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The Photochemical Reactions of Ethylene Glycol and Its Ethers in the Presence of Ferric Chloride

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The photochemical reactions of ethylene glycol, ethylene glycol monomethyl ether and ethylene glycol dimethyl ether with ferric chloride have been carried out under a nitrogen atmosphere and with irradiation by ultraviolet light. These reactions have involved the cleavage of the carbon-carbon bond to give formaldehyde and chloromethyl methyl ether; of the carbon($-CH_2-$)-oxygen bond to give acetaldehyde, methanol and water, or of the carbon(CH_3-)-oxygen and hydrogen-oxygen bonds to give methane, ethane, hydrogen chloride and methyl chloride. Furthermore, they have been accompanied by the photo-reduction of ferric chloride to ferrous chloride. From these results, it has been assumed that ferric chloride acts as an oxidizing reagent and Lewis acid in the photochemical reactions.

It has well been known that a transition metal ion can serve as an oxidation-reduction or Lewis acid reagent in some thermal reactions. Recently, an interest in the behavior of a transition metal ion in the photochemical reactions has been taken by several investigators. The catalysis of the photo-oxidation of ethanol by copper ions,(1) and the photochemical reactions of peresters in the presence of copper ions, have been reported on.(2) The properties of a transition metal ion in the excited state would be different from those in the normal state, and an excited transition metal ion may have a characteristic effect on a substrate through the formation of a transition metal ion-substrate complex. In this paper, we will describe our studies of the photochemical reactions of ethylene glycol and its ethers with ferric chloride under a nitrogen atomosphere. Ethylene glycol and its ethers were chosen in this study because their photo-oxidation by oxygen has well been studied in our previous paper.(3)

Experimental

Meterials.—Anhydrous ferric chloride, ethylene glycol and ethylene glycol monomethyl ether were of a commercial grade. Ethylene glycol dimethyl ether

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1) H. R. Cooper and B. M. Talbot, *Trans. Faraday Soc.*, **61**, 506 (1965).

2) G. Sonsnovsky, *J. Org. Chem.*, **28**, 2934 (1963).

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

was prepared according to the methods described in the literature.[4] These materials were purified by the manner described in a previous paper.[3]

The Procedure of the Photo-reaction.—A weighed amount of ferric chloride was dissolved into an appropriate amount of ethylene glycol or its ethers. This solution was then introduced into a cylindrical reaction vessel with a capacity of about 250 ml., and a 100 W. mercury lamp with a water-cooling jacket was placed in this vessel. After nitrogen gas had been bubbled in for about 5 min., the vessel was connected with a gas burette, the air space of which had previously been filled with nitrogen gas. The solution was then irradiated for 24 hr.

The Analysis of the Products.—The analysis of the products was mainly accomplished by means of gas chromatography (g. c.), using a Hitachi KGL-2 gas chromatograph. The irradiated solution was analyzed by immediately withdrawing 5 to 10 μl. of the solution into a syringe. A column containing polyethylene glycol-1600 and/or high vacuum silicon grease was used in the g. c. analyses. The major product peaks in the gas chromatogram were identified by a comparison of their retention times with those of authentic materials, if possible. Acetaldehyde, acetaldehyde ethylene acetal and methanol were identified by the methods described in the previous paper.[3] Chloromethyl methyl ether and ethylene glycol dimethyl ether were identified by trapping the materials from the column, and by then comparing the infrared spectra of the trapped materials with those of authentic materials. Besides the analyses by g. c., the total amounts of the compounds containing carbonyl groups were determined as their 2, 4-dinitrophenylhydrazones (2, 4-D.). The components of 2, 4-D.'s were identified by paper chromatography according to Horner's method.[5] Here, the 2, 4-D.'s of acetaldehyde and formaldehyde were confirmed to be the main components.

