The Ullmann Condensation Reaction of Haloanthraquinone Derivatives with Amines in Aprotic Solvents. V.[1] The Formation of Active Catalyst by the Partial Oxidation of Copper(I) with Molecular Oxygen

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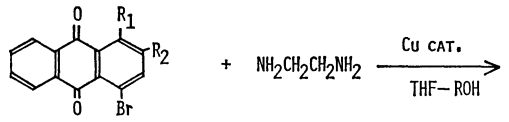
Although copper(I) is a more effective catalyst than copper(II) in the Ullmann condensation reaction of haloanthraquinones with ethylenediamine in aprotic solvents under a nitrogen atmosphere, the oxidation products of copper(I) by molecular oxygen enhanced the reaction rate compared to copper(I) catalyst. From the studies on the effect of Cu(II) salt addition to Cu(I) salt, solvent effects, and ESR spectra, it was concluded that alkoxycopper(II) species, formed by the oxidation of Cu(I) with molecular oxygen in alcohol–ethylenediamine solution, acted cooperatively with Cu(I) to increase the catalytic activity. The idea was also supported by the fact that the condensation was remarkably accelerated by the combination of Cu(I) and chloromethoxycopper-(II). Reaction pathways including the alkoxo and halogen bridged Cu(I)···Cu(II) mixed valence complex are proposed and discussed.

The Ullmann condensation reaction, a nucleophilic aromatic substitution with the aid of copper catalyst, is used as an important synthetic tool of various aromatic compounds, especially dyestuffs and drugs.[2] The detailed mechanisms, however, remain ambiguous. From our continuing studies on the Ullmann condensation reaction of haloanthraquinones with amines in aprotic solvents, it was clarified that Cu(II) species, formed by an electron transfer from Cu(I) to haloanthraquinone under a nitrogen atmosphere, plays a very interesting role, though Cu(I) salts are more effective catalysts than Cu(II) salts.[3,4] On the basis of the kinetic studies it was concluded that the resulting Cu(II) species acted cooperatively with Cu(I) to increase the catalytic activity of Cu(I) in the condensation with 2-aminoethanol,[5] while in the condensation with ethylenediamine(EN) only Cu(I) was active and the reaction rate decreased with the formation of the Cu(II) species.[1]

We now have found that in the condensation with EN the partial oxidation of Cu(I) catalyst by molecular oxygen unexpectedly enhanced the reaction rate, while the Cu(I) species will be oxidized into inactive Cu(II) by oxygen.

In this paper we will report the unexpected oxygen effect on the condensation with EN and propose that the alkoxycopper(II) species increase the catalytic activity of Cu(I) species.



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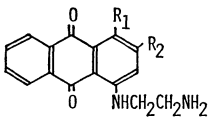
2 : $R_1 = R_2 = H$

3 : $R_1 = NH_2$, $R_2 = Br$



4 : $R_1 = NH_2$, $R_2 = H$

5 : $R_1 = R_2 = H$

6 : $R_1 = NH_2$, $R_2 = Br$

Experimental

Materials. 1-Amino-4-bromoanthraquinone (**1**) and 1-bromoanthraquinone (**2**) were prepared as before.[3] 1-Amino-2,4-dibromoanthraquinone (**3**) was prepared from sodium 1-amino-4-bromoanthraquinone-2-sulfonate by bromination and purified by recrystallization from benzene–ethanol: Found: C, 44.00; H, 1.69; N, 3.63%. Mp 229.4—229.7 °C (cor) (lit,[6] 214 °C). Copper(I) bromide and copper(I) chloride were prepared and purified as described in the literature.[7] Commercially available copper(I) iodide was used without further purification. Copper(II) bromide was purified according to the literature.[8] Copper(II) chloride was dried at 100 °C under vacuum. Chloromethoxycopper-(II) was prepared by the reaction of copper(I) chloride with molecular oxygen in methanol[9] (Found: Cu, 49.0%. Calcd for CH_3OClCu: Cu, 48.87%). All solvents were dried and purified by standard procedure, and stored under a nitrogen atmosphere.

