CHEMISTRY 80 RESEARCH

THESIS

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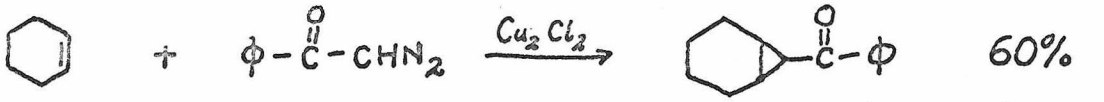
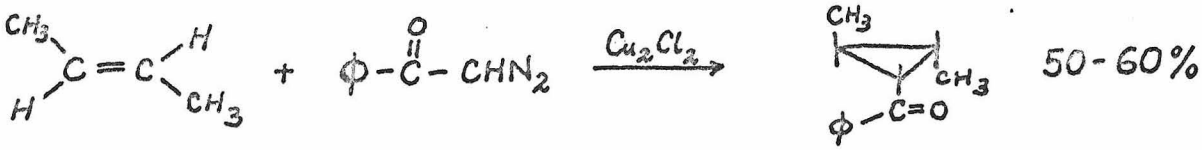
SYNTHESES OF CYCLOPROPENE AND BICYCLOBUTANE

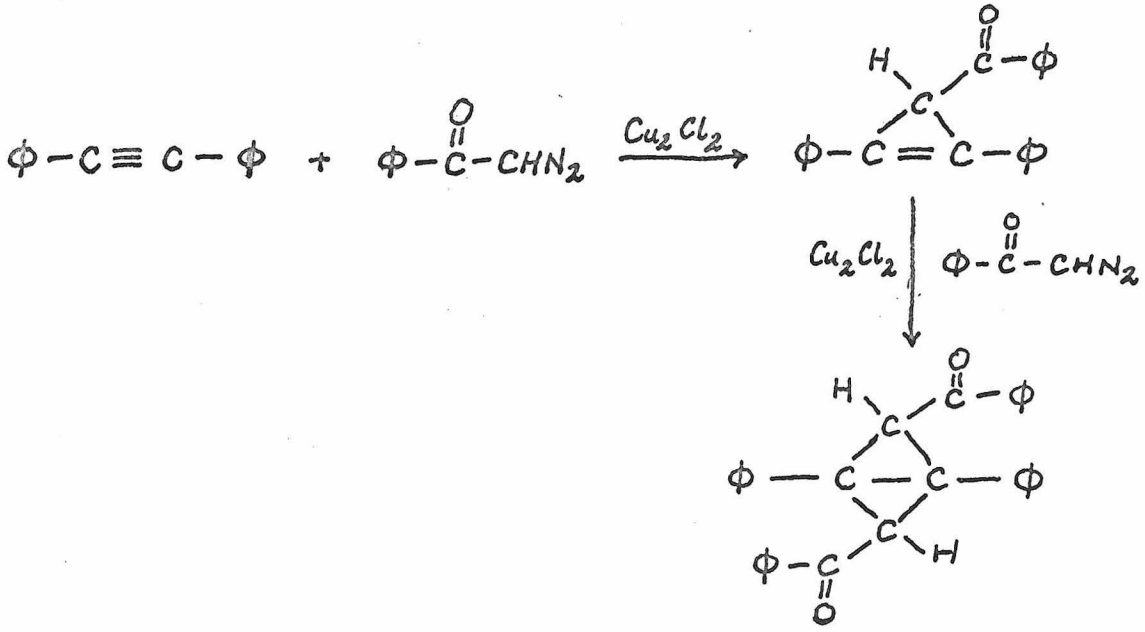
Introduction:

It is known that diazoacetophenone adds to carbon-carbon double bonds with a suitable catalyst.[1] The following reactions have been observed:





We decided to investigate similar reactions of additions to carbon-carbon triple bonds. We hoped that additions would lead to cyclopropene and/or bicyclobutane. The acetylenic compounds used were diphenylacetylene and 3-hexyne.