The Spectrophotometric Study of the Photo-reaction.—Solutions of 0.05 mol. of ferric chloride in 20 ml. of ethylene glycol, ethylene glycol monomethyl ether or ethylene glycol dimethyl ether were introduced into a spherical ampule (2 cm. radius). The sample solutions were cooled with a dry ice - acetone bath; the air was removed under the reduced pressure of 1—2 mmHg, and then the ampule was filled with nitrogen gas. After the procedure of the replacement by nitrogen gas had been repeated 4—5 times, the sample solution was poured into a reaction cell, which consisted of a spectrophotmeter cell ($1\times1\times4$ cm.) and the upper part of which was connected to the above ampule. The apparatus used is shown in Fig. 1. The cell was irradiated at a distance of 4 cm. from a light source, a 100 W. mercury lamp, at room temperature. At various time intervals, the sample cell was taken out and the absorption spectra were measured with a Hitachi spectrophotometer.

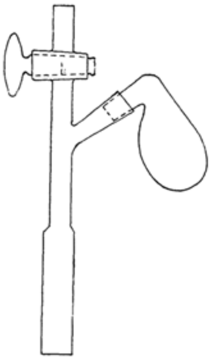

Fig. 1. Spectrophotometer cell.

Results and Discussion

Spectrophotometric Studies. — The visible absorption spectra of ferric chloride in ethylene glycol, ethylene glycol monomethyl ether and ethylene glycol dimethyl ether showed large absorption bands lower than 550 mμ and absorption peaks at 600, 620 and 685 mμ in all cases, as is shown in Figs. 2, 3 and 4. The visible spectra of these solutions varied with the irradiation of light.

In the case of ethylene glycol monomethyl ether and ethylene glycol dimethyl ether, the large band lower than 550 mμ and the peaks at 600, 620 and 685 mμ decreased with the irradiation time and two new peaks appeared, at 532 and 1000 mμ, as is shown in Figs. 3 and 4. The former new peak, at 532 mμ, corresponds to that of H^+FeCl_4 in diisopropyl ether reported by Metzler.[6] We also observed absorption peaks at 532, 600, 620 and 685 mμ in a ferric chloride - ethylene glycol monomethyl or ethylene glycol dimethyl ether - hydrochloric acid or methyl chloride system, as is shown in Fig. 5.

On the basis of these results, we are now able to suggest that in the course of the photo-reaction hydrochloric acid or methyl chloride is produced and that this forms a complex with ferric chloride according to the following scheme:

$$FeCl_3(\text{solvent}) \xrightarrow{RCl} RFeCl_4(\text{solvent})$$

This new peak, at 532 mμ, also decreased with the irradiation time. On the other hand, the latter new peak, at 1000 mμ, corresponded to the peak in a ferrous chloride - ethylene glycol system. This peak increased with the irradiation time. These results indicate that ferric chloride is photoreduced by ether to ferrous chloride.

In the case of ethylene glycol, the peaks at 600, 620 and 685 mμ decreased with the irradiation. However, the decrease in the large band lower than 550 mμ could not be observed. This may result from the fact that the large band in the ferric chloride - ethylene glycol system does not vary even upon the addition of hydrochloric acid. A new peak appeared at 1000 mμ. The intensity

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[4] A. L. Kanzfelder and R. R. Vogt, *J. Am. Chem. Soc.*, **60**, 1714 (1938).

[5] L. Horner and W. Kirmse, *Ann.*, **597**, 48 (1955).

[6] D. E. Metzler and R. J. Myers, *J. Am. Chem. Soc.*, **72**, 3777 (1950).

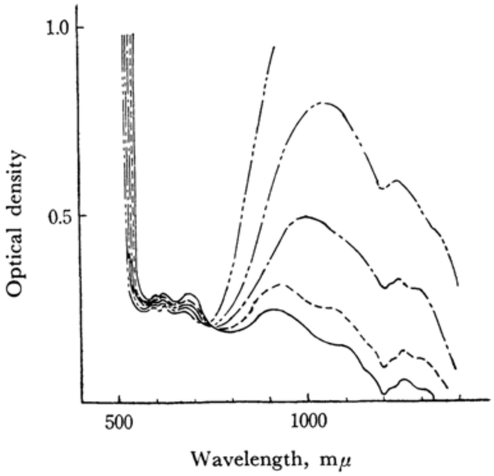


Fig. 2. The variation of visible spectrum to irradiated time (ethylene glycol - FeCl$_3$ system). Concn. of FeCl$_3$: 0.90 mol./l.

