

PHOTODECOMPOSITION OF THE
ETHYLENEDIAMINETETRAACETATOFERRATE(III) ION

by

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A THESIS

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INTRODUCTION

When the ethylenediaminetetraacetatoferrate(III) ion, Fe(III)EDTA^- , is radiated with ultraviolet light, the Fe(III) is reduced to Fe(II) .

The photosensitivity of this complex has been noted by Lambert, et al., (11) and compared to the photosensitivity of other metal chelates.

Jones and Long (8) have noted the photosensitivity of the complex formed between Fe(III) and di-sodium EDTA and have proposed the following scheme for the photodecomposition:

- (1) $\text{Fe(III)EDTA}^- + \text{light} = \text{Fe(II)EDTA}^{2-} + \text{decomposition products}$
- (2) $\text{Fe(II)EDTA}^{2-} + \frac{1}{2} \text{H}_2\text{O} + \frac{1}{4} \text{O}_2 = \text{Fe(III)EDTA}^- + \text{OH}^-$
- (3) Repeated photoreduction and oxidation leads to the formation of $\text{Fe(OH)(III)EDTA}^{2-}$ and eventually Fe(OH)_3 .

Hill-Cottingham (7) has investigated the photoreduction of Fe(III)EDTA^- spectrophotometrically and has found that the EDTA chelate is decomposed on exposure to daylight.

The trioxalatoferrate(III) ion is also reduced on exposure to ultraviolet light. Parker and Hatchard (6,13,14,15) have used potassium trioxalatoferrate(III) as a standard chemical actinometer and have proposed the following mechanism for the photoreduction:

- (1) $\text{Fe(III)(Ox)}_3^{3-} + h\nu = \text{Fe(III)(Ox)}_3^{3-*}$ (activated complex)
- (2) $\text{Fe(III)(Ox)}_3^{3-*} = \text{Fe(II)(Ox)}_2^{2-} + \text{Ox}^{\cdot-}$ (oxalate radical)
- (3) $\text{Fe(III)(Ox)}_3^{3-} + \text{Ox}^{\cdot-} = \text{Ox}^{2-} + \text{Fe(III)(Ox)}_2(\text{Ox}^{\cdot-})^{2-}$
(dioxalatoferrate(III) attached to oxalate radical)
- (4) $\text{Fe(III)(Ox)}_2(\text{Ox}^{\cdot-})^{2-} = \text{Fe(II)(Ox)}_2^{2-} + 2 \text{CO}_2$

Since Fe(III)EDTA^- ion and the trioxalatoferrate(III) ion both possess chelated carboxyl groups, it is possible that mechanisms of decomposition are similar. Carbon dioxide could be a photodecomposition product of Fe(III)EDTA^- .

Bent and Crawford (3) have observed an absorption peak at 2350 cm.^{-1} in the infrared spectrum of nitrocellulose in potassium bromide disk after thermal decomposition. This absorption was assumed to be due to the formation of carbon dioxide which was trapped in the potassium bromide lattice. The absorption peak remained after the disk was repressed at pressures up to 125,000 p.s.i.

In the present work HFe(III)EDTA was irradiated by ultraviolet light in a potassium bromide disk so that any carbon dioxide formed would be trapped in the potassium bromide lattice. The changes in structure of HFe(III)EDTA during radiation were studied by observing the changes in the infrared spectrum. Trapped carbon dioxide was also detected in potassium bromide disks.

EXPERIMENTAL

Reagents

The ethylenediaminetetraacetic acid, H_4EDTA , used in the preparation of HFe(III)EDTA was Fisher certified reagent and was used without further purification. The di-sodium ethylenediaminetetraacetate, di-sodium EDTA, used in the pH titrations was Eastman practical grade. It contained considerable water insoluble particles which were filtered from solution before use. For the precipitation of ferric hydroxide, B&A (Baker and Adamson) reagent quality ferric nitrate and Dupont C.P. ammonium hydroxide (30% NH_3) were used. The

sodium hydroxide and barium chloride used to prepare the standard sodium hydroxide solution were B&A reagent quality. Infrared quality potassium bromide obtained from Harshaw Chemical Co. was used for preparation of potassium bromide disks. Standard ferrous-dipyridyl solutions were made from B&A reagent quality ferrous sulfate, and from 2,2'-dipyridyl obtained from Matheson Chemical Co. The compounds used in the magnetic susceptibility measurements were B&A reagent quality copper(II) sulfate, nickel(II) sulfate, cobalt(II) sulfate, iron(II) sulfate, iron(III) sulfate, manganese(II) sulfate, and potassium chromium(III) alum.