Experimental:

N-Nitroso-N-methylurea was prepared according to the method described by F. Arndt.[2] Urea was added to a slightly acidic solution of methyamine chloride, and then sodium nitrite was added. The product was isolated by adding the mixture to a cold sulfuric acid solution and collecting the crystalline foamy precipitate which rose to the surface. (66.5% yield)

Diazomethane was prepared according to the method described by F. Arndt.[3] N-Nitroso-N-methylurea was added to a cold ether-water potassium hydroxide solution. The ether was distilled and collected together with the diazomethane evolved. Concentration of diazomethane was determined by titrating an aliquot of the ethereal solution with a known amount of benzoic acid added against a standard base. (58.5% yield)

Diazoacetophenone was prepared according to the method described by M. S. Newman and P. Beal, III.[4] An ethereal solution of benzoyl chloride was added to a well-stirred cooled solution of diazomethane and triethylamine (previously dried over barium oxide) in ether. After filtering off the triethylamine hydrochloride, the solvent was removed under reduced pressure and the crude crystals were recrystallized from low-boiling petroleum ether. 88.5% yield)

Reaction of Diazoacetophenone with Diphenylacetylene.

Diazoacetophenone, 4.5 g (0.0308 mole), in 40 ml ether and 120 ml of isooctane was added slowly to a well-stirred solution of 0.5 g (0.0034 mole) diazoacetophenone, 2.39 g (0.0134 mole) diphenylacetylene, and 0.1 g cuprous chloride in 30 ml of isooctane. The nitrogen evolved was collected, and after eight hours the calculated amount of nitrogen was collected. The mixture was filtered, yielding a yellow filtrate (A) and an oily brown residue remained in the flask.

The filtrate (A) was concentrated by distillation. On cooling yellow rosette-like crystals (I) were formed. On further standing in the refrigerator, white, spherical crystals (II) appeared. The crystals were recrystallized separately from isooctane, m.p. 106.3-109° for (I) and 134.5° for (II). About 1/3 of the original isooctane solution was chromatographed on a neutral alumina column. Colorless crystals (III) (0.8 g, m.p. 60-61.5°) were eluted with pentane. No further products were eluted with benzene, ether, and ethanol. Mixtures of crystals were found to be separable by first adding hexane from which crystals (I) (m.p. 107-112°) and (III) (m.p. 60-67.5°?) can be fractionally crystallized, and the residue of the original mixture dissolved in isooctane yielded (II) (m.p. 130.4-136°). On standing, (I) in hexane turned to (II), which after recrystallization melted at 135.8-137.9°. Mixed melting point of (II) with cis-dibenzoyl-

ethylene (m.p. 138-139°) gave 135.8-142.3°(?).

The residue (B) was dissolved in carbontetrachloride, and was not decolorized with Norite. An attempt was made to chromatograph on a neutral alumina column. The carbontetrachloride solution when evaporated left a reddish colored oil which dissolved in a benzene-hexane mixture. On evaporation an oil was again obtained, which yielded few long needle-like crystals. Unfortunately these were unable to be separated from the oil.

Reaction of Diazoacetophenone with 3-Hexyne.

A similar procedure and stoichiometric amounts were used as in the diphenylacetylene, except cupric sulfate catalyst and benzene solvent were used. After warming to 60° for five hours, only 1/10 of the expected nitrogen was evolved. A little cuprous chloride was added, upon which a total of about 1/4 of the expected nitrogen was evolved.

After removal of solvent, a brownish oil was obtained. Isooctane was added and decanted as a yellow solution (C), and an oily residue (D) was left. (C) on concentration yielded 0.03 g yellow crystals (m.p. 94-104°). 1/3 of (D) was vacuum evacuated, collecting the solvents which by v.p.c. showed two compounds. The residue yielded some cubic crystals (m.p. 98-111°) having a u.v. spectrum identical with that of trans-dibenzoylethylene. Vacuum distillation of a fraction of the oily residue in a sealed "Y" tube gave a colorless liquid which showed two compounds

on v.p.c. of similar retention time as mixtures of benzene and hexyne.

Reaction of Diazoacetophenone with Excess 3-Hexyne.

Diazoacetophenone, 3.07 g, was dissolved in 25 ml of 3-hexyne. (1:10 diazoacetophenone to hexyne) To the solution 0.1 g of cuprous chloride was added. The expected volume of nitrogen was evolved. 2/3 of the hexyne was then distilled. The remaining solvent was removed by vacuum pump. The liquid collected showed one compound on v.p.c. Vacuum distilled part of the remaining oil with liquid nitrogen as coolant. An explosion of the sealed "Y" tube resulted when an attempt was made to open the tube. No time was available to work further on this reaction.