——— 0.0 hr. ------ 2.5 hr.
---- 6.0 hr. ---- 9.0 hr.
---- 24.0 hr.

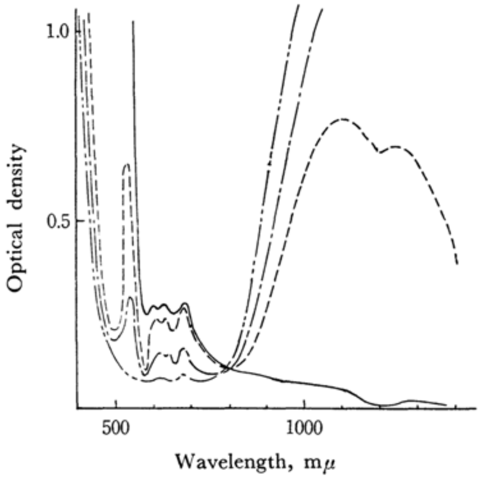


Fig. 3. The variation of visible spectrum to irradiated time (ethylene glycol monomethyl ether - FeCl$_3$ system). Concn. of FeCl$_3$: 0.64mol./l.

——— 0.0 hr. ------ 2.5 hr.
---- 8.5 hr. ---- 24.0 hr.

of this peak increased at an extremely slower rate than that in the case of ethers.

We may, therefore, assume that the photoreduction of ferric chloride by ethylene glycol proceeds very slowly.

A Comparison between the Photochemical and Thermal Reactions of Ethylene Glycol in the Presence of Ferric Chloride. — *Thermal Reaction.* — The thermal reaction of ethylene glycol in the presence of ferric chloride was investigated. A solution of 1.44 g. of anhydrous ferric chloride in 10 ml. of ethylene glycol was placed into a reaction vessel equipped with a condenser which had been connected to a trap cooled with a dry ice - acetone bath; the solution was then heated at 130°C for 5 hr. During this period no products were obtained in the trap. Although the reaction mixture was analyzed by g. c. and 2, 4-D. methods, no reaction products were observed. When 6.0 g. of the reaction mixture was distilled at 83—85°C/8 mmHg, most

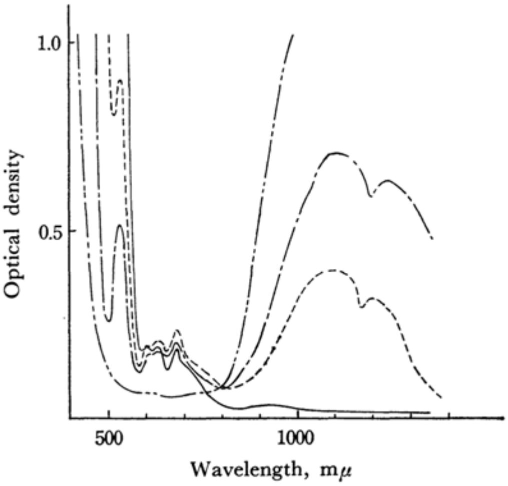


Fig. 4. The variation of visible spectrum to irradiated time (ethylene glycol dimethyl ether - FeCl$_3$ system). Concn. of FeCl$_3$: 0.47 mol./l.

——— 0.0 hr. ------ 1.5 hr.
---- 3.0 hr. ---- 18.0 hr.

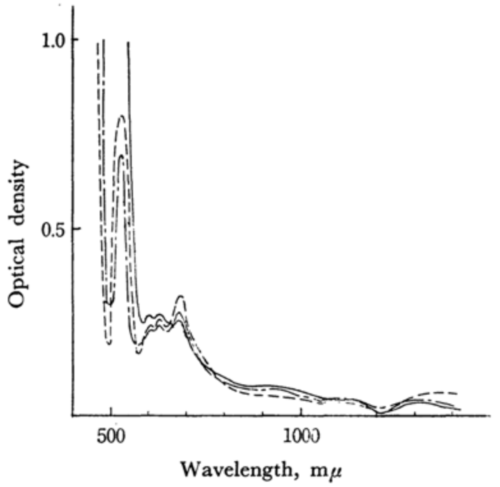


Fig. 5. The effect of hydrochloric acid or methyl chloride on visible spectrum of ferric chloride - ethylene glycol monomethyl ether system.
Concn. of FeCl$_3$: 0.64 mol./l.

