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## The Photochemical Reaction of Ethylene Glycol with Ferric Chloride-Pyridine Complex\*<sup>1</sup>

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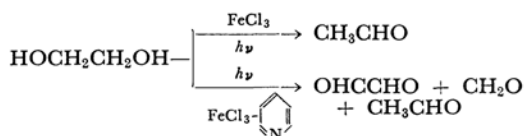
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The photochemical reaction of ethylene glycol with ferric chloride-pyridine complex are carried out under a nitrogen atmosphere with 100 W mercury lamp at room temperature. Glyoxal, formaldehyde, acetaldehyde and water are obtained as the main products. When the molar ratio of pyridine to ferric chloride is below 1—2, the amounts of glyoxal and formaldehyde produced increase with increasing the amount of pyridine, though that of acetaldehyde decreases. In the process, Fe(III) is photo-reduced to Fe(II). Thus, the remarkable effect of pyridine on the photochemical reaction is observed. From these results, the mechanisms of the action of the excited Fe(III) in the presence and absence of pyridine are assumed here.

In the preceding paper,<sup>1)</sup> we have reported that the photochemical reaction of ethylene glycol with ferric chloride proceeds *via* a Fe(III)-complex to give acetaldehyde as the main product, whereas acetaldehyde is not obtained in the thermal reaction. The reactivity of the Fe(III) ion in the excited state must be altered by variation of the ligand field around the Fe(III) ion. Also, a part of the ligand in a complex may be cleaved in the excited state and the cleaved ligand may contribute to the photochemical reaction together with the Fe(III) ion. From these points of view, we investigated the photochemical reaction of ethylene

glycol with a Fe(III) complex which contains pyridine as a part of the ligands. As the consequence, it was confirmed that the photochemical reaction of ethylene glycol with a ferric chloride-pyridine complex differs from that in the case of ferric chloride alone as is shown in the following equations.



In this paper, the results were described and the reaction mechanisms were discussed. And the mechanism proposed for the formation of acetaldehyde in the previous paper<sup>1)</sup> was again discussed.

\*<sup>1</sup> Presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

1) H. Inoue, K. Tamaki, N. Komakine and E. Imoto, This Bulletin, in press.

## Experimental

**Materials.** Anhydrous ferric chloride, ethylene glycol and ethylene glycol dimethyl ether used here were purified by the method described in the previous papers.<sup>1,2)</sup> Pyridine, 2-, 3- and 4-methylpyridine and 2,6-dimethylpyridine were of a commercial grade and were dried on sodium hydroxide and distilled through a Vigreux column before use.

**Procedures of the Photochemical Reaction.** A typical procedure for the irradiation was as follows. Weighed amounts of anhydrous ferric chloride and pyridine or the relative compounds were dissolved into 20 ml of ethylene glycol or ethylene glycol dimethyl ether. Ten milliliters of this solution was pipetted out and admitted into a vycor tube (inner diameter, 20 mm; thickness of the wall, 1 mm). After nitrogen gas had been bubbled in it for about 5 min, the vycor tube was sealed immediately and irradiated for 20 hr at an equidistant place of 4 cm from a 100 W mercury lamp at room temperature. In order to isolate the reaction products, another procedure was attempted at large scale by using the 300 ml cylindrical reaction vessel by the method described in the previous paper.<sup>2)</sup>

**Analyses of the Products.** The analyses of the products were mainly accomplished by the methods described in the previous papers.<sup>1,2)</sup> Acetaldehyde, acetaldehyde ethylene acetal (this amount was calculated as that of acetaldehyde in this paper.), chloromethyl methyl ether, methyl chloride, methanol and water were determined by means of gas chromatography (g. c.). The carbonyl compounds such as formaldehyde, glyoxal and acetaldehyde were determined as 2,4-dinitrophenylhydrazones. The isolation of carbonyl compounds was carried out by paper chromatography. In addition to the methods described above, the determinations of formaldehyde and ferrous ion were made spectrophotometrically by using Schiff's reagent and *o*-phenanthroline methods respectively.<sup>3,4)</sup>

