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The Photochemical Reactions of Fe(III) Complexes with 1,2-Glycols. Dehydration and Dehydrogenation*[1]

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Ferric chloride reacts with 1,2-glycols, when irradiated with light, to afford dehydration and dehydrogenation products. The reaction course is influenced by the structure of the 1,2-glycols, the kind of ligand around the Fe(III) ion, and the solvent in the reaction system. When the number of hydrogen atoms on carbon having a hydroxyl group of 1,2-glycol increases, the yield of the dehydration product increases in comparison with that of the dehydrogenation product; the photochemical reaction of ferric chloride with ethylene glycol or pinacol gives, selectively, acetaldehyde or acetone respectively. The photochemical reaction of ferric acetate with the ethylene glycol shows a highly selective dehydrogenation, giving only formaldehyde, though it is in a good yield. Furthermore, the addition of aniline or acetic acid to the ferric chloride-ethylene glycol system results in an increase in the production of glyoxal or acetaldehyde respectively. In the photochemical reaction of ferric chloride with ethylene glycol or *cis*- and *trans*-1,2-cyclohexanediol, acetonitrile as a solvent causes the formation of the dehydrogenation products, that is, acetoxyacetaldehyde and glyoxal or 1,2-cyclohexanedione respectively.

The photochemical reaction of ethylene glycol with ferric chloride affords, selectively, the dehydration product, acetaldehyde.(1) The ferric chloride - pyridine complex, however, causes the formation of the dehydrogenation product, glyoxal and formaldehyde, from ethylene glycol.(2) The reactions are mediated by a Fe(III) ion - ethylene glycol complex in solution. The selectivity of the reaction may be interpreted in terms of the interaction of a ligand with the hydrogen of either the carbon or hydroxyl group of ethylene glycol, which is close to the ligand. Moreover, the electronic nature of the Fe(III) in a Fe(III) complex may also contribute to the selective reaction. The present paper deals with a study of the effects of the ligand of a complex, of the solvent, and of the structure of 1,2-glycols on the dehydration or dehydrogenation course. Ethylene glycol, propylene glycol, 2,3-butanediol, pinacol, and *cis*- and *trans*-1,2-cyclohexanediol as 1,2-glycols, and ferric chloride and ferric acetate as ferric salts, were used here.

Experimental

Materials. The ethylene glycol, propylene glycol, 2,3-butanediol, aniline, and acetic acid were purchased from commercial sources, while the pinacol and *cis*- and

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1) H. Inoue, K. Tamaki, N. Komakine and E. Imoto, This Bulletin, **39**, 1577 (1966).

2) H. Inoue, K. Tamaki, N. Komakine and E. Imoto, This Bulletin, **40**, 875 (1967).

trans-1,2-cyclohexanediol were synthesized by the methods described in the literature.3-5) These materials were dried by the usual methods and distilled through a Vigreux column before use. Ethylene glycol: bp 76—77°C/4 mmHg, n_D^{22} 1.4321. Propylene glycol: bp 185—189°C, n_D^{32} 1.4291. 2,3-Butanediol: bp 72—73°C/5 mmHg, n_D^{31} 1.4343. Pinacol: bp 80°C/15 mmHg (lit.3,6) bp 75°C/13 mmHg). *cis*-1,2-Cyclohexanediol: mp 97—98°C (lit.4) mp 98°C). *trans*-1,2-Cyclohexanediol: mp 102—104°C (lit.5) mp 101.5 103°C). The anhydrous ferric chloride and ferric acetate, and thallium oxide (Tl_2O_3) were of a commercial grade; they were dried over phosphorus pentoxide at 100°C under the reduced pressure of 10 mmHg. The acetonitrile was purified by two distillations after having been dried on calcium hydride.

General Procedure of the Photochemical Reaction. The photochemical reactions were carried out by the methods described in previous papers.1,2) Glycols and ferric chloride or ferric acetate were transferred, under a nitrogen atmosphere, to a vycor tube. The tube was then sealed and irradiated for 20—24 hr at an equidistant place (4 cm) from a 100W mercury lamp, which irradiated waves at 2500, 3200, 3600, 4400, 5500, and 5800 Å at room temperature unless otherwise stated. The reactions of *cis*- and *trans*-1,2-cyclohexanediol with anhydrous ferric chloride or ferric acetate were carried out in an acetonitrile solvent. In the case of pinacol, chelate complexes consisting of pinacol and ferric chloride or cupric chloride were prepared, dissolved in an acetonitrile solvent, and irradiated as has been described above. The concentration of a solution of the chelate complex in acetonitrile was about 22 g/*l*. In order to isolate the reaction products, another procedure was attempted on a large scale by using a cylindrical, 300-m*l* reaction vessel.1)

Analyses of the Products. The analyses of the products were mainly accomplished by means of gas chromatography, using Hitachi KGL-2 and Yanagimoto 5DH gas chromatographs. A column containing polyethylene glycol-6000 and -20 M and/or high-vacuum silicone grease was used in the gas chromatography analyses. Helium gas was used as the carrier gas.