——— Ferric chloride - ethylene glycol monomethyl ether
------ Addition of 0.60 mol./l. of hydrochloric acid
------ Addition of methyl chloride

TABLE I. THE AMOUNTS OF THE MAIN PRODUCTS IN THE PHOTOCHEMICAL REACTIONS*

Starting material	Amount mol.	$FeCl_3$ mol.	Amount of products obtained mol. $\times 10^2$				Total amount of gas mol. $\times 10^2$	Recovery %
			H_2CO	CH_3CHO	CH_3OCH_2Cl	CH_3OH		
$HOCH_2CH_2OH$	3.56	0.18	0	13.3	0	0	0.4	81
$CH_3OCH_2CH_2OH$	2.84	0.14	4.9	2.1	Trace	3.9	1.4	90
$CH_3OCH_2CH_2OCH_3$	1.64	0.08	2.1	0	1.2	0.8	0.2	91

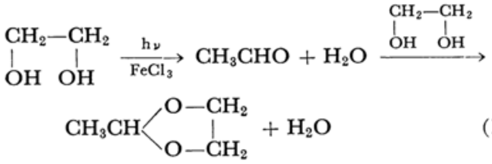
* Reaction time: 24 hr.

of the ethylene glycol was recovered, and 1.2 g. of the polymeric material was obtained as the distilled residue.

Photochemical Reaction. — A solution of 28.8 g. of anhydrous ferric chloride in 200 ml. of ethylene glycol was irradiated with a 100 W. mercury lamp according to the method described above. In the course of the photo-reaction, the evolution of 0.4×10^{-2} mol. (at S. T. P.) of gas was observed. An analysis of the gas by g. c. showed that its gas mainly consisted of hydrogen, methane and carbon monoxide.

The reaction mixture was then fractionated through a Vigreux column to give (1) a fraction of b. p. 25—80°C/8 mmHg (trapped by a dry ice - acetone bath; approximately 26 g.), (2) a fraction containing mainly unchanged ethylene glycol (approximately 180 g.), and (3) a distilled residue (approximately 40 g.). From fraction 1, acetaldehyde ethylene acetal, acetaldehyde and water were confirmed and determined by g. c. The amounts of these products are shown in Table I. The distilled residue was a dark brown oily material; this material was not, however, analyzed in detai. Besides these products, a small amount of glyoxal was isolated as the 2, 4-D.

As has been described above, apparent differences between the photochemical and thermal reactions were observed. The photochemical reaction of ethylene glycol in the presence of ferric chloride proceeds via the dehydration of ethylene glycol to give acetaldehyde, followed by the reaction 1 with ethylene glycol to produce acetaldehyde ethylene acetal. The reaction mechanism will be discussed later.



$$\underset{OH}{CH_2}-\underset{OH}{CH_2} \xrightarrow[FeCl_3]{h\nu} CH_3CHO + H_2O \xrightarrow{\underset{OH}{CH_2}-\underset{OH}{CH_2}} CH_3CH\left\langle\begin{array}{l} O-CH_2 \\ \quad\;\; | \\ O-CH_2 \end{array}\right. + H_2O \quad (1)$$

