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THE CHARGE TRANSFER PHOTOCHEMISTRY
OF SELECTED IRON(III) SPECIES

BY

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Submitted to the Department of Chemistry
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The undersigned recommend to the Faculty of Graduate Studies and Research acceptance of the thesis "The Charge Transfer Photochemistry of Selected Iron(III) Species", submitted by John Hugh Carey, B.Sc., M.Sc., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

Irradiation of simple iron species in their charge transfer regions produces simple radicals which can react with other molecules in solution.

The irradiation of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ in the presence of radical scavengers caused an increase in yield as the concentration of scavenger increased. Tertiary butanol as a scavenger gave rise to a plateau at $\bar{I}_{\text{Fe(II)}} = .130$ which agreed well with previous results. With other scavengers, such as methanol, isopropanol, and formic acid, the yield continued to rise linearly with scavenger concentration. This was interpreted as a direct reaction between the iron excited state and the scavenger which was in a reactive position in the solvation shell.

The dihydroxobridged ferric dimer $(\text{Fe}(\text{H}_2\text{O})_4\text{OH})_2^{4+}$ also exhibited this new reaction. The tertiary butanol yield for this species was close to zero.

Irradiation of $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ in the chloride-to-metal charge transfer region produced a complicated dependence of $\bar{I}_{\text{Fe(II)}}$ upon chloride and scavenger concentration. At low chloride, behaviour similar to the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ system was observed. The behaviour is consistent with the photo-production of chlorine atoms which react competitively with chloride and scavengers. The excited state reaction

was also observed for methanol and isopropanol in this system.

The photodecarboxylation of ferric-EDTA complexes was studied at 3500Å. The hydrolytic forms present at pH 8.00 and 9.00 were observed to have yields below 0.10 and varying from species to species. The oxo-bridged dimer was unreactive, possibly as a result of population of ligand field bands, either by direct irradiation or relaxation processes. The products were similar to other aminopoly-carboxylate systems. The excited state reaction also appears to occur in the presence of scavengers.

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I. INTRODUCTION

(A) General Introduction

Although the production of an excited state via the absorption of light energy by a ground state molecule is the initial step in all photochemical reactions, the absorption process itself is only of limited interest in the study of the mechanisms of these reactions. The principles that

i) only light which is absorbed by a molecule can result in a photoreaction

ii) one quantum produces one excited state

which evolved early in this century can be taken as axiomatic.⁽¹⁾ The Frank-Condon Principle,⁽²⁾ which also deals with the absorption processes, is more significant. This principle states that the absorption process is so fast compared with molecular motion that the atoms of a molecule do not change position or momentum during an electronic transition. Since the new electronic configuration may have its potential energy minimum at some other nuclear configuration than that of the ground state, the Frank-Condon Principle predicts that the excited state initially produced will be the result of a vertical transition from the ground state to the excited state potential surface, as depicted in Fig. I-1, and, depending on the relative positions of the excited and ground state potential minima,

FIG. I-1

Vertical transitions between the ground state and
(a) a slightly distorted excited state, and (b) a greatly
distorted excited state.

may produce an electronic excited state that is not in its vibrational ground state. This excited state is assumed to rapidly lose its excess vibrational energy to produce a vibrationally-equilibrated excited state, from which emission and reaction are assumed to occur. (3)

The processes by which an excited state loses its excitation energy can be subdivided into

- i) radiative transitions (emission)
- ii) radiationless transitions
- iii) energy transfer

Radiative transitions generally occur from the lowest excited state of a given multiplicity back to the initial reactant in its ground state. Radiationless transitions can lead back to the original ground state configuration, but they may also lead to another excited state or to a new molecule in its electronic ground state. The process in which a molecule in an excited configuration relaxes to a photochemical product rather than the ground state has been discussed by Hammond. (4) Both are relaxation, but the distortion of the excited state can favour relaxation to product if the distortion makes the geometry of the excited state resemble the product. Conversely, if the excited state is not distorted relative to the ground state, relaxation back to this ground state configuration is favoured. Radiationless transitions between excited states are sometimes called internal conversion (IC) or intersystem crossing (ISC)

depending on whether the multiplicities of the two states are the same or different. Energy transfer occurs between two molecules in which the original excited state is deactivated by producing an excited state in the second molecule through transfer of some of its excitation energy.

Hammond⁽⁴⁾ has suggested that the study of photoreactions should be divided into two parts.

- i) the study of reaction mechanisms
- ii) the establishment of structure-reactivity relationships

In order to completely describe the mechanism of a photoreaction, a knowledge of all excited states involved in radiative and radiationless processes leading into and away from the photoreactive state is required. Ideally, both the geometry and vibro-electronic structure of these states, and the transition probabilities of the paths connecting them should be known. Photochemical studies are generally concerned with complex polyatomic molecules in solution which have poorly resolved spectra. This makes the derivation of structural information about excited states difficult. In cases where spectra have been resolved, if a molecular orbital treatment can be applied, useful mechanistic information can be obtained. For example, a molecular orbital treatment of the photodecomposition of formaldehyde⁽⁵⁾ has successfully correlated spectroscopic analysis with photochemical reactivity. This type of anal-

ysis may be extended to predict the reactivities of symmetrical and cyclic ketones, thus providing one example of knowledge of a mechanism leading to a useful structure-reactivity relationship. Most predictions, however, result from empirical observations based on structures, eg. Adamson's rules for photosubstitution in transition metal complexes,⁽⁶⁾ rather than from a knowledge of the mechanism.

In order to overcome the difficulties imposed by lack of knowledge of the natures of excited states, some simplifications must be made. In general, relaxation of excess vibrational energy and radiationless conversion processes between states are thought sufficiently rapid that one need only be concerned with the lowest states of a given multiplicity.⁽³⁾ This is a good approximation in organic chemistry, possibly because most irradiations in the visible or near ultra-violet involve population of the π^* levels and the σ bonds are left intact after the excitation. In many cases the excited state minima lie above one another, with relatively slight distortion, permitting good communication between excited states and hence rapid relaxation. It should be noted that if a molecule like benzene is irradiated in the far ultra-violet, the σ bonds are broken and the photochemical behaviour is in sharp contrast to that observed when the transition involves the π orbitals. Thus the approximation that only the lowest energy states need be considered needs to be qualified so that only those states which are similar are

assumed to relax rapidly among themselves.

In the photochemistry of transition metal complexes, excited states of two different types occur. Ligand field excitations produce changes in electron density among the 'd' orbitals of the metal. There is little change in electronic population between the metal and ligand atoms.

Since the 'd' orbitals are π^* or σ^* , the vibrationally equilibrated excited state of a ligand field band probably resembles a distorted version of the ground state, with the atomic electronic populations intact.

In contrast to ligand field excitation, charge transfer transitions result in a net change in total electronic population between the metal and the ligands. A simplified approach neglects overlap between orbitals and visualizes the transition as the transfer of one electron from one atom to another.⁽⁷⁾ The excited state differs from the ground state not only in geometry but in "oxidation state" of the metal and of the ligands involved in the transition. A traditional distinction is therefore made between charge transfer photochemistry, which is primarily redox in character, and ligand field photochemistry which is primarily substitutional.

Some ligand field redox processes occur in systems containing reducing substances such as oxalate⁽⁸⁾ or ferrocyanide⁽⁹⁾ or where a charge transfer state is thermally accessible to the vibrationally equilibrated excited state.⁽¹⁰⁾ The degree to which charge transfer states relax through

7.
radiationless processes involving ligand field excited states is very much an open question since the substitution that sometimes accompanies charge transfer excitation may result from dissociation of an excited state which is redox in character, and not from one of ligand field character. (7)

One interesting aspect of charge transfer photochemistry concerns the fate of the ligand. In systems where the ligand involved in the transition is a halide or is derived from water, radicals such as halogen atoms, hydrogen atoms or hydroxyl radicals can form as a result of excitation. (7) A large fraction of these radicals recombine with their metal partner due to the cage effect. Those which escape recombination undergo the same thermal reactions observed with these radicals when they are produced in other ways.

When the ligand is more complex, for example an amino acid or an aminopolycarboxylate, the charge transfer excitation can result in decomposition of the ligand. (11-13) This type of reaction raises some interesting possibilities concerning the importance of charge transfer photochemistry in systems such as natural waters.

Aminopolycarboxylates such as NTA are used as detergent builders and are found in industrial wastes. It has been suggested that since the nonbiological degradation of these compounds, as well as amino acids, is slow, photooxidation of their metal complexes may be an important pathway in their decomposition in natural waters. (11) These compounds are good

complexing agents and possess the ability to leach metals from bottom sediments.⁽¹⁴⁾ An examination of stability constants for NTA complexes reveals that the iron and copper complexes are thermally very stable.⁽¹⁵⁾ Photochemical investigations, however, reveal that these complexes undergo an efficient photoredox process resulting in decarboxylation of the ligand and reduction of the metal.^(11,12)

Although in the past, iron charge transfer photochemistry has received much attention, the results are difficult to inter-relate since the studies were performed in a wide variety of media, and the effects of the medium on the products and stoichiometry has not received sufficient study to separate primary photoeffects from medium effects. For example, a study of products and quantum yields in the photolysis of ferric chloride in a variety of media has led several authors to question whether the chloride-to-metal charge transfer, which absorbs strongly in the photolysis mixtures, is really photoactive.⁽¹⁶⁻¹⁸⁾

Alcohols and other organic compounds have been used as radical scavengers in a wide variety of systems. Although changes in stoichiometry have been observed, they have not been explained in detail.⁽¹²⁾

We have undertaken a systematic study of the charge transfer photochemistry of several selected iron species in the hope of clearing up some of the discrepancies which have arisen due to differing reaction conditions that were

employed by previous researchers.

(B) Alcohol Scavenging of Free Radicals

The high reactivity of simple aliphatic alcohols towards radicals has proven useful in attempts to elucidate the reactive intermediates produced in the radiolysis of aqueous solutions and in photolysis reactions producing radical species. Hydrogen atoms, hydroxyl radicals and halogen atoms react via hydrogen abstraction with alcohols. The possible hydrogen abstraction reactions of the hydroxyl radical can be illustrated by the following scheme:

Optical absorption spectra do not give evidence for the alkoxy radical produced in reaction I-1(a) so it is probable that if this radical is formed, it reacts rapidly, abstracting a hydrogen from another alcohol to form one of the other types of radicals. (19) Both reaction I-1(b) and I-1(c) produce hydroxyalkyl radicals, the difference being whether the hydrogen abstracted is from the α - or β -carbon from the hydroxyl group. Since tertiary alcohols have no α -hydrogens, they cannot form α -radicals, while secondary and primary alcohols (other than methanol) can produce either α - or β -radicals

The determination of rate constants for the reactions of hydroxyl radicals and hydrogen atoms produced by radiolysis with various substrates has been an area of intensive study. Some rate constants for the reactions of these radicals with various reactants are given in TABLE I-1. (20,21)

Three alcohols were used as scavengers for the reactive species in the present study; methanol, which forms only α -radicals; isopropanol, which can form either α - or β -radicals and tertiary butanol which gives only β -radicals.

Pulse radiolysis experiments confirm that both α - and β -radicals are formed with isopropanol with 90% in the α -form. (19) There may exist an equilibrium such as that shown in which α - and β -radicals interconvert.