Equipment

The Beckman models H-2 and G pH meters were used for the pH titrations. External shielded electrodes were used.

All infrared spectra were recorded on a Perkin-Elmer Infracord spectrophotometer. The potassium bromide disks were molded in a hard steel die which could be evacuated. To form these disks pressure was applied by means of a hydraulic jack mounted in a steel framework. A 275 watt General Electric Sun Lamp was used as the source of ultraviolet radiation. The distance from the lamp to the samples was 27 cm. In order to control the temperature during irradiation, the disks were placed in a 100 ml. beaker which was located in a constant temperature water bath controlled at 25° C. Absorbance of the ferrous-dipyridyl solutions was measured in a Beckman DU spectrophotometer at 522 millimicrons using a slit width of 0.08 mm.

The apparatus used for magnetic susceptibility measurements consisted of an electromagnet, which provided a constant field strength, and an analytical balance, which was used to measure the force exerted on the samples by the

magnetic field. The cores of the electromagnet were made of five-inch diameter soft iron and were connected by a U-shaped arrangement of five-inch square bars of soft iron. Water was circulated through Tygon tubing which was wrapped around the coils to reduce the rate of heating of the core. The pole faces were 3.2 cm. in diameter and spaced 1.3 cm. apart. The left pan of the balance was replaced by a counter-weight. From the counter-weight a gold chain was suspended through an opening in the bottom of the balance case. Sample tubes were attached to the lower end of the gold chain by means of a nylon stirrup and were allowed to swing freely between the pole faces. More detailed description of the apparatus is given by Duell (4).

Magnetic Susceptibility Measurements

Samples of compounds containing one, two, three, four, and five unpaired electrons, including HFe(III)EDTA , were ground to a fine powder by means of a mortar and pestle. The powder samples were then packed into glass sample tubes of known volume and weight and their densities were determined by difference in weight. On comparison of relative molar susceptibilities of the samples, HFe(III)EDTA was found to be similar to iron(III) sulfate and manganese(II) sulfate indicating that the compound is ionic.

Preparation of Potassium Bromide Disks

The potassium bromide and samples were stored in a desiccator over night to remove most of the moisture. All disks were prepared by weighing on an analytical balance 2.0 mg. of sample and adding enough potassium bromide to make the total weight 600 mg. The samples were placed in the die for 10

minutes under vacuum and then under vacuum at 5,000 p.s.i. pressure for 10 minutes. Reground disks were pressed at 7,000 p.s.i. pressure. The disks obtained were 13 mm. in diameter and 1.4 mm. thick.

Preparation of HFe(III)EDTA

Forty grams of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 100 ml. of distilled water and the iron oxide which coated the ferric nitrate was filtered from solution. The ferric nitrate solution was added dropwise to an ammonium hydroxide solution containing 50 ml. concentrated ammonium hydroxide and 50 ml. of distilled water. The mixture was stirred by a magnetic stirrer during the precipitation. Excess ammonium hydroxide prevented the formation of colloidal iron oxide. The ferric hydroxide formed was washed five times by centrifugation or until the odor of ammonia could no longer be detected.

The ferric hydroxide was collected in 100 ml. of distilled water. Thirty five grams of H_4EDTA was added and the mixture was heated over a steam cone while being stirred for one hour or until there was no residue. Any excess H_4EDTA precipitated when the solution was cooled to room temperature and was filtered from solution.

Acetone was added in small amounts and the volume of the acetone-water mixture was reduced by boiling over a steam cone. When the HFe(III)EDTA crystals began to form on the sides of the beaker, the solution was removed from the steam cone and allowed to cool to room temperature. The crystals were removed from solution by filtering under vacuum and redissolved in a minimum amount of water. Acetone was added until the HFe(III)EDTA was again crystallized from solution. The bright yellow crystals of pure HFe(III)EDTA

were removed by filtering under vacuum and dried on the filtering funnel by drawing air through the funnel with an aspirator. About twenty grams of pure HFe(III)EDTA was collected.

