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Oxidative Dehydrogenation of Bis(salicylideneaminato)copper(II) Complex in Pyridine and Formation of 2-Cyanophenolato Complex

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The copper(II) complex of salicylideneamine (salamH) reacts with molecular oxygen in pyridine to give the 2-cyanophenolato complex, $[Cu(2\text{-}CNphO)_2(py)_2]$, in good yield, where 2-CNphOH and py denote 2-cyanophenol and pyridine, respectively. This complex was characterized by the infrared and electronic spectra and by its magnetic susceptibilities, and was compared with the authentic complex, $[Cu(2\text{-}CNphO)_2(py)_2]$. The mechanism for the oxidation of the coordinated imino groups is discussed.

It is well known that copper(II) salts catalyze significantly the oxidation of organic substances by molecular oxygen.[1] Brackman *et al.*[2] have reported that the ammoxidation of alcohols and aldehydes catalyzed by copper(II) salts gives the corresponding nitriles in good yields, and have proposed that the imino function (RCH=NH) which formed by condensation of aldehyde with ammonia was oxidized to nitrile via an intermediate of an imino radical (RCH=N·), involving a Cu(II)/Cu(I) redox system. Misono *et al.*[3] have investigated the kinetics of the formation of benzonitrile from benzaldehyde and ammonia catalyzed by some copper compounds, and have proposed that benzilideneamine is an important intermediate. They have reported that 2-cyanophenol was formed by thermal decomposition of bis(salicylideneaminato)copper(II), $[Cu(salam)_2]$.[4]

The oxidative dehydrogenation of amino and alkylamino groups coordinated to metal ions has been reported.[5] Diamond *et al.*[6] have found that pentaammine(benzylamine)ruthenium(II) ion reacts with molecular oxygen to give pentaammine(benzonitrile)-ruthenium ion. Keene *et al.*[7] have reported that the complexes, $[Ru(bpy)_2(NH_2CH_2R)_2]^{+2}$($NH_2CH_2R$= allylamine, benzylamine, and butylamine) were oxidized chemically and electrochemically to give the corresponding bis(nitrile) complexes, $[Ru(bpy)_2(NCR)_2]^{+2}$ and proposed that the reactions proceed by initial oxidation of Ru(II) to Ru(III), followed by a series of stepwise dehydrogenation reactions which occur via the imine intermediate. Recently, the oxidative dehydrogenation of the coordinated secondary amine moieties to the copper atom has been reported for Cu(II)–4,4′-(ethane-1,2-diyldiimino)bis(pent-3-en-2-one) complex[8] and bi-Cu(I)–macrocyclic complex.[9]

In this paper we wish to report that $[Cu(salam)_2]$ reacts with molecular oxygen to give quantitatively the 2-cyanophenolato complex. This reaction should afford good information on the mechanism of the ammoxidation catalyzed by copper compounds.

Experimental

Preparation of Copper(II) Complexes with Salicylideneamine and Its Analogs. All the complexes with the Schiff bases used in this work were obtained by the method described in the literature. They are abbreviated as follows: Bis(salicylideneaminato)copper(II): $[Cu(salam)_2]$[10a]; bis(substituted salicylideneaminato)copper(II): $[Cu(X\text{-}salam)_2]$[10b], where X can be 5-Me, 3-Me, 3-MeO, 4-Cl, 5-Br, 5,6-Benzo, and 5-NO_2; bis[1-(*o*-hydroxyphenyl)ethylideneaminato)copper(II): $[Cu(hpam)_2]$[10c]; bis(*N*-methylsalicylideneaminato)-copper(II): $[Cu(N\text{-}Mesalam)_2]$[10c].

Isolation of Oxidized Products. *Oxidized Product of* $[Cu(salam)_2]$: A pyridine solution (300 cm^3) of $[Cu(salam)_2]$ (1.0 g) was kept at 70 °C, with dried air bubbled through it. The green solution turned brown gradually. The reaction was followed by monitering the visible absorption spectra of small portions of the solution at regular intervals. The spectral changes were no longer observed after *ca.* 7 h; the resulting solution was evaporated under reduced pressure. The brown solids were collected on a glass filter, washed with hexane, and dried *in vacuo*. The yield was quantitative. The product is soluble in pyridine (py), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), slightly soluble in dichloromethane, methanol, and benzene, but insoluble in water. This was reprecipitated from a mixture of pyridine and ether.

The oxidized product of $[Cu(salam)_2]$ could be obtained from the reaction between its pyridine solution and an aqueous solution of hydrogen peroxide (30%) at room temperature. This was identified to be the same product as the above. The reaction of $[Cu(salam)_2]$ with molecular oxygen in dioxane was found to give the pale brown product. This is soluble in pyridine, but insoluble in noncoordinating solvents; its formula is $[Cu(2\text{-}CNphO)(OH)]$.