**Spectrophotometric Measurement of the Photochemical Reaction.** The measurements of ultraviolet and visible absorption spectra were made according to the same methods used in the previous paper.<sup>1)</sup>

## Results and Discussion

**Thermal Reaction of Ethylene Glycol with Ferric Chloride - Pyridine Complex.** The thermal reaction of ethylene glycol with ferric chloride in the presence of pyridine was investigated at first. A solution of 1.4 g of anhydrous ferric chloride and 0.7 g of pyridine in 20 ml of ethylene glycol was placed in a reaction vessel equipped with a condenser which had been connected to a trap cooled with a dry ice-acetone bath and was then heated at 130°C for 5 hr. During this period no product was obtained in the trap. From the

reaction mixture a small amount of glyoxal was isolated as 2,4-dinitrophenylhydrazone, but other product was not confirmed by g. c. and 2,4-D analyses.

**Photochemical Reaction of Ethylene Glycol with Ferric Chloride - Pyridine Complex.** A solution of 18.1 g of anhydrous ferric chloride and 8.8 g of pyridine in 250 ml of ethylene glycol was irradiated with a 100 W mercury lamp according to the method described above. At various intervals of the reaction time, 5 ml of the solution was pipetted out and the reaction products were confirmed and determined by the methods described above. Glyoxal, formaldehyde, acetaldehyde and water were contained as the main products and trace amounts of gas components were detected as the by-products. Ferric ion was reduced to ferrous ion in the course of the photochemical reaction. The variation of the amounts of the main products to the reaction time is shown in Fig. 1. The amounts of glyoxal, acetaldehyde and

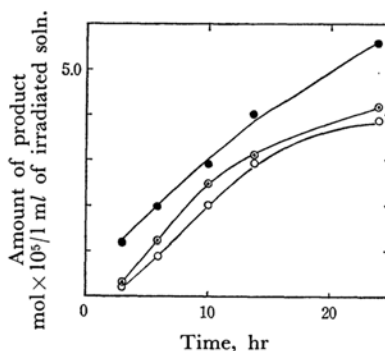


Fig. 1. Plot of the amounts of the main products vs. irradiate time: Internal irradiation method, ethylene glycol; 4.35 mol,  $\text{FeCl}_3$ ; 0.11 mol and pyridine; 0.11 mol.

● Glyoxal      ◐ Acetaldehyde  
○ Formaldehyde

formaldehyde produced increased with the reaction time, and the amount of glyoxal produced was more than those of acetaldehyde and formaldehyde produced in the reaction process. On the other hand, the amount of ferrous ion increased with increase of the amounts of all products. After the reaction time of 24 hr, unchanged ethylene glycol and low-boiling-point products were removed in vacuo under a nitrogen atmosphere, and 32 g of the brown distilled residue was obtained. The distilled residue was a hygroscopic dark brown clay-like material. We could not carry out the elemental analysis of this material, since it was very unstable under air or moisture. However, the results of the qualitative tests showed the presence of ferrous or ferric ion, chloride ion and an organic compound in the material. The infrared spectrum of the material showed the characteristic absorption bands to pyridinium salt at

2) H. Inoue, K. Tamaki and E. Imoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 654 (1966).

3) A. Kubo, "Jikken Kagaku Koza," Vol. 15, II, Maruzen, Tokyo (1958), p. 278.

4) R. I. Veksler, *Zhur. Anal. Khim.*, **1**, 301 (1946); **4**, 14 (1949); **5**, 32 (1950).

about 2750, 1632, 1602, 1528 and 1480  $\text{cm}^{-1}$ . Among these bands the absorption band at about 2750  $\text{cm}^{-1}$  corresponded to  $\text{=N}^+-\text{H}$  stretching band. From the results the material seems to be a complex which consists of pyridinium hydrogen chloride and ferric or ferrous chloride.