Preparation of $\text{NH}_4\text{Fe(III)EDTA}$

Ten grams of HFe(III)EDTA , prepared according to the above procedure, was dissolved in 100 ml. of distilled water and the solution titrated to the first equivalent point with ammonium hydroxide, using the model H-2 pH meter. Water was removed by evaporation over a steam cone until the crystals were almost dry. The crystals were removed from the steam cone while they were still moist since complete drying on the steam cone gave a partially reduced product. The yellow-brown crystals were completely dried by evaporation at room temperature.

Determination of Structure of HFe(III)EDTA and $\text{NH}_4\text{Fe(III)EDTA}$

The spectra of HFe(III)EDTA and $\text{NH}_4\text{Fe(III)EDTA}$ were recorded and compared in the region of 5.7 micron where unionized carboxyl groups absorb (2) (Fig. 1 and 2). According to these spectra all of the acetate groups of the acid are not ionized while all the acetate groups of the ammonium salt are ionized.

Sodium hydroxide solution was prepared by dissolving sodium hydroxide pellets in water and adding BaCl_2 to remove carbon dioxide. The solution was standardised against potassium acid phthalate using phenolphthalein indicator. The sodium hydroxide concentration was 0.1244 N.

A 0.1900 gram sample of HFe(III)EDTA was dissolved in 50 ml. of distilled water and titrated with standard sodium hydroxide using the model H-2 pH meter to determine the total number of acid equivalents in the compound (Fig. 4). Two acid equivalents were observed at 5.3 and 10.6 milliequivalents of base.

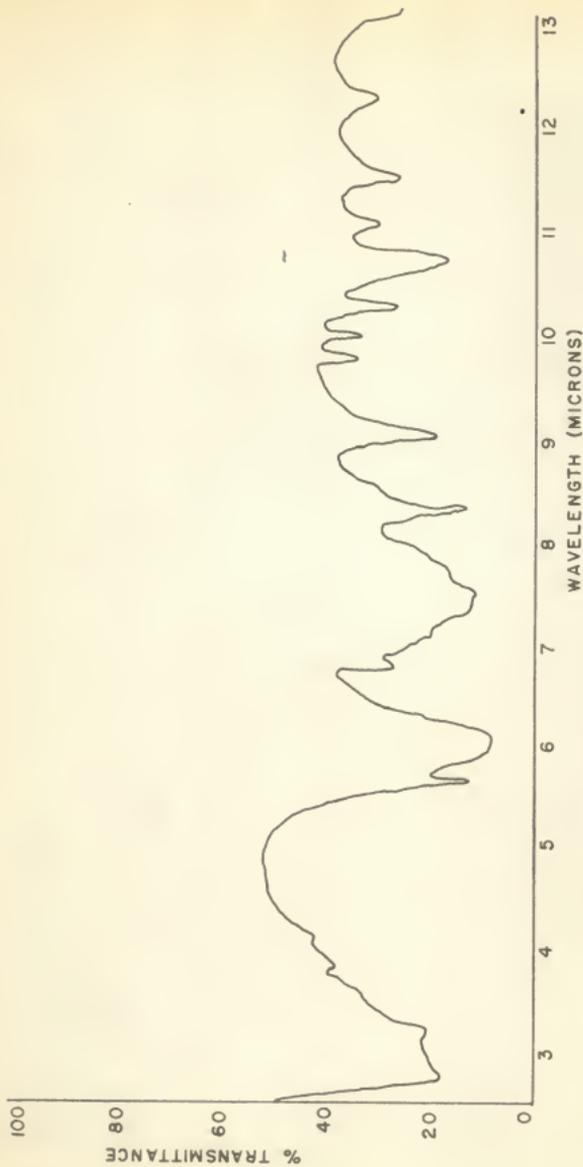


Figure 1. Spectrum of HFe(III)EDTA before radiation.