Acetone, propionaldehyde, acetaldehyde, methyl ethyl ketone, 2-ethyl-4-methyl-1,3-dioxolane, 2,4-dimethyl-1,3-dioxolane, 2,2,4-trimethyl-1,3-dioxolane, 2,4,5-trimethyl-1,3-dioxolane, and 2-ethyl-2,4,5-trimethyl-1,3-dioxolane were identified by a comparison of their retention times with those of authentic materials, and by trapping the materials from the column and by then comparing the infrared spectra of the trapped materials with those of authentic materials. The amounts of these compounds were determined by means of gas chromatography, and by the paper chromatography of their 2,4-dinitrophenylhydrazones. The amounts of the oxolanes are described as those of the corresponding carbonyl compounds in Tables 1, 2, 3 and 4. 1,2-Propanedione, 1,2-cyclohexanedione, adipaldehyde, 2,3-butanedione, and glyoxal were isolated as their 2,4-dinitrophenylhydrazones, which were purified by recrystallization from ethanol or ethanol - ethyl acetate, and which were identified by comparing their infrared spectra and their melting points with those of authentic materials. The diketones were determined by measuring the weights of their 2,4-dinitrophenylhydrazones. Acetoxyacetaldehyde was isolated as the 2,4-dinitrophenylhydrazone, mp 150—151°C (lit.7) mp 152°C), the infrared absorption spectrum of which has the absorption of the carbonyl group of the ester at 1730 cm^{-1}. Its elementary analysis indicates:

Found: C, 42.40; H, 3.44; N, 19.72%. Calcd for $C_{10}H_{10}N_4O_6$: C, 42.57; H, 3.55; N, 19.86%.

Formaldehyde and the ferrous ion were determined spectrophotometrically by using the Schiff's reagent and the 1,10-phenanthroline methods respectively.8,9)

Analysis of Fe(III) in Fe(III) Complex. A weighed amount of the Fe(III) complex was decomposed by refluxing it in concentrated nitric acid for 3—4 hr. The solution was then diluted with distilled water, and adjusted to pH 2—3 with 1 N sodium acetate - acetic acid, after which a 2% tiron solution was added. The solution was then titrated with a 0.01 M EDTA solution by a volumetric method.

Preparations of Complexes. *Ferric Chloride - Pinacol.* Ferric chloride (7.1 g) in acetonitrile (20 g) was mixed with a solution of pinacol (10 g) in acetonitrile (2 g). The solution was heated at 70—80°C for 1—2 min, then cooled with dry ice and acetone. Pale green crystals of the complex, which decomposed above 100°C without melting, were filtered off and washed with boiling chloroform (yield, 3.8 g).

Found: C, 26.15; H, 5.26%. Calcd for $C_6H_{14}O_2$-$FeCl_3$: C, 25.70; H, 5.03%.

Ferric chloride content, 4.2×10^{-3} mol/g. Pinacol content, 3.8×10^{-3} mol/g.

The determination of the pinacol present in the complex was carried out by the following method: a portion of 0.3 g of 8-quinolinol was added to a solution of 0.1 g of the complex in 10 m*l* of acetonitrile. The mixture was then allowed to stand at 30°C for 30 min to give the precipitate of the 8-quinolinol-ferric ion complex. The pinacol thus removed was analyzed by means of gas chromatography. The infrared absorption spectrum of the complex showed absorptions at 3270, 2960, 1460, 1380, 1340, 1140, 950, 920, 880, and 690 cm^{-1}, as Fig. 1 shows.

