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Effects of Chelated and Non-chelated Transition Metal Ions on the Photoreactions of Pyridinecarboxylic Acids in Aqueous Solutions

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Iron(III) and copper(II) chelated by 2-pyridinecarboxylate bring about the photochemical decarboxylation of the ligand *via* the electron transfer from carboxylate to metal ions to give pyridine and 2,2′-bipyridine (for Fe(III)) or 2-pyridinol (for Cu(II)). In the presence of iron(III), ruthenium(III), and copper(II), 3-pyridinecarboxylic acid gives photochemically 2,2′-bipyridine-3,5′-dicarboxylic acid without decarboxylation. 4-Pyridinecarboxylic acid is photo-resistant both in the presence and in the absence of iron(III) and copper(II).

Metal ions, especially transition metal ions, have profound effects on the photoreactions of organic compounds.[1)] Recently, long range electron transfer mechanism has been proposed for the metal ion-catalyzed photo-oxidation of olefins.[2)] Effects of metal ions on the photoreactions of carboxylic acids have extensively been studied,[3)] together with their photoreactions in the absence of metal ions.[4)] A metal ion may have different effects on the photoreaction depending on whether it is coordinated by an organic ligand or not. Pyridinecarboxylic acids afford a good system to investigate the differences between the coordinated and the non-coordinated metal ions: 2-pyridinecarboxylic acid forms very stable chelate bonds with many metal ions, whereas 3- and 4-pyridinecarboxylic acid form no such stable chelate bonds.[5)]

We have reported some results on the photoreactions of 2- and 3-pyridinecarboxylic acid in the absence of metal ions. The irradiation of 3-pyridinecarboxylic acid in an aqueous solution with 254 nm light gives 2-hydroxy-3-pyridinecarboxylic acid in the pH range of 0—2 and 2,3′-bipyridine-5-carboxylic acid in the pH range of 4—6.[6)] 2-Pyridinecarboxylic acid gives photochemically 6-hydroxy-2-pyridinecarboxylic acid in an acidic aqueous solution.[7)]

Results and Discussion

The photoreactions of pyridinecarboxylic acids in the presence of several metal ions are summarized in Tables 1 and 2. Among the metal ions, iron(III) and copper(II) have remarkable effects on the photochemical processes of the acids. The metal ion effects on 2-pyridinecarboxylic acid (**1**) are different from those on 3-pyridinecarboxylic acid (**2**). In the case of **1**, which forms stable chelate bonds with metal ions,[8)] the products *via* decarboxylation are significant. The 254 nm light irradiation of 2-pyridinecarboxylatoiron(III) complex gives pyridine (**3**), 2,2′-bipyridine (**4**) and a trace of 2-pyridinol. The photoreaction

Table 1. Photoreactions of 2-pyridinecarboxylatometal complexes in aqueous solutions
2-PyCOO = 2-Pyridinecarboxylato, Irradiated with a low pressure mercury lamp.

Complex	10^4[Complex] / mol dm^{-3}	Additive and its concn	Irr. time / h	Yield of product/%[a)] **3**	**4**	**5**	Recovery of starting material/%
[Fe_2(2-PyCOO)$_4$(OH)$_2$]	1.34		2.5	12	8		56[b)]
	1.34		6	17	15	3	39[b)]
	1.34	Hydroquinone 6.7×10^{-6} mol dm^{-3}	6	62	trace		23[b)]
[Cu(2-PyCOO)$_2$]	2.0		6	trace		15	24[b)]
[Cr(2-PyCOO)$_3$]	1.0		48			trace	
[Zn(2-PyCOO)$_2$]	1.0		3			trace	
[Mg(2-PyCOO)$_2$]	1.0		3			trace	67[c)]

a) $\text{Yield}=\dfrac{\text{Amount of product with respect to pyridine nucleus}}{\text{Amount of 2-pyridinecarboxylate contained in the starting complex}}$. b) With respect to 2-pyridinecarboxylate. c) With respect to metal complex.

Table 2. Photoreactions of 3-pyridinecarboxylic acid–metal salt systems in aqueous solutions
[3-Pyridinecarboxylic acid] = 6×10^{-4} mol dm^{-3}, Irradiated with a low pressure mercury lamp.

Metal salt	10^4[Metal salt] / mol dm^{-3}	pH	Irr. time / h	Yield of product/%[a)] **7**	**8**	Recovery of **2** / %
$FeCl_3$	1.0	4.9—5.3	4	12	24	41
$RuCl_3$	1.0	4.4—4.8	4	6	17	31
$CuSO_4$	3.0	4.9—5.2	4	7	4	53

a) The yields of the bipyridine derivatives are expressed with respect to the pyridine nucleus.