Discussion:

We were unable to isolate any addition products to diphenylacetylene. It seemed not much, if any, of the diphenylacetylene had reacted. The melting points of the crystals obtained corresponded to diphenylacetylene, and to cis and trans-dibenzoylethylene.

$$2\ \phi-\overset{O}{\overset{\|}{C}}-CHN_2 \longrightarrow \phi-\overset{O}{\overset{\|}{C}}-CH=CH-\overset{O}{\overset{\|}{C}}-\phi + 2N_2$$

After the failure of the first experiment, we decided to try 3-hexyne. It was known that cupric sulfate catalyzed reactions were slower.[5] Therefore cupric sulfate was used in the hope that coupling products would not form. The deficient amount of nitrogen evolved indicated the

possibility of incomplete reaction of diazoacetophenone or the formation of azo and azine compounds. Dibenzoylethylene was also formed, but there was no indication of products resulted from addition to hexyne.

We decided to take advantage of the liquid state of 3-hexyne. With excess hexyne, we hoped to form cyclopropene. Complete evolution of nitrogen was observed with cuprous chloride catalyst. Time permitted only an attempt to vacuum distill the oily residue. We have no explanation for the explosion of the vacuum distillation tube, except the possibility of an inadequately sealed vacuum tube and oxygen had condensed by the liquid nitrogen coolant. The detonation could have resulted from the evaporation of the oxygen and reaction with compounds in the tube.

We cannot conclude whether any addition products were obtained in the reactions. The highly strained bicyclobutane or cyclopropene may be too unstable to be isolated under our experimental conditions. A more thorough analysis of the excess hexyne mixture would have been helpful.

PHOTOLYSIS OF Fe^{III} CHELATES

Introduction:

The photolysis of ferric dipivaloylmethide, $Fe(DPM)_3$, in toluene with benzophenone as sensitizer, degassed and sealed *in vacuo*, yields a green colored solution which rapidly returns to the red-brown color when exposed to air.[6] It is believed that the green solution may be due to a specie of Fe^{II}. It has been known that β-diketone chelates of Fe^{II} are difficult to prepare because of their reactivity toward oxygen.[7]

We decided to investigate further the irradiation of ferric chelates of dipivaloylmethide (DPM^-), dibenzoylmethide (DBM^-), and acetylacetonate (AA^-) under various conditions. We also tried to find some evidence of Fe^{II} species by ferricyanide tests, n.m.r. and u.v. spectroscopy, and chelate to iron ratio determination.

Experimental:

The samples were placed in 15 x 125 mm. pyrex test tubes, degassed, and sealed *in vacuo*. The tubes were irradiated with a 450-watt mercury vapor lamp in a water-cooled pyrex jacket.

Spectra were taken with the samples in the sealed tubes using Beckman cell holders adapted for the Cary spectrophotometer.

Table I lists the samples irradiated.

Analysis of Irradiated $Fe(DBM)_3$.

The sealed tubes were opened in a nitrogen-filled drybox. The solution was filtered. Concentrated hydrochloric acid was added to the filtrate, and the solution was tested for Fe^{II} with ferricyanide solution. The solution remained yellow. However, when water was added, a deep blue color was obtained. But similar color was obtained with a solution of unirradiated $Fe(DBM)_3$. Therefore the test was inconclusive.

The crystals lost the crystalline shape when filtered from the solution. The residue was analyzed for total iron and ligand contents. Separation was performed by hydrolyzing the sample, and the ligand was extracted from the aqueous portion with chloroform. Iron was analyzed by o-phenanthroline and thiocyanate methods. Ligand was analyzed by ultraviolet spectroscopy.

The results of the analysis are listed in Table II.

Discussion:

We found that $Fe(DPM)_3$ irradiated in a mesitylene or xylene solution with benzophenone also resulted in a green colored solution. This led us to believe that toluene, xylene, and mesitylene may be hydrogen sources.