The hydroxyalkyl radicals undergo a deprotonation in base just as the hydroxyl radical which has a pK of 11.9

The hydroxyalkyl radical anion is also produced by reactions between hydrated electrons and carbonyls. (23)

TABLE I-1

Rate constants of the hydroxyl radical
and the hydrogen atom in solution

Reactions of the hydroxyl radical

<u>reactant</u>	<u>$k \times 10^{-8} (M^{-1} s^{-1})$</u>
acetone	1.0
benzoate ion	52.
methanol	9.0
ethanol	19.
n-propanol	28.
i-propanol	22.
n-butanol	42.
t-butanol	5.2
formate ion	35.
Fe^{2+}	2.3
Br^-	10.
H	70.
OH	

$$-d[OH]/dt = 1.2 \times 10^{10} [OH]^2$$

Reactions of the hydrogen atom

<u>reactant</u>	<u>$k \times 10^{-8} (M^{-1} s^{-1})$</u>
benzoic acid	9.0
methanol	.016
ethanol	.25
n-propanol	.26
i-propanol	.70
n-butanol	.38
formic acid	.010
formate ion	2.3
H	

$$-d[H]/dt = 2.6 \times 10^{10} [H]^2$$

This is followed by the equilibrium in equation I-3.

The β -radical derived by hydrogen abstraction from tertiary butanol is not dissociated up to pH of 13.5. In alkaline solution, electron transfer from hydroxyalkyl radicals is observed for several alcohols but not for tertiary butanol. (24)

Two reactions are possible for hydroxyalkyl radicals in the absence of oxidizing agents.

It is known that for hydroxymethyl radicals, pathway I-6(a) is preferred over pathway I-6(b) and it has been possible to differentiate between behaviour within the solvent cage and in solution from the products derived from hydroxymethyl radicals produced in the photolysis of H_2O_2 in methanol-water mixtures. (25,26)

In the presence of excess $Fe(III)$, α -hydroxyalkyl radicals are oxidized to ketones according to equation I-7

The reaction between Fe(III) and β -hydroxyalkyl radicals, although it proceeds with the reduction of the iron, may not lead to the carbonyl product. Copper seems to be a better oxidizing agent than iron, kinetically, for β -hydroxyalkyl radicals and the product in the copper case is the diol. (27,28) There is no evidence for elimination in the case of tertiary butanol which would give a ketone via an enol intermediate.

Relative reactivities of α - and β -hydroxyalkyl radicals towards iron and copper has been shown through product studies for the iron, H_2O_2 , isopropanol system. (27,28) With iron alone, acetone is the major product and 2,5-hexanediol which is the product of the combination of two β -hydroxyisopropyl radicals is a minor product. When copper is added to compete with combination for the radicals, the hexanediol product almost

<u>Product</u>	<u>Fe^{3+}</u>	<u>$\text{Cu}^{2+}/\text{Fe}^{3+}$</u>
acetone	93%	84%
1,2-propanediol	---	11.2%
2,5-hexanediol	4.4%	0.7%

disappears and is replaced by a new minor product, 1,2-propanediol. There is also a decrease in the acetone yield, possibly representing the effect of added copper upon the equilibrium in equation I-2. (27,28)

Thus the copper oxidation of β -radicals may be represented by the equation

Since the reaction of β -radicals does not lead to ketones in the copper-hydroxyl radical system, the product of the hydroxybutyl radical in the iron system may not give acetone. The reaction of the hydroxyl radical with tertiary butanol in the presence of copper leads to 2-methyl-1,2-propanediol.

Another area of current interest in the study of radicals of species produced in the irradiation of water-alcohol glasses. (29,30,31)

Irradiations of $[(CN)_5FeNO]^{2-}$ and $[Fe(CN)_6]^{3-}$ are explained in terms of charge transfer from ligand to metal followed by a redox process involving electron transfer from the methanol to the ligands which gives the hydroxymethyl radical $\cdot CH_2OH$. (29) The process has been represented by

The net result is reduction of the metal and oxidation of the alcohol. The irradiation of tris-(bipy)-ruthenium(II) cation in alcohol-water glasses has been shown to occur with reduction of the alcohols to $CH_3C\cdot HOH$. (30)

The photooxidation of alcohols by electron transfer has also been reported to occur using 1,1'-dimethyl-4,4'-bipy-

ridylium (paraquat) salts as the absorbing species. The reactive complex leading to alcohol oxidation was an alcohol separated paraquat cation-counter anion pair or a free alcoholated paraquat dication. The rate of oxidation was controlled by the ability of the alcohol to come into contact with the cation in the ground state rather than the oxidation potential of the alcohol.⁽³²⁾ In order for electron transfer to occur, the alcohol must be in direct contact with the excited state and because of the short lifetime of the excited state must have been in intimate contact in the ground state.

(C) Some Aspects of the Photochemistry of Iron (III)

Although known to occur for centuries, explanations of the photoreduction of iron salts were unsatisfactory until Rabinowitch⁽³³⁾ interpreted the spectra of ferric-halide ion pairs as ligand-to-metal charge transfer and showed that radicals were produced in the irradiation of these systems. The absorption process was thus depicted as

I-10

and the yield of the reaction was dependent on that fraction of Fe^{2+}X which released free X into solution.

The principle difficulty encountered in studying the photochemistry of simple iron systems is the high efficiency of the back reaction in solution.

I-11

Net photoreduction occurs only when X is provided an alternate fate either by using high enough light intensities so that the radical-radical reaction, I-12, is efficient or by providing chemical scavengers which will react with X. In this type of

I-12

system, a careful distinction must be made between a true primary quantum yield and a net quantum yield for reaction. We chose to begin our investigations of the charge transfer photochemistry of iron with potentially the simplest system, ferric perchlorate in aqueous acid.

Ferric ion is known to form hydrolytic species in solution, several of which have been characterized and their absorption bands recorded. The principle species in strongly acidic solutions is $Fe(H_2O)_6^{3+}$ which has an absorption maximum at $\lambda=240nm$ corresponding to the water to iron charge transfer.⁽³³⁾ In less acidic solutions the equilibrium represented by I-13 is established. The hydroxo-monomer has an hydroxide to iron charge transfer transition centered at $300nm$.⁽³⁴⁾ When appreciable quantities of hydroxo-monomer are formed, a dimerization reaction takes place. This dimer has been shown to have a dihydroxo-bridged structure by mag-

netic measurements⁽³⁵⁾ and has an absorption maximum at 330nm,⁽³⁶⁾ presumably a charge transfer from the bridging hydroxide to iron. After the dimer forms, if the pH is raised still further, precipitation occurs. Thus, the species present in dilute aqueous iron solutions can be represented by the equilibria

A species which absorbs at 330nm has been observed in ferric perchlorate solutions in alcohol-water mixtures. This has been claimed to be an alcohol complex by one author⁽³⁷⁾ while another suggests that the effect of the alcohol may be to displace equilibrium, I-14, to the right due to a decrease in the activity of water.⁽³⁸⁾ Since the addition of concentrated acid causes this peak to disappear, the second explanation seems the most likely.

Irradiation of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ using labelled iron to detect reactions between added ferrous iron and hydroxyl radicals produced in the photolysis has led to the assignment of the quantum yield as .05 at 2°C,⁽³⁹⁾

When the small effect of temperature was corrected for using experimental results, the quantum yield at 25°C was estimated to be $.07 \pm .02$. This value is an unambiguous assign-

ment for the primary yield of hydroxyl radicals at room temperature. This reaction as well as the primary dark reactions in the absence of scavengers were assumed to be

Reaction I-18 is responsible for the net yield of Fe(II) observed in this photolysis. Several authors have studied this reaction and found the yield of oxygen to be very low.⁽⁴⁰⁾ The bar above the products in I-15 represents species still in the solvent cage.

Irradiation of $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ at 300nm also results in hydroxyl radicals based on chemical scavenging studies assigns the primary yield of this radical as .13 - .14 at room temperature.⁽⁴¹⁾ The photoreaction is

followed by I-17 and I-18

Organic scavengers have been employed to react with

hydroxyl radicals produced in reaction I-16 and I-19. Among these scavengers were methanol, ethanol, isopropanol, benzoic acid, benzyl alcohol and p-toluic acid. Methanol, ethanol, and isopropanol scavengers led to formaldehyde, acetaldehyde and acetone, respectively, as products. Benzoic acid substitution formed o-, m-, and p-hydroxybenzoic acid in a ratio of 2:2:1. Benzyl alcohol was attacked at the side chain only and quantitatively oxidized to benzaldehyde. Substitution of the benzene group also occurred for m- and p-toluic acid. (42,43)

Benzene was also oxidized by irradiation of $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ to give phenol and biphenyl. The ratio of phenol to biphenyl was dependent upon the concentration of Fe(III). The relative rates of the reaction of $\text{Ph}\cdot$ with Fe^{2+} , Fe^{3+} , and Cu^{2+} was 1:4:30. (41) The reaction sequence was given as

Similar reactions convert the alcohols above to aldehydes or ketones. For example, the reaction of $\cdot\text{OH}$ with methanol in the presence of Fe(III) produces formaldehyde (44) by the

following reactions

These reactions are identical to those which occur with organic compounds when hydroxyl radicals are produced by other reagents, eg. Fenton's reagent.

The irradiation of ferric ion pairs FeCl^{2+} , FeBr^{2+} , FeSCN^{2+} , FeOH^{2+} , can result in initiation of vinyl polymerization.⁽⁴⁵⁾ Some particular attention has been paid to FeCl^{2+} since results from the irradiation of this species appear confusing.

When this system is used to initiate polymerization, hydroxyl end groups were observed in the polymers. This led to the suggestion that hydroxyl radicals were produced in the excitation rather than chlorine atoms.⁽¹⁸⁾

In an attempt to solve this confusion, David has irradiated FeCl^{2+} and studied the net quantum yield for photo-reduction as a function of pH and Cl^- concentration. He concludes, that since the net yield decreases as chloride (and presumably FeCl^{2+}) concentration increases, FeCl^{2+} is not the photoactive species. He suggests that FeOH^{2+} is really the photoactive species in these solutions. As pH increases, a decrease in quantum yield is observed which is attributed

to the dihydroxo-bridged dimer being unreactive photochemically. (18)

The investigators in these studies concluded that hydroxyl radicals rather than chlorine atoms were primary photoproducts in the irradiation of FeCl^{2+} .

We therefore decided to study the scavenging behaviour of several organic scavengers in a system that was known to produce hydroxyl radicals, ie. $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ in strong acid. With this knowledge in hand, we hoped to compare the behaviour of the same scavengers in the FeCl^{2+} system and demonstrate whether or not hydroxyl radicals were produced in the FeCl^{2+} irradiation.