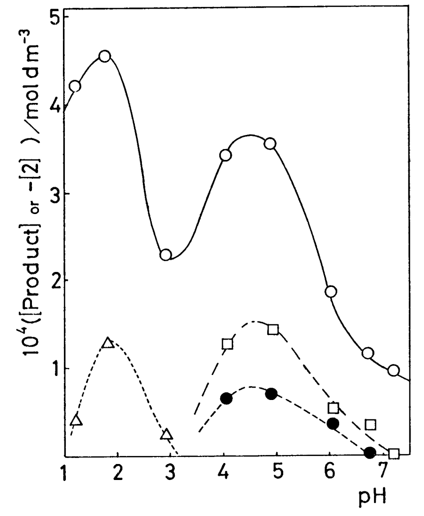
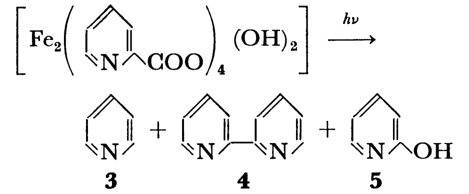
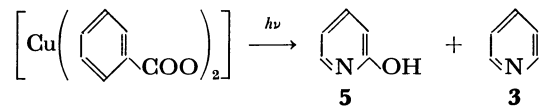


Fig. 1. Dependence of photoreactions of 3-pyridinecarboxylic acid–$FeCl_3$ systems on pH. [3-Pyridinecarboxylic acid]$=6\times10^{-4}$ mol dm^{-3}; [$FeCl_3$]$=1\times10^{-4}$ mol dm^{-3}; Irradiation time, 4 h. The yields of the bipyridine derivatives are expressed with respect to the pyridine nucleus. ···△···: **6**, --●--: **7**, —·—□—·—: **8**, —○—: **2** reacted.

of 2-pyridinecarboxylatocopper(II) complex gives 2-pyridinol and a trace of pyridine.

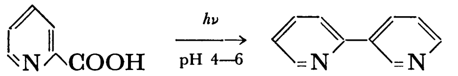


3 **4** **5**



5 **3**

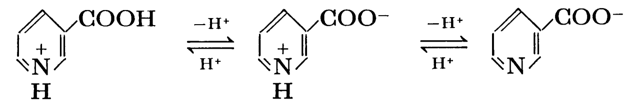
In the absence of metal ions, the UV-irradiation of 2-pyridinecarboxylic acid in the pH range of 4—6 gives 2,3′-bipyridine in 20% yield.



The addition of hydroquinone, a radical scavenger, to the iron(III) complex solution inhibits the formation of 2,2′-bipyridine and increases the yield of pyridine.

The coordinated cobalt(II) and magnesium(II), the lower oxidation states of which are unstable, stabilyze the coordinating 2-pyridinecarboxylate under illumination.

The photoreaction of 3-pyridinecarboxylic acid, which forms no stable chelate bond with metal ions, is affected by iron(III) ions differently from that of 2-pyridinecarboxylic acid. 3-Pyridinecarboxylic acid exists in three forms depending on the pH of the solutions. The effects of iron(III) on the photoreaction of 3-pyridinecarboxylic acid is pH dependent (Fig. 1). At pH 4—6, where the form of 3-pyridinecarboxylic acid is a mixture of **2b** and **2c**, the UV-irradiation in the presence of Fe(III) gives 2,2′-bipyridine-3,5′-dicarboxylic acid (**7**), which is obtained as an iron(II) complex, in addition to 2,3′-bipyridine-5-carboxylic acid (**8**), which is the main product in the absence of Fe(III).[6)]

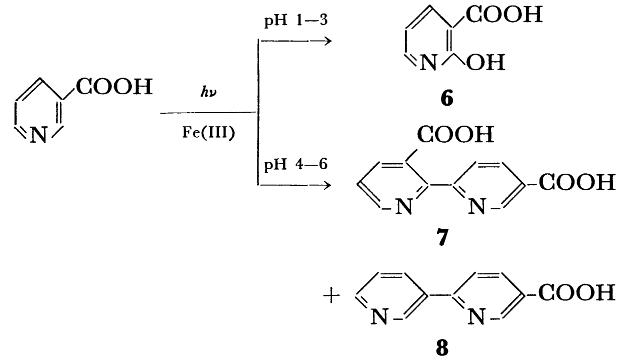


2a **2b** **2c**

pK_a at 25 °C, 2.07[9)] pK_a at 25 °C, 4.81[9)]

At pH 1—3, where the form of 3-pyridinecarboxylic acid is **2a**, the irradiation in the presence of Fe(III) gives 2-hydroxy-3-pyridinecarboxylic acid (**6**), the same product as in the photoreaction in the absence of Fe(III).[6)]

In higher pH range, iron(III) is precipitated as hydroxide or oxide, and hence the effect of iron(III) can not be studied.