TABLE I

Photolysis of Ferric Chelates

Chelate	Other	Solvent	Radiation Time (hr)	Remarks
0.05 M $Fe(DPM)_3$	-	Benzene	150.5	darker solution
0.05 M $Fe(DPM)_3$	0.05 M EtOH	Benzene	120	very dark solution
0.05 M $Fe(DPM)_3$	0.05 M EtOH 0.05 M ϕ_2CO	Benzene	120	very dark solution
0.05 M $Fe(DPM)_3$	0.05 M ϕ_2CO	Benzene	120	darker solution
0.05 M $Fe(DPM)_3$	0.05 M ϕ_2CO	Toluene	120	yellow-green solution
0.05 M $Fe(DPM)_3$	-	Toluene	83	no visible reaction
0.05 M $Fe(DPM)_3$	0.05 M ϕ_2CO	Cumene	83	no visible reaction
0.05 M $Fe(DPM)_3$	0.05 M ϕ_2CO	Mesitylene	102	brown-green solution
0.05 M $Fe(DPM)_3$	0.05 M ϕ_2CO	Xylene	47.5	yellow-green solution
0.0001 M $Fe(DPM)_3$	0.0001 M ϕ_2CO	Toluene	25 min.	colorless
0.0003 M $Fe(DPM)_3$	0.3 M $(\phi_2COH)_2$	Benzene	(heat)	colorless solution with green ppt.
0.003 M $Fe(DPM)_3$	0.3 M $(\phi_2COH)_2$	Benzene	(heat) 61.5	green solution with black ppt. green-yellow solution with green-black ppt.
0.005 M $Fe(DPM)_3$	0.005 M aceto-naphthone	Toluene	117	ppt.
0.05 M $Fe(AA)_3$	0.05 M ϕ_2CO	Toluene	61.5	needle-like crystals
0.0001 M $Fe(AA)_3$	0.05 M ϕ_2CO	Toluene	61.5	colorless
0.005 M $Fe(DBM)_3$ (almost saturated)	0.005 M ϕ_2CO	Toluene	61.5	black, needle-like crystals purple-pink solution
0.0001 M $Fe(DBM)_3$	0.0001 M ϕ_2CO	Toluene	61.5	colorless
0.0025 M $Fe(DBM)_3$	0.0025 M ϕ_2CO	Toluene	117	crystals; dissolved on heating, recrystallized on cooling
0.005 M $Fe(DBM)_3$	0.005 M ϕ_2CO	Toluene (under N_2)	117	crystals
0.005 M $Fe(DBM)_3$	-	Toluene	64	no visible reaction
0.005 M $Fe(DBM)_3$	0.1 M $(\phi_2COH)_2$	Toluene	64	no visible reaction

TABLE II

Analysis of Precipitate from Photolyzed $Fe(DBM)_3$

		Fe Content (moles) By o-phen.	Fe Content (moles) By SCN	HDBM (moles)	HDBM/Fe By o-phen.	HDBM/Fe By SCN
I.	Unknowns					
	Sample (1)	5.32×10^{-6}	4.95×10^{-6}	8.71×10^{-6}	1.64	1.76
	Sample (2)	2.22×10^{-6}	2.03×10^{-6}	3.00×10^{-6}	1.35	1.48
II.	Control Run					
	$Fe(DBM)_3$	1.45×10^{-6}	1.21×10^{-6}	4.06×10^{-6}	2.80	3.36
	Correction factors	0.96	1.15	1.03		
III.	Corrected Values of Unknowns					
	Sample (1)	5.11×10^{-6}	5.69×10^{-6}	8.97×10^{-6}	1.76	1.58
	Sample (2)	2.13×10^{-6}	2.34×10^{-6}	3.09×10^{-6}	1.45	1.32