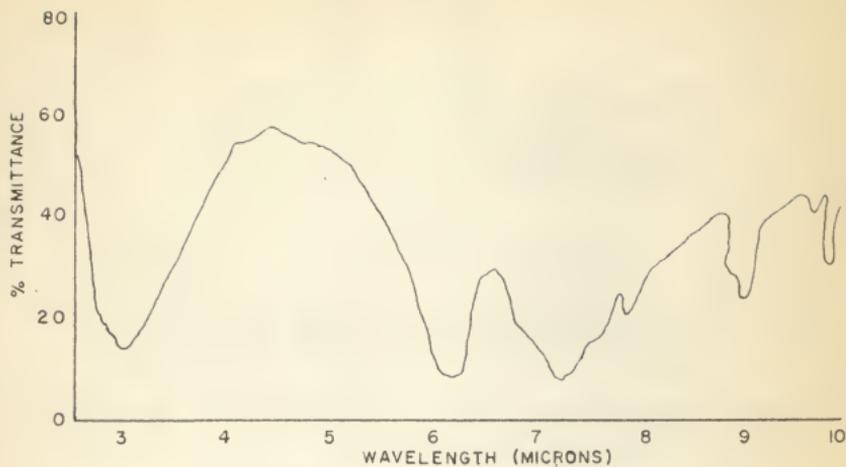


Figure 2. Spectrum of $\text{NH}_4\text{Fe(III)EDPA}$.

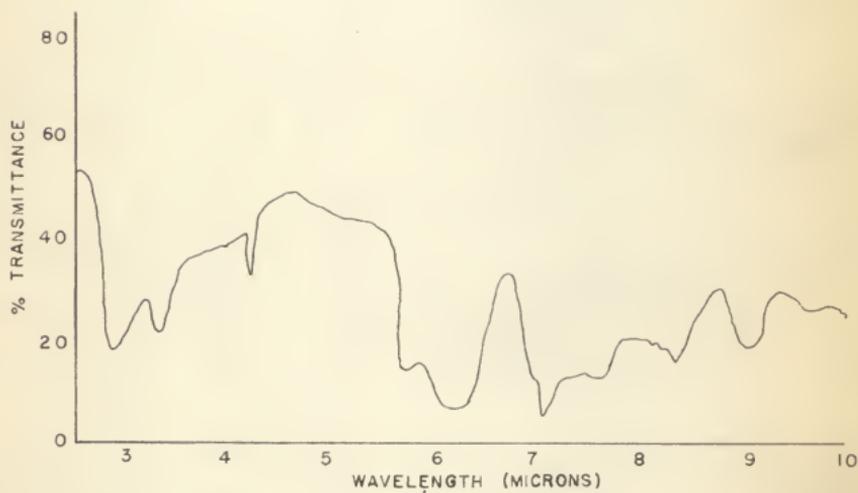


Figure 3. Spectrum of Fe(III)EDPA after radiation, regrinding and repressing.

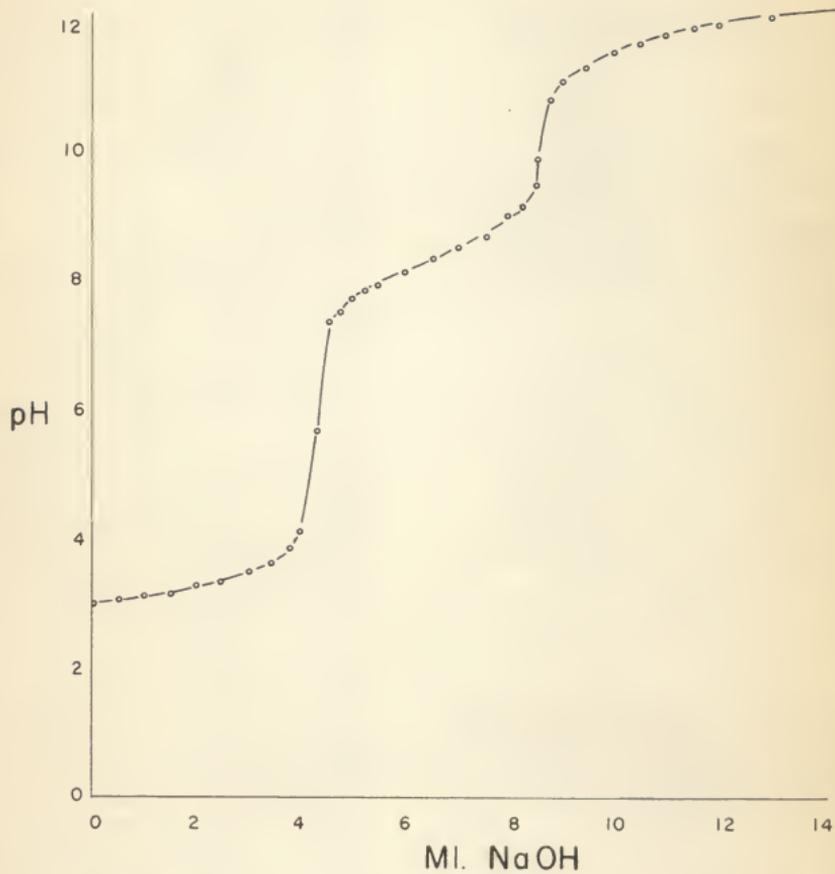


Figure 4. Titration of $\text{Mg}(\text{OH})_2/\text{EDTA}$ to determine the total number of acid equivalents.