All the reaction conditions are summarized in Table 1, together with the empirical formulas of the products. The

TABLE 1. OXIDATION CONDITIONS FOR COPPER(II) COMPLEXES AND THEIR PRODUCTS

Complex[a)]	Solvent[b)]	Temp/°C	Time/h	Atmosphere	Reaction product: Yield/%	Formula	Color
$[Cu(salam)_2]$	Pyridine	70	7	Air	95	$[Cu(2\text{-}CNphO)_2(py)_2]$	Greenish brown
$[Cu(salam)_2]$	Pyridine[c)]	30	0.5	Air	90	$[Cu(2\text{-}CNphO)_2(py)_2]$	Greenish brown
$[Cu(salam)_2]$	Dioxane	70	7	Air	60	$[Cu(2\text{-}CNphO)(OH)]$	Pale brown
$[Cu(hpam)_2]$	Pyridine	80	10	Air	90	$[Cu(2\text{-}CNphO)_2(py)_2]$	Greenish brown
$[Cu(N\text{-}Mesalam)_2]$	Pyridine	110	100	O_2		No reaction	

a) Complex: 3 mmol. b) Solvent: 300 cm^3. c) Addition of aqueous H_2O_2 solution (30%, 6 mmol).

TABLE 2. ANALYTICAL DATA, MAGNETIC MOMENTS, AND ν(CN) FREQUENCIES FOR 2-CYANOPHENOLATO COPPER COMPLEXES

Complex	Found (%)			Calcd (%)			μ_{eff}[b)]	ν(CN)[c)]
	C	H	N	C	H	N	BM	cm^{-1}
$[\mathrm{Cu(2\text{-}CNphO)_2(py)_2}]$[a)]	62.75	3.65	12.50	62.94	3.96	12.23	2.05	2220, 2205
$[\mathrm{Cu(2\text{-}CNphO)_2(py)_2}]$	62.91	3.93	12.07	62.94	3.96	12.23	1.91	2220, 2205
$[\mathrm{Cu(2\text{-}CNphO)_2(bpy)}]$	63.03	3.43	11.90	63.22	3.54	12.29	1.91	2220, 2208
$[\mathrm{Cu(2\text{-}CNPhO)(OH)}]$	42.46	2.32	7.16	42.31	2.53	7.05	1.46	2238

a) Oxidized product. b) Measured at room temperature. c) Measured in Nujol mulls. ν(CN): 2237 cm^{-1} for 2-CNphOH; 2205 cm^{-1} for 2-CNphONa.

analytical data for these products are given in Table 2, along with their magnetic moments determined at room temperature and the frequencies due to ν(CN).

Isolation of 2-Cyanophenol from the Oxidized Product of $[\mathrm{Cu(salam)_2}]$. The oxidized product (0.1 g) of $[\mathrm{Cu(salam)_2}]$ was dissolved in pyridine (10 cm^3). A solution (100 cm^3) of 1 M (1 M = 1 mol dm^{-3}) hydrochloric acid was added to it. Hydrogen sulfide gas was passed through the solution for 10 min, followed by passing nitrogen gas for 20 min. The black precipitates were filtered and washed with ether. The filtrate was extracted with ether (50 cm^3). The ethereal washings and extract were combined and dried over anhydrous sodium sulfate, and then evaporated under reduced pressure to yield tan-yellow solids. They were recrystallized from hexane to give white crystals. The yield was 0.04 g. This was identified to be 2-cyanophenol from the elemental analysis, infrared spectrum, and melting point (96.5 °C).

Preparation of 2-Cyanophenolato Complexes. *Bis(2-cyanophenolato)bis(pyridine)copper(II),* $[\mathrm{Cu(2\text{-}CNphO)_2(py)_2}]$: This complex was obtained by a modification of the method described in the literature.[11)] To an aqueous solution (20 cm^3) containing $\mathrm{CuSO_4\cdot 5H_2O}$ (0.75 g, 3 mmol) and pyridine (0.48 g, 6 mmol), an aqueous solution (15 cm^3) of 2-cyanophenol (0.72 g, 6 mmol) and sodium hydroxide (0.24 g, 6 mmol) was added dropwise with stirring. The olive green solids which precipitated were collected on a glass filter, and washed with water, and with small volumes of ethanol and ether, and then dried *in vacuo*. They were recrystallized from dichloromethane to give greenish brown crystals.