Cupric Chloride - Pinacol. A portion of 1 g of cupric chloride was added to a solution of 2 g of pinacol in 10 g of acetonitrile. The solution was heated at 70—80°C for 1—2 min, and then cooled with a dry ice - acetone mixture. Pale green crystals of the complex, which decomposed above 100°C without melting, were filtered off and washed with boiling chloroform (yield, 1.5 g). Pinacol content, 5.7×10^{-3} mol/g. The infrared absorption spectrum of the complex showed absorptions at 3400, 3125, 3025, 2750, 2550, 2330, 1460, 1375, 1210, 1160, 1140, 1113, 947, 895, and 827 cm^{-1}.

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Results

Photochemical Reaction of Ferric Chloride. *Eethylene Glycol.* Ethylene glycol reacts with ferric chloride under the irradiation of ultraviolet light for 24 hr to afford acetaldehyde in a 74% yield,[1] based on the amount of ferric chloride used. The addition of pyridine to the ferric chloride-ethylene glycol system, however, results in the production of glyoxal, formaldehyde, and acetaldehyde in 44, 5 and 6% yields respectively, when 60% of the Fe(III) is photo-reduced to Fe(II).[2] In this paper, aniline or acetic acid was added to a solution of ferric chloride in ethylene glycol, with the molar ratio of aniline or acetic acid to ferric chloride, of 1/2 or 1 respectively, and irradiated in an atmosphere of nitrogen at a distance of 4 cm from the light source for 24 hr at room temperature. As Table 1 shows, the addition of aniline to the reaction system gave glyoxal and acetaldehyde in 12 and 9% yields, while Fe(III) was photo-reduced to Fe(II) in a 84% yield. Thus, the product yields became considerably lower than the photo-reduction yield of Fe(III) to Fe(II). Probably, this means that aniline itself is photo-oxidized by ferric chloride. On the other hand, in the case of acetic acid, acetaldehyde was obtained as the main product in a yield which corresponded to the photo-reduction yield of Fe(III) to Fe(II). Thus, the acidic or basic ligand in the reaction system tends to contribute to the formation of the dehydration or dehydrogenation product respectively.

Propylene Glycol. When a solution of ferric chloride in propylene glycol was heated at about 100°C under a nitrogen atmosphere for 5.5 hr, no product was detected. However, the ultraviolet light irradiation of a solution of ferric chloride in propylene glycol gave mainly acetone, propionaldehyde, acetaldehyde, and formaldehyde, as is shown in Table 2. During the photo-reaction, the Fe(III) is photo-reduced to Fe(II). Acetone or propionaldehyde is produced by the elimination of the primary or the secondary hydroxyl group respectively (dehydration).

The formations of acetaldehyde and formaldehyde mean the occurrence of the oxidative cleavage of

Table 1. The effects of the ligands added on the photochemical reaction of ethylene glycol with ferric chloride*

Ligand	Molar ratio Ligand/$FeCl_3$	Yield of product (%)**			
		CH_3CHO	CH_2O	OHCCHO	Fe(II) ion
None***	—	74	0	0	—
Pyridine***	1	6	5	44	60
Aniline	0.5	9	0	12	84
Acetic acid	1	18	0	4	22

* The amounts of ethylene glycol and ferric chloride used for the cases of none, pyridine, aniline and acetic acid were 3.56, 0.18, 0.18, 4.5×10^{-3}; 0.18, 9×10^{-3}; and 0.18, 9×10^{-3} mol, respectively. Irradiation time: 24 hr for none and 20 hr for the other cases. Irradiation method: Cylindrical vessel for none, and light irradiation at the distance of 4 cm for the other cases.

** The yields of the products were calculated by (amount of CH_3CHO)/(amount of $FeCl_3$)×100 for CH_3CHO, (amount of CH_2O)/(amount of $FeCl_3$)×100 for CH_2O, and 4×(amount of OHCCHO)/(amount of $FeCl_3$)×100 for OHCCHO.

*** H. Inoue, K. Tamaki, N. Komakine and E. Imoto, This Bulletin, **39**, 1577 (1966); *ibid.*, **40**, 875 (1967).

Table 2. The photochemical and thermal reactions of propylene glycol with ferric chloride or hydrogen peroxide*

$FeCl_3$ or H_2O_2	Reaction type	Yield of product (%)**					
		CH_3COCH_3	CH_3CH_2CHO	CH_3CHO	CH_2O	CH_3COCHO	Fe(II) ion
$FeCl_3$	P***	12	23	17	1	0	64
H_2O_2	P	83	7	trace	1	8	—
$FeCl_3$	T	trace	trace	0	0	0	0
H_2O_2	T	2	10	trace	0	0	—

* The amounts of propylene glycol, ferric chloride and hydrogen peroxide were 4.04, 0.19 and 0.18 mol respectively. Irradiation time: 20 hr. Thermal reaction: temperature, 100°C and time, 5.5 hr.