**Relationship between the Amounts of the Reaction Products and Pyridine Added.** A form of a ferric chloride-pyridine complex in ethylene glycol must be changed to various forms by the amount of pyridine added. Therefore the photochemical reaction of ethylene glycol with ferric chloride-pyridine complex also must be varied by the amount of pyridine added. Here the relationship between the amounts of reaction products and pyridine added was investigated. A weighed amount of pyridine was added into a solution containing 0.72 g of ferric chloride in 20 ml of ethylene glycol. Ten milliliters of this solution was admitted in a vycor tube, and irradiated at a distance of 4 cm from light source at room temperature for 20 hr. The relationship between

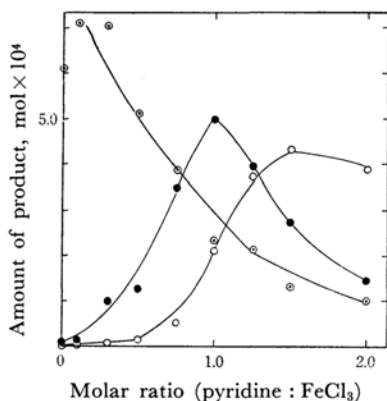


Fig. 2. Plot of the amounts of the main products vs. the molar ratio of pyridine to ferric chloride: External irradiation method, ethylene glycol; 0.18 mol,  $\text{FeCl}_3$ ;  $4.5 \times 10^{-3}$  mol and irradiation time; 20 hr.

● Glyoxal      ⊙ Acetaldehyde  
○ Formaldehyde

the amount of formaldehyde, acetaldehyde or glyoxal produced and the molar ratio of pyridine to ferric chloride are shown in Fig. 2. As is shown in Fig. 2, the amount of acetaldehyde produced decreased with increase of the amount of pyridine added. On the other hand, the amount of glyoxal or formaldehyde produced became maximum when the molar ratio of pyridine to ferric chloride is about 1 or 1.5 respectively, as is shown in Fig. 2. Thus, the amount of pyridine added seems to determine the reaction course resulting in the formation of acetaldehyde, formaldehyde and glyoxal. Furthermore, we can suggest that the mechanism for the formation of acetaldehyde may differ from that in the case of formaldehyde and glyoxal.

**Effects of Pyridine Derivatives.** The effects of various pyridine derivatives on the photochemical reaction of ethylene glycol with ferric chloride were investigated. Pyridine derivatives used here were 2-, 3- and 4-methylpyridine and 2,6-dimethylpyridine. Weighed amounts of anhydrous ferric chloride and pyridine derivatives were dissolved into 20 ml of ethylene glycol. Ten milliliters of this solution was irradiated for 20 hr according to the same manner as in the case of pyridine. The amounts of products obtained are presented in Table 1. In each case glyoxal and formaldehyde in addition to acetaldehyde were obtained. The difference between the cases of pyridine and pyridine derivatives was not distinct. This result seems to give some additional support for the results described in the case of pyridine.

**Photochemical Reaction of Ethylene Glycol Dimethyl Ether with Ferric Chloride-Pyridine Complex.** The characteristic reaction of ethylene glycol with ferric chloride-pyridine complex under irradiation may depend on the specific structure of ethylene glycol. Therefore ethylene glycol dimethyl ether in place of ethylene glycol was used here as a substrate and was irradiated by the method described above.

When a weighed amount (0.19 g) of pyridine was added into 10 ml of the solution of ethylene glycol dimethyl ether containing 0.39 g of anhydrous ferric chloride (the molar ratio of pyridine, ferric

TABLE 1. THE AMOUNTS OF THE MAIN PRODUCTS IN THE PHOTOCHEMICAL REACTION OF ETHYLENE GLYCOL WITH FERRIC CHLORIDE IN THE PRESENCE OF PYRIDINE OR PYRIDINE DERIVATIVES\*

Pyridine derivative	$\text{pK}_a^{**}$	Fe(II) ion $\text{mol} \times 10^4$	Amount of product, $\text{mol} \times 10^4$		
			$\text{CH}_3\text{CHO}$	$\text{CH}_2\text{O}$	$\text{OHCCCHO}$
Pyridine (P)	5.17	27	2.5	2.4	5.0
2-Methyl-P	5.97	28	2.5	3.8	4.9
3-Methyl-P	5.68	34	2.7	3.7	4.8
4-Methyl-P	6.02	32	3.6	3.5	4.6
2,6-Dimethyl-P	6.75	28	2.2	5.2	3.9

\* Ethylene glycol; 0.18 mol,  $\text{FeCl}_3$ ;  $4.5 \times 10^{-3}$  mol, pyridine or pyridine derivatives;  $4.5 \times 10^{-3}$  mol and irradiation time; 24 hr.