Another area of interest in the photochemistry of iron complexes is decarboxylation reactions. Many reports of carboxylic acids being oxidized upon irradiation of their solutions containing Fe^{3+} have appeared. These are reviewed by Balzani and Carasitti. (46) The formation of radicals is supported by kinetic and stoichiometric evidence, and by the fact that vinyl polymerization can be initiated by the irradiation of ferric citrate. The process seems to involve

As mentioned earlier this reaction is potentially important

in the decomposition of amino acids and aminopolycarboxylates. Previous studies of the photoreduction of FeNTA^- and CuNTA^- have indicated that the photoefficiency decreased with increasing pH.⁽¹¹⁾ Since these species were known to exist in various forms, interrelated by hydrolysis reactions, it was suggested that one of the hydrolytic forms, the dimer, was photochemically inactive. The hydrolytic reactions of the iron aminopolycarboxylate, FeEDTA^- , are well studied and the dimer is known to have an oxo-bridge.⁽⁴⁷⁻⁹⁾

In sharp contrast to most ferric complexes, the dimer is strongly coloured with a very intense peak in the visible region. This large absorbance has been attributed to a relaxation of the spin selection rule in the dimer due to magnetic coupling across the oxo-bridge. This coupling is also thought responsible for a decrease in the magnetic moment of FeEDTA upon dimerization.⁽⁴⁸⁾

Since the ligand field bands of the dimer are less forbidden by the spin selection rule it was suggested that efficient relaxation of charge transfer excited states into ligand field excited states might occur and thus excitation in the CT region might not lead to photoreduction.⁽¹¹⁾

To investigate this possibility, we chose to study the changes in quantum yield as FeEDTA^- was allowed to undergo hydrolysis.

II. EXPERIMENTAL

Irradiations were performed at either 2537Å or 3500Å in a Rayonet photochemical reactor.⁽⁵⁰⁾ Cells of two different designs were used and each was secured in the photoreactor by a different method as illustrated in Fig. II-1(a) and (b).

The temperature inside the Rayonet with sixteen lamps in use stabilized in the neighbourhood of 35°C. Hexaaquoiron(III), chloropentaaquoiron(III) and the dihydroxo-bridged dimer were irradiated in anunjacketed quartz cell, 20mm I.D., which was suspended through the top of the reactor with a copper pipe as shown in Fig. II-1(a). Another cell from the same piece of quartz tubing was constructed with a stopcock and ball and socket joint so that degassing by a freeze-thaw process could be carried out. Unfiltered light from medium pressure mercury lamps was used to irradiate hexaaquoiron(III). Approximately 98% of the emission from these lamps occurs at 2537Å⁽²⁾, a wavelength at which hexaaquoiron(III) is strongly absorbing. Another set of mercury lamps, which were coated so that their emission was centered at 3500Å, was used to irradiate chloropentaaquoiron(III) and the dihydroxo-bridged dimer. The ferric-ethylenediaminetetraacetate (FeEDTA) species were also irradiated at 3500Å.

Irradiations of the FeEDTA species were performed in a jacketed pyrex cell, 20mm I.D., which was thermostated to 30.0 ± .1°C by distilled water from a Haake circulating bath

FIG. II-1(a)

Quartz cell and method of suspension used for
irradiations of simple iron species.

FIG. II-1(b)

Pyrex cell used to irradiate FeEDTA species.

flowing through the outer jacket. This constant temperature was necessary to control the hydrolytic equilibria. The experimental setup is depicted in Fig. II-1(b).

Irradiations to determine quantum yields were carried to less than 5% conversion while stoichiometric experiments varied from 25% to >90%.

Solutions to be irradiated were freshly made from stock solutions of the required reagents. Hexaaquoiron(III) perchlorate stock solution was made by precipitating the iron as a hydroxide from a freshly prepared ferric sulfate solution. The precipitate was centrifuged and washed many times with distilled water. This precipitate was dissolved in HClO_4 which was diluted to 1l. The total iron in the stock solutions was analyzed by two methods which gave good agreement. One method involved the addition of excess EDTA and measuring the optical density at 260nm according to the procedure of Uzumasa et al. (51) The second method involved the reduction of the ferric ion to ferrous using prolonged irradiation at 2537Å. After a thiocyanate test showed that all ferric ion had been reduced, the total ferrous ion was measured as the trisphenanthroline ferrous complex. (52)

The two ferric perchlorate stock solutions used in this study were found to have iron concentrations of .125 and .248M. Ferric nitrate was unsuitable for the preparation of the ferric stock since even small amounts of nitrate were found to interfere with the iron(II) analysis.

The $\text{NaFe(III)EDTA} \cdot 3\text{H}_2\text{O}$ was prepared according to standard procedures⁽⁴⁷⁾ and recrystallized twice from distilled water. Synthesis and recrystallizations were conducted under red safelight and the product was stored in foil-wrapped vials.

Solutions to be irradiated were made up in the following manner:

(a) hexaaquoiron(III) perchlorate

Five ml of iron stock, 10ml 4.0M NaClO_4 , 25ml 4.50M HClO_4 and various volumes of scavenger were added to 50ml volumetric flasks and diluted to the mark. These solutions were stored in a dark cupboard until irradiated. In general, 5 to 15 different samples were prepared at the same time and were irradiated within 48 hours of preparation.

(b) chloropentaaquoiron(III) perchlorate

To a 50ml volumetric flask, 5ml iron stock, 25ml 4.50M HClO_4 , and various volumes of scavenger were added. Then 4.0M NaClO_4 and 2.0M NaCl were added in amounts such that the total sodium ion concentration was 0.8M after the mixture was diluted to 50ml. For some of the higher chloride concentrations, 4.0M NaCl was used.

(c) dihydroxo-bridged ferric dimer

To a 50ml volumetric flask was added 5ml iron stock, 34ml 4.50M NaClO_4 , and various amounts of scavengers and enough distilled water to dilute to 50ml.

(d) ferric-EDTA species

Solutions were made from a 0.1M FeEDTA stock solution

and were buffered in $1.15 \times 10^{-2} \text{M}$ Na_2EDTA . The pH was adjusted to 8.00 and 9.00 using a Fisher "accumet" pH meter. It was found that when 0.1M NaOH was added to the more concentrated iron solutions ($>.02\text{M}$) precipitation of some of the iron occurred, even when rapid mixing was accomplished with the use of a magnetic stirrer. This problem was eliminated by changing the order of additions. The amount of 0.1M NaOH needed was estimated with the aid of a trial run. The Na_2EDTA buffer, 5ml of $6.25 \times 10^{-2} \text{M}$, was added to the required amount of base and various amounts of FeEDTA stock solution were added and the solution was diluted to 24ml. The pH of this solution was adjusted to 8.00 or 9.00 using 0.01M NaOH and then was diluted to 25ml. With suitably pure FeEDTA, no precipitate appeared at concentrations below .040M.

Irradiations of FeEDTA with the alcohol scavengers were performed on solutions made without the Na_2EDTA buffer. These solutions were made by taking 5ml 0.1M FeEDTA stock, 5ml 1M HClO_4 , and various amounts of scavenger.

Oxygen was known to have an effect on the "colour" of a FeEDTA solution which had been irradiated. (51,53) For this reason, in the irradiations of all FeEDTA species, the solutions were deaerated by sealing the solutions with a serum cap and bubbling nitrogen through the solution for 20 minutes. Stainless steel hypodermic needles, injected through the serum cap, were used to pass nitrogen to and from the cell. These were removed prior to irradiation.

In order to determine the effect of oxygen upon yield in the hexaquoiron(III) system, several irradiations were performed in which solutions had been degassed by successive freeze-thaw cycles. This process was found preferable to passing nitrogen since, when nitrogen was bubbled through the alcohol-water solutions, alcohol evaporated and the alcohol:water concentration ratio was a function of degassing time.

After irradiation, analysis of the reduced iron was performed using ortho-phenanthroline.⁽⁵⁴⁾ In the case of hexaquoiron(III) and chloropentaaquoiron(III), the acid had to be neutralized before analysis. The direct addition of NaOH caused the precipitation of ferric hydroxide and the following method was devised to avoid precipitation. To a 100ml flask containing approximately 90ml distilled water was added 2ml buffered phenanthroline (phen-buffer) and 2.5ml 1.00M NaOH for each ml of photolyte analyzed. After photolysis, 1 or 2 ml of photolyte was added and the mixture diluted to 100ml and allowed to sit 30 minutes in the dark. After sitting, the optical density at 510nm was determined and from this value the concentration of iron(II) was determined.

The buffered phenanthroline (phen-buffer) used throughout this study was similar to that used by Hatchard and Parker⁽⁵⁴⁾ except that the concentration of phenanthroline was increased. Solution A was made by dissolving 1g of ortho-

phenanthroline in 20ml 95% ethanol and diluting to 100ml with distilled water. Solution B was the sodium acetate-sulfuric acid buffer described by Hatchard and Parker. The phen-buffer was made by mixing 2 volumes of solution A with 3 volumes of solution B.

Since it was reported that perchlorate might interfere in the determination of ferrous ion with phenanthroline⁽⁴⁴⁾, a check was made on the analytical method. The results are depicted in Fig. II-2. The molar absorptivity of 1.08×10^4 from this curve agrees well with that of 1.11×10^4 obtained by Hatchard and Parker⁽⁵⁴⁾ and reported by Calvert and Pitts.⁽²⁾ At higher perchlorate concentrations than those encountered in this analysis, trisphenanthrolineiron(II) perchlorate can precipitate, causing low absorbance values. This was found to occur in the irradiations of the dihydroxo-bridged dimer if the photolyte was mixed directly with phen-buffer before dilution. This problem could be avoided by dilution of the phen-buffer to 90ml before the addition of the photolyte.

Photolytes from the FeEDTA system were also analysed for Fe(II) using phen-buffer. In this case, 100ml of phen-buffer was placed in a polyethylene bottle which was sealed with a serum cap and parafilm. This solution was deaerated by bubbling nitrogen for 30 minutes. The deaerated phen-buffer was injected directly through the serum cap into the irradiated FeEDTA. The mixture was then diluted to 25ml in a volumetric flask and stored for 30 minutes before the optical density was

Fig. II-2

Absorbance at 510nm of the ferrous pheranthroline complex
as a function of concentration of Fe(II).

determined.

Light intensities were determined using ferrioxalate actinometry⁽⁵⁴⁾, from the slope of a plot of concentration of Fe(II) produced vs. irradiation time, ie, conversion rate (C.R.). Quantum yields were calculated from the conversion rate for various irradiations among the following formula.

$$\Phi = \frac{(\text{C.R.})_{\text{exp.}}}{(\text{C.R.})_{\text{ferrioxalate}}} \times \Phi_{\text{ferrioxalate}} \quad (\text{II-1})$$

where (C.R.)exp. and (C.R.)ferrioxalate were determined by experiment and $\Phi_{\text{ferrioxalate}}$ was taken as 1.21 at 3500Å and 1.25 at 2547Å.⁽⁵⁴⁾

Products of the irradiations were also determined. Derivatives of aldehydes and ketones were made and precipitated directly from the photolyte with 2,4-dinitrophenylhydrazine reagent prepared according to Vogel.⁽⁵⁵⁾ The 2,4-dinitrophenylhydrazones were recrystallized from ethanol and identified by melting point, in comparison with those prepared from pure samples. Quantitative determination of carbonyl products was made following the procedure of Lappin and Clark⁽⁵⁶⁾ using experimentally derived molar absorptivities for acetone and formaldehyde.

Identification of the organic products of the alcohol scavenging was confirmed by gas chromatography. Carbon tetrachloride or chloroform extracts of the photolytes were injected into a Beckman GC-2 gas chromatograph equipped with a 5ft. 10%

ethofat on Chromasorb W column. All gas chromatography was performed at room temperature. Retention times were compared with retention times of the pure substances.