Condensation with Ethylenediamine. Catalyst solution was prepared by the reaction of copper(I) bromide with oxygen in ethanol and EN solution. In a typical experiment, copper(I) bromide (71.7 mg, 5×10^{-4} mol) was weighed into a 40 ml Schlenk type flask equipped with a magnetic stirrer and with a gas inlet connected with a gas buret containing air. After evacuation, N_2 was introduced and the same procedure was repeated several times. Ethanol (5 ml) and EN (8 ml, 1.2×10^{-1} mol) were added into the flask with stirring under a nitrogen atmosphere to give a homogeneous Cu(I) solution. Then oxygen was introduced to the solution with stirring and oxygen consumption was measured by a gas buret. On the other hand, **1** (75.5 mg, 2.5×10^{-4} mol) and the solvent (THF 24 ml, C_2H_5OH 23 ml) were mixed in a 50 ml three necked flask equipped with a reflux condenser, thermometer, and a three-way stopcock. After this solution was brought to the reaction temperature, the reaction was initiated by the addition of the catalyst solution (2.7 ml, Cu content 1.04×10^{-4} mol) with the help of a pipette. The condensation was performed under a dry and oxygen-free nitrogen atmosphere. At regular time intervals, 0.5 ml aliquots of the reaction solution were taken out, diluted in 25 ml of ethanol, and subjected to visible spectral measurements. The yields of **4** based on **1** were determined by use of the absorbance of **4** at 615 nm.[1]

Instruments. UV and visible spectra were measured

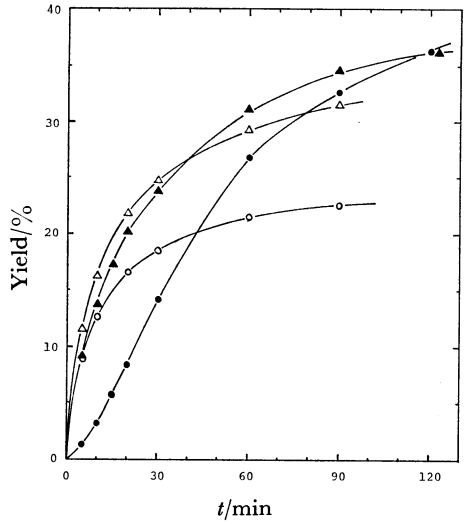


Fig. 1. Time course of the reaction of **1** with EN by Cu catalyst.
$[\mathbf{1}]_0=5.0\times10^{-3}$ mol dm^{-3}, $[EN]_0=0.5$ mol dm^{-3}, $[Cu]_0=2.1\times10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF–EtOH 1:1. ○: $r([O_2]/[CuBr])=0$, △: $r=0.166$, ▲: $r=0.258$ ●: $r=0.562$.

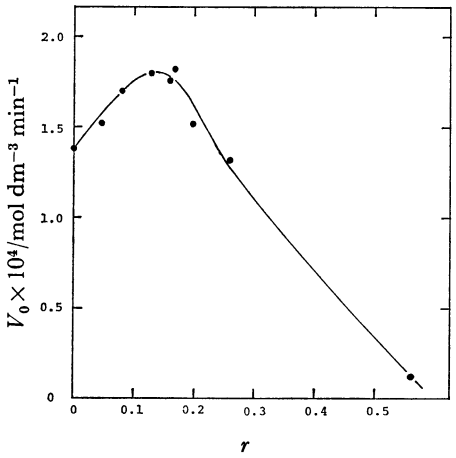


Fig. 2. The dependence of the initial rates (V_0) on the molar ratio $r([O_2]/[CuBr])$ in the reaction of **1** with EN by Cu catalyst.
$[\mathbf{1}]_0=5.0\times10^{-3}$ mol dm^{-3}, $[EN]_0=0.5$ mol dm^{-3}, $[Cu]_0=2.1\times10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF–EtOH 1:1.

on a Shimadzu UV-210 spectrophotometer. ESR spectra were measured by the use of a JEOL-PE-3X ESR spectrometer, equipped with a 100 KHz field modulation unit.

