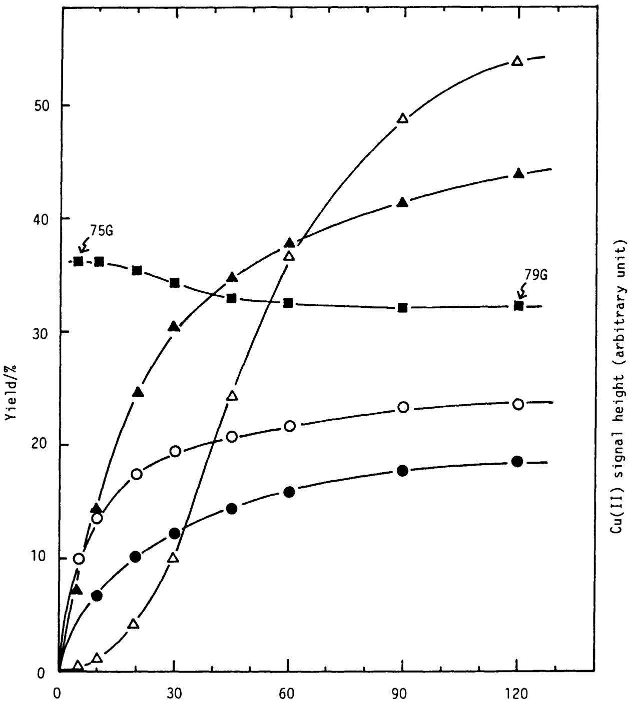


Fig. 8. Time course of the reaction of **1** with EN by Cu catalyst in the presence of glucose.
$[\mathbf{1}]_0=5.0\times10^{-3}$ mol dm^{-3}, $[EN]_0=0.5$ mol dm^{-3}, $[Cu]_0=2.1\times10^{-3}$ mol dm^{-3}, $[\text{glucose}]_0=2.27\times10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF-EtOH 1 : 1.
○: Yield of **3** by CuCl catalyst, ●: yield of **3** by CuCl catalyst in the presence of glucose, △: yield of **3** by $Cu(OH)_2$ catalyst, ▲: yield of **3** by $Cu(OH)_2$ catalyst in the presence of glucose, ■: Cu(II) signal height of the reaction system by $Cu(OH)_2$ in the presence of glucose.

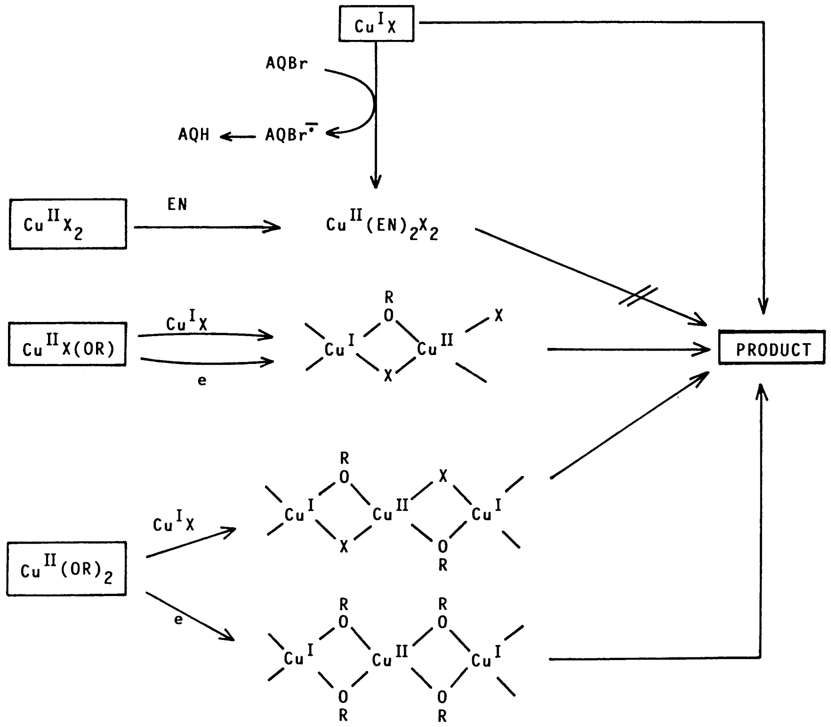


Fig. 9. Reaction pathways.

Cu(I) was observed in the systems using ineffective $Cu(EN)_2X_2$ with a planar structure (A= 80 G).

As Fig. 8 shows, upon the addition of glucose to the condensation system (**1**-EN-$Cu(OH)_2$), little induction period was observed and the Cu(II) signal height decreased very little. Since the coupling constant was observed to be 75 G, even at 4 min, it was concluded that during the first stage of the reaction the Cu(II) species was reduced to active Cu(I) by glucose and then reoxidized to an inactive Cu(II) species. The yield of **3** in **1**-EN-CuCl was decreased upon the addition of glucose. These results suggest that the coordination of glucose to the Cu(I) species interrupts the coordination of haloanthraquinone.

Reaction Pathways. The reaction pathways of the Ullmann condensation using $Cu(OR)_2$ or CuX(OR) are shown in Fig. 9.20) As discussed above, all of the observed results support the reaction pathways including a Cu(I)···Cu(II) mixed valence complex. Although Cu(I) halide is an active catalyst, the reaction rate decreases along with the formation of inactive $Cu(EN)_2X_2$. The alkoxo- or hydroxo-bridged mixed valence complex would be formed by the reaction between the Cu(I)X and the alkoxo or hydroxo Cu(II) species, or by the reduction of the alkoxo- or hydroxo-bridged Cu(II) species.

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