Another 0.8000 gram sample of HFe(III)EDTA was titrated to the first equivalence point with the standard sodium hydroxide using the model E-2 pH meter to obtain a more accurate value for the molecular weight. 2.22 milliequivalents of base were used (Fig. 5).

To determine if one of the two acid equivalents observed was due to an unchelated acetate group, a 0.2000 gram sample of HFe(III)EDTA was dissolved in a solution containing 5.00 ml. of a 0.0125 M di-sodium EDTA solution in 50 ml. of distilled water (Fig. 6). The acid strength of an unchelated acetate group was expected to be very similar to the remaining acid equivalents of the di-sodium EDTA. As was expected, the three acid equivalents were titrated simultaneously. The solution was titrated with the standard sodium hydroxide solution using the model G pH meter.

For comparison a solution containing 5.00 ml. of the 0.125 M di-sodium EDTA in 50 ml. of distilled water was titrated with standard sodium hydroxide (Fig. 6). The two remaining acid equivalents were titrated simultaneously and the rise in pH was similar to that of the solution containing HFe(III)EDTA and di-sodium EDTA.

Ultraviolet Radiation of HFe(III)EDTA

The HFe(III)EDTA was irradiated with ultraviolet light in potassium bromide disks so that any carbon dioxide formed could be trapped in the potassium bromide lattice. The carbon dioxide formation was observed at 4.2 microns.

In order to determine the rate of formation of carbon dioxide in the disk, a single disk was irradiated and the spectrum recorded at regular intervals during irradiation. The intensity ratio, I_0/I , was determined by the baseline method (19) as illustrated in Fig. 9.