2,2′-Bipyridinebis(2-cyanophenolato)copper(II), $[\mathrm{Cu(2\text{-}CNphO)_2(bpy)}]$. This complex was obtained in a similar way to that used for the above complex, using 2,2′-bipyridine in place of pyridine.

The analytical data for the 2-cyanophenolato complexes are given in Table 2, together with their magnetic moments determined at room temperature and the frequencies due to ν(CN).

Materials. All reagents were of reagent grade. The solvents were purified in the usual manner.

Measurements. The UV, VIS, and NIR spectra were recorded on a Hitachi 340 recording spectrophotometer. The diffused reflectance spectra were obtained by using the above instrument along with a Hitachi R-10 A integrating sphere unit and a NIR integrating sphere unit. The infrared spectra and magnetic susceptibilities were obtained by the method described elsewhere.[12)]

Results and Discussion

We have found that a pyridine solution of $[\mathrm{Cu(salam)_2}]$ changed the color from green to greenish brown on being allowed to stand for a few days at room temperature under air. We are interested in the cause of such a color change.

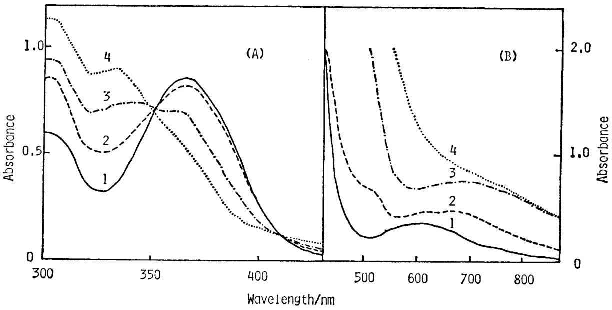


Fig. 1. Absorption spectral changes of pyridine solutions of $[\mathrm{Cu(salam)_2}]$ at 70 °C under air. (A); [Complex] = 8×10^{-5} M, 1): reaction time = 0, 2): 265, 3): 325, 4): 385 min. (B); [Complex] = 8×10^{-3} M, 1): reaction time = 0, 2): 26, 3): 80, 4): 385 min. Cell length: 1 cm.

Absorption Spectral Changes. Figure 1 shows the absorption spectral changes of a pyridine solution of $[\mathrm{Cu(salam)_2}]$ at 70 °C under air. The absorption bands at 366 and 598 nm observed for the original spectrum can be assigned to charge-transfer and ligand field transitions, respectively. The absorption spectrum changes remarkably with time, showing the isosbestic points at 351 and 408 nm; the absorption band at 366 nm decreased in intensity and a new absorption band appeared at 333 nm (in Fig. 1-A), and the absorption band at 598 nm was shifted to lower energies with increasing the intensity around 500 nm (in Fig. 1-B). These spectral changes indicate that a marked change occurred in the coordinated ligand and the environment around the central copper atom.

Characterization of the Reaction Product. The analytical data for the reaction product of $[\mathrm{Cu(salam)_2}]$ in pyridine are in agreement with an empirical formula of $[\mathrm{Cu(2\text{-}CNphO)_2(py)_2}]$. The magnetic moment is 2.05 BM. The electronic spectrum measured in pyridine shows an intense absorption band around 23000 cm^{-1} and a broad absorption band around 14000 cm^{-1} (Fig. 2). These bands can be assigned to a charge-transfer transition between the phenolic oxygen atom and copper atom and the ligand field transitions from higher energies.[13)] Figure 3 shows the infrared spectra of $[\mathrm{Cu(salam)_2}]$ and its reaction product. In the latter compound, the absorption bands at 3280 and 1625 cm^{-1} are due to ν(N–H) and ν(C=N), respectively, which were observed for [Cu(salam)$_2$], disappeared and new absorption bands were observed at 2220 and 2205 cm^{-1} and at 1221, 1072, and 691 cm^{-1}. The bands at 2220 and 2205 cm^{-1} can be assigned to the stretching vibrations of nitrile group from their frequencies. The latter three bands can be assigned to the characteristic bands of the coordinated pyridine. These results indicate that the imino groups coordinated to the copper atom were oxidized to the nitrile groups by the oxidative dehydrogenation.

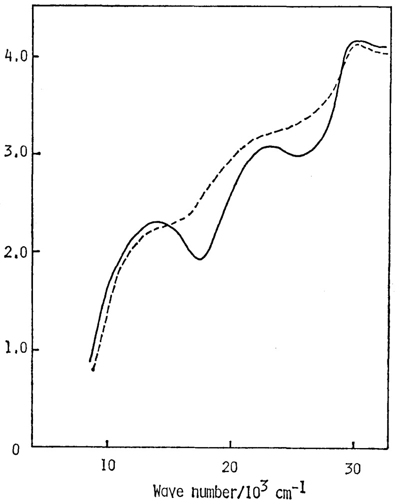


Fig. 2. Electronic spectra in pyridine.
- - -: Oxidized product of [Cu(salam)$_2$] in pyridine, ——: authentic complex, [Cu(2-CNphO)$_2$(py)$_2$].