TABLE III

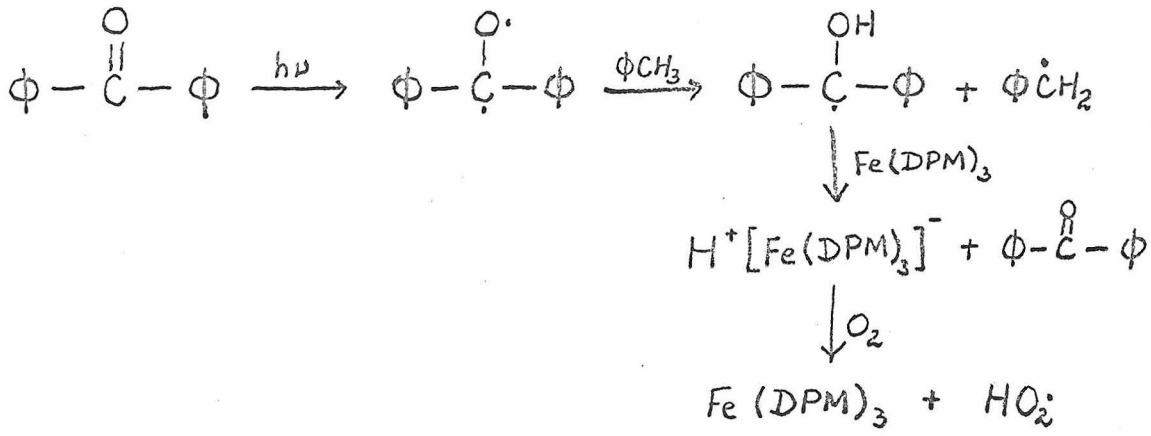
N.M.R. Analysis

	Sample (Toluene Solvent)	Peaks (Relative to TMS)	Peak to Peak
I.	0.08 M $Fe(DPM)_3$ 0.05 M ϕ_2CO (TMS in capillary tube)	- 3 cps -298 cps	295 cps
II.	0.08 M $Fe(DPM)_3$ 0.05 M ϕ_2CO	-278 cps + 17 cps	295 cps
III.	0.08 M $Fe(DPM)_3$ 0.05 M ϕ_2CO Irradiated 278.5 hrs.	-244 cps + 51 cps	295 cps
IV.	0.16 M $Fe(DPM)_3$ 0.05 M ϕ_2CO TMS	-210 cps + 85 cps (+213 cps)	295 cps
V.	0.16 M $Fe(DPM)_3$ 0.05 M ϕ_2CO	-205 cps + 90 cps	295 cps

TABLE IV

Absorptions and Extinction Coefficients

Compound	Solvent	Absorption (Å)	Extinction Coeff.
$Fe(DPM)_3$	Toluene	4300 3560	$\epsilon_{4300} = 5380$ $\epsilon_{3560} = 3560$ $\epsilon_{3660} = 4545$
$Fe(AA)_3$	Toluene	4370 3510	$\epsilon_{4370} = 4400$ $\epsilon_{3510} = 5380$ $\epsilon_{3660} = 3960$
$Fe(DBM)_3$	Toluene	~4800 (broad) 4090 3350 2550	$\epsilon_{4800} = 4200$ $\epsilon_{4090} = 5480$
HDBM	$CHCl_3$	3420 2520	$\epsilon_{3420} = 2.48 \times 10^4$ $\epsilon_{2520} \approx (1.0\text{-}1.1) \times 10^4$
Benzpinacol	$CHCl_3$	2710 (shoulder) 2610 2560 (shoulder)	
Benzophenone	$CHCl_3$	3790 (shoulder) 3600 (shoulder) 3480 3380 (shoulder)	



However, the use of ethanol in benzene showed no reaction. Anattempt to reduce $Fe(DPM)_3$ directly in benzene with $LiAlH_4$ showed only a slight fading of the color of solution. Another possible method to reduce the chelate could be with tri-n-butyltin hydride.

The green solution of $Fe(DPM)_3$ in toluene was found to have an absorption peak at 7730Å. Solutions of 10^{-4}M chelate concentration gradually turned colorless in 25 minutes of irradiation time. Ultraviolet spectra showed a gradual disappearance of the chelate peaks. However, on exposure to air, no chelate spectra was obtained.

We thought that benzophenone may form benzpinacol which then in turn complex with some form of iron causing the green colored solution. We found that when a chelate-benzpinacol benzene solution was heated or irradiated, a light green solution was formed, sometimes with green-black precipitate. The spectra showed no absorption at 7730Å. We also noted spectrally that the iron chelate concentration

decreased on heating, and at the same time ligand absorption appeared.

We also found that irradiation of $Fe(DBM)_3$ and $Fe(AA)_3$ yielded crystals. $Fe(DBM)_3$ also showed a change of solution color from brown-red to purplish pink. On exposure to air, the crystals disappeared and the solution returned to the original color. The crystals dissolved when the sealed tube was heated on the steam bath, but recrystallized on cooling. The pink solution showed an absorption peak at 5200Å.