Several solutions of 0.1M FeEDTA were deaerated and irradiated until decolourization was obtained. The iron was reoxidized and precipitated by adding NaOH and bubbling air through the solution for 12 hours. Complete precipitation was confirmed by allowing the solution to settle and adding more NaOH to the clear supernatant. The precipitate was removed by centrifugation and the supernatant was concentrated on a rotary evaporator. Addition of ethanol precipitated a gummy white solid which was filtered, washed with ethanol, and air dried. This material was assumed to contain product aminopolycarboxylate ligands and EDTA. Cobalt complexes of these ligands were synthesized and separated by ion exchange. (57) NMR spectra were recorded in D₂O in a Varian T-60 spectrophotometer and uv-vis measurements were made on either a Cary 14 or a Gilford 240 spectrophotometer.

Sources of supply for chemicals used in this study are listed in Appendix A.

III. THE IRRADIATION OF FERRIC PERCHLORATE SOLUTIONS

The absorption spectra of iron(III) species irradiated in this study are depicted in Fig. III-1. The spectrum of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, obtained in strongly acidic media, agrees well with that previously reported.⁽³³⁾ There is only one major peak, occurring at $\lambda=240\text{nm}$ ($a=4350$) corresponding to the water-to-iron charge transfer band. This transition was excited using $2537\text{\AA}$ light.

The spectrum obtained in weakly acidic solutions exhibits another band at 335nm ($a=8300$) which is attributed to the dihydroxo-bridged dimer.⁽³⁶⁾ Irradiations performed at 350nm excite this band since $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ absorbs very weakly at this wavelength.

Although the hydroxo monomer, $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ is known to have a maximum at 300nm ⁽³⁴⁾, this species could not be selectively irradiated since at the high concentrations needed to assure total absorbance over short path lengths, most of the hydroxo monomer underwent dimerization and the dimer was the strongest absorbing species in solution.

The irradiation of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ at 254nm in the absence of scavengers produced Fe(II) as a product at a rate which initially was not constant but after several minutes attained a constant value. This behaviour, as depicted in Fig. III-2 has been observed in the photochemistry of Fe(II) where the initially increased rate is due to impurities act-

FIG. III-1

Absorption spectra of (a) the dihydroxo-bridged dimer and (b) hexaaquoiron(III).

FIG. III-2

The absorbance at 510nm (directly related to $[\text{Fe(II)}]$),
as a function of irradiation time with no added scavengers.

ing as scavengers. (58) The net quantum yield is determined from the slope in the region where production of Fe(II) is linear with time of irradiation after the impurities have been consumed. As can be seen in the figure, linear behaviour was obtained after 5 minutes of irradiation and the quantum yield calculated from the slope, $\Phi_{\text{Fe(II)}}$, is 0.06.

As observed in other studies, the addition of organic compounds caused an increase in the rate at which Fe(II) was produced. The quantum yields observed at various scavenger concentrations for a variety of organic scavengers are given in TABLE III-1. The largest increases in quantum yields were observed using alcohols and formic acid as scavengers. Tertiary butanol was particularly interesting since a plateau was reached after which $\Phi_{\text{Fe(II)}}$ became independent of alcohol concentration. The value of the quantum yield on this plateau, $\Phi_{\text{Fe(II)}} = .130$, is taken to be twice the primary quantum yield for free $\cdot\text{OH}$.* The value agrees well with Dainton's Fe isotope exchange estimate (39) for this primary yield of $.07 \pm .03$ at 25°C ($2 \times .07 = 0.14$).

The other two alcohols, methanol and isopropanol, and also formic acid, exhibit a linear increase with scavenger concentration that is independent of the scavenger employed. Extrapolation back to zero scavenger concentration gives a limiting yield of 0.125 which is assumed equal within experi-

* A detailed exposition on this point appears on p.41.

TABLE III-1

at 2537Å

Quantum yields as a function of scavenger concentration

[methanol]	Fe(II)
.0494M	.123 ± .002
.0988	.126
.988	.154
1.482	.170
1.976	.167
2.470	.197
[isopropanol]	Fe(II)
.0262M	.123 ± .002
.118	.134
.131	.134
.262	.137
.524	.140
.786	.154
1.048	.167
2.358	.198
2.620	.212
.262 degassed	.122
2.620 degassed	.208

[t-butanol]

Fe(II)

.0212	.100 $\pm$.003
.0424	.116
.106	.131
.212	.134
.424	.129
.636	.130
1.060	.129
2.120	.132

[formic acid]

Fe(II)

.691M	.152 $\pm$.004
1.414	.172
2.231	.216
3.257	.230

[acetic acid]

Fe(II)

.914	.023 $\pm$.003
1.148	.025

[malonic acid]

Fe(II)

.630	.031 $\pm$.003
------	-----------------

FIG. III-3

Quantum yields for production of Fe(II) as a function of scavenger concentration using (●) tertiary butanol, (■) formic acid, (▲) isopropanol and (●) methanol as scavengers. Degassed isopropanol determinations are also depicted (△):

mental error to the tertiary butanol plateau. In agreement with previous experiments, degassing has no measurable effect on the quantum yield.⁽⁴⁴⁾ Since the organic radicals are known to react with O_2 ⁽⁵⁹⁾, this result indicates that at the high Fe(III) concentration employed, the reaction with oxygen has been overwhelmed. If the iron concentration were decreased, the oxygen reaction would have to be considered. This behaviour has been observed in other radical producing systems.⁽⁶⁰⁾

Moderate concentrations of acetone, acetic acid and malonic acid each caused a small increase in quantum yield but the limiting plateau was not attained. This seems reasonable since both acetic acid and acetone⁽⁵⁹⁾ are known to be poor scavengers for hydroxyl radicals. For this reason, they were dropped from the study.

The assignment of the limiting yield for Fe(II) as being twice the primary yield for $\cdot OH$ is based on the assumption that the reaction follows the path

At the high concentrations of scavenger employed, reaction (III-3) will predominate over reaction (III-5) which can then be omitted. Thus there exists a competition between Fe^{2+} and HS for the hydroxyl radicals. The high concentration of Fe(III) ensures that reaction (III-4) will predominate over reaction (III-6) which will also be omitted for low conversions.

Applying a steady state treatment to this scheme gives the following kinetics.

$$\Phi_{\text{Fe(II)}} = \frac{V}{I} \times \frac{d[\text{Fe(II)}]}{dt} \quad \text{III-7}$$

$$= \frac{V}{I} \left(\frac{2k_1k_3[\text{Fe}^{3+}][\text{HS}]}{k_2[\text{Fe}^{2+}] + k_3[\text{HS}]} \right) \quad \text{III-8}$$

If I, V and (Fe^{3+}) and assumed constant

$$\Phi_{\text{Fe(II)}} = \frac{c [\text{HS}]}{k_2[\text{Fe}^{2+}] + k_3[\text{HS}]} \quad \text{III-9}$$

It can be seen from this expression that if the (Fe^{2+}) is kept low by short irradiation times (low conversions) and the scavenger concentration is increased, a point will be reached where $k_3(\text{HS}) > k_2(\text{Fe}^{2+})$ and the expression will simplify to

$$\Phi_{\text{Fe(II)}} = C$$

III-10

Expression (III-10) illustrates that when the scavenger concentration is high enough to react with all free $\cdot\text{OH}$, and thus eliminate reaction (III-2), the quantum yield becomes independent of scavenger concentration giving rise to the observed plateau. Since there are two iron molecules reduced for each $\cdot\text{OH}$ scavenged, this limiting quantum yield represents twice the primary yield of free $\cdot\text{OH}$.

The organic products, S, resulting from methanol and isopropanol scavenging were identified by gas chromatography and by their 2,4-dinitrophenylhydrazones to be formaldehyde when methanol was used as scavenger and acetone when isopropanol was used. Melting points and retention times are given in TABLE III-2. For these alcohols, the reaction is therefore

The assumption that the CH bond is broken rather than the O-H bond is based on reports of the ESR spectra of these radicals from pulse radiolysis studies.⁽²²⁾ If the $\text{RCHR}(\text{O}\cdot)$ radical is formed, it seems to readily abstract a C-H hydrogen to produce the $\text{RC}\cdot\text{R}(\text{OH})$ radical in agreement with bond energy data.

TABLE III-2

Melting points of 2,4-Dinitrophenylhydrazones
from methanol and isopropanol scavenging

(i) methanol scavenging

reported formaldehyde derivative m. p.	164°C
found for formaldehyde derivative	166.3
found for irradiated solution derivative	166.1

(ii) isopropanol scavenging

reported acetone derivative m. p.	126°
found for acetone derivative	124.3
found for irradiated solution derivative	124.4

TABLE III-3

Retention times on 10% Ethofat column

formaldehyde	45 seconds	tert-butanol	200 seconds
acetone	60	isobutyraldehyde	85
methanol	130	CCl ₄	118
isopropanol	160	ether	30

irradiated solution, methanol scavenging, CCl₄ extract
48 seconds, 96 seconds, 140 seconds

irradiated solution, isopropanol scavenging, chloroform
extract

33 seconds, 62 seconds, 100 seconds

irradiated solution, tert-butanol scavenging, ether extract
34 seconds, 85 seconds, 210 seconds

Irradiated solution, tert-butanol scavenging, ether extract
and acetone

34 seconds, 65 seconds, 85 seconds, 210 seconds

Acetone analysis performed in conjunction with Fe(III) analysis confirmed the 2:1 stoichiometry and are given in TABLE III-3.

The product of the tertiary butanol scavenging was harder to determine. Neither acetone nor methanol were produced indicating that elimination of a $\cdot\text{CH}_3$ was not a reaction pathway. There was a small but undetermined yield of isobutyraldehyde which was identified by GC in comparison with a known sample. Neutralization, filtration, and evaporation of both an irradiated and an unirradiated sample left a white solid (mainly NaClO_4). Carbon tetrachloride extracts of this solid showed the presence of organic material for the irradiated sample but not for the unirradiated one. There were two peaks in the NMR in the 2-2.5 ppm region of approximate 3:1 intensity.

The high boiling nature of this organic product as well as the nature of the other produce, isobutyraldehyde, are indications that isobutylene glycol, $\text{CH}_2^{\text{OH}} - \text{C}^{\text{OH}}(\text{CH}_3) - \text{CH}_3$, which was proposed as a product by Walling⁽²⁷⁾ for the tert-butanol scavenging of $\cdot\text{OH}$ in the presence of Fe^{3+} and Cu^{2+} , may also be present here. Since the intercept of .130 for Fe(II) indicates that two Fe(II) are produced for each $\cdot\text{OH}$ scavenged (when compared with Dainton's value), the reaction path may be

With the isobutylaldehyde resulting from the pinacol type rearrangement of the glycol or some rearrangement of the radical prior to reaction with Fe^{3+} .

The increase above 0.13 in Fe(II) with increasing scavenger concentration which occurs when methanol, isopropanol, and formic acid are used as scavengers is taken to indicate a new reaction not included in the path given above. The similarity between the intercept of this line and the tertiary butanol plateau indicate that this behaviour occurs in addition to scavenging for free $\cdot\text{OH}$ radicals and the lack of dependence upon the nature of scavenger concentration suggests that this is not a scavenging for $\cdot\text{OH}$ radicals but some other reaction. This matter will be discussed more fully in a later section.