** The yields of CH_3COCH_3, CH_3CH_2CHO, CH_3CHO, CH_2O and Fe(II) ion: (amount of the product)/(amount of $FeCl_3$ or H_2O_2)×100, and the yield of CH_3COCHO: 2×(amount of CH_3COCHO)/(amount of H_2O_2)×100. The total amount of gas evolved was 4×10^{-3} and 1.5×10^{-3} mol for the photo-reactions in the case of ferric chloride and hydrogen peroxide respectively.

*** P and T are the abbreviations for the photochemical and thermal reactions.

Table 3. The photochemical and thermal reactions of 2,3-butanediol with ferric chloride*

Reaction type	Yield of product (%)			
	$CH_3COCH_2CH_3$	CH_3CHO	$CH_3COCOCH_3$	Fe(II) ion
P	14	24	0	50
T	0	0	0	0

* The starting amounts of 2,3-butanediol and ferric chloride were 0.1 and 5×10^{-3} mol respectively. Irradiated time: 24 hr. Distance of irradiation: 4 cm. Thermal reaction: temperature, 100°C and time, 5.5 hr. The evolution of gas was not observed. The yield of the product was based on the starting amount of ferric chloride.

the bond between 1- and 2-carbons (dehydrogenation). The dehydration occurs twice as easily as does the dehydrogenation and, furthermore, involves twice as much elimination of the secondary hydroxyl group as of the primary hydroxyl group.

The ultraviolet-light irradiation of propylene glycol in the presence of hydrogen peroxide resulted in the formation of acetone in a 83.3% yield. This reaction is initiated by the hydroxyl radical produced by the photo-decomposition of hydrogen peroxide, followed by the abstraction of hydrogen on 2-carbon and the elimination of the primary hydroxyl group. Thus, there were remarkable differences between the photochemical behavior of ferric chloride and hydrogen peroxide in relation to propylene glycol. Probably, this is because the excited ferric chloride reacts with propylene glycol through a complex between them. Furthermore, the fact that the secondary hydroxyl group is more easily eliminated than the primary hydroxyl group supports the interpretation of the elimination mechanism by means of ferric chloride, as will be discussed later.

2,3-Butanediol. When a solution of ferric chloride in 2,3-butanediol was heated at about 100°C under a nitrogen atmosphere for 5.5 hr, no product was confirmed. However, the ultraviolet-light irradiation of the solution involving ferric chloride in 2,3-butanediol gave acetaldehyde, methyl ethyl ketone, and Fe(II) in 24, 14 and 50% yields respectively, as is shown in Table 3. That is, the yields of acetaldehyde and methyl ethyl ketone, based on the amount of Fe(III) converted to Fe(II), were 48 and 28% respectively. This would mean that the carbon-carbon bond cleavage occurs in a ratio similar to the elimination of the hydroxyl group.

Pinacol. A complex consisting of ferric chloride and pinacol was isolated as a pale green plate by mixing a solution of ferric chloride in acetonitrile with that of pinacol in acetonitrile. The combination of the elementary analyses of carbon and hydrogen, and the quantitative analyses of Fe(III) and pinacol in the crystals, showed that the molar ratio of the ferric chloride to the pinacol present in the complex is nearly 1, as is shown in Table 4. Furthermore, the infrared absorption spectrum of the crystals had absorptions characteristic of pinacol and ferric chloride.

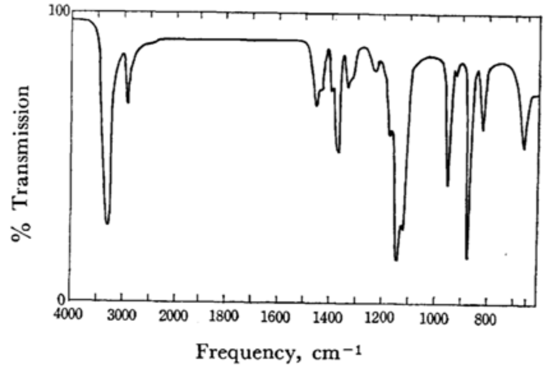


Fig. 1. Infrared spectrum of ferric chloride-pinacol complex (KBr disk).