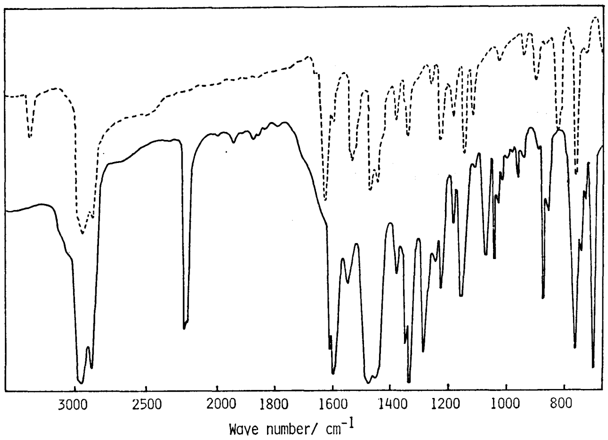
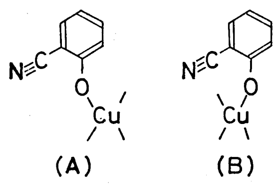


Fig. 3. Infrared spectra in Nujol mulls.
- - -: [Cu(salam)$_2$], ——: oxidized product of [Cu(salam)$_2$] in pyridine.

The authentic complex which was prepared by the reaction of $CuSO_4$, 2-cyanophenol, and pyridine has the same composition, formulated as [Cu(2-CNphO)$_2$(py)$_2$], and shows the same infrared spectrum as that for the oxidized product (Table 2). In the electronic spectra, the absorption maxima for the oxidized product are in agreement with those for the authentic complex (Table 3). However, the intensities around 19000 cm^{-1} are slightly higher in the oxidized product than those in the authentic complex. This may be caused by the difference in orientation of the coordinated 2-cyanophenolato ligands between these complexes as shown below. A molecular model for them suggests that a free rotation of the 2-CNphO at the Cu–O bond is restricted by the coordinated pyridine molecules. Therefore, on the basis of steric repulsion, the form (A) is a possible configuration for the authentic complex. On the contrary, the form (B) may be maintained in the oxidized product, because the original [Cu(salam)$_2$] has a *trans*-planar configuration. In this form, a planar configuration around the central copper atom may distort to a tetrahedral configuration by steric requirement. This is one reason why high intensities are observed in the oxidized product.



The magnetic moment of the authentic complex is a slightly lower value (1.91 BM) than that of the oxidized product. This may be caused by a slight difference between configurations of the authentic and the oxidized complexes, as mentioned above.

It should be noted that the doublet bands due to ν(CN) are observed for the 2-cyanophenolato complexes and both peaks are of equal intensity. Moreover, the C–O stretching vibrations of the coordinated 2-cyanophenol are observed around 1320 cm^{-1} as doublet bands. These results suggest that 2-cyanophenolato ligands coordinate to the copper atom in two different fashions. It has been reported that nitrile groups can coordinate to metal ions through either nitrogen atom or π-bond of nitrile.[14] In the former

TABLE 3. ELECTRONIC SPECTRAL DATA FOR 2-CYANOPHENOLATO COPPER COMPLEXES

Complex	Solvent	$\frac{\nu_{max}}{10^3\ cm^{-1}}$ (log ε)				
[Cu(2-CNphO)$_2$(py)$_2$]	Pyridine		14.0(2.23)	23.2(3.10)	30.3(4.15)	
	DMF	12.4 sh	14.4(1.86)	23.4(2.80)	30.3(3.38)	33.4(4.00)
	Solid	12.7 sh	16.2	23.1	31.1	33.1
[Cu(2-CNphO)$_2$(py)$_2$][a]	Pyridine		14.4(2.20)	22.5(3.20)	30.5(4.11)	
	Solid	13.0 sh	15.8 sh	23.1	31.1	33.1
[Cu(2-CNphO)$_2$(bpy)]	Solid		15.9	23.1	30.0	34.1

a) Oxidized product. sh: Shoulder.