The results of the irradiation of $\text{Fe(H}_2\text{O)}_6^{3+}$ in the presence of organic scavengers clearly show that tertiary butanol is the best choice to determine primary yields of hydroxyl radicals in this system.

Irradiations performed on solutions containing dihydroxobridged dimer at $3500\text{\AA}$ are depicted in Fig. III-3. Again an increase in yield is noted for methanol and isopropanol but not for tertiary butanol. This time, the yield observed for

FIG. III-4

Quantum yields for production of Fe(II) as a function of scavenger concentration for irradiation of the dihydroxo-bridged dimer, for methanol (Δ), isopropanol ($\bigcirc$), and tertiary butanol ($\bigcirc$), as scavengers.

5

TABLE III-4

Irradiation of the dihydroxo-bridged dimer at 3500Å

[methanol](M)	Fe(II)
0	.010
.988	.030
1.975	.035
2.963	.058
3.950	.062
4.938	.079
[isopropanol](M)	Fe(II)
1.301	.032
[tert-butanol](M)	Fe(II)
.408	.014
.816	.013

tertiary butanol is close to the yield for unscavenger dimer irradiation.

The increase in yield that occurs for methanol has a lower slope than that of the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ system. The primary yield of this reaction determined using tertiary butanol is .011 at 350nm.

IV. THE IRRADIATION OF $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$

The absorption spectrum of iron solutions in 2.25M HClO_4 containing various amounts of HCl are shown in Fig. (IV-1). A peak arises at 335nm ($\epsilon=1490$) which is assigned as chloride-to-metal charge transfer. (33)

Direct irradiation of this band with 350nm light in the absence of scavengers results in photoreduction with a net quantum yield of .0010 to .0030, dependent upon chloride concentration. Irradiations were performed using tertiary butanol, methanol, and isopropanol as scavengers.

Tertiary butanol was studied first since the results of the hydroxyl radical scavenging indicated it could give direct access to primary quantum yields of Fe^{3+} reduction. The results of the irradiation of $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ in tertiary butanol solutions are listed in TABLE IV-1. There is a complicated dependence of Fe(II) upon both concentration of scavenger and concentration of chloride. This suggests competition between the two species for the photoproduct radicals since increase in tertiary butanol at constant chloride concentration results in an increased yield while increasing chloride for a constant tertiary butanol concentration decreases the yield. In order to explain this behaviour, the following reactions are assumed to take place.

FIG. IV-1

Absorption spectra for ferric perchlorate in (a) 0,
(b) .002, (c) .004, (d) .006, (e) .010M, HCl, 2.10M HClO₄,
and 0.8M NaClO₄.

TABLE IV-1

Quantum yields at 3500Å as a function of
scavenger and chloride concentrations

[tert-butanol](M)	[Cl ⁻](M)	Fe(II)
.424	.01	.186 ± .003
.636	.01	.182
.816	.08	.140
.816	.16	.104
.816	.24	.084
.816	.32	.070
.848	.01	.182
1.224	.16	.120
1.224	.24	.100
1.224	.32	.092
1.632	.16	.135
1.632	.24	.118
1.632	.32	.102
2.04	.08	.162
2.04	.16	.139
2.04	.24	.123

$$[\text{Fe}]^{3+} = .0248 \text{ M}$$

For simplicity we have assumed that the effects due to reactions

are negligible due to the high concentrations of tertiary butanol and chloride.

The scheme then gives the following kinetics

$$\Phi_{\text{Fe(II)}} = \frac{V}{I} \times \frac{d[\text{Fe(II)}]}{dt} \quad \text{IV-8}$$

$$= \frac{V}{I} \left(\frac{2k_2k_1[\text{FeCl}^*][\text{t-butOH}]}{k_2[\text{t-butOH}] + k_4[\text{Cl}^-]} \right) \quad \text{IV-9}$$

therefore,

$$\frac{1}{\Phi_{\text{Fe(II)}}} = \frac{I}{V} \left(\frac{k_2[\text{t-butOH}] + k_4[\text{Cl}^-]}{2k_1k_2[\text{FeCl}_4][\text{t-butOH}]} \right) \quad \text{IV-10}$$

If I , V , and $[\text{Fe}^{3+}\text{Cl}]$ are assumed constant then,

$$\frac{1}{\Phi_{\text{Fe(II)}}} = C_1 + \frac{C_2[\text{Cl}^-]}{[\text{t-butOH}]} \quad \text{IV-11}$$

A plot of $1/\Phi$ vs $[\text{Cl}^-]$ should be linear and have a slope dependent on each tertiary butanol concentration. The intercept would represent the value of $1/\Phi$ if reaction IV-4 (and hence reaction IV-5) did not occur.

If the limiting quantum yield is independent of butanol concentration, a plot of $1/\Phi$ vs $[\text{Cl}^-]/[\text{t-but}]$ would be linear.

These plots are shown in Fig. IV-2 and IV-3 and are in excellent agreement with the above predictions. The limiting yield of Fe(II) is .186 from the extrapolation and thus the primary yield of chlorine atoms is .093 (ie. .186/2).

If the chloride concentration is lowered relative to the tertiary butanol concentration the chloride dependent term will become smaller and the quantum yield may be determined directly. Irradiations of this system in 0.01M NaCl and .424, .636, and .848M tertiary butanol gave $\Phi_{\text{Fe(II)}}$ of .186, .182, and .182, respectively.

These values, along with those obtained from the intercepts in Fig. IV-2 are included in those depicted in Fig. IV-5.

FIG. IV-2

The reciprocal quantum yield for production of Fe(II) as a function of concentration of chloride for irradiation of chloropentaaquoiron(II) using tertiary butanol as scavenger. Concentrations of tertiary butanol were .816M (O), 1.224M (Δ), 1.632M (O), 2.04M ($\square$).

FIG. IV-3

The reciprocal quantum yield for production of Fe(II) as a function of concentration of chloride/concentration of tertiary butanol. Concentrations of tertiary butanol were .816M (O), 1.224M (Δ), 1.632M (O), 2.04M ($\square$).

When methanol is used as a scavenger the results are chloride dependent as before, but the plot of $1/\bar{I}$ vs $[Cl^-]$ gives a different intercept for each methanol concentration as shown in Fig. IV-4. Irradiations were also performed in 0.01M NaCl using methanol and isopropanol as scavengers. These results are listed in TABLE IV-2. When these values of $\bar{I}$ Fe(II) are plotted against concentration of scavenger they exhibit a linear dependence upon scavenger concentration as did the $Fe(H_2O)_6^{3+}$ system. As before, tertiary butanol does not exhibit this effect. Fig. IV-5 allows a comparison of these two types of behaviour. We conclude that the additional reaction which was present in the $Fe(H_2O)_6^{3+}$ system is also present in the $Fe(H_2O)_5Cl^{2+}$ system. Furthermore, the primary quantum yield of chlorine atoms is .092 which is a factor of 10 greater than the primary yield for hydroxyl radical production in the dimer could be.

The products in this system were found to be formaldehyde and acetone for methanol and isopropanol scavenging respectively. Isobutyraldehyde was present in small yield (detected by G.C.) on tert-butanol scavenging. No acetone, methanol or chloro-alcohols were detected by G.C.. Melting points and retention times are given in TABLE IV-3.

It is apparent that the conclusions reported by David⁽¹⁸⁾ that the chloro species could not be the photoactive species are not supported by the limiting quantum yields. These conclusions were based on the decrease in photoreduction

yields observed as chloride concentrations increase. Since this behaviour has now been shown to be due to Cl^- scavenging for $\text{Cl}^\bullet$, we now believe the chloro-species is the most photoactive at 350nm.

Previous reports⁽¹⁶⁾ that vinyl polymerization initiated by ferric chloride photolysis contained hydroxo-end groups can be explained if the reaction which terminates the chain involves termination by $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ or by one of the waters of $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$. Since $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is known to terminate vinyl polymerization and produce hydroxy end groups, appearance of $-\text{OH}$ end groups in the polymer may not indicate hydroxyl radicals produced in the photoreaction.

The conclusions from this series of experiments seem to be that although $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ is very photoactive at 300nm, irradiations of ferric chloride performed at 350 or 365 will excite either $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ or $\text{Fe}(\text{OH})_2\text{Fe}^{4+}$ and produce chlorine atoms as the radicals in the primary process.

TABLE IV-2

The irradiation of chloropentaquoiron(III) at 3500Å

[methanol](M)	[Cl ⁻](M)	Fe(II)
.247	.01	.202
.494	.01	.213
.988	.01	.213
1.482	.01	.232
1.975	.08	.180
1.975	.16	.151
1.975	.24	.139
1.975	.32	.130
2.963	.08	.196
2.963	.16	.180
2.963	.24	.165
2.963	.32	.152
3.95	.16	.207
3.95	.24	.193
3.95	.32	.181
4.94	.08	.238
4.94	.16	.219
4.94	.24	.210
[isopropanol](M)	[Cl ⁻](M)	Fe(II)
.0650	.01	.155
.130	.01	.185
.260	.01	.196
.520	.01	.209
.780	.01	.226
1.300	.01	.236

FIG. IV-5

Quantum Yield for production of Fe(II) at low chloride as a function of scavenger concentration for irradiation of chloropentaaquoiron(III) using (Δ) isopropanol, ($\circ$) methanol, and ($\bullet$) tertiary butanol as scavengers.

TABLE IV-3

Melting points and retention times in chloropentaaquoiron(III)
photolysis

Melting Points

found for formaldehyde derivative	166.3°C
found for methanol scavenging	166.0
found for acetone derivative	124.3
found for isopropanol scavenging	124.3

Retention Times

irradiated solution, methanol scavenging, CCl_4 extract

48 seconds

118

130

irradiated solution, isopropanol scavenging, ether extract

30 seconds

55

165

irradiated solution, tert-butanol scavenging, CCl_4 extract

85 seconds (small)

125

210

yields observed as chloride concentrations increase. Since this behaviour has now been shown to be due to Cl^- scavenging for $\text{Cl}^\bullet$, we now believe the chloro-species is the most photoactive at 350nm.

Previous reports⁽¹⁶⁾ that vinyl polymerization initiated by ferric chloride photolysis contained hydroxo-end groups can be explained if the reaction which terminates the chain involves termination by $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ or by one of the waters of $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$. Since $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is known to terminate vinyl polymerization and produce hydroxy end groups, appearance of $-\text{OH}$ end groups in the polymer may not indicate hydroxyl radicals produced in the photoreaction.

The conclusions from this series of experiments seem to be that although $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ is very photoactive at 300nm, irradiations of ferric chloride performed at 350 or 365 will excite either $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ or $\text{Fe}(\text{OH})_2\text{Fe}^{4+}$ and produce chlorine atoms as the radicals in the primary process.

V. THE IRRADIATION OF FERRIC-EDTA

The iron-EDTA system was selected for irradiation because of the possible importance of the photochemistry of iron-amino acid and iron-aminopolycarboxylate complexes in natural waters. The pH region of interest is therefore 6.0 to 8.0. When FeEDTA was irradiated in solutions at various pH values, the quantum yield was a constant in the region from pH 3 to pH 6, decreasing as pH was increased from 6 to 9. These results are listed in TABLE V-1.