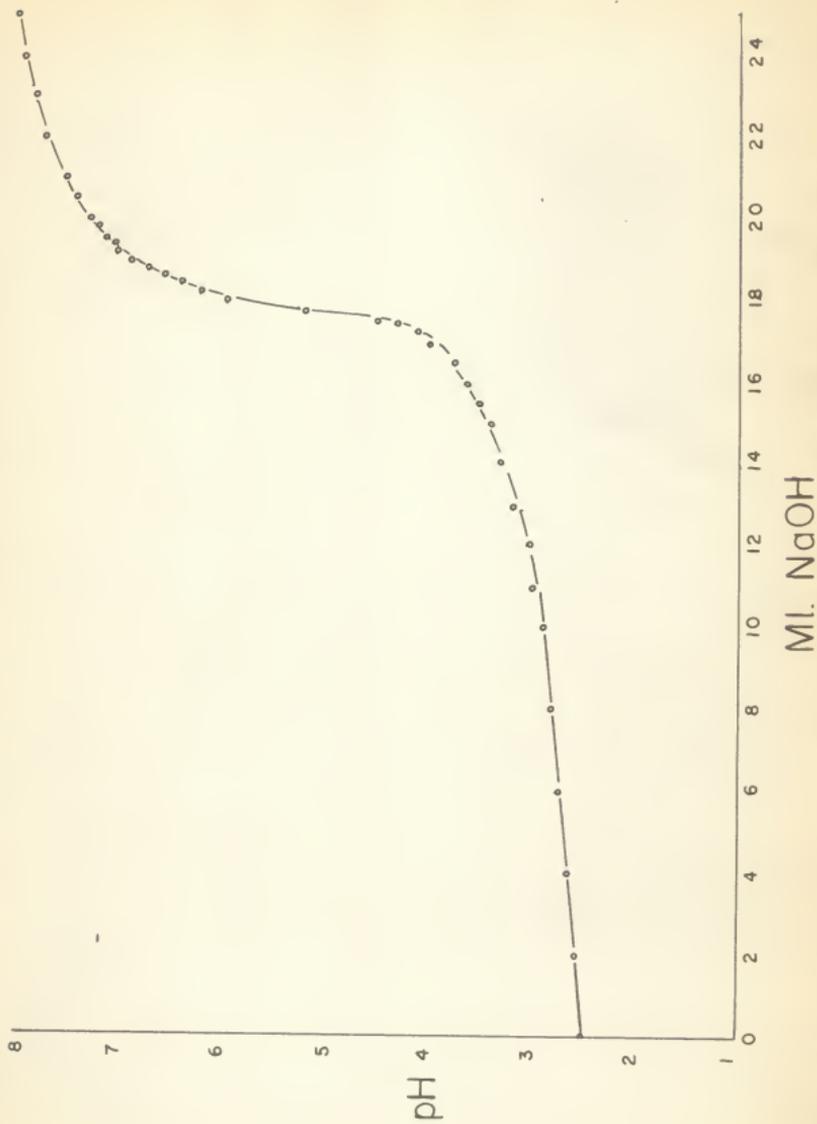
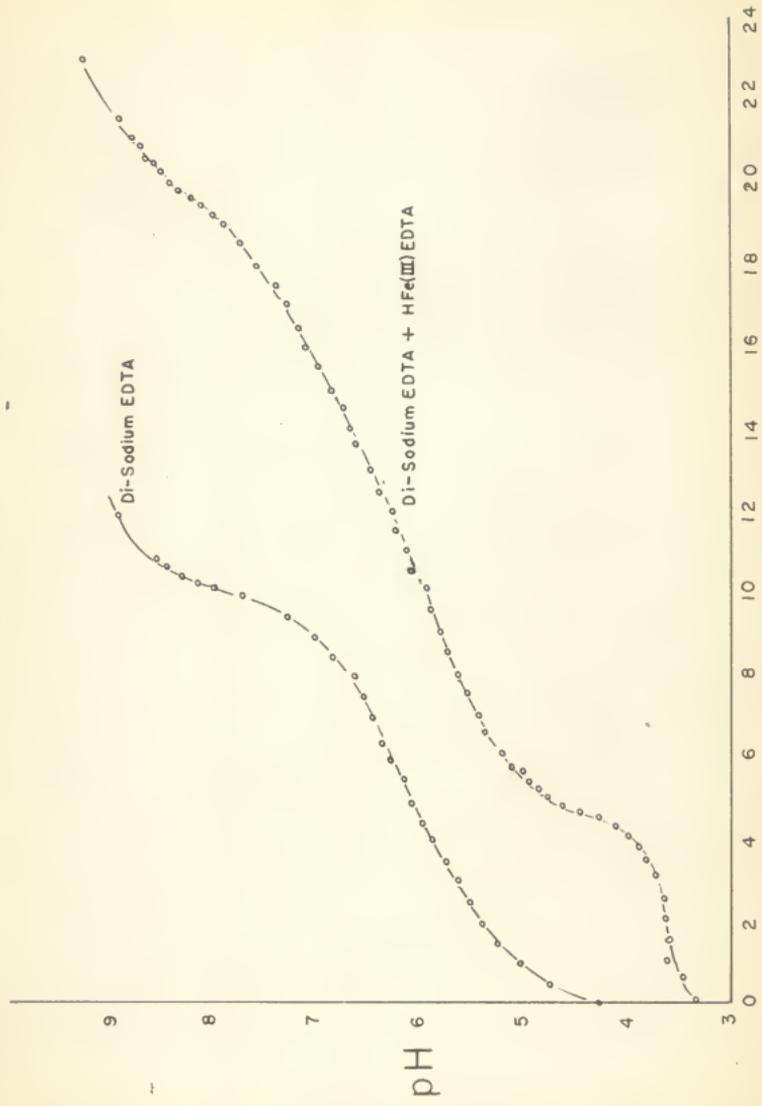


Figure 5. Titration of Fe(III)EDTA to determine the molecular weight.



ml. NaOH

Figure 6. Titration of di-sodium EDTA with and without HFe(III)EDTA.

The rate of formation of ferrous ion during radiation was determined for the reaction in the potassium bromide disk so that the kinetics could be compared to that of carbon dioxide formation. The disks were irradiated for various periods of time ranging from 5 minutes to 60 minutes. After irradiation the disks were dissolved in 50 ml. of 5×10^{-4} molar dipyriddy solution and the absorbance was measured at 522 millimicrons in a Beckman DU