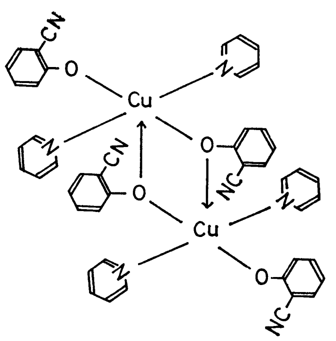


Fig. 4. Proposed structure for $[Cu(2\text{-}CNphO)_2(py)_2]$.

case, the ν(CN) frequencies shifted to higher energies than that of the free ligand, whereas in the latter case, they shifted to lower energies. In the present copper complexes, the ν(CN) frequencies are within a range of 2237 cm^{-1} for 2-CNphOH to 2205 cm^{-1} for 2-CNphONa (Table 2). This indicates that coordination of nitrile groups is not involved in these copper complexes. Therefore, we propose a binuclear structure for $[Cu(2\text{-}CNphO)_2(py)_2]$ as shown in Fig. 4 in which the copper atoms are bridged by the phenolic oxygen atoms. This structure could be easily broken up in pyridine solution. The infrared spectra taken on pyridine solutions of the oxidized and authentic complexes showed only one band due to ν(CN) at 2212 cm^{-1}. Such a binuclear structure has been revealed by X-ray analysis of [Cu(salen)], where salen denotes dianion of *N,N'*-disalicylideneethylenediamine, and its magnetic data (1.84 to 2.0 BM) are not inconsistent with the present results.[15] The facts that the original complex, $[Cu(salam)_2]$, has a *trans*-configuration[16] and that the two bands due to ν(CN) are of equal intensity suggest that a *trans*-form is probable for the oxidized complex, although either a *trans*- or *cis*-configuration is possible for $[Cu(2\text{-}CNphO)_2(py)_2]$. On the other hand, the complex, $[Cu(2\text{-}CNphO)_2(bpy)]$, may have a *cis*-configuration and the infrared spectrum shows two absorption bands due to ν(CN). Thus, this complex also may have a binuclear structure in the solid state.

Mechanism for Oxidative Dehydrogenation. In order to clarify the mechanism for the oxidative dehydrogenation of $[Cu(salam)_2]$ the following effects on the oxidation were investigated.

Solvent Effects: The $[Cu(salam)_2]$ complex was allowed to react with molecular oxygen in various solvents such as pyridine, dioxane, ethanol, and benzene under these conditions: The concentration of the complex was 8×10^{-5} M, at 70 °C, and under air. Absorption spectral changes were observed in the former three solvents, but no spectral change was observed in benzene. The time required for the oxidation increased in the order of: pyridine (4.5 h)<dioxane (5 h)<ethanol (20 h). The oxidized product could be obtained from the dioxane solution of $[Cu(salam)_2]$ and was identified to be [Cu(2-CNphO)(OH)], as mentioned in Experimental.

Effects of Added Bases: The oxidative dehydrogenation of $[Cu(salam)_2]$ in dioxane has been found to be accelerated by the addition of organic aromatic bases such as 1,10-phenanthroline (phen), 2,2'-bipyridine (bpy), and pyridine as shown in Fig. 5. The apparent reaction rates increased in the order of phen> bpy>py, and increased with an increase in concentration of the added base.

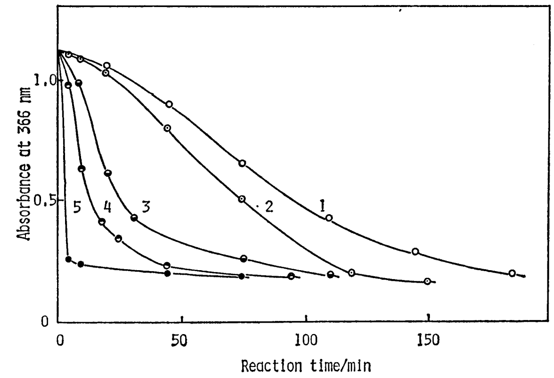


Fig. 5. Effects of added bases to dioxane solutions of $[Cu(salam)_2]$ on oxidation at 70 °C under air. Added bases; 1): none, 2): pyridine (10^{-3} M), 3): 2,2'-bipyridine (10^{-3} M), 4): bpy (10^{-2} M), 5): 1,10-phenanthroline (10^{-3} M). [Complex]=10^{-4} M, Cell length: 1 cm.