Since in basic solution, the iron-EDTA exists in at least three hydrolytic forms, according to the following equilibria, the quantum yield variation raises the possibility that photoreaction efficiency may be dependent on which hydrolytic species absorbs the light.

In order to find quantum yields for each species, it is necessary to know the fraction of light absorbed by each species. At pH of 8.00, both hydroxo and aquo monomers are present, along with some oxo bridged dimer.⁽⁴⁹⁾ When the pH is increased to 9.00, 97% of the monomer present is in the form of hydroxo and the aquo monomer is not a significant

TABLE V-1

Fe(II) quantum yields as a function of pH

pH	[Fe] _{tot} (M)	Fe(II)
2.0	.020	.094 ± .003
6.0	.020	.091
6.0	.010	.073
6.0	.002	.078
7.0	.020	.084
8.0	.020	.031

TABLE V-2

Dimer concentrations as a function of total iron at pH = 9.00

[Fe] _{tot} (M)	A _d (540nm)	10 ⁴ x [dimer] (M)
.00300	.341	2.23
.00500	.488	6.45
.00500	.468	6.03
.00700	.527	10.33
.0100	.550	15.95
.0150	.586	27.11
.0200	.608	38.84
.0250	.623	51.07
.0300	.628	62.48
.0350	.634	74.21
.0400	.634	84.71

absorber at this pH. Thus the light need only be partitioned between two species, the hydroxo monomer and the dimer. In very dilute solution, at pH=11.00, only hydroxo monomer is present and a molar absorbtivity at 350nm of 970 was estimated. Using this value and the absorption spectra recorded at pH=9.00 in short (0.1 mm) path length cells, a dimer absorbtivity of 5100 at 350nm was estimated. (The dimer concentrations were obtained from the absorbance at 540nm⁽⁴⁹⁾ using a molar absorbtivity of 121.) These calculations are given in Appendix B.

The dimer/monomer ratio could be adjusted by varying the total iron concentration, and the variation of dimer concentration with total iron at pH 9.00 is depicted in Fig. V-1. Based on data from TABLE V-2 the dimer concentration increases non-linearly with total iron until the total concentration is approximately 0.10M. After this point the dimer concentration exhibits a linear dependence upon total iron concentration.

The quantum efficiencies for photoreduction based on production of iron(II), for various total iron concentrations are given in TABLE V-3. After an initial decrease in yield as total iron increased, a plateau value was reached for each pH as shown in Fig. V-2(a) and (b). A comparison of Fig. V-1 and Fig. V-2(b) reveals that the limiting value for quantum yield was reached at the same total iron concentration as the curve in Fig. V-1 became linear. Thus, when the dimer/monomer ratio became constant, the quantum yield also became constant.

This behaviour indicates that the monomer and the dimer

TABLE V-3

Fe(II) quantum yields as a function of
total iron concentration. $T = 30^{\circ}$

pH = 8.00		pH = 9.00	
[Fe] _{tot} (M)	obs	[Fe] _{tot} (M)	obs
.00500	.059	.00300	.042
.00800	.056	.00500	.037
.0100	.055	.00500	.035
.0100	.054	.00700	.034
.0110	.047	.0100	.025
.0130	.047	.0150	.026
.0150	.038	.0200	.024
.0150	.039	.0250	.021
.0160	.031	.0300	.022
.0200	.029	.0350	.025
.0280	.026	.0400	.024
.0320	.026		
.0360	.026		

TABLE V-4

Quantum yields for CH₂O production at pH = 9.00

[Fe]	CH ₂ O	Fe(II)	Fe(II)/CH ₂ O
.00600	.021	.035	1.8
.00800	.019	.032	1.7

FIG. V-1

The variation of dimer concentration with total iron concentration at pH 9.00.

FIG. V-2

The quantum yield for production of Fe(II) as a function of total iron concentration at pH=8.00 ($\blacktriangle$) and pH=9.00 ($\blacksquare$).

have different quantum yields for photoreduction.

If A_d is the fraction of light absorbed by the dimer and A_m is the fraction of light absorbed by the monomer, Φ_d is the quantum yield of the dimer and Φ_m the quantum yield of the hydroxo monomer, then the observed quantum yield Φ_{obs} can be represented by equation V-3.

$$\Phi_{obs} = A_d \Phi_d + A_m \Phi_m \quad V-3$$

Since, $A_m = 1 - A_d$, substitution in V-3 gives

$$\Phi_{obs} = A_d \Phi_d + \Phi_m - A_d \Phi_m \quad V-4$$

$$\Phi_{obs} = \Phi_m - A_d(\Phi_m - \Phi_d) \quad V-5$$

From equation V-5 it can be seen that the desired values for Φ_m and Φ_d can be obtained from a plot of Φ_{obs} vs A_d by extrapolation to A_d values of 0 and 1 respectively. Such a plot is shown in Fig. V-3. From the intercepts, quantum yields for hydroxo monomer and dimer can be estimated as $\Phi_m = 0.065$ and $\Phi_d = 0$. This confirms speculation that the drop in quantum yield with pH is due to hydrolysis of the $[\text{FeEDTA}(\text{H}_2\text{O})]^-$ monomer to form oxo-bridged dimer.

The previous chapter revealed that the limiting yield for the dihydroxo-bridged dimer $\text{Fe}(\text{OH})_2\text{Fe}^{4+}$ was low, and the present work indicates that the oxo-bridged dimer also has a

FIG. V-3

Quantum yield for production of Fe(II) as a function
of fraction of light absorbed by the dimer (A_d).

the 2:1 ratio of Fe(II) to formaldehyde. This data is given in TABLE V-4.

In a separate experiment, 'decolourized' solution was re-oxidized and the iron precipitated. The ligand mixture which was expected to contain 50% EDTA and 50% ED3A (ED3A=ethylenediaminetriacetic acid) was reacted with Co(II) in air, producing the corresponding Co(III) complexes. These complexes were separated by ion exchange as aquo complexes and the chloro derivatives were made following an approach to identification of aminopolycarboxylate ligands introduced by Blackmer, Hamm and Legg.⁽⁵⁷⁾ The NMR of the chloro complexes were recorded in HCl/D₂O mixtures to limit solvent ¹H concentration. The spectra obtained are shown in Figs. V-4, 5. Spectrum V-5 resembles that reported by Day and Reilley⁽⁶³⁾ for Co(EDTA)Cl. The second spectrum is similar to the spectrum of Co(ED3A)NO₂. In particular, both the oxidized ligand complex and Co(ED3A)NO₂ exhibit a broad band at 6.5 p.p.m. indicative of an amine proton. Both spectra have doublets at 3.2 and 3.5 p.p.m. and a singlet at 4.7 p.p.m. The assignment of an amino function was confirmed by a ninhydrin test which was positive for the oxidized ligand mixture but not for pure EDTA. The absence of a methyl proton singlet at 2.0 - 2.5 p.p.m. in the NMR rule out the N-CH₃ as a product since such a peak occurs for Co(MEDTA)NO₂⁽⁶⁴⁾ (MEDTA=N-methyl-ethylenediaminetriacetic acid).

In another experiment, the oxidized ligand mixture was dissolved in water and HCl was added. A white precipitate

2 OF/DE 2

the monomer, presumably due to relaxation of the spin selection rules through spin-spin coupling across the Fe-O-Fe bridge. (48) Thus a pathway for radiationless relaxation which involved coupling of the charge transfer excited state with the ligand field states may be more efficient in the dimer. The relaxation of the spin selection rules is reported to be the reason that the oxo-bridged dimer is deep red in colour. Irradiating this ligand field band of the dimer at 540nm, a wavelength where only the oxo-bridged dimer absorbs, produced no photoreduction.

In the uv spectrum of the oxo-bridged dimer, however, there are several absorption maxima which have been assigned as simultaneous-pair electronic (s.p.e.) bands. (61) These correspond to simultaneous excitation to ligand field states on both iron centres by absorption of one photon. It is claimed that pair transitions in which spin does not change on excitation are fully allowed. Thus, the s.p.e. bands may be very intense and 350nm light absorbed by the oxo-bridged dimer may not excite the molecule to predominantly charge transfer excited states but to excited ligand field states on both iron atoms. As indicated above, photoredox would not be expected if the light produced ligand field excited states.

Unfortunately, no assignment can be made as to the degree to which charge transfer or s.p.e. states are excited at 350nm. This distinction may not be necessary, however, since the existence of s.p.e. bands isoenergetic with charge transfer bands may allow strong coupling to occur between these states.

Thus, the charge transfer excited state may be deactivated via energy transfer to ligand field states with which they are strongly coupled. The facts that the quantum yield for oxo-bridged dimer photoreduction is very near zero and that some degree of charge transfer state population should be produced in the excitation may, when taken together, indicate that such a relaxation does in fact occur. Neither s.p.e. bands nor relaxation of the spin selection rule (as evidenced by enhanced ligand field band intensity) has been observed for the dihydroxo bridged dimer.

Thus, although the quantum yields for both dimers are very low compared to the corresponding monomers, the underlying reasons for this behaviour are probably different. In the dihydroxo-bridged dimer, the low yield is probably caused by the structure of the dimer preventing escape of the radical prior to recombination while in the oxo-bridged dimer, the low yield is probably due to the populating of ligand field bands, either directly or through relaxation.

Attempts were also made to determine the products and stoichiometry of the photoreduction. In the Fe-NTA irradiation⁽¹¹⁾, carbon dioxide, formaldehyde and the iron (II) complexes of NTA and IDA were found. In the Fe-EDTA system, the presence of formaldehyde was confirmed by the 2,4-dinitrophenylhydrazine derivative (mp 163-165%). Formaldehyde quantum yields determinations, performed in conjunction with Fe(II) analysis confirmed, within the limits of uncertainty

the 2:1 ratio of Fe(II) to formaldehyde. This data is given in TABLE V-4.

In a separate experiment, 'decolourized' solution was re-oxidized and the iron precipitated. The ligand mixture which was expected to contain 50% EDTA and 50% ED3A (ED3A=ethylenediaminetriacetic acid) was reacted with Co(II) in air, producing the corresponding Co(III) complexes. These complexes were separated by ion exchange as aquo complexes and the chloro derivatives were made following an approach to identification of aminopolycarboxylate ligands introduced by Blackmer, Hamm and Legg.⁽⁵⁷⁾ The NMR of the chloro complexes were recorded in HCl/D₂O mixtures to limit solvent ¹H concentration. The spectra obtained are shown in Figs. V-4, 5. Spectrum V-5 resembles that reported by Day and Reilley⁽⁶³⁾ for Co(EDTA)Cl. The second spectrum is similar to the spectrum of Co(ED3A)NO₂. In particular, both the oxidized ligand complex and Co(ED3A)NO₂ exhibit a broad band at 6.5 p.p.m. indicative of an amine proton. Both spectra have doublets at 3.2 and 3.5 p.p.m. and a singlet at 4.7 p.p.m. The assignment of an amino function was confirmed by a ninhydrin test which was positive for the oxidized ligand mixture but not for pure EDTA. The absence of a methyl proton singlet at 2.0 - 2.5 p.p.m. in the NMR rule out the N-CH₃ as a product since such a peak occurs for Co(MEDTA)NO₂⁽⁶⁴⁾, (MEDTA=N-methyl-ethylenediaminetriacetic acid).