\*\* H. C. Brown, D. Gintis and L. Domash, *J. Am. Chem. Soc.*, **78**, 5387 (1956).

chloride and ethylene glycol dimethyl ether is 1 : 1 : 40), a brown solid in the colloidal state appeared on the wall of the reaction vessel. This solid probably may be a complex which consists of ferric chloride, pyridine and ethylene glycol dimethyl ether. This heterogeneous solution was irradiated for 15 hr. In addition to this experiment, the homogenous solution, of which the molar ratio of pyridine, ferric chloride and ethylene glycol dimethyl ether is 0.75 : 1 : 40, was irradiated for 15 hr. The amounts of the products obtained are shown in Table 2.

TABLE 2. THE AMOUNTS OF THE MAIN PRODUCTS IN THE PHOTOCHEMICAL REACTION OF ETHYLENE GLYCOL DIMETHYL ETHER WITH FERRIC CHLORIDE IN THE PRESENCE OF PYRIDINE\*

Amount of compound added, mol $\times 10^3$		Amount of product mol $\times 10^4$		
FeCl <sub>3</sub>	Pyridine	CH <sub>2</sub> O	ClCH <sub>2</sub> OCH <sub>3</sub>	CH <sub>3</sub> OH
2.4	0	6.2	3.0	1.5
2.4	1.8	8.3	trace	1.3
2.4	2.4	6.5	trace	2.0

\* Ethylene glycol dimethyl ether;  $9.6 \times 10^{-2}$  mol, and irradiation time; 15 hr.

In all cases, formaldehyde and methanol were obtained as the main products. Gas components and two other products (the amounts of these products are less than 10% of that of methanol formed) were obtained as by-products, but glyoxal was not detected. Chloromethyl methyl ether was scarcely obtained when pyridine was added. This seems to mean that chloromethyl methyl ether is converted to formaldehyde and methyl

chloride in the presence of pyridine. Thus, the action of ferric chloride on ethylene glycol dimethyl ether under irradiation seems not to be influenced by the presence of pyridine.

**Spectral Studies.** Ultraviolet and visible absorption spectra of a mixture of ferric chloride and pyridine in ethylene glycol are shown in Fig. 3. The ultraviolet spectrum showed weak broad band at about 345 m $\mu$  and strong bands at about 252, 257 and 263 m $\mu$ , and did not correspond to the sum of the spectra of ferric chloride and pyridine. Furthermore, the weak band at about 345 m $\mu$  shifted to lower wavelength when the amount of pyridine increased. Therefore, the ferric chloride must form a complex with pyridine in ethylene glycol.

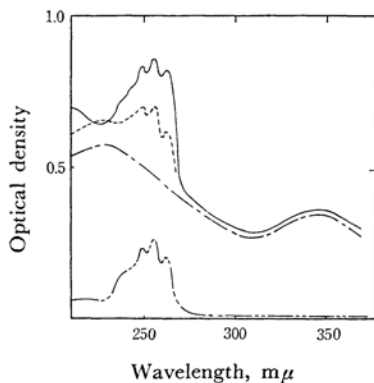


Fig. 3. The ultraviolet absorption spectrum of pyridine, ferric chloride and a mixture of pyridine and ferric chloride in ethylene glycol: ——— Pyridine only;  $1.23 \times 10^{-4}$  mol/l, ——— FeCl<sub>3</sub> only;  $1.19 \times 10^{-4}$  mol/l, ——— a mixture of pyridine ( $1.23 \times 10^{-4}$  mol/l) and FeCl<sub>3</sub> ( $1.19 \times 10^{-4}$  mol/l) and ——— calculated curve (pyridine plus FeCl<sub>3</sub>).