Results and Discussion

In the condensation with EN using CuBr catalyst under a N_2 atmosphere, the reaction rate decreased with time. The result is interpreted in terms of the formation of ineffective Cu(II) species by an electron transfer from Cu(I) to haloanthraquinone.[1] Upon the introduction of oxygen to the catalyst solution (CuBr–EN–EtOH), the colorless solution turned immediately to deep blue, which indicated the formation of Cu(II) species. By the use of this blue catalyst, the yield of **4** increased unexpectedly, as shown in

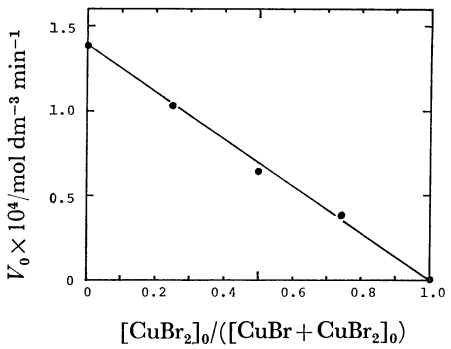


Fig. 3. The effect of the addition of $CuBr_2$ on the initial rates (V_0) in the reaction of **1** with EN by CuBr catalyst.
$[\mathbf{1}]_0=5.0\times10^{-3}$ mol dm^{-3}, $[EN]_0=0.5$ mol dm^{-3}, $[CuBr+CuBr_2]_0=2.1\times10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF–EtOH 1:1.

Fig. 1. Figure 2 illustrates the plots of the initial rate (V_0) *vs.* the molar ratio(r) of the absorbed oxygen to CuBr. Figures 1 and 2 indicated the following characteristics of the reaction:

i) The initial rate markedly depends on the amount of the oxygen absorbed; the maximum initial rate was observed at the ratio r of about 0.13.

ii) By the catalyst-absorbed small amounts of oxygen, both initial rate and final yield were larger than those obtained by Cu(I) catalyst alone.

iii) In the region of the larger molar ratio(r) the initial rate decreased but the final yield tends to increase. Comparing at 2 h, the catalyst system with a ratio r of 0.56 gave the largest yield, after a clear induction period.

Similar results were observed in other condensation systems such as **1**–EN–CuCl, **2**–EN–CuBr, **2**–EN–CuI, **3**–EN–CuBr, and **3**–EN–CuI. These facts reveal that the oxygen effect is not specific to either haloanthraquinones or copper(I) halides.

Effect of Copper(II) Bromide Addition to Copper(I) Bromide Catalyst System. If copper(II) bromide is used as an alternative to the copper(II) species, formed by the partial oxidation of Cu(I) with molecular oxygen, the reaction rate will increase similarly to the case of the condensation with 2-aminoethanol.[4,5] Figure 3 shows the results of the addition of $CuBr_2$ to CuBr, keeping the total copper amount to be constant, in the condensation with EN under a N_2 atmosphere. Contrary to our expectation, the initial rate decreased linearly with the increase in the molar ratio of $CuBr_2$ to the total copper amount ($CuBr+CuBr_2$). This result shows that $CuBr_2$ does not act as a promoter and only Cu(I) is active in the condensation with EN under N_2. From this result it was concluded that Cu(II) species of the CuBr–EN–EtOH–O_2 catalyst system is different from that of the CuBr–$CuBr_2$–EN–EtOH catalyst system.

Solvent Effects on the Formation of Active Catalyst. The solvent effects on the oxidation of Cu(I) catalyst solution by molecular oxygen were examined as shown in Table 1. These results are compared at the molar ratios(r) ranging from about 0.12 to 0.16: In this region the initial rate revealed a maximum (Fig. 2).