In another experiment, the oxidized ligand mixture was dissolved in water and HCl was added. A white precipitate

formed overnight which was shown to be EDTA by NMR. The resulting solution was evaporated and precipitated with ethanol. The gummy white solid obtained was redissolved in NaOH/D₂O and the NMR spectrum shown in Fig. V-5(a) was recorded when compared with the ligand spectrum obtained from an unirradiated sample, (which was identical to a bench sample of EDTA), shown in Fig. V-5(b), the results indicate that one end of the EDTA is now different from the other since the peak due to the N-CH₂-CH₂-N protons is split into two approximately equal peaks. The peak due to N-CH₂-COO⁻ protons is also split but in approximately a 2:1 ratio. Both these observations are consistent with removal of one acetate group and substitution of a proton which would exchange rapidly in D₂O. Thus, the photodecarboxylation of ferric amino polycarboxylates can be represented by equations V-7 - V-9.

Since comparable behaviour has been noted for CuNTA, and the non-biological decomposition of amino acids in natural waters is slow⁽⁶⁵⁾, this reaction may be a significant pathway for degradation of aminopolycarboxylates and amino acids

FIG. V-4

The NMR spectra of the ligands obtained after
~~p~~recipitation of the iron from two solutions of FeEDTA;
(a) a sample irradiated to decolorization and reoxidized and
(b) an unirradiated sample.

FIG. V-5(a) & (b)

The NMR spectra of the cobalt complexes prepared by treating cobalt(II) with the ligand mixture obtained by precipitation of the iron from a photolyzed sample of FeEDTA. The complexes were separated by ion exchange since species (a) was neutral at pH = 5.00, while species (b) was anionic at pH = 5.00.

in natural waters.

The effect of methanol and tertiary butanol on Fe(II) yields for $[\text{Fe}(\text{EDTA})\text{H}_2\text{O}]^-$ was also briefly examined in acidic solutions. Tertiary butanol produced no noticeable change in the quantum yield, while methanol caused an observable increase. It was difficult to correlate this increase to concentrations since some scavenger was removed during the degassing procedure and thus concentration of scavenger is a function of degassing time.

We are able to confirm, however, that an increase in yield is seen in moderately concentrated methanol solutions and not in tertiary butanol and the behaviour thus parallels that observed in the previous two chapters. The results of this study are listed in TABLE V-5 and depicted in Fig. V-6.

TABLE V-5

Irradiation of FeEDTA with methanol at 3500Å

[methanol](M)	Fe(II)
0	.071
.244	.067
.536	.080
.944	.077
1.47	.087
1.88	.091
2.56	.087

FIG. V-6

The quantum yield as a function of scavenger concentration in the irradiation of FeEDTA^- .

VI. EFFECTS OF THE MEDIUM

As can be seen from Fig. III-2 and IV-5, there is a difference in behaviour among scavengers in the concentration range where the scavenger should be reacting with all free radicals. The fact that tertiary butanol scavenging reaches a plateau at a value which is equal within experimental error to the intercept of the linear portion of the curve obtained when methanol, isopropanol, and formic acid are scavengers, confirms that the increase in quantum yield occurs as a result of some process not included in the previous kinetic schemes. One rather obvious possibility was that at high scavenger concentrations scavengers could enter the primary co-ordination sphere of the iron giving rise to a new charge transfer transition between the scavenger and the iron which may have been populated during the excitation. Several facts do not support this contention, however.

The equilibrium between formic acid and iron, in which formate becomes co-ordinated to iron is known to have an equilibrium constant, K , equal to 8.5×10^{-4} (66). Thus, less than 1% of the formate would be co-ordinated at unit H^+ activity. The acid strength in question is $2.25M HClO_4$. Fig. III-2 reveals that formic acid exhibits the same behaviour as methanol and isopropanol and since formic acid is not co-ordinated it seems unlikely that the reactions of the two alcohols are to be attributed to co-ordinated alcohol.

Since iron is para-magnetic the ^1H NMR line widths of the solvent molecule should exhibit para-magnetic broadening. A technique making use of this phenomenon has been developed to investigate solvation of para-magnetic ions. (67,68)

The transverse relaxation time, T_2 , of the solvent protons is reduced by para-magnetic solutes and therefore the ^1H NMR line widths of the -OH protons from the alcohols and water should exhibit broadening due to the para-magnetic ion, Fe^{3+} . Where exchange between the solvation shell and the bulk solvent is rapid, McConnell's equation can be applied. (67)

$$1/T_2 = P_D/T_{2D} + P_M/T_{2M} \quad \text{VI-1}$$

$$(\delta\nu)_{1/2} = 1/\pi T_2 \quad \text{VI-2}$$

$$(\delta\nu)_{1/2} = P_M(\delta\nu_M)_{1/2} \quad \text{VI-3}$$

Where P_D is the probability that a solvent molecule is in the diamagnetic environment (bulk) and P_M is the probability that a solvent molecule is in the paramagnetic environment (solvate shell), and $(\delta\nu)_{1/2}$ as the corresponding peak widths at half-height.

If contributions to the line width of the bulk water proton peak are assumed to be negligible when compared to the contributions to the line width from the water molecules surrounding the ferric ion, (ie. $(\delta\nu_A)_{1/2}$ is small), then equation IV-1 reduces to IV-3.

A more complete derivation is given in Appendix C along

with expressions to calculate it. δ_M can be evaluated since it is assumed equal to the line width at half peak height in the absence of added organic solvents. NMR spectra of the ferric perchlorate solutions to be irradiated were recorded. The line widths at half peak height for both water protons and alcohol methyl protons are given in TABLE VI-1. Predicted line widths calculated from IV-3 by the method shown in Appendix C, are also given assuming that the value for the line width of the water proton in the absence of organic solvents was accurate to ± 1 Hz. These results show a substantial broadening of the water proton line width which increases with increasing concentration of added organic. One interesting feature of this broadening is that it is greater than the predicted broadening in which alcohols were assumed not to enter the co-ordination sphere. This is clearly demonstrated in Fig. VI-1. If alcohols had become co-ordinated the observed broadening could be expected to be less than the predicted value. The observed values are greater than the predicted values since line broadening of the second co-ordination sphere was neglected in the calculation although it has been known to be 5 to 10% of the broadening observed in the primary co-ordination sphere. (69,70) It is important to note that no difference in the NMR behaviour was observed between methanol and tertiary butanol. Therefore, we can rule out co-ordination of the scavengers in this system giving rise to the observed differences in scavenging behaviour.

A second possibility to account for this behaviour is

TABLE VI-1

Concentration scavenger (M)	Predicted line widths based on		Observed line widths (Hz)
	53Hz	55Hz	
methanol			
.615	55	57.1	56
1.185	57.7	59.9	62
1.793	60.0	62.3	65
2.351	61.4	63.7	70
2.996	65.5	67.9	72
3.555	71.8	74.5	79
isopropanol			
1.078	60.0	62.3	60
1.786	75	77.8	87
tert-butanol			
.236	55	57.1	58
.705	59.1	61.3	68
.942	62.3	64.6	73
1.202	67.3	70.3	79
1.428	75.5	78.3	86

FIG. VI-1

Observed line widths at half peak height vs.
predicted line widths at half peak height for (▲)
methanol, (●) tertiary butanol, and (●) isopropanol.

direct reaction of the scavenger with the excited state. In the past such a reaction has been assumed not to occur, since the lifetime of an excited state is so short compared to diffusion processes, that a scavenger and an excited state cannot come together during the lifetime of the excited state. Such an assumption neglects the possibility that the scavenger and absorbing reactant were in encounter at the time of birth of the excited state.

Noyes has developed expressions for the scavenging of radicals produced in pairs which become separated by one or more solvent molecules.⁽⁷¹⁾ He assumes that two types of free radicals exist in solution, those which are separated by only one or two solvent molecules but which diffuse back together and recombine with their original partners, and those which become separated by many solvent molecules and react with radicals produced from other reactants. He develops expressions which show that scavenging for the former should be described by time dependent kinetic expressions while scavenging for the latter should be described by conventional kinetics. From this analysis, he derives an expression similar to III-9 for scavenging of free radicals which would not have reacted with their original partners and derives an expression dependent upon the square root of the scavenger concentration in the case where scavenger concentration was high enough to compete with 'primary' recombination. From Fig. VI-2 it can be seen that the behaviour observed for methanol, isopropanol, and formic

FIG. VI-2

Quantum yields vs. square root of scavenger concentration for methanol, isopropanol and formic acid, for irradiation of hexaaquoiron(III) perchlorate. Scavengers were methanol (Δ), isopropanol ($\circ$), formic acid ($\square$), and tertiary butanol ($\circ$).

acid does not fit the square root relationship, and therefore is not due to Noyes type scavenging.

Another treatment was developed by Waites and Hammond in order to explain results in which quantum yield varied linearly with scavenger concentration.⁽⁷²⁾ It was assumed that the scavenger was reacting directly with the excited state and that the linear behaviour represented the probability that the scavenger was in encounter with the excited state at the time of absorption. This behaviour is similar to that observed in the present system. When reaction VI-5 is included in the kinetic treatment in Chapters III or IV, the resulting expression for quantum yield is VI-5.

$$\Phi_{\text{Fe(II)}} = c_1[\text{HS}] + \frac{c_2[\text{HS}]}{k_2[\text{Fe(II)}] + k_3[\text{HS}]} \quad \text{VI-5}$$

This expression reduces to that obtained in the previous kinetic treatment, Chapter III or IV, when scavenger concentration approaches zero. Thus, scavengers which can react with the excited state and those which cannot should have the same intercept at zero scavenger concentration.

Since the three scavengers fall on the same line in the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ irradiation, and methanol and isopropanol fall on the same line in the $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}$ irradiation, it seems reasonable to assume that the scavengers are reacting at unit efficiency in these cases. The slopes of the linear portions of the curves in Fig. III-2 and Fig. IV-2 are the same within

experimental error, ie. 0.031 for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$; 0.034 for $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ indicating little difference in this behaviour for two different excited states, and lending support to the notion that the excited state is reacting with the scavenger at unit efficiency.

Since in the case of $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ the transition occurs between the chloride and the metal, scavengers which are situated on the opposite side of the complex from the chloride may not react. The yield for this reaction between excited state and scavenger would therefore be dependent upon the scavenger occupying the correct position in the solvation shell. The identical slopes for the two species indicate that the excited states probably have similar geometries and therefore the same statistical factors for the excited state reaction. This would happen if, in the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ excited state, one water was different from the other five and the excited state may therefore be represented by $\text{Fe}(\text{H}_2\text{O})_5^{2+}(\text{H}_2\text{O})^+$.

A clue to the nature of the excited state reaction is given by the difference in reactivity observed between tertiary butanol and the other scavengers. Tertiary butanol has no α -hydrogens while the others do. Thus the excited state reaction likely involves the α -hydrogen of the scavengers. In the introduction it was mentioned that tertiary hydroxy-

butyl radicals do not participate in electron transfer reactions while the radicals formed by abstraction of an α -hydrogen from primary or secondary alcohols readily undergo electron transfer. This behaviour is parallel to the behaviour observed for the excited state reaction. It is therefore possible that the reaction observed for primary and secondary alcohols with the excited state involves electron transfer from the alcohol in the excited state. This reaction is schematicized by the following sequence:

The lower slopes observed for the reaction of the dihydroxo-bridged dimer excited state with the alcohols and the Fe(EDTA) excited state with the alcohols probably represent either a larger steric factor or a decreased efficiency for the reaction.

