

PHOTOREACTIONS OF HETEROAROMATIC COMPOUNDS VI\*

EFFECTS OF COORDINATING METAL IONS ON THE PHOTOREACTION OF  
2-PYRIDINECARBOXYLATE IN AQUEOUS SOLUTIONS

Tsutomu KIMURA, Junji KAMIMURA, Kōtarō TAKADA,  
and Akira SUGIMORI

Department of Chemistry, Faculty of Science and Technology,  
Sophia University, Kioi-cho 7, Chiyoda-ku, Tokyo 102

Coordinating iron(III) to 2-pyridinecarboxylate brings about the photochemical formation of 2,2'-bipyridine and pyridine. Coupled oxidation and reduction between 2-pyridinecarboxylate and copper(II) gives 2-hydroxypyridine and copper(0).

Remarkable effects of coordinating metal ions, especially transition metal ions, on the photoreactions of ligands have been reported. Among them the photochemistry of oxalato metal complexes<sup>1)</sup> and of amino acids<sup>2)</sup> has been extensively investigated. We report here the effects of coordinating iron(III), copper(II), cobalt(II), zinc(II), and magnesium(II) on the photochemical behavior of 2-pyridinecarboxylate in aqueous solutions.

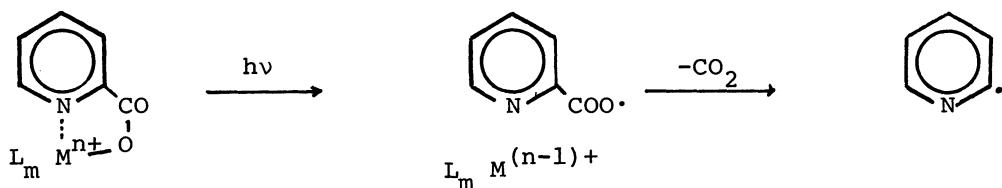
Aqueous solutions of 2-pyridinecarboxylatometal complexes ( $1 \sim 2 \times 10^{-4}$  mol dm<sup>-3</sup> with respect to the complexes) were irradiated with a low pressure mercury lamp under nitrogen. After irradiation the products were separated by means of extraction with dichloromethane and anion exchange chromatography (column, Dowex-1; eluent aqueous formic acid).

The results are shown in Table 1. The most remarkable effect of metal ion is observed in the photoreaction of the iron(III) complex.<sup>3)</sup> In contrast to the formation of 2,3'-bipyridine in the absence of metal ions (at pH, 6 ~ 7), 2,2'-bipyridine (as tris(2,2'-bipyridine)iron(II)) and pyridine are formed, accompanied by a small amount of 2-hydroxypyridine.

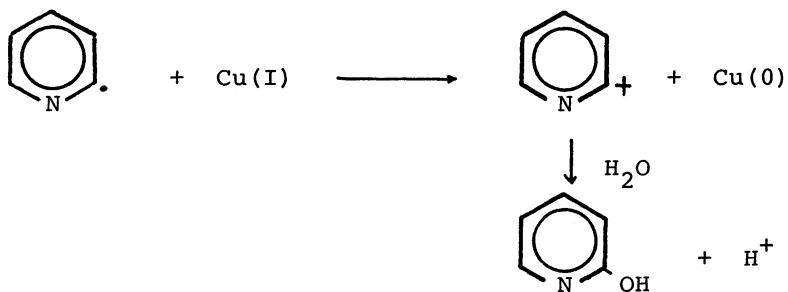
The formation of 2,2'-bipyridine *via* pyridine in the photochemical reaction of the iron(III) complex can be excluded, because the irradiation of aqueous pyridine solutions containing iron(III) or iron(II) gave no 2,2'-bipyridine under the same irradiation conditions.

It should be noted that iron(III) and copper(II) act in different ways. The copper(II) complex<sup>4)</sup> gives photochemically 2-hydroxypyridine and a small amount of pyridine.

The photoproducts from the iron(III) and copper(II) complex are the decarboxylation products from 2-pyridinecarboxylic acid. Similar to other carboxylatometal complexes, the first step of the photoreaction is probably decarboxylation which results from the photochemical electron transfer from carboxylate to metal ions.

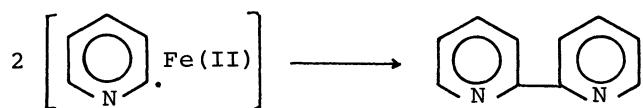


Copper(I) can further oxidize 2-pyridyl radicals to give copper(0) and 2-pyridyl cations, the latter of which is converted finally to 2-hydroxypyridine. A copper mirror was observed on the wall of vessels when the copper(II) complex was irradiated.



On the other hand, iron(II) can not oxidize 2-pyridyl radicals, and 2,2'-bipyridine and pyridine are formed. The fact that the dimerization of 2-pyridyl radicals occurs in high efficiency under the condition where the rapid reaction of the radicals with iron(III) is expected, suggests the stabilization of 2-pyridyl radicals by iron(II). The interaction between iron(II) and 2-pyridyl radicals would facilitate the dimerization of the radicals. A similar effect of iron(II) was observed in the dimerization of  $R_2NCH_2CH=CH-CH_2\cdot$  radicals.<sup>5)</sup>

The mechanism for the formation of pyridine has not yet been clarified.