Table 1. Initial rates (V_0) for the reaction of **1** with EN by Cu catalyst[a)]

Entry	Catalyst solution	r[b)]	$V_0 \times 10^4$/mol dm^{-3} min^{-1}
1	CuBr-EN-EtOH	0.0	1.38
2	CuBr-EN-EtOH-O_2	0.128	1.80
3	CuBr-EN-O_2	0.151	0.91
4	CuBr-EN-O_2+EtOH[c)]	0.130	1.48
5	CuBr-EN-MeOH	0.0	1.32
6	CuBr-EN-MeOH-O_2	0.119	1.74
7	CuBr-EN-py-O_2	0.158	1.53
8	CuBr-EN-*i*-PrOH-O_2	0.135	1.37
9	CuCl-EN-MeOH	0.0	1.45
10	CuCl-EN-MeOH-O_2	0.158	1.58

a) $[\mathbf{1}]_0 = 5.0 \times 10^{-3}$ mol dm^{-3}, $[EN]_0 = 0.5$ mol dm^{-3}, $[Cu]_0 = 2.1 \times 10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF-EtOH 1:1. b) The molar ratio of the absorbed oxygen to CuX. c) Ethanol was added to CuBr-EN-O_2 system.

The reaction of copper(I) bromide with oxygen in EN–EtOH solution afforded a blue solution containing a blue solid. By this catalyst solution, the yield increased as shown in Fig. 1 (Table 1, Entry 2). The reaction of oxygen with CuBr in EN gave a dark greenish brown solution containing a brown solid. This catalyst solution markedly decreased the initial rate compared with that obtained with CuBr catalyst (Entry 3). However, by the addition of ethanol to the CuBr–EN–O_2 catalyst solution, the color of the solution turned to dark blue and the initial rate increased (Entry 4), though the catalytic activity was smaller than that for the catalyst system CuBr–EN–EtOH–O_2. This result shows that alcohol converted inactive copper(II) species into active ones. The dark greenish brown solution, generated by the reaction of CuBr with O_2 in EN–pyridine solution, also increased the catalytic activity (Entry 7). These results may suggest that ethanol in the condensation solution is related to the formation of active Cu(II) species (see Experimental). The blue catalyst solution formed by the oxidation of CuBr or CuCl with molecular oxygen in EN–MeOH also increased the catalytic activity (Entries 6 and 10). These results indicated that alcohols play a very important role in the formation of active catalyst.

The Role of Alkoxycopper(II) Species. The oxygen uptake by CuBr in methanol was extremely slow without EN, while the reaction of CuCl with oxygen in methanol proceeded moderately and gave a yellowish green solid. The solid is known to be chloromethoxycopper(II) formed by the following stoichiometry:[9)]

$$4CuCl + O_2 \xrightarrow[MeOH]{} 4CuCl(OMe) + 2H_2O. \quad (1)$$

By the addition of CuCl(OMe) the catalytic activity of CuCl increased in spite of the absence of oxygen (Figs. 4 and 5). Further, in the case of CuCl(OMe) alone, an induction period was observed. These results were analogous to the case of oxygen addition.

Figure 6 shows the ESR spectra of the catalyst solution CuCl–EN–MeOH–O_2 (r=0.13), $CuCl_2$–EN–MeOH, and CuCl(OMe)–EN–MeOH at room temperature. The CuCl–EN–MeOH–O_2 system revealed only Cu(II) species as electron paramagnetic species. The coupling constants obtained from the spacing of the third and fourth peaks of the Cu(II) signal are summarized in Table 2. The coupling constant was smaller in the CuX–EN–ROH–O_2 system than in the CuX_2–EN–ROH system. This suggests that the former Cu(II) species has a stronger covalent bond between Cu(II) and the ligand than the latter.[10)] On the other hand, CuCl(OMe) has a more covalent bond character because of strongly electron donating CH_3O ligand than $CuBr_2$ has, and the CuCl(OMe)–EN–MeOH system also indicated a Cu(II) signal with a small coupling constant. These ESR data will also suggest the presence of an alkoxo ligand in the Cu(II)