The EDTA case is especially interesting since it is possible that the reaction between alcohols and the excited states can take place prior to decarboxylation and thus the product of this reaction is a reduced Fe(EDTA) and an alcohol radical. This may explain the hitherto unexplained difference

in stoichiometry of this reaction which occurred on the addition of large concentrations of primary and secondary alcohols.⁽¹²⁾ In the case of CoEDTA, a 1:1 ratio of carbon dioxide to reduced metal was observed in the absence of scavengers but when scavengers were added (50% isopropanol) the ratio of carbon dioxide to reduced metal approached 1:2.⁽¹²⁾ Thus, in the absence of scavengers this reaction may be

Whereas, in the presence of 50% isopropanol the reaction may be

The assignment of the excited state reaction as electron transfer is not without precedents. ESR studies of $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_5\text{NO}^{3-}$ have both demonstrated electron transfer from

the alcohol to the excited state. (29,31) In the former case, the excited state was produced as a result of charge transfer from NO to iron while in the case of $\text{Fe}(\text{CN})_6^{3-}$, the excited state involved an intra-ligand transition and the iron was not reduced in initial transition. Both species, however, produced alcohol radicals as a result of excitation. Moreover, another ESR study involving uranyl iron and Ce has demonstrated that different radicals are produced for the same alcohol. (73,74) Irradiation of Ce(IV) in alcohol water mixtures showed that methanol was unreactive, ethanol produced formaldehyde and methyl radicals. Higher primary alcohols produced formaldehyde and the corresponding alkyl radical. In contrast to this, irradiation of UO_2^{2+} in alcohol-water mixtures produced radicals derived by abstraction of an α -hydrogen. Similar behaviour was observed for carboxylic acids, Ce(IV) excitation producing an alkyl radical and CO_2 while uranyl excitation produce a radical derived by abstraction of a hydrogen atom α to the carboxyl group. When taken together, these results allow a comparison since the photochemistry of carboxylic acids has been studied. In the case of Ce(IV) carboxylic acid system, the transition which was excited is carboxylate-to-metal charge transfer while the excitation of UO_2^{2+} presumably produces an excited state which does not involve the carboxylic acid. The behaviour of each of these systems is depicted in Fig. VI-3(a) and (b). If a similar reaction occurred between each metal and an alcohol, the observed radicals would be

FIG. VI-3(a) & (b)

Radical production from carboxylic acids for
irradiation of UO_2^{2+} and Ce(IV) .

(a).

(b).

FIG. VI-4

The proposed radical production from alcohols
for irradiation of UO_2^{2+} and Ce(IV) .

(a)

(b)

produced, as shown in Fig. VI-4.

Finally, recent reports on the emission of VO_2^{2+} indicate that alcohols can react directly with this excited state and that the emission is quenched by methanol and isopropanol but not by tertiary butanol.⁽⁷⁵⁾ This behaviour parallels the iron system and supports the conclusion that the increase in yields seen with methanol and isopropanol is due to direct reaction of the alcohols with the charge transfer excited states.

The implications of this new reaction are great since alcohols have often been used as radical scavengers in photolysis. The confusion which has been generated in the photolysis of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Tl}(\text{H}_2\text{O})_6^{3+}$, and $\text{Ce}(\text{IV})^{3+}$ in alcohols may be a result of electron transfer from the alcohol to excited state.⁽⁷⁶⁾ In the case of $\text{Ce}(\text{IV})^{3+}$, there may also be products from the direct charge transfer from alcohol to metal.

SUMMARY

As a result of the work presented here, several new facts have emerged.

The pattern of reactivity for the tertiary butanol scavenging in the chloropentaaquoiron(III) irradiation leads to the conclusion that, other reports to the contrary, chlorine atoms are the product of chlorine-to-iron charge transfer irradiation. The effects previously noted by David can be attributed to chloride ion scavenging for chlorine atoms.

From the behaviour of methanol and isopropanol in comparison to tertiary butanol, it can be deduced that electron transfer from a suitable substrate to a ligand-to-metal charge transfer excited state can occur if the substrate is in the reactive position at the time of excitation. Many studies which have been conducted in aqueous alcohols and other scavengers in which changes in stoichiometry or yield were noted should be amended to include this new reaction. Since many studies of solvated electron production from ferrous species were conducted with scavengers, it may be valuable to conduct a similar study on metal-to-ligand and metal-to-solvent charge transfer excitation.

Another interesting point to emerge from this and other recent work is that, since a species need not be co-ordinated to participate directly in a photo-reduction, different products may be expected if the species is in a position to

react via electron transfer to the excited state. The realization that two reaction paths are possible may be useful in elucidating the mechanism of the oxidation of alcohols via cerium photolysis which, as noted in Balzani and Carasitti can give confusing results.

A final point which has been learned concerns the photodecomposition of ferric-aminopolycarboxylates. It has now been demonstrated that the decrease in yield observed with increasing pH is due to dimerization. Since concentrations of these species are low enough in natural waters that dimerization is not significant, it can be expected that even where the pH of natural waters may be basic, a significant lowering of quantum yield may not be observed.

Several extensions into new areas seem logical as a result of this work. Charge transfer systems of other types should be investigated with suitable scavengers. The question of reaction products, depending upon co-ordination or solvent effects, also might prove fruitful. Finally, the irradiation of ferric-amino acid complexes should also be investigated with close attention paid to the hydrolytic species absorbing the light.

APPENDIX A

<u>Chemical</u>	<u>Supplier</u>	<u>Grade</u>
tertiary-Bu-tyl Alcohol	Fisher	Certified ACS
Carbon Tetrachloride	Fisher	Certified Spectra-analyzed
Chloroform	Fisher	Certified Spectra-analyzed
Cobalt Carbonate	BDH	Reagent
Cobalt Chloride	Anachemia	Purified
Deuterium Oxide	Stohler Isotope	99.9%
2,4-Dinitrophenyl-hydrazine	Eastman	---
Ethylenediaminetetra-acetate Disodium Salt	Fisher	Certified ACS
Ferric Chloride	Fisher	Anhydrous, sublimed
Ferric Nitrate	Fisher	Certified ACS
Ferric Sulfate	Anachemia	Reagent
Ferrous Ammonium Sulfate	Anachemia	Reagent
	General Chem., N. Y.	Reagent
Formaldehyde Solution	Fisher	Certified ACS
Formic Acid	BDH	90% Reagent
Glycine	Eastman	---
Hydrogen Peroxide, 30%	Fisher	Reagent
Iminodiacetic Acid	BDH	Certified Spectra-analyzed
	Aldrich	Spectrophotometric
Ninhydrin	Nat. Biochem.	---
Nitrilotriacetic Acid	BDH	Reagent

iso-Propyl Alcohol	Fisher	Certified Spectra-analyzed
o-Phenanthroline, monohydrate	Fisher	Certified ACS
Potassium Hydroxide	Merck	Reagent
Sodium Chloride	Fisher	Certified ACS
Sodium Hydroxide	Anachemia	Reagent
Sodium Perchlorate	BDH	Analar
	G. F. Smith	Anhydrous

Nitric, Hydrochloric, Sulfuric, Perchloric Acids, Allied Chemical, Reagent Grade

APPENDIX B

(i) Total iron concentration = 1.95×10^{-5}

A₃₅₀ = 1.095, pH = 11.0, path = 5cm

$$a_m = .094/5 \times 10^5/1.95$$

$$= 974$$

$$a_m = 970$$

(ii) [dimer] = .00678, [monomer] = .008

$$A_{350} = .210/.005 = 42.0$$

$$42.0 = a_m \times .008 + a_d \times .0068$$

$$a_d = 42/.0068 - .008/.0068 a_m$$

$$= 5035$$

(iii) [dimer] = .0106, [monomer] = .0094

$$A_{350} = .319/.005 = 64$$

$$64 = a_m \times .0094 \times a_d \times .0106$$

$$a_d = 64/.0106 - .0094/.0106 a_m$$

$$= 5177$$

(iv) $5035 + 5177/2 = 10212/2 = 5106$

$$a_d = 5100$$

APPENDIX C

For the purpose of this study we have assumed that six solvent species are co-ordinated to the iron and comprise the primary solvation sphere. We also disregard the possibility that the second co-ordination sphere can be preferentially solvated or can be broadened by a paramagnetic ion. In this case, we have six paramagnetic solvent sites and the remainder of the solvent is assumed to be in a diamagnetic environment. Since each water has two protons, the total environment is twelve. This can be related to the total number of protons from the weights of iron, alcohol, acid, and water used.

From this information, P_M , the probability that a proton will be found in the paramagnetic environment will be

$$P_M = \frac{12 \times \# \text{ moles Fe(III)}}{\# \text{ moles HClO}_4 + 12 \times \# \text{ moles Fe(III)} + 2 \times \# \text{ moles H}_2\text{O} + \# \text{ moles alcohol}}$$

and P_A , the probability that a proton will be in the diamagnetic environment will be

$$P_A = 1 - P_M$$

The relaxation time is related to the width of the NMR signal at half height by

$$(\delta v)_{\frac{1}{2}} = 1/\pi T_2$$

When exchange is rapid between environments,

$$1/T_2 = P_D/T_{2D} + P_M/T_{2M}$$

If contributions to the peak width from protons in the diamagnetic environment is assumed to be negligible when compared to that from the paramagnetic environment.

$$(\delta v)_{\frac{1}{2}} = P_M (\delta v_M)_{\frac{1}{2}}$$

If # moles alcohol = 0, $(\delta v_M)_{\frac{1}{2}}$ can be evaluated from the observed line width $(\delta v)_{\frac{1}{2}}$ and

$$P_M = \frac{12 \times \# \text{ moles of iron(III)}}{2 \times \# \text{ moles H}_2\text{O} + 12 \times \# \text{ moles iron(III)} + \# \text{ moles HClO}_4}$$

Using this value for $(\delta v)_{\frac{1}{2}}$ and values of P_M calculated for alcohol water mixtures, a predicted peak width can be calculated.

In this case, P_p for water only, was calculated to be .00116 and $v_{\frac{1}{2}} = 53 \text{ Hz}$.

$$\text{Thus } (\delta v_M)_{\frac{1}{2}} = 53/.001166 = 45,455 \text{ Hz}$$

or

$$(\delta v_M)_{\frac{1}{2}} = 55/.001166 = 47170$$

assuming the observed value of 54 Hz was good to ± 1 Hz.

Calculated from the amounts of reagent used, P_M was found for each mixture to be

[methanol]

	P_M
.615	.00121
1.185	.00127
1.793	.00132
2.351	.00135
2.996	.00144
3.555	.00158

[isopropanol]

1.078	.00132
1.786	.00165

[tert-butanol]

.236	.00121
.705	.00130
.942	.00137
1.202	.00149
1.428	.00166

From these values for P_M and $(\delta v_M)_{\frac{1}{2}}$ the predicted peak widths given in the text were calculated.

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