The coordinating cobalt(II) and magnesium(II), the lower oxidation state of which is unstable, stabilize the coordinated 2-pyridinecarboxylate under illumination.

Table 1 Photochemical reactions of some 2-pyridinecarboxylatometal complexes<sup>a)</sup>

Complex	Conc. ( $10^{-4}$ . mol dm $^{-3}$ )	Irr. time (h)	Product and yield <sup>b)</sup>			
$[\text{Fe}_2(\text{PyCOO})_4(\text{OH})_2]^{3)}$	1.3	2.5	12	8	—	56 <sup>c)</sup>
	1.3	6	17	15	3	39 <sup>c)</sup>
$[\text{Cu}(\text{PyCOO})_2]^{4)}$	2.0	6	trace	—	15	24 <sup>c)</sup>
$\text{Na}[\text{Co}(\text{PyCOO})_3]^{6)}$	1.0	6	—	—	trace	83 <sup>d)</sup>
$[\text{Zn}(\text{PyCOO})_2]$	1.0	3	—	—	trace	
$[\text{Mg}(\text{PyCOO})_2]$	1.0	3	—	—	trace	67 <sup>d)</sup>

a) PyCOO = 2-pyridinecarboxylate

Amount of product with respect to pyridine nucleus

b) Yield =  $\frac{\text{Amount of product with respect to pyridine nucleus}}{\text{Amount of 2-pyridinecarboxylate contained in the starting complex}}$

c) With respect to 2-pyridinecarboxylate

d) With respect to metal complex (Determined by UV-spectra)

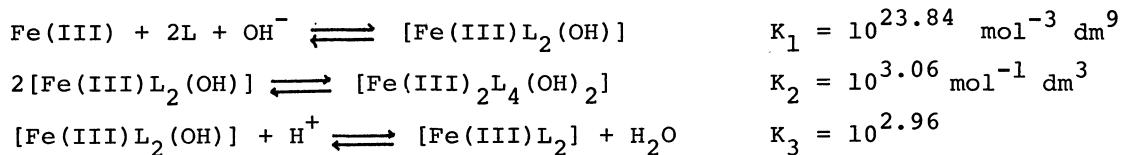
\* Part V T.Sugiyama, T.Furihata, Y.Edamoto, R.Hasegawa, A. Sugimori, and G.P.Sato, *Tetrahedron Lett.*, 1974, 4339.

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G.B.Porter, J.G.W.Doering, and S.Karanka, *J. Amer. Chem. Soc.*, 84, 4027 (1962).

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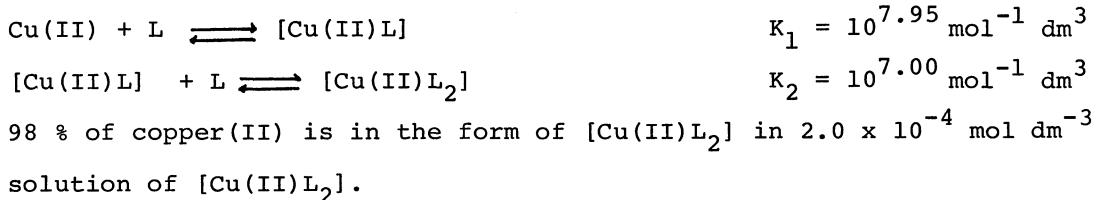
3) Considering the following equilibria,



where L represents 2-pyridinecarboxylate, 30 % of iron(III) is in the form of  $[\text{Fe(III)}_2\text{L}_4(\text{OH})_2]$  and 70 % of iron(III) is in the form of  $[\text{Fe(III)}\text{L}_2(\text{OH})]$  in  $1.3 \times 10^{-4} \text{ mol dm}^{-3}$  solution of  $[\text{Fe(III)}_2\text{L}_4(\text{OH})_2]$ .

G.Anderegg, *Helv. Chim. Acta*, 43, 1530 (1960).

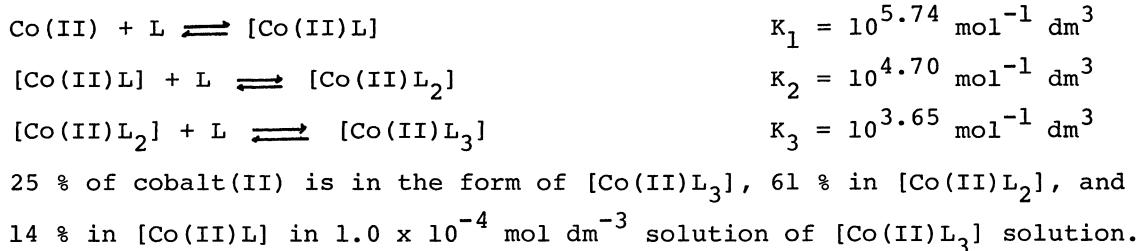
4) Considering the following equilibria,



G.Anderegg, *Helv. Chim. Acta*, 43, 414 (1960).

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6) Considering the following equilibria,



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