The ferric chloride - pinacol complex dissolved in acetonitrile was irradiated with ultraviolet light for 24 hr at room temperature. As Table 4 shows, acetone was obtained as the sole product in a nearly 100% yield, based on the amount of ferric chloride in the complex as a starting material. The theoretical amount of the unreacted pinacol was recovered. When water instead of acetonitrile was used as the solvent, pinacol did not react with ferric chloride under the ultraviolet-light irradiation. This must be due to the decomposition of the ferric chloride - pinacol complex by the coordination of water.

On the other hand, when a solution of the complex in acetonitrile or water was refluxed under a nitrogen atmosphere for 6 hr, no product was detected, and pinacol was recovered in an almost 100% yield.

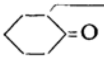
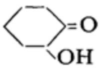
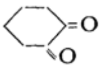
Although the production of pinacolone by pinacol rearrangement was predicted in the photochemical reaction of pinacol with ferric chloride, no pinacolone was detected at all. Pinacol also formed a complex with cupric chloride; the photochemical reaction of the complex gave acetone in a lower yield than in the case of the ferric chloride - pinacol complex, as is shown in Table 4. The photochemical reactions of binary metal salts, such as ferric chloride-cupric chloride and ferric chloride-thallium oxide, with pinacol gave unfavorable results, as Table 4 also shows. Thus, pinacol is photo-oxidized by ferric chloride in acetonitrile

TABLE 4. THE PHOTOCHEMICAL REACTION OF PINACOL-Fe(II) OR Cu(II) ION COMPLEX*

Complex pinacol-metal salt	Amount (g)	Component (mol×10^3)		Metal salt added (mol×10^3)	Solvent	Reaction type	Yield of CH_3COCH_3 (%)	Recovery % pinacol
		Metal salt	Pinacol					
$FeCl_3$	0.22	0.7	0.8	0	CH_3CN	P	100	55
$FeCl_3$	0.33	1.4	1.3	0	H_2O	P	0	100
$FeCl_3$	0.50	1.4	2.7	0	CH_3CN	T	0	90
$FeCl_3$	0.12	0.5	0.4	0	H_2O	T	0	100
$CuCl_2$	0.42	1.0	2.4	0	CH_3CN	P	40	83
$FeCl_3$	0.12	0.5	0.5	$CuCl_2$ (0.3)	CH_3CN	P	100	48
$FeCl_3$	0.13	0.5	0.5	Tl_2O_3 (0.3)	CH_3CN	P	114	37

* Irradiated time: 24 hr. Distance of irradiation: 4 cm. Thermal reaction: temperature, 100—110°C and time, 6 hr. The yield of acetone was based on the starting amount of ferric chloride or cupric chloride, and the recovery yield of pinacol was based on that of pinacol.

TABLE 5. DEHYDRATION AND DEHYDROGENATION PRODUCTS IN THE PHOTOCHEMICAL REACTION OF *cis*- AND *trans*-1,2-CYCLOHEXANEDIOL WITH FERRIC CHLORIDE OR FERRIC ACETATE*

1,2-Diol	Fe(III) salt	Yield of product (%)			
			 or 	$OHC(CH_2)_4CHO$	Fe(II) ion
cis-	$FeCl_3$	trace	4—8	0	38
trans-	$FeCl_3$	trace	4—8	0	50
cis-	$Fe(OCOCH_3)_3$	trace	0	2	—
trans-	$Fe(OCOCH_3)_3$	trace	0	1	—

* The starting amounts of 1,2-cyclohexanediol, ferric chloride and ferric acetate all were 5×10^{-3} mol. Acetonitrile was used as a solvent. Irradiation time: 48 hr for ferric chloride and 24 hr for ferric acetate. Distance of irradiation: 4 cm. The yield of the product was based on the starting amount of ferric chloride or ferric acetate.

TABLE 6. THE PHOTOCHEMICAL AND THERMAL REACTIONS OF ETHYLENE GLYCOL WITH FERRIC ACETATE*

Ethylene glycol (mol)	$Fe(OCOCH_3)_3$ (mol×10^3)	Reaction type	Yield of product (%)			Recovery %
			CH_3CHO	CH_2O	OHCCHO	
0.33	7.8	P	0	12	0	97
0.33	16.1	T	0	0	9	—
0.32	3.2	P	0	13	0	—

* Irradiated time: 24 hr. Distance of irradiation: 4 cm. Thermal reaction: temperature, 100—110°C and time, 5—6.5 hr. No gas was evolved and the other products were not detected from the measurement of gas chromatography. The yield of the product and the recovery yield of ethylene glycol were based on the starting amount of ferric acetate and ethylene glycol respectively.