We also attempted to find the ratio of ligand to iron in the crystals. The results (Table II) indicated that the number of ligands per iron decreased, but we were unable to interpret as to whether the iron is Fe^{II} or Fe^{III}.

We failed to find positive evidence of Fe^{II} species in irradiated samples of iron chelates. We found that benzophenone and/or benzpinacol are necessary to obtain the green colored solution.

Ferrous Chloride Catalyzed Oxidation of Dihydroxyfumaric Acid in Methanol at 30°C and 1 Atm. O_2

Introduction:

The ferrous chloride ($FeCl_2 \cdot 2H_2O$) catalyzed oxidation of ascorbic acid has been studied by Dr. Chin-Hua Wu. It was found that the rate of oxidation is first order with respect to ascorbic acid and ferrous chloride. Ascorbic acid belongs to the "Class I co-substrates," among which is also dihydroxyfumaric acid (trans-HOOC(HO)C=C(OH)COOH).

We attempted to elucidate the mechanism and the reaction orders of the ferrous chloride catalyzed oxidation of dihydroxyfumaric acid. Of special interest was the attempt to prove or disprove the postulated existence of a peroxy radical transient, $Cl_2FeO\cdot$, and the subsequent trapping of the transient. That is:

$$FeCl_2 + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cl_2FeO_2$$

$$Cl_2FeO_2 + DH_2 \xrightarrow{slow} Cl_2FeO\cdot + D + H_2O$$

$$Cl_2FeO\cdot + DH_2 \xrightarrow{fast} Cl_2Fe + D + H_2O$$

$$Rate = K[FeCl_2][DH_2][O_2]$$

Thus, according to this mechanism the rate should be first order with respect to ferrous chloride, dihydroxyfumaric acid, and oxygen.

Experimental:

The ferrous chloride ($FeCl_2 \cdot 2H_2O$) used in the experiments was two samples obtained from Dr. Chin-Hua Wu.

One was sample W5-124 and the second was W11-120-1 and W11-121-1. The purity of these samples was checked spectrophotometrically and by titration with potassium dichromate. The corrections for purity were made accordingly in the calculations.

The dihydroxyfumaric acid (trans-HOOC(HO)C=C(OH)COOH) used was from the stock bottles from Nutritional Biochemical Corporation.

The methanol used as reaction solvent was specially treated, dried, and distilled by Dr. Chin-Hua Wu.

The experiments were performed with the constant-temperature-and-pressure gas apparatus. The normal procedure was to place the ferrous chloride and dihydroxyfumaric acid in a covered spoon, and the methanol solution in the reaction flask. After the process of degassing and filling the system with oxygen, the ferrous chloride and dihydroxyfumaric acid were added to the solution. The uptake of oxygen was then measured at regular intervals. The result of the change of volume of oxygen was plotted versus time. The initial rate, $\left(\frac{\partial O_2}{\partial t}\right)_{t=0}$, was measured from the slope at time equals zero or shortly thereafter. When the reaction was not carried to completion, the reaction solution was analyzed immediately for Fe^{II}, Fe^{III} and co-substrate by spectrophotometric analysis. This yielded the ratio of the number of moles of oxygen to moles of iron or co-substrate. The results of the experiments are tabulated in Tables V and VI.

TABLE V

Ferrous Chloride Catalyzed Autoxidation of Dihydroxyfumaric Acid in Methanol at 30°C and 1 Atm. O_2