6 **7** **8**

The effects of ruthenium(III) and copper(II) are practically the same as those of iron(III). The UV-irradiation of **2** in the presence of Ru(III) or Cu(II) in the pH range of 4—5 gives **7** and **8**.

Figure 2 shows the effects of iron(III) as a function of iron(III) concentration. Here the efficiency of Fe(III) effect (Q) on the photoreaction is expressed on the basis of the light absorbed by 3-pyridinecarboxylic acid according to the following equation.

$$Q=\frac{[\text{Product}]\ \text{or}\ -[\mathbf{2}]}{\dfrac{\text{Light absorbed by }\mathbf{2}}{\text{Light absorbed by }\mathbf{2}\text{ and }FeCl_3}}$$

(The Q-value is a relative quantum yield calculated for the light absorbed by 3-pyridinecarboxylic acid.)

The saturation of the effect of Fe(III) at relatively low concentration and the constant Q-values over the wide range of Fe(III) concentration suggest that the photoreaction originates from the excited **2** not from the excited Fe(III), and the reaction between the excited **2** and Fe(III) should be rapid.

For the photoreaction of 4-pyridinecarboxylic acid, iron(III) and copper(II) have practically no effects. Four hours' irradiation of 5×10^{-4} mol dm^{-3} solutions of 4-pyridinecarboxylic acid at pH 4.7 gave slight UV-spectral changes both in the presence and in the absence of iron(III) and copper(II).

The photochemical decarboxylation of 2-pyridinecarboxylate attached to iron(III) and copper(II) under

TABLE 3. COMPOSITION OF 2-PYRIDINECARBOXYLATOMETAL COMPLEXES
2-PyCOO = 2-Pyridinecarboxylato

Complex	Found (%)			Calcd (%)		
	C	H	N	C	H	N
$[Fe_2(2\text{-PyCOO})_4(OH)_2]$	44.78	2.68	8.82	45.46	2.86	8.83
$[Cu(2\text{-PyCOO})_2]$	46.32	2.72	8.87	46.83	2.62	9.10
$[Zn(2\text{-PyCOO})_2]4H_2O$	37.52	3.99	7.33	37.96	4.25	7.38
$[Cr(2\text{-PyCOO})_3]H_2O$	49.69	2.96	9.73	49.55	3.23	9.63
$[Mg(2\text{-PyCOO})_2]2H_2O$	45.76	3.97	8.89	47.33	3.97	9.20

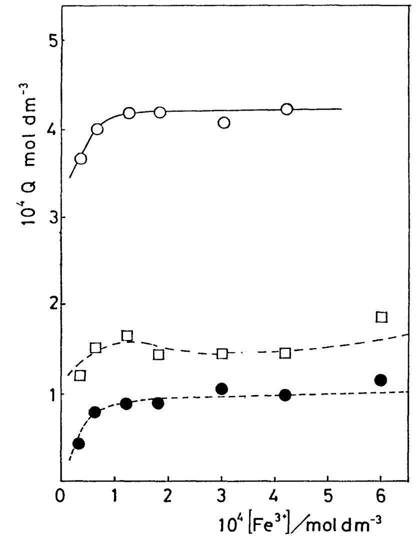


Fig. 2. Dependence of photoreactions of 3-pyridinecarboxylic acid on Fe(III) concentration ([**2**]=6×10^{-4} mol dm^{-3}, pH≈4.4).
The efficiency of the photoreaction is defined as,

$$Q = \frac{[\text{Product}] \text{ or } -[\mathbf{2}]}{\dfrac{\text{Light absorbed by } \mathbf{2}}{\text{Light absorbed by } \mathbf{2} \text{ and } \mathrm{FeCl_3}}}\,.$$

--●--: **7**, —·—□—·—: **8**, —○—: **2** reacted.

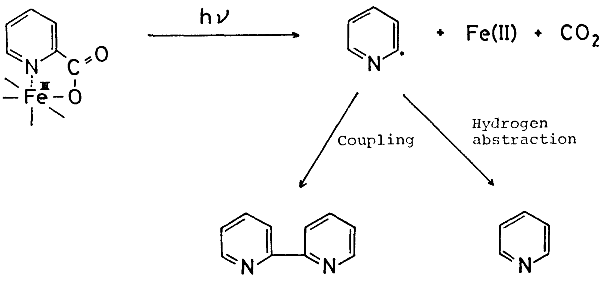
illumination can be explained by the effective electron transfer from the carboxylate to the coordinated metal ions to give carbonyloxy radicals which easily decarboxylate to form 2-pyridyl radicals.