TABLE 7. THE EFFECT OF ACETONITRILE ON THE PHOTOCHEMICAL REACTION OF FERRIC CHLORIDE WITH ETHYLENE GLYCOL

Ethylene glycol (mol)	$FeCl_3$ (mol)	CH_3CN (g)	Yield of product (%)					Recovery %
			CH_3CHO	CH_2O	OHCCHO	CH_3COOCH_2CHO	Fe(II) ion	
3.56	0.18	0	74	0	0	0	—	81
0.11	0.11	158	0	0	1	8	50	80

* Irradiated time: 24 hr in the absence of acetonitrile and 48 hr in the presence of acetonitrile. Reaction method: cylindrical vessel. The yield of the product was based on the starting amount of ferric chloride.

to afford, selectively, acetone in a good yield. This seems to be characteristic of the photochemical action of ferric chloride.

cis- and trans-1,2-cyclohexanediol. As Table 5 shows, the photochemical reaction of ferric chloride with *cis-* and *trans-*1,2-cyclohexanediol in acetonitrile afforded, selectively, a dehydrogenation product, 1,2-cyclohexanedione or 2-hydroxycyclohexanone, in a low yield of about 10%, when Fe(III) was reduced to Fe(II) in about a 40% yield. Although we attempted to recover *cis-* or *trans-*1,2-cyclohexanediol from the reaction mixture, it was difficult to recover it completely because of the formation of a complex between *cis-* or *trans-*1,2-cyclohexanediol and ferric chloride. By means of the ligand-exchange of the complex by 8-quinolinol, about 45—50% of *cis-* or *trans-*1,2-cyclohexanediol was, however, recovered. Thus, the yield of the product was low because of the photochemical reaction of ferric chloride with acetonitrile as a solvent; no remarkable differences were observed in the cases of *cis-* and *trans-*1,2-cyclohexanediol. The coordination of acetonitrile to Fe(III) may affect the selectivity and the yield in the formation of the dehydrogenation product.

Photochemical Reaction of Ethylene Glycol with Ferric Acetate. The photochemical reaction of ethylene glycol with ferric acetate was carried out under conditions similar to those used with ferric chloride. As Table 6 shows, formaldehyde was obtained as the sole product. During the photochemical reaction, white crystals appeared on the wall of the reaction vessel. In the photochemical reaction of 0.17 mol of ethylene glycol and 0.008 mol of ferric acetate, 0.16 g of the crystals was collected by filtration after the reaction. The crystals rapidly turned from white to brown upon exposure to air. The infrared absorption spectrum of the crystals, measured by a KBr disk, shows absorptions at 3400, 2950, 2870, 1555—1530, 1450—1430, 1350, 1055, 1030, 893, and 660 cm^{-1}, absorptions characteristic of those of ferric or ferrous acetate and ethylene glycol. The iron content of the complex was 4.8×10^{-3} mol/g; this corresponded to the amount of ferric acetate required for the formation of formaldehyde. The crystals are probably a complex between ferrous acetate and ethylene glycol.

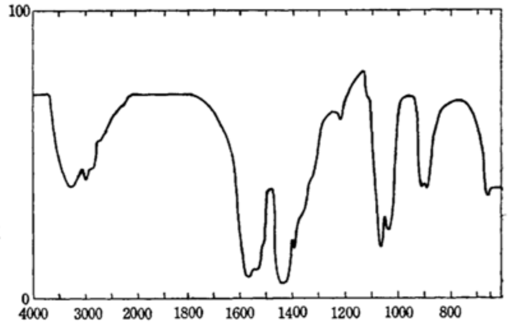


Fig. 2. Infrared spectrum of ferricacetate-ethylene glycol complex (KBr disk).