Concentration of Complex: The reaction of $[Cu(salam)_2]$ in pyridine was made by varying the concentration from 8×10^{-5} M to 1.6×10^{-3} M. All the reactions showed some induction periods. Thus, the maximal rate constants (k_{obsd}) were calculated graphically from the constant slopes after the induction periods obtained in the plots of $\ln(a-x)$ *vs.* reaction time, where a and x are the concentrations at time equal to t_0 and t, respectively, with assumption of the following equation:

$$[Cu(salam)_2] + O_2 \xrightarrow[py]{k_{obsd}} [Cu(2\text{-}CNphO)_2(py)_2] + 2H_2O. \qquad (1)$$

A plot of $\log(k_{obsd})$ *vs.* $\log a$ shows a linear relation with a slope nearly equal to unity, as shown in Fig. 6. This indicates that the oxidative dehydrogenation of $[Cu(salam)_2]$ depends on the first order of the complex concentration. The induction periods are found to be decreased with an increase in the complex concentration.

Effects of Substituents on Aromatic Ring: Figure 7 shows the plots of the decreases in the complex concentration against reaction time. The complex concentration was calculated according to the following equation:

$$x = a(A_0-A_t)/(A_0-A_\infty), \qquad (2)$$

where A_0, A_t, and A_∞ represent the absorbances at time equal to t_0, t, and at the final state, respectively. Clearly, the induction periods and the maximal rate constants are affected by the substituents on the aromatic ring; the electron-donating groups accelerate the reaction, whereas the electron-withdrawing groups retard it. The maximal rate constants increased in the order of 5-Me>3-Me>H>3-MeO>5-Br>4-Cl> 5,6-Benzo>5-NO_2, as listed in Table 4. It should be noted that $[Cu(5\text{-}NO_2salam)_2]$ did not show any spectral changes under the same conditions.

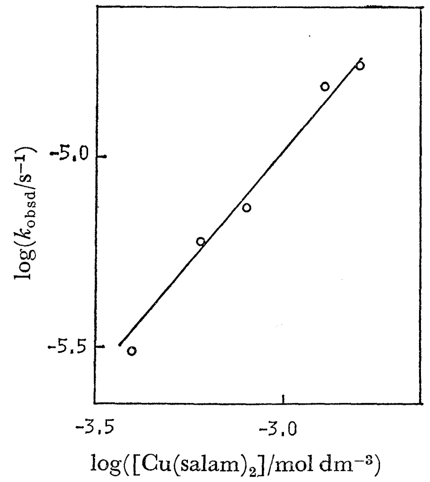


Fig. 6. A plot of $\log(k_{obsd})$ *vs.* $\log[Cu(salam)_2]$.

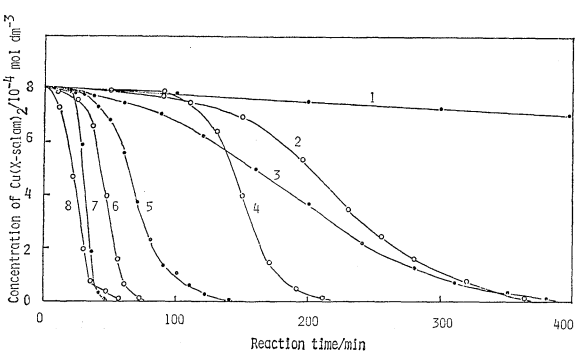


Fig. 7. Effects of substituents of $[Cu(X\text{-}salam)_2]$ on oxidation in pyridine at 70 °C under air. $[Complex]=8\times10^{-4}$ M, 1): X=5-NO_2, 2): 4-Cl, 3): 5,6-Benzo, 4): 5-Br, 5): 3-MeO, 6): H, 7): 5-Me, 8): 3-Me.

TABLE 4. EFFECTS OF THE SUBSTITUENTS OF AROMATIC RING ON THE MAXIMAL RATE CONSTANTS AND THE INDUCTION PERIODS FOR THE OXIDATIVE DEHYDROGENATION OF $[Cu(X\text{-}salam)_2]$ IN PYRIDINE AT 70 °C UNDER AIR

Substituent X	Maximal rate constant $\frac{k_{obsd}}{10^{-4}\ s^{-1}}$	Induction period $\frac{Time}{min}$
5-Me	27.8	25
3-Me	15.2	8
H	13.5	40
3-MeO	8.8	50
5-Br	8.7	110
4-Cl	2.8	180
5,6-Benzo	2.1	95
5-NO_2	—	—

Concentration of complexes was 8×10^{-4} M.

Effects of Substituents on Nitrogen and Carbon Atoms of Imino Groups: Several copper(II) complexes, $[Cu(hpam)_2]$, $[Cu(N\text{-}Mesalam)_2]$, $[Cu(salen)]$, and $[Cu(N\text{-}OHsalam)_2]$, were made to react in pyridine at 70 °C under air, where *N*-OHsalamH denotes salicylaldehyde oxime. Among them, the carbon atom-substituted complex, $[Cu(hpam)_2]$, gave the oxidized product, $[Cu(2\text{-}CNphO)_2(py)_2]$, while the other nitrogen atom-substituted complexes did not show any oxidation under the above conditions. These results indicate that the oxidative dehydrogenation of $[Cu(salam)_2]$ may be initiated by a splitting of the N–H bond of the coordinated imino groups.