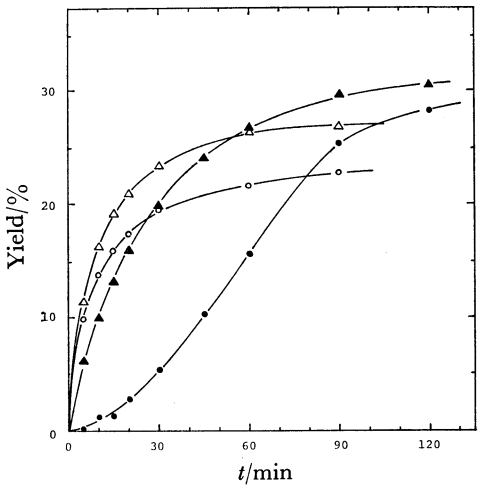


Fig. 4. Time course of the reaction of **1** with EN by CuCl–CuCl(OMe) catalyst.
$[\mathbf{1}]_0 = 5.0 \times 10^{-3}$ mol dm^{-3}, $[EN]_0 = 0.5$ mol dm^{-3}, $[CuCl + CuCl(OMe)]_0 = 2.1 \times 10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF–EtOH 1:1. ○: $r'([CuCl(OMe)]_0/[CuCl + CuCl(OMe)]_0) = 0$, △: $r' = 0.309$, ▲: $r' = 0.751$, ●: $r' = 1.0$.

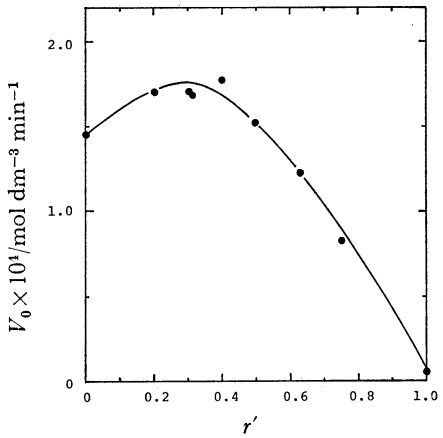


Fig. 5. The dependence of the initial rates (V_0) on the ratio $r'([CuCl(OMe)]_0/[CuCl + CuCl(OMe)]_0)$ in the reaction of **1** with EN.
$[\mathbf{1}]_0 = 5.0 \times 10^{-3}$ mol dm^{-3}, $[EN]_0 = 0.5$ mol dm^{-3}, $[CuCl + CuCl(OMe)]_0 = 2.1 \times 10^{-3}$ mol dm^{-3}, temp 50 °C, solvent THF–EtOH 1:1.

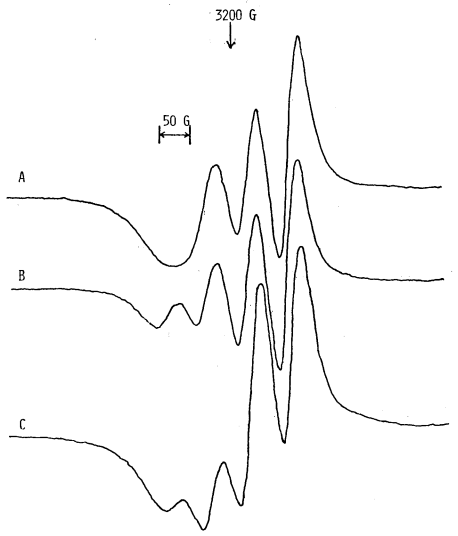


Fig. 6. ESR spectra of Cu catalyst solution at room temperature.
[Cu]$=3.8\times10^{-2}$ mol dm^{-3}, [EN]$=9.2$ mol dm^{-3}. A: CuCl–EN–MeOH–O_2 ($r=0.13$), B: CuCl(OMe)–EN–MeOH, C: $CuCl_2$–EN–MeOH.