The next phenomenon concerns the photochemical reaction of a complex consisting of ethylene glycol and ferric acetate (Fe(III) ion content; 1.58×10^{-2} mol/3.8 g) in acetonitrile. The complex was prepared as follows. When a solution of 3.8 g of ferric acetate in 20.1 g of ethylene glycol was allowed to stand at room temperature for a day, there were precipitated 2.4 g of a pale prism, decomposing gradually above 100°C. After this had been filtered and then washed with acetonitrile. it was dried on calcium chloride under the reduced pressure of 10 mmHg at room temperature. The dispersion of the crystals in a solution of 8-quinolinol in acetonitrile removed the ethylene glycol from the crystals. Thus, it was confirmed that no organic compounds other than ethylene glycol and acetate anion were present in the crystals. Furthermore, the infrared absorption spectrum of the crystals, as measured by the use of a KBr disk, had absorptions at 3300—3100, 2950, 2870, 1580—1560, 1455—1420, 1390, 1300, 1245, 1230, 1070, 1040, 910, 895, and 660 cm^{-1}, absorptions characteristic of ferric acetate and ethylene glycol, as Fig. 2 shows. The absorption of the complex at 1560—1580 cm^{-1} was shifted toward a wave number shorter by about 30 cm^{-1} than that of ferric acetate. The determination of the Fe(III) present in the crystals showed the amount to be 4.1×10^{-3} mol/g. These results indicate that the crystals are a complex consisting of ferric acetate and ethylene glycol, with a molar ratio of 6.

A dispersed solution of 0.1 g of the ferric acetate-ethylene glycol complex in 10.0 g of acetonitrile was irradiated in an atmosphere of nitrogen at a distance of 4 cm from the light source for 24 hr at room temperature. Formaldehyde was obtained as the sole product in a 100% yield.

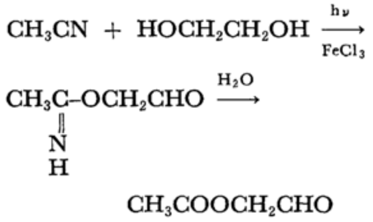
It has thus been confirmed that the photochemical reaction of ferric acetate with ethylene glycol shows a highly selective oxidative cleavage of a carbon-carbon bond to formaldehyde. Furthermore, the photochemical action of ferric acetate on *cis-* and *trans-*1,2-cyclohexanediol was also similar to that for ethylene glycol; that is, it resulted in the production of adipaldehyde, as is shown in Table 5.

On the other hand, the thermal reaction of ferric acetate with ethylene glycol afforded only a dehydrogenation product, glyoxal. Thus, there was a remarkable difference between the photochemical and thermal reactions of ferric acetate with ethylene glycol.

Solvent Effect of Acetonitrile. As Table 7 shows, the photochemical reaction of ferric chloride with ethylene glycol in acetonitrile afforded glyoxal and acetoxyacetaldehyde in 1 and 8% yields respectively, while Fe(III) was photo-reduced to Fe(II) in a 50% yield. About 80% of the ethylene glycol was recovered. Acetaldehyde and formaldehyde, which are the products of the photochemical reactions of ethylene glycol with ferric chloride and ferric acetate respectively, were not detected at all. Furthermore, when the solution of a mixture of ferric chloride and ethylene glycol in acetonitrile was allowed to stand at room temperature without any light irradiation, no acetoxyacetaldehyde was obtained. A reaction (1) involving the formation of hydroxyethyl esters by thermal interaction between nitriles and ethylene glycol has already been reported.[10] In the photochemical reaction

$$\mathrm{RCN + HOCH_2CH_2OH \xrightarrow[reflux]{} RCOO(CH_2)_2OH} \qquad (1)$$

described above, acetoxyacetaldehyde would be produced *via* the following process, that is, by the addition to one hydroxyl group of ethylene glycol to a nitrile group of acetonitrile coordinated to ferric chloride, and by the oxidation of the other hydroxyl group of ethylene glycol by the excited ferric chloride, as is indicated in Eq. (2):

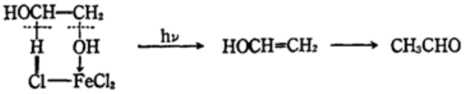


$$\mathrm{CH_3CN + HOCH_2CH_2OH \xrightarrow[FeCl_3]{h\nu} CH_3\underset{\substack{\| \\ N \\ H}}{C}{-}OCH_2CHO \xrightarrow{H_2O} CH_3COOCH_2CHO} \qquad (2)$$