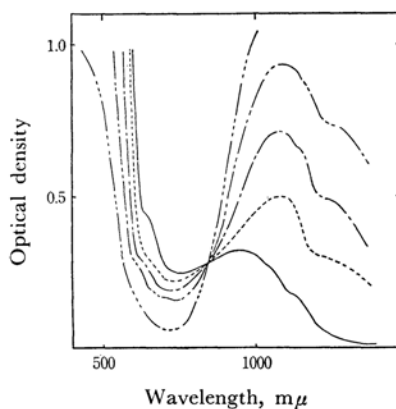


Fig. 4. The variation of the visible absorption spectrum to the irradiation time (ethylene glycol-FeCl<sub>3</sub>-pyridine system): The concentration of FeCl<sub>3</sub> and pyridine; 0.45 mol/l and 0.45 mol/l. — Before irradiation, ---- 6 hr, ——— 10 hr, ..... 14 hr and ——— 24 hr.

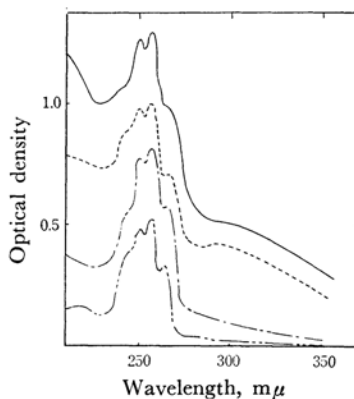


Fig. 5. The variation of the ultraviolet absorption spectrum to the irradiation time (ethylene glycol-FeCl<sub>3</sub>-pyridine system): The concentration of FeCl<sub>3</sub> and pyridine;  $4.2 \times 10^{-4}$  mol/l and  $4.2 \times 10^{-4}$  mol/l. — Before irradiation, ---- 6 hr, ——— 14 hr, and ..... 24 hr.

When a mixture of ferric chloride and pyridine in ethylene glycol was irradiated with a 100 W mercury lamp, the peaks at 252, 257 and 263  $m\mu$  decreased with the irradiated time, and new band appeared at about 1050  $m\mu$ , of which the peak increased with the irradiation time, as shown in Figs. 4 and 5. The new peak corresponded to the peak in a ferrous chloride-ethylene glycol system. Furthermore, the ultraviolet absorption spectrum of the solution at the irradiated time of 24 hr closely corresponded to the spectrum of a mixture of  $0.3 \times 10^{-4}$  mol/l of ferric chloride,  $3.9 \times 10^{-4}$  mol/l of ferrous chloride,  $3.9 \times 10^{-4}$  mol/l of hydrogen chloride and  $4.2 \times 10^{-4}$  mol/l of pyridine.

These phenomena show that ferric chloride-pyridine complex is more easily reduced by ethylene glycol to give ferrous chloride and pyridinium hydrogen chloride in comparison with the case of ferric chloride alone described in the previous paper.<sup>1)</sup>