TABLE 2. ESR DATA OF CATALYST SOLUTION AT ROOM TEMPERATURE[a)]

Catalyst solution	Coupling constants/G[b)]
CuBr–EN–EtOH–O_2[c)]	72.9
CuCl–EN–MeOH–O_2[d)]	71.2
CuCl(OMe)–EN–MeOH	70.9
$CuBr_2$–EN–EtOH	75.8
$CuCl_2$–EN–MeOH	75.4

a) [Cu] $=3.8\times10^{-2}$ mol dm^{-3}, [EN] $=9.2$ mol dm^{-3}. b) 1 G$=10^{-4}$ T. c) $r([O_2]/[CuBr])=0.142$. d) $r=0.205$.

species formed by the oxidation of Cu(I) with molecular oxygen in EN–ROH solution. Consequently, it is concluded that alkoxycopper(II) species is responsible for the activation of Cu(I) catalyst.

In order to clarify the difference between CuX–EN–EtOH–O_2 ($r=0.1$) and CuX–EN–EtOH catalyst system, the apparent activation energy(ΔE^*) was obtained from Arrhenius plots of the initial rate. Partially oxidized catalyst systems have larger activation energies than CuX systems: ΔE^* of **2**–EN–CuI–O_2 and **2**–EN–CuI were 48.5 kJ mol^{-1} and 37.2 kJ mol^{-1} respectively and ΔE^* of **3**–EN–CuI–O_2 and **3**–EN–CuI was 45.2 kJ mol^{-1} and 38.1 kJ mol^{-1}. On the other hand, the preexponential term(A) was increased by the partial oxidation: The ratio of A between **2**–EN–CuI–O_2 and **2**–EN–CuI was 124, and that between **3**–EN–CuI–O_2 and **3**–EN–CuI was 16. These data indicate that the active copper species in the partially oxidized solution differ from the simple Cu(I) species.

In the preparation of the CuBr–$CuBr_2$–EN–EtOH mixture, blue solids were precipitated and these blue precipitates were also observed, though in much smaller amounts, in the CuBr–EN–EtOH–O_2 system. Both of the blue precipitates indicated the same IR spectra and turned to violet (570 nm) when dissolved into THF–MeOH(2:3) solution. It was reported that the colors of $Cu^{II}(EN)$ and $Cu^{II}(EN)_2$ were pale blue and violet respectively, and that the blue $Cu^{II}(EN)_3$ were very unstable and turned to violet $Cu^{II}(EN)_2$ in solution.[11)] Consequently, the blue precipitate formed in the presence of large excess EN is considered to be $Cu^{II}(EN)_3$ and it will readily turn to violet $Cu^{II}(EN)_2$ in the reaction mixture(THF–EtOH 1:1).

The blue $Cu^{II}(EN)_3$ or violet $Cu^{II}(EN)_2$ obtained from the CuBr–$CuBr_2$–EN–EtOH system were ineffective to the condensation with EN. Therefore, it was considered that the reaction of CuX and oxygen in EN–ROH generated an inactive copper(II) species and an active alkoxycopper(II) species.

In the CuCl–CuCl(OMe) system, the maximum initial rate appeared when the molar ratio(r') of CuCl(OMe) to total copper was about 0.30 (Fig. 5). On the other hand, in the case of oxygen addition, the maximum rate appeared when the ratio(r) was 0.13 (Fig. 2). If the stoichiometry of the oxidation of Cu(I) by molecular oxygen in EN–ROH solution could be followed by Eq. 2 as done for the oxidation of CuCl in pyridine,[12)] these results may be reasonably understood. In Eq. 2, "CuO" and "CuX_2" are active

$$4CuX + O_2 \xrightarrow[\text{EN-ROH}]{} 2\text{"CuO"} + 2\text{"}CuX_2\text{"} \qquad (2)$$

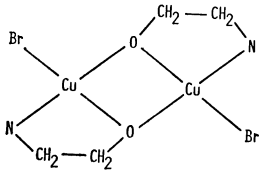
and inactive Cu(II) species, respectively. Thus, in the case of oxygen addition, the maximum initial rate appeared when about a half of the Cu(I) was oxidized. Therefore, the ratio of active Cu(II) to total Cu(II) was 0.25. Thus, the molar ratio of active Cu(II) species to the active copper species was $0.25/(0.5+0.25)=0.33$. This value is in accord with the ratio 0.30 in the CuCl–CuCl(OMe) system under a N_2 atmosphere. The initial rate of CuX–EN–EtOH–O_2 was smaller than that of CuCl–CuCl(OMe). This result can also be understood by the idea that the inactive Cu(II) species was formed along with active Cu(II) species in the CuX–EN–ROH–O_2 system followed by Eq. 2.