Run No.	$[FeCl_2 \cdot 2H_2O]_o$ M	$[DHF]_o$ M	Reaction Period (min.)	$R_o \times 10^3$ ml min^{-1} (ml soln)$^{-1}$	$\frac{\Delta[Fe]}{[FeII]_o}$	$\frac{\Delta O_2}{\Delta[DHF]}$	$\frac{\Delta[DHF]}{[DHF]_o}$
W11- 78	0.050	-	134	1.16	0.17		
W11-101	0.050	-	134	1.16	0.17		
H 2- 62	0.138	-	90	12.6	0.29		
W 9-119	0.059	0.045	100	23.4	0	1.61	1
W 9-122	0.060	0.047	95	23.0	0	1.68	1
W 9-130	0.134	0.055	36	48.7	<0.01	1.60	~1
H 2- 22(A)*	0.027	0.026	60	14.5	0.06	2.58	1
H 2- 52(B)*	0.049	0.026	97	26.0	0.08	1.50	1
H 2- 96(B)*	0.049	0.026	97	22.9	0.09	1.57	1
H 2- 14(A)*	0.050	0.026	123	16.8	0.11	1.91	1
H 2- 98(A)*	0.051	0.028	123	26.5	0.10	1.65	1
H 2-100(C)*	0.050	0.027	120	19.5	0.10	1.57	1
H 2- 18(A)*	0.053	0.050	144	18.1	0.11	1.55	1
H 2- 60(C)*	0.138	0.012	60	50.4	0.13	1.24	
H 2- 56(C)*	0.137	0.025	30	81.7	0.07	1.62	1
H 2- 54(C)*	0.139	0.049	37	88.0	0.05	1.54	
H 2- 76(C)*	0.141	0.100	45	310	0.01	2.73	1

*Letters refer to the sample of $FeCl_2 \cdot 2H_2O$ used: (A) W 5-124, 101.6%
(B) W11-120, 99.13%
(C) W11-121, 101.6%

TABLE VI

Catalyzed Autoxidation of Dihydrofumaric Acid in Methanol at 30°C and 1 Atm. O_2

Run No.	$[FeCl_2 \cdot 2H_2O]_o$ M	$[DHF]_o$ M	M		Reaction Period (min.)	$R_o \times 10^3$ ml min^{-1} (ml soln)$^{-1}$	$\frac{\Delta[Fe]}{[FeII]_o}$	$\frac{\Delta O_2}{\Delta[DHF]}$
H2- 12(A)*	0.050	-	LiCl	0.47	59	15.2	0.60	-
			p-TSA	0.099				
H2- 26(A)*	0.055	0.026	LiCl	0.47	60	28.9	0.91	-
			p-TSA	0.103				
H2- 70(C)*	0.139	0.026	LiCl	0.47	30	339	0.27	0.74
			p-TSA	0.09				
H2- 30(A)*	0.053	0.026	LiCl	0.0	60	2.7	0.009	2.73
			p-TSA	0.103				
H2- 72(C)*	0.139	0.025	LiCl	0.0	61	35	0.08	1.27
			p-TSA	0.10				
H2- 92(C)*	0.045	0.027	$HgCl_2$	0.097	60	86.3	0.05	1.46
H2- 34(A)*	0.052	0.025	$HgCl_2$	0.20	30	93.3	0	1.59
H2- 64(C)*	0.138	0.027	$HgCl_2$	0.20	125	89.5	0.03	1.79
H2- 94(B)*	0.044	0.028	$HgCl_2$	0.289	70	163	0.13	1.46
H2- 38	-	0.026	$HgCl_2$	0.20	30	1.1	-	6.02
H2- 40	-	0.026	$HgCl_2$	0.21	30	1.9	-	4.03
H2- 42(A)*	0.052	0.023	$ZnCl_2$	0.212	60	46.0	0.033	2.37
H2- 68(C)*	0.139	0.026	$ZnCl_2$	0.21	60	125	0.03	2.05
H2-102(B)*	0.049	0.029	$FeCl_3$	0.004	135	12.7	(0.11)	(1.52)
H2-104(B)*	0.049	0.027	$FeCl_3$	0.009	160	8.2	(0.11)	(1.64)

*Letters refer to the sample of $FeCl_2 \cdot 2H_2O$ used: (A) W 5-124, 101.6%
(B) W11-120, 99.13%
(C) W11-121, 101.6%

Discussion:

Table V shows that the rate showed erratic and minor changes when the concentration of ferrous chloride was changed. However, the increase of the concentration of dihydroxyfumaric acid caused increases in the rate of oxidation, but not a first order increase.