2,2′-Bipyridine is considered to be a coupling product of 2-pyridyl radicals. The fact that the addition of hydroquinone, an effective hydrogen donor, inhibits the photochemical formation of 2,2′-bipyridine and promotes that of pyridine supports the suggested mechanism (Scheme 1).

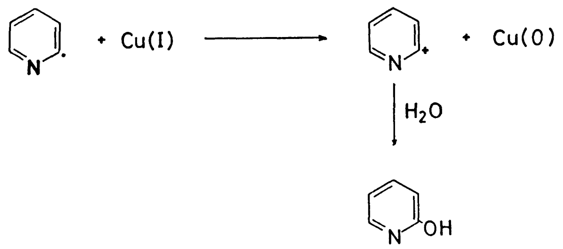
The promotion of radical coupling in the presence of transition metal ions has been reported,[10] and a long lived free radical-metal complex has been proposed.[11]

The formation of 2-pyridinol in the photoreaction of 2-pyridinecarboxylatocopper(II) complex can be explained by the subsequent oxidation of 2-pyridyl radicals by copper(I). The formation of a copper mirror on the reaction vessel was observed during the irradiation (Scheme 2).

The process of the formation of 2,2′-bipyridine-3,5′-dicarboxylic acid in the photoreaction of the 3-pyridinecarboxylic acid–iron(III) system is different from that of the formation of 2,2′-bipyridine in the photoreaction of 2-pyridinecarboxylatoiron(III) complex.



Scheme 1.



Scheme 2.

The formation of a bipyridine derivative and iron(II) indicates the electron transfer from 3-pyridinecarboxylic acid to iron(III). At pH=5, no evidence for the complex formation between 3-pyridinecarboxylic acid and iron(III) in the ground state, because the UV-absorption spectrum of the mixture of 3-pyridinecarboxylic acid and iron(III) is almost the same as the sum of those of the components. As is shown earlier, only the light absorbed by 3-pyridinecarboxylic acid is effective for the formation of **7**. These facts suggest that the formation of **7** occurs *via* charge transfer interaction between an excited 3-pyridinecarboxylic acid and a ground state iron(III) ion.

Thermal oxidation of pyridine by iron(III) at high temperature is an example in which the oxidation of pyridine gives bipyridine.[12]

Experimental

Materials. Commercial 2-, 3-, and 4-pyridinecarboxylic acid (G.R. grade reagents of Tokyo Kasei Co. or Wako Junyaku Co.) were used without further purification. 2-Pyridinecarboxylatometal complexes were prepared in the crystalline form by refluxing the metal salt and sodium 2-pyridinecarboxylate in water. The composition of the metal complexes were determined by elemental analysis (Table 3).

UV-irradiation. The solutions of 2-pyridinecarboxylatometal complexes were prepared by dissolving the complexes in water. The sample solutions of 3- and 4-pyridinecarboxylic acid–transition metal salt systems were prepared by adding the metal salts to the solutions of sodium pyridinecarboxylates. The pH of the solution was adjusted with hydrochloric acid or sodium hydrogencarbonate.

For the identification of the photoproducts 2—3 dm^3 of the solution were irradiated with a low pressure mercury lamp under the bubbling of nitrogen. For the quantitative analysis 50—100 cm^3 of the solution deaerated by bubbling nitrogen or argon for at least 30 min were irradiated with a low pressure mercury lamp under magnetic stirring.

Separation, Identification, and Quantitative Analysis of the Photoproducts. *Photoproducts from 2-Pyridinecarboxylatometal Complexes*: Pyridine was extracted with dichloromethane from the irradiated solutions and identified by means of UV-spectra. Other products were separated by anion exchange chromatography (column, Dowex-1 formate; eluent, formic acid).

2,2′-Bipyridine was obtained as tris(2,2′-bipyridine)iron(II). 2,2′-Bipyridine liberated by refluxing it in a sodium hydroxide solution was steam-distilled. By comparing its NMR spectra with those of the authentic 2,2′-bipyridine, 2,2′-bipyridine in the photoproducts was identified. The UV- and visible spectra of the iron(II) complex supports this conclusion.

2-Pyridinol and 2,3′-bipyridine were identified by the comparison of UV-, IR-, and NMR spectra with those of the authentic samples.