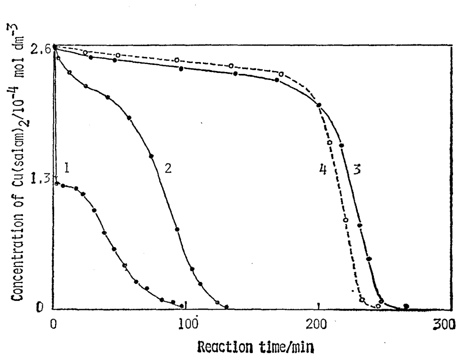


Fig. 8. Effects of added hydrogen peroxide on oxidation of $[Cu(salam)_2]$ in pyridine at 70 °C under air. $[Complex]=2.6\times10^{-4}$ M, 1): $[H_2O_2]=2.6\times10^{-4}$ M, 2): 2.6×10^{-5} M, 3): 2.6×10^{-6} M, 4): no addition.

Effects of Addition of Hydrogen Peroxide: Figure 8 shows the plots for the oxidation of $[Cu(salam)_2]$ *vs.* reaction time when various concentrations of hydrogen peroxide were added to the pyridine solutions of the complex at 70 °C under air. With the addition of an equimolar amount of hydrogen peroxide to the complex, a nearly half-mole of the complex was oxidized within 5 min, and the oxidation was completed within 100 min after showing a short induction period (curve 1). With the addition of one-tenth amount of hydrogen peroxide, the initial induction period disappeared, but the reaction rate retarded with time, and a fast oxidation again occurred after 50 min (curve 2). On the other hand, with the addition of one-hundredth of hydrogen peroxide, the reaction pattern (curve 3) was similar to the case of no addition (curve 4).

The available results suggest that the oxidative dehydrogenation of the coordinated imino groups in pyridine may occur according to the following scheme:

$$Cu(II)(R\text{-}CH{=}NH)_2 \rightleftharpoons Cu(I)(R\text{-}CH{=}\dot{N}H^+)(R\text{-}CH{=}NH) \qquad (3)$$

$$Cu(I)(R\text{-}CH{=}\dot{N}H^+)(R\text{-}CH{=}NH) + O_2 \longrightarrow Cu(II)(R\text{-}CH{=}\dot{N})(R\text{-}CH{=}NH) + HO_2\cdot \qquad (4)$$

$$Cu(II)(R\text{-}CH{=}\dot{N})(R\text{-}CH{=}NH) + HO_2\cdot \longrightarrow Cu(II)(R\text{-}CN)(R\text{-}CH{=}NH) + H_2O_2 \qquad (5)$$

$$Cu(II)(R\text{-}CN)(R\text{-}CH{=}NH) + H_2O_2 \xrightarrow{py} Cu(II)(R\text{-}CN)_2(py)_2 + 2H_2O. \qquad (6)$$

The initiation reaction is considered to be a thermal one-electron transfer from the imino nitrogen atom to the copper atom, as shown in Eq. 3. The induction periods observed in the oxidation investigated here may be due to the back reaction in Eq. 3, which is the oxidation of copper(I) to copper(II) by the imino radical. In the presence of molecular oxygen, the reactions shown in Eqs. 4 and 5 may occur in competetion with the above back reaction.

The effects of the added aromatic bases (Fig. 5) can be related to Eq. 3. That is, these bases can function as an acceptor of proton (H^+) liberated and as a promoter of electron transfer from the imino group to the copper atom by coordination. Thus the increasing order of the apparent reaction rates (phen>bpy>py) is not correlated to the order of the pK_a values (py>phen>bpy).