Although it has been established that one equivalent of molecular oxygen oxidized 4 molar equivalents of Cu(I),[13–16)] Fig. 2 shows that the oxygen consumption in EN–EtOH solution exceeds the molar ratio $r(O_2/CuBr)=0.25$. Davies *et al.* reported that O_2 consumption of more than $r=0.25$ was observed in the reaction of copper(I) chloride with oxygen in pyrrolidine, piperidine, or cyclam, and they described the possibility of the proton removal from N–H groups.[17)] In our case, the side reaction such as the oxidation of EN may take place, but the side reaction may occur very slowly and would be negligible at the maximum initial rate, since the oxygen uptake of more than the molar ratio of 0.25 took a very long time.

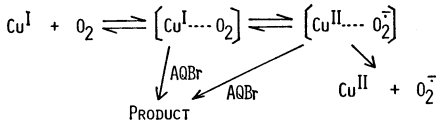
The Presence of an Induction Period. The induction period is observed when CuBr–EN–EtOH–O_2 ($r=0.56$) or CuCl(OMe) only was used (Figs. 1 and 4). The ESR measurement of these condensation systems showed that the Cu(II) signal height gradually decreased. On the contrary, AQBr–EN–$CuBr_2$ system showed no

decrease of Cu(II) signal height under heating. These facts may indicate that a part of the active alkoxycopper(II) species was reduced to active Cu(I), which accelerates the reaction by the combination with the active Cu(II).

These results will shed light on the cooperative behavior between Cu(I) and Cu(II) in the condensation with 2-aminoethanol(AE). As described in the previous papers,[4,5] the induction period in the condensation system of **1** or **2**–AE–CuBr vanished by the addition of $CuBr_2$, which did not activate the condensation with EN. This fact may be reasonably understood by the idea that 2-aminoethanol itself has a OH group and functions as an alkoxide. Hodgson *et al.* reported the molecular structure of Cu(II) complex, prepared by treating $CuBr_2$ with 2-dibutylaminoethanol, to be an oxygen-bridged dimer:[18]

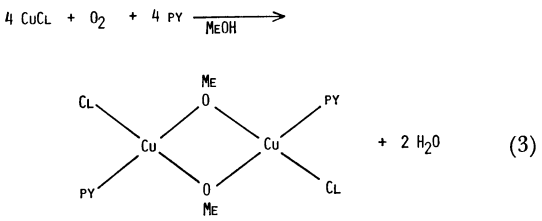


Reaction Pathway. All of the observed results eliminate the possibility of a mechanism as described by Scheme 1,[19] where Cu(I)···O_2 or Cu(II)···superoxide complex functions to activate the condensation reaction:



Scheme 1.

The most plausible reaction pathways are shown in Scheme 2.[19] Under a N_2 atmosphere, only Cu(I) is active; the inactive $Cu^{II}(EN)_2$ is formed by an electron transfer from Cu(I) to AQBr and then the reaction rate decreases with the formation of Cu(II) species. In the presence of oxygen there may be several possible reaction pathways. The reaction of Cu(I) with molecular oxygen in EN–ROH solution affords the active alkoxycopper(II) species and inactive $Cu^{II}(EN)_2$. The CuCl(OMe) and $Cu(OMe)_2$ have been known to exist as a polymer.[20] An oxidation of CuCl in methanol containing pyridine generated di-μ-methoxo-bis[chloropyridinecopper(II)], the structure of which was established by X-ray analysis to be the methoxo bridged dimer (Eq. 3):[14]