Table VI shows the effects upon addition of p-toluene sulfonic acid (p-TSA) and/or Lewis acids. The presence of Lewis acids seemed to increase the rate of oxidation as shown by comparing runs H2-26 to H2-30, and H2-70 to H2-72. But the presence of p-toluene sulfonic acid reduced the rate as shown by comparing runs H2-30 to H2-98 and H2-100, and H2-72 to H2-56. These observations do not appear to support the peroxy radical as postulated in the mechanism above. However, they do seem to imply an association of dihydroxyfumaric acid with ferrous chloride. Possibly the partial mechanism is:

$$FeCl_2 \rightleftharpoons FeCl^{\oplus} + Cl^{\ominus}$$

$$FeCl^{\oplus} + HDHF \rightleftharpoons ClFe(DHF) + H^{\oplus}$$

$$ClFe(DHF) \xrightarrow{\text{oxidation}}$$

The curious negative rate observed in the oxidation process, which we call the "discontinuous point," is shown in Table VII. This "point" occurred when most of the dihydroxyfumaric acid has been oxidized. A very sudden rapid uptake of oxygen occurred and simultaneously the reaction solution turned to a yellow color. When a maximum of the

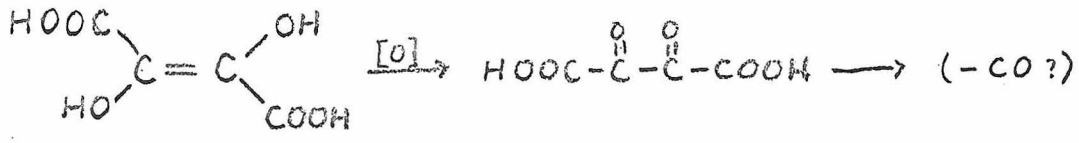
TABLE VII

"Discontinuous Point" of Catalyzed Autoxidation of Dihydroxifumaric Acid in Methanol at 30°C and 1 Atm. O_2

Run No.	$[FeCl_2 \cdot 2H_2O]_o$ M	$[DHF]_o$ M	M	$R_o \times 10^3$ ml min^{-1} (ml soln)$^{-1}$	Disc. Point (min.)	ΔV (ml)
H2- 52	0.049	0.026		26.0	80	1.40
H2- 96	0.049	0.026		22.9	85	1.30
H2- 14	0.0506	0.026		16.8	92	1.10
H2- 98	0.051	0.026		26.5	81	1.05
H2-100	0.050	0.027		19.5	100	1.35
H2- 18	0.053	0.050		18.1	136	1.80
H2- 60	0.137	0.025		50.4	7.4	0.12
H2- 56	0.137	0.025		81.7	17.5	0.45
H2- 94	0.044	0.028	$HgCl_2$ 0.289	163	43	2.15
H2- 92	0.045	0.027	$HgCl_2$ 0.097	86.3	40.5	1.65
H2- 64	0.138	0.027	$HgCl_2$ 0.052	89.5	18	0.6
H2- 42	0.052	0.023	$ZnCl_2$ 0.212	46.0	35	0.20
H2- 68	0.159	0.026	$ZnCl_2$ 0.21	125	(too fast to observe)	
H2-102	0.0494	0.029	$FeCl_3$ 0.005	12.7	125	1.10
H2-104	0.0493	0.027	$FeCl_3$ 0.009	8.2	145	1.20

uptake was reached, a negative rate was observed until approximately where the original reaction curve was prior to the "discontinuous point." (The ΔV shown in Table VII refers to the sudden uptake of oxygen since this could be measured more accurately.) Analysis for Fe^{III} before this point occurred showed almost none present. The ΔV seemed to vary with the concentration of dihydroxyfumaric acid when only ferrous chloride was present.

The fact that the "discontinuous point" occurred at the same time as the appearance of the yellow color, which was presumed to be due to oxidation of Fe^{II} to Fe^{III}, and the change of ΔV depended on the concentration of dihydroxyfumaric acid indicates and supports the formation of a DHF-Fe^{II} complex. The negative rate was probably due to the decomposition of the oxidized dihydroxyfumaric acid:



The reaction solutions were not analyzed for decomposition products. However, it seems that an easy analysis could be done on the gas by mass spectrometry.

The measurements of the initial rates are variable and inaccurate, depending on how the slopes are drawn. They depend to a large extent on how many points are obtained from the early phase of the experiments. Therefore, a fast rate yields a much more inaccurate initial rate.

We failed to find evidence for the existence of the postulated peroxy radical, $Cl_2FeO\cdot$. However, our experiments do not exclude the existence of the radiccal.

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