Quantitative analysis was done by means of the ion exchange chromatography and spectroscopy.

Photoproducts from the 3-Pyridinecarboxylic Acid–FeCl$_3$ System: After the irradiated solution was concentrated under reduced pressure, iron(II) and iron(III) were precipitated with hydrogen sulfide. The photoproducts were separated by means of the anion exchange chromatography (column, Dowex-1 formate; eluent, formic acid) and by means of gel-filtration with Sephadex G-10. Two photoproducts were identified.

Iron(II) Complex of 2,2′-Bipyridine-3,5′-dicarboxylic Acid. In order to liberate the ligand the complex was refluxed with aqueous sodium hydroxide. After the evaporation of the solvent the residue was extracted in a Soxhlet's extractor with dry 1,4-dioxane. The crystalline product thus obtained was converted to the methyl ester by diazomethane. The compound was identified as dimethyl 2,2′-bipyridine-3,5′-dicarboxylate from the following data; mp 115—116 °C; IR (KBr disk) 2900 (CH$_3$), 1735, 1730, 1720 (C=O), and 1295 cm^{-1} (ester C–O); NMR (CDCl$_3$) δ=9.25 (1H, dd, J=2.1 and 0.9 Hz, H at the 6′-position), 8.82 (1H, dd, J=4.9 and 1.6 Hz, H at the 6-position), 8.49 (1H, dd, J=8.0 and 2.1 Hz, H at the 4′-position), 8.27 (1H, dd, J=8.0 and 0.9 Hz, H at the 3′-position), 8.10 (1H, dd, J=7.8 and 1.6 Hz, H at the 4-position), 7.44 (1H, dd, J=7.8 and 4.9 Hz, H at the 5-position), 4.00 (3H, s, CH$_3$), and 3.82 (3H, s, CH$_3$); The above assignment is based on the decoupling experiment; MS (70 V) *m/e*(relative intensity), 272(20), 257(54), 242(19), 241(100), 214(10), 213(8), 198 (7), 183(11), 105(12), 91(12), 78(10), 77(10). Found: C, 61.62; H, 4.41; N, 10.43%; M$^+$, 272. Calcd for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44; N, 10.29%; M, 272.

UV spectra of the iron(II) complex, λ_{max}=515 (shoulder) and 550 nm.

2,3′-Bipyridine-5-carboxylic Acid. The product eluted by 0.5 mol dm^{-3} formic acid was identified as 2,3′-bipyridine-5-carboxylic acid by comparing its spectra with those reported previously.[6)]

Determination of the Yields of Products. The quantitative analyses of the photoproducts from 3-pyridinecarboxylic acid–metal salt systems were carried out spectrophotometrically after the separation with anion exchange chromatography.

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8) Considering the following equilibria,

$\mathrm{Fe(III)+2L+OH^-} \rightleftharpoons \mathrm{[Fe(III)L_2(OH)]}$ $K_1=10^{23.84}$ mol^{-3} dm^9

$\mathrm{2[Fe(III)L_2(OH)]} \rightleftharpoons \mathrm{[Fe(III)_2L_4(OH)_2]}$ $K_2=10^{3.06}$ mol^{-1} dm^3

$\mathrm{[Fe(III)L_2(OH)]+H^+} \rightleftharpoons \mathrm{[Fe(III)L_2]+H_2O}$ $K_3=10^{2.96}$

where L represents 2-pyridinecarboxylate, it was found that 30% of iron(III) is in the form of [Fe(III)$_2$L$_4$(OH)$_2$] and 70% of iron(III) is in the form of [Fe(III)L$_2$(OH)] in 1.3×10^{-4} mol dm^{-3} solution of [Fe(III)$_2$L$_4$(OH)$_2$] at pH=6. Almost all the iron(III) ions are coordinated by 2-pyridinecarboxylate (G. Anderegg, *Helv. Chim. Acta*, **43**, 1530 (1960)).

A similar calculation on the following equilibria:

$\mathrm{Cu(II)+L} \rightleftharpoons \mathrm{[Cu(II)L]}$ $K_1=10^{7.95}$ mol^{-1} dm^3

$\mathrm{[Cu(II)L]+L} \rightleftharpoons \mathrm{[Cu(II)L_2]}$ $K_2=10^{7.00}$ mol^{-1} dm^3

showed that 98% of copper(II) is in the form of [Cu(II)L$_2$] in 2.0×10^{-4} mol dm^{-3} solution of [Cu(II)L$_2$] at pH=6 (G. Anderegg, *Helv. Chim. Acta*, **43**, 414 (1960)).

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