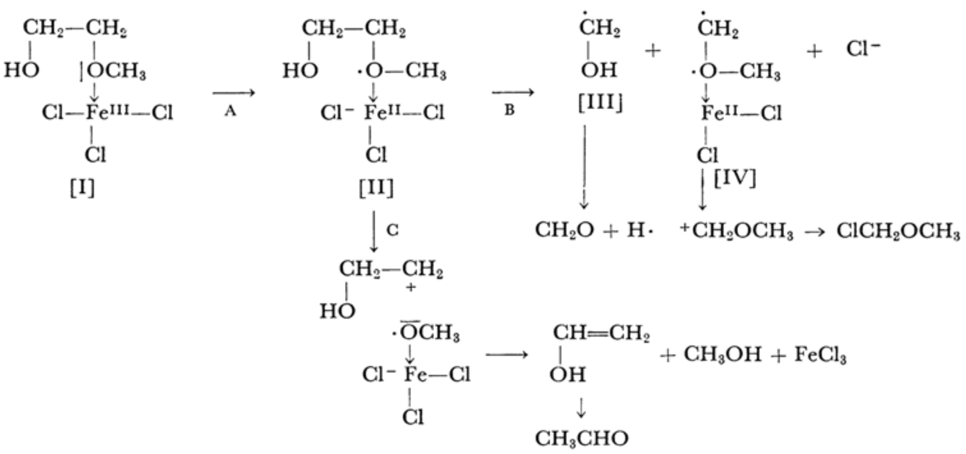
Photochemical and Thermal Reactions of Ethylene Glycol Monomethyl Ether with Ferric Chloride.—*Thermal Reaction.*—A solution of 2.08 g. of anhydrous ferric chloride in 20 ml. of ethylene glycol monomethyl ether was refluxed for 5 hr. The reaction mixture was then fractionated through a Vigreux column to give (1) a fraction of b. p. 80—90°C (approximately 3 g.), (2) a fraction containing mainly unchanged ethylene glycol monomethyl ether (approximately 15 g.), and (3) the distilled residue (approximately 3 g.). Ethylene glycol dimethyl ether was obtained from the fraction 1. The distilled residue was a black-brown clay-like solid containing ferric ions and chlorine ions.

As has been described above, the thermal reaction of ethylene glycol monomethyl ether with ferric chloride gave mainly ethylene glycol dimethyl ether. The reaction probably proceeds by a disproportionation 2. Although ethylene glycol was not confirmed in this investigation, it may be present in the distilled residue in the form of a complex with ferric chloride, or in the form of the polymeric material.

$$2\,CH_3OCH_2CH_2OH \xrightarrow{FeCl_3} CH_3OCH_2CH_2OCH_3 + HOCH_2CH_2OH \quad (2)$$

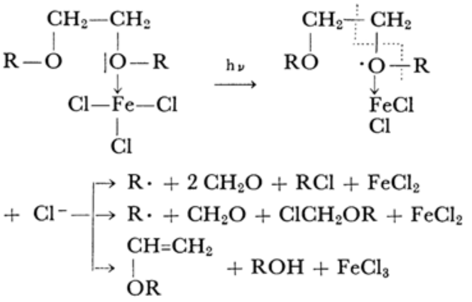
Photochemical Reaction. — The irradiation of ethylene glycol monomethyl ether with ferric chloride was made by the same procedure as in the case of ethylene glycol. In the course of irradiation, methane, ethane, hydrogen and carbon monoxide evolved. Among the products present in the reaction mixture, acetaldehyde, chloromethyl methyl ether, methanol, methoxymethyl methoxyethyl ether, methyl chloride and water were determined by g. c. In addition to these products, formaldehyde was determined by the 2, 4-D. method. The results are shown in Table I.

These results show that the mechanism of the photochemical reaction is different from that of the thermal reaction. Ferric chloride and ethylene glycol monomethyl ether form a complex, though the structure of the complex is not certain. (The formation of a complex was observed by spectrophotometric studies.) Ferric ions in a complex are reduced by ethylene glycol monomethyl ether to ferrous ions under ultraviolet irradiation. This means that the transfer of a lone-pair electron on an oxygen atom of a hydroxy or methoxy group to the excited ferric chloride occurs. This step is the primary process in the photochemical reaction. The formation and the amount of formaldehyde and chloromethyl methyl ether show the cleavage of the carbon-carbon bond (reaction 4), while those of acetaldehyde and methanol or water show the cleavage of the carbon-oxygen bond ($-CH_2-O-$) (reaction 5). From the results of the spectrophotometric studies, it may also be supposed that the



Scheme 1

reactions 4 and 5 are accompanied with the reaction 3, that is, the cleavage reaction of the R–O– bond to R^+ and ^-O–, because in the course of the reaction the formation of methyl chloride or hydrogen chloride was observed.