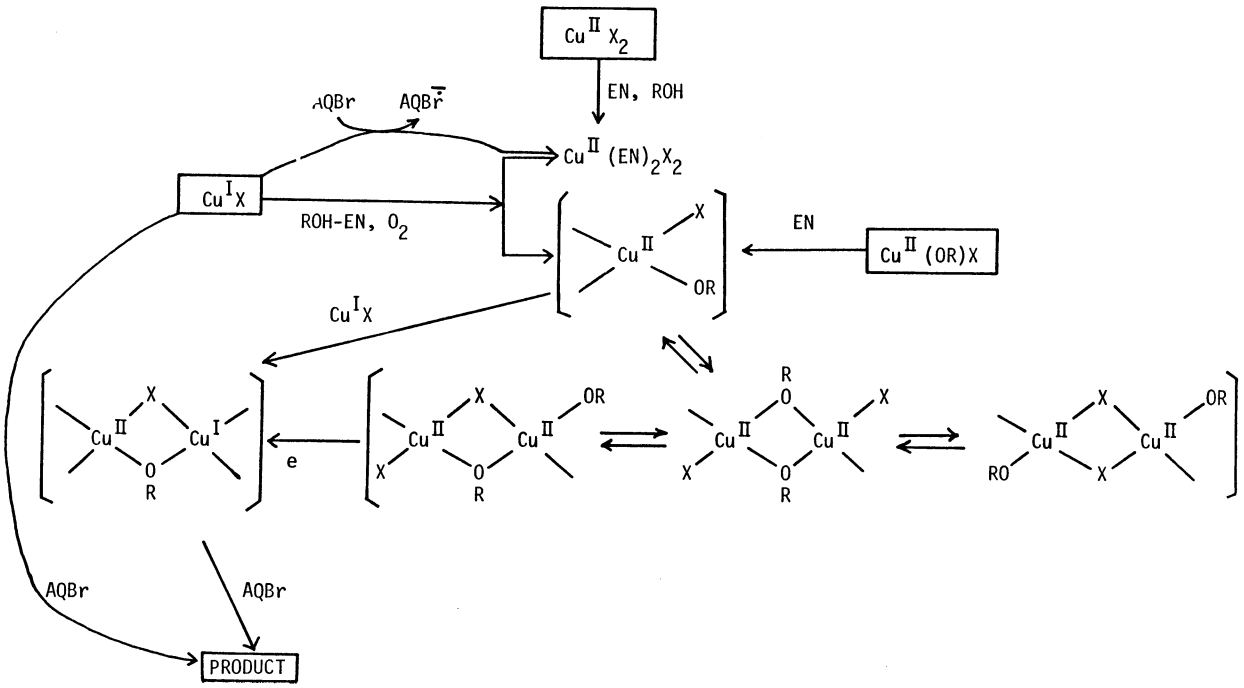


(3)

Therefore, the alkoxycopper(II) species formed by the partial oxidation of Cu(I) in EN–EtOH solution would probably have an ability to form a dimeric structure with Cu(I) or Cu(II) by alkoxo bridge.

One possible pathway is as follows: The Cu^{I}···Cu^{II} mixed valence complex is formed by the reaction between monomeric alkoxycopper(II) species and Cu(I). The cooperative behavior of Cu(I) and Cu(II) may be caused by this dimeric species. The pathway catalyzed by Cu(I) alone also operates independently. On the other hand, in the case of CuCl(OMe) alone the catalytic activity increased gradually with the formation of Cu(I). This result may suggest that alkoxo and/or halogen bridged dimeric species is reduced to give active Cu^{I}···Cu^{II} mixed valence complex.

However, the present data do not exclude another



Scheme 2.

pathway on which Cu(I) and Cu(II) do not form any dimeric species but act cooperatively to enhance the catalytic activity.

These results are helpful in exploration of the more active catalyst of the Ullmann condensation reaction.

Further detailed examinations of the cooperative behavior of Cu(I) and Cu(II) are progress and will be reported in the near future.

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