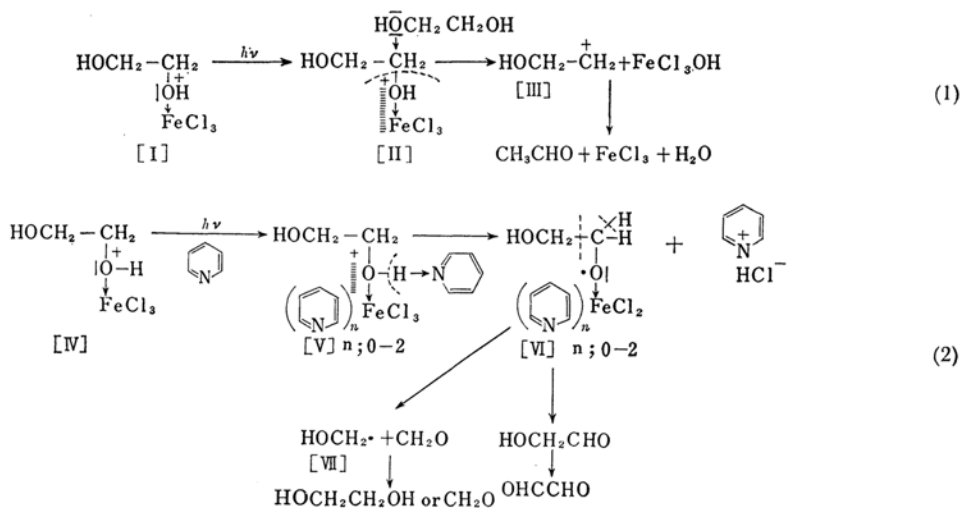
**Presumption of a Mechanism for the Action of Ferric Chloride or Ferric Chloride-Pyridine Complex on Ethylene Glycol.** In the photochemical reaction of ethylene glycol with ferric chloride in the presence of pyridine, the amounts of glyoxal and formaldehyde produced increased with increasing the amount of pyridine when the molar ratio of pyridine to ferric chloride is below 1. In the process Fe(III) was photo-reduced to Fe(II). In the absence of pyridine, however, only acetaldehyde was obtained as a product, and the photo-reduction of Fe(III) to Fe(II) proceeded slowly in comparison with the case in the presence of pyridine. In the case of ethylene glycol dimethyl ether, the remarkable effect of pyridine on the photochemical reaction was not observed.

From these results, the mechanism of the action of the excited Fe(III) in the presence and absence

of pyridine are discussed here. At first it appears plausible to consider that the excited Fe(III) initiates the various reactions. The excited Fe(III) has higher oxidation potential in comparison with Fe(III) in the ground state. Therefore the oxidative ability of Fe(III) or the property of Fe(III) as an electron acceptor seems to increase under irradiation. If the orbital of the lone pair electron of oxygen atom of ethylene glycol can overlap with the d-orbitals of Fe(III) ion, the electron on an oxygen atom may be spread over the unoccupied orbitals of Fe(III) ion. Consequently, the oxygen atom of ethylene glycol under irradiation must become more positive than that in the ground state. In this state, however, an electron transfer from the oxygen atom to Fe(III) ion, that is, the oxidation does not occur. This state is symbolized as the process of I—II or IV—V in reactions (1) and (2). The dotted lines show the electron distribution between an oxygen atom and Fe(III) ion. If an electron transfer from an oxygen atom to Fe(III) ion occurs under irradiation, it will become to produce a radical on the oxygen atom. Consequently, the cleavage of the carbon-carbon bond will be expected.

In the photochemical reaction of ethylene glycol described above, the presence of pyridine gives the oxidation products. However there is no reason why the presence of pyridine in the complex results in the electron transfer, since in the case of ethylene glycol dimethyl ether the effect of pyridine is not observed. Therefore, in order to explain the difference of the photochemical reaction between with and without pyridine, we must consider the action of (a) ethylene glycol itself and (b) the free base such as pyridine in the reaction medium in addition to that of the excited Fe(III) ion.

(a) Ethylene glycol must be arranged by the hydrogen bridge in the reaction medium, and the



oxygen atom of one molecule may be placed at the vicinity of the carbon atom of the other molecule. When the oxygen atom of one molecule is charged positively, the nucleophilic participation to the carbon atom by the oxygen atom of the other molecule must occur, and then the carbon-oxygen bond will be cleaved ionically to give III (reaction (1)). III is converted to give acetaldehyde and water.

(b) In the photochemical process, a free base may be present in the reaction medium. When the oxygen atom of ethylene glycol is positively charged by the action of the excited Fe(III), the

hydrogen of the hydroxy group may transfer to the free base as the proton. Consequently, the transition of an electron from the oxygen atom to ferric ion is facilitated to give VI, which has a radical on the oxygen atom, as is shown in reaction (2). VI is converted to give VII with the cleavage of the carbon-carbon bond or hydroxyacetaldehyde with the cleavage of the carbon-hydrogen bond. Furthermore hydroxyacetaldehyde will be oxidized to give glyoxal *via* the same process as reaction (2). On the other hand, VII must be converted to give formaldehyde or ethylene glycol, as is shown in reaction (2).

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