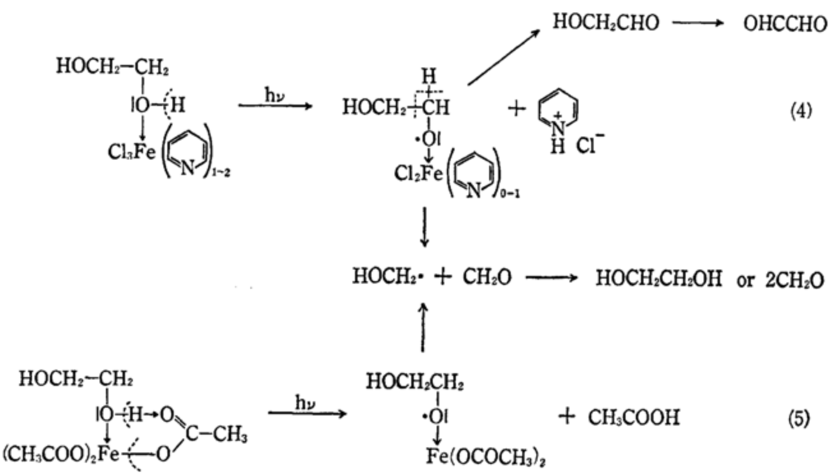
Discussion

Ferric salts form a complex with 1,2-glycols in the reaction system. The ferric chloride - pinacol and ferric acetate - ethylene glycol complexes were isolated as crystals. The excitation of the Fe(III) of the complex with light resulted in the competition of the dehydration and the dehydrogenation of the 1,2-glycols coordinated with the Fe(III). When the number of hydrogen on carbon with a hydroxyl group increased, the dehydration increased in comparison with the dehydrogenation: the yield of the dehydration product became lower in the order of ethylene glycol> propylene glycol> 2,3-butanediol> pinacol, while that of the dehydrogenation showed the reverse order. Furthermore, in the case of propylene glycol, the secondary hydroxyl group was eliminated more readily than the primary hydroxyl group. In addition, no rearrangement product was obtained in any case. On the other hand, the irradiation of a complex consisting of ferric acetate and ethylene glycol in acetonitrile gave, selectively, the dehydrogenation product, and addition of pyridine or acetonitrile to the ferric chloride - ethylene glycol system resulted in an increase in the formation of the dehydrogenation product. Thus, there were significant effects of the ligand, the solvent, and the structure of 1,2-glycol on the selectivity for the dehydration and the dehydrogenation.

The mechanisms for the two reactions may be explained reasonably by considering the interaction of the ligand or the base with hydrogen of either the carbon or hydroxyl group of 1,2-glycol. That is, for a dehydration mechanism, we assume a mechanism involving the intramolecular abstraction of hydrogen radical or proton by a chlorine radical or anion, followed by the simultaneous elimination of the hydroxyl radical or anion by the excited Fe(III), as is shown in Eq. (3). For the occurrence of the dehydration, the existence



(3)



(4)

(5)

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[10] B. Robinson, *J. Chem. Soc.*, **1963**, 2417.

of hydrogen on the carbon with a hydroxyl group and an exact stereochemical arrangement of the 1,2-glycol and ferric chloride in the complex are required.

The dehydrogenation by ferric acetate or the ferric chloride - pyridine system resembles Criegee's oxidation of glycols by lead tetraacetate.[11] Furthermore, it has been proposed that the excitation of Fe(III) complexes with OH^-, Br^-, I^-, NCS^- or $C_2O_4{}^{2-}$ as the ligand results in the transfer of an electron from the ligand to the Fe(III).[12] In a previous paper,[2] we have assumed the interaction of pyridine with the hydrogen of the hydroxyl group of glycol and the transfer of an electron from the oxygen of glycol or the glycol anion to the Fe(III), as is indicated in Eq. (4). The dehydrogenation by ferric acetate may also involve a mechanism similar to that of the case of pyridine, that is, the intramolecular interaction of acetate anion with the hydroxyl group and the oxidation of glycol or the glycol anion by the excited ferric acetate, thus producing formaldehyde *via* the cleavage of a carbon-carbon bond.

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[11] R. Criegee, E. Höger, C. Huber, P. Kruck, F. Marktscheffel and H. Schellenberger, *Ann.*, **599**, 81 (1956).

[12] N. Uri, *Chem. Revs.*, **50**, 375 (1952); E. Rabinowitch, *Rev. Modern Phys.*, **14**, 112 (1942); C. A. Parker, *Trans. Faraday Soc.*, **50**, 1213 (1954); C. A. Parker and C. G. Hatchard, *J. Phys. Chem.*, **63**, 22 (1959).