$$+\ Cl^- \rightarrow R\cdot + 2\,CH_2O + RCl + FeCl_2 \quad (3)$$

$$\rightarrow R\cdot + CH_2O + ClCH_2OR + FeCl_2 \quad (4)$$

$$\rightarrow \underset{OR}{CH=CH_2} + ROH + FeCl_3 \quad (5)$$

The cleavage of the carbon-carbon or carbon-oxygen bond is caused by the electron transfer in the primary process. It is not clear whether the cleavage of the carbon-carbon bond is ionic or homolytic. If the structure of a complex is I, and if the cleavage of the carbon-carbon bond is homolytic, the reaction proceeds via Paths A and B; that is, I is converted to II by the electron transfer, and then the cleavage reaction of II gives formaldehyde and chloromethyl methyl ether via the intermediate, III and IV. On the other hand, acetaldehyde and methanol are produced by the reaction paths A and C, in which the oxidative cleavage of the carbon-oxygen bond occurs, as is shown in Scheme 1. The fact that the amount of chloromethyl methyl ether is small (Table I) seems to show that chloromethyl methyl ether is converted into methanol, formaldehyde and methoxymethyl methoxyethyl ether by the following thermal reactions:

$$CH_3OCH_2Cl + H_2O \rightarrow CH_3OH + CH_2O + HCl$$

$$CH_3OCH_2Cl + CH_3OCH_2CH_2OH \rightarrow CH_3OCH_2OCH_2CH_2OCH_3 + HCl$$

Methyl vinyl ether, which can be produced by the dehydration of ethylene glycol monomethyl ether, and its polymer were not confirmed. The polymer may be present in the distilled residue.

Photochemical and Thermal Reactions of Ethylene Glycol Dimethyl Ether in the Presence of Ferric Chloride. — The photochemical and thermal reactions and the identification of the products were carried out by the same methods as in the cases of ethylene glycol and ethylene glycol monomethyl ether.

Thermal Reaction.—No reaction products were confirmed by g. c. and 2, 4-D. methods.

Photochemical Reaction. — In the course of irradiation, methane, ethane, hydrogen and carbon monoxide evolved, and crystals in the form of colorless prisms appeared on the walls of the lamp. These crystals were collected by filtration, washed with dry ether, and dried on phosphorus(V) oxide overnight. Attempts to measure the infrared spectrum and to make an elemental analysis of those crystals failed, since they were very unstable in relation to air or moisture. However, the results of the combustion test, Beilstein's test, and the other qualitative tests showed the presence of ferrous or ferric ions, chlorine ions and an organic compound in the crystals. When the crystals were allowed to stand under an air atmosphere they turned yellow, and the form of the crystals changed from colorless prisms to a semi-crystalline mush, the infrared spectrum of which showed large absorption bands at 3400, 1630 and 1600 cm^{-1} and other broad absorption bands at 1780, 1450, 1365, 1240, 1190, 1090 and 1045 cm^{-1}. The large absorption bands at 3400, 1630 and 1600 cm^{-1} corresponded to those of $FeCl_2 \cdot 4H_2O$.[7] Although the components of the colorless crystals are not clear, they seem to be a complex of ferrous chloride and an organic compound. The method of formation and the amounts of chloromethyl methyl ether and

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[7] I. Gamo, This Bulletin, **34**, 1495 (1961).

formaldehyde seem to support the assumption of the oxidative cleavage mechanism described above. However, an inbalance in the amounts of the products was observed, as is shown in Table I. This may be caused by the formation of colorless crystals under ultraviolet irradiation. A reaction would proceed by steps analogous to the steps of the reactions 3, 4 and 5, that is, an oxidative cleavage of a carbon-carbon bond to $\cdot CH_2OCH_3$ and $^+CH_2$-OCH_3.

Summary

The photochemical reactions of ethylene glycol, ethylene glycol monomethyl ether and ethylene glycol dimethyl ether in the presence of ferric chloride involve the cleavage process of the carbon-carbon bond to give formaldehyde and chloromethyl methyl ether; of the carbon($-CH_2-$)-oxygen bond to give acetaldehyde, methanol and water, or of the carbon(CH_3-), hydrogen-oxygen bond to give methane, ethane, hydrogen chloride and methyl chloride. These reactions are accompanied by the photoreduction of ferric chloride to ferrous chloride.