The substituent effects that the electron-donating groups on the aromatic ring accelerated the reaction rates and shortened the induction periods can be explained by taking account of Eqs. 3 and 4; the electron-donating groups may facilitate the electron transfers from the imino group to the copper atom (Eq. 3) and from the copper atom to molecular oxygen (Eq. 4). Such a behavior has been found in the autoxidation of the substituted phenylhydroxylamines.[17] And also the autoxidation of phenylhydroxylamine has been found to be accelerated by copper(II) ion.[18]

As described above, the oxidative dehydrogenation investigated here proceeded rapidly after showing induction periods. This indicates that the radical chain autoxidation may be involved in this system. The chain reaction may propagate by the direct attack of molecular oxygen to the imino radical and by the catalytic decomposition of hydrogen peroxide with the copper complex. A tentative scheme for the radical chain autoxidation is proposed, as follows:

$$\mathrm{Cu(II)(R\text{-}CH{=}\dot{N})(R\text{-}CH{=}NH)} + O_2 \longrightarrow \mathrm{Cu(II)(R\text{-}CN)(R\text{-}CH{=}NH)} + HO_2\cdot \qquad (7)$$

$$\mathrm{Cu(II)(R\text{-}CN)(R\text{-}CH{=}NH)} + HO_2\cdot \longrightarrow \mathrm{Cu(II)(R\text{-}CN)(R\text{-}CH{=}\dot{N})} + H_2O_2 \qquad (8)$$

$$\mathrm{Cu(II)(R\text{-}CN)(R\text{-}CH{=}\dot{N})} + O_2 \longrightarrow \mathrm{Cu(II)(R\text{-}CN)_2} + HO_2\cdot \qquad (9)$$

Decomposition of hydrogen peroxide

$$\mathrm{Cu(II)(R\text{-}CH{=}NH)_2} + H_2O_2 \longrightarrow \mathrm{Cu(I)(R\text{-}CH{=}NH)_2} + HO_2\cdot + H^+ \qquad (10)$$

$$\mathrm{Cu(I)(R\text{-}CH{=}NH)_2} + H_2O_2 \longrightarrow \mathrm{Cu(II)(R\text{-}CH{=}NH)_2} + HO\cdot + HO^- \qquad (11)$$

$$\mathrm{Cu(I)(R\text{-}CH{=}\dot{N}H^+)(R\text{-}CH{=}NH)} + H_2O_2 \longrightarrow \mathrm{Cu(II)(R\text{-}CH{=}\dot{N})(R\text{-}CH{=}NH)} + HO\cdot + H_2O \qquad (12)$$

followed by abstraction of hydrogen atom with $HO_2\cdot$ and $HO\cdot$. The above reaction scheme is supported by the results that the reactions of [Cu(salam)$_2$] with O_2^-[19] and H_2O_2 in pyridine occurred readily at room temperature.

In the catalytic decomposition of hydrogen peroxide, Sigel *et al.*[20] have found that coordinately saturated copper(II) complexes (four-coordinate complexes) are essentially inactive. And Kochi has pointed out that in the reaction of hydrogen peroxide catalyzed by iron ion the reaction represented in Eq. 13 is more facile than that represented in Eq. 14, because hydrogen peroxide is a strong oxidizing agent but only a mild reducing agent.[21]

$$Fe^{II} + H_2O_2 \longrightarrow Fe^{III} + HO\cdot + HO^- \qquad (13)$$

$$Fe^{III} + H_2O_2 \longrightarrow Fe^{II} + HO_2\cdot + H^+ \qquad (14)$$

Therefore, in the present oxidation, the reaction represented in Eq. 12 is considered to be more important than those represented in Eqs. 10 and 11.

As shown in Fig. 8, the initial induction period was made to disappear by the addition of an equimolar amount of hydrogen peroxide to the complex, but a short induction period was observed again after producing about a half oxidation of the complex. Furthermore, the catalytic amount of hydrogen peroxide ($[H_2O_2]$:[complex]=1:100) had no effect on the reaction. These results indicate that the radical chain sequence induced by decomposition of hydrogen peroxide may be not so long. These facts suggest that the rate-determining step in the present oxidative dehydrogenation of [Cu(salam)$_2$] is the splitting of the N–H bond of the coordinated imino group, along with the reduction of copper(II) to copper(I), as shown in Eq. 3.

We have also found that [Ni(salam)$_2$] and [Co^{II}(salam)$_2$] were oxidized by molecular oxygen in pyridine to give their 2-cyanophenolato complexes. In the nickel complex, the severe conditions were required to obtain the fully oxidized product: for 120 h at 115 °C under O_2 1 atm. This suggests that the oxidative dehydrogenation of [Ni(salam)$_2$] may be initiated by the electron transfer from the coordinated imino group to molecular oxygen without change in the oxidation state of the nickel ion. On the other hand, the oxidized product of [Co^{II}(salam)$_2$] was obtained in the conditions similar to the case of [Cu(salam)$_2$]. In the cobalt complex, the initial reaction is considered to be the oxidation of Co(II) to Co(III) by molecular oxygen, followed by the stepwise dehydrogenation of the coordinated imino groups through a redox couple of Co(II)/Co(III) as in the copper case. Details on the oxidation of these Ni(II) and Co(II) complexes will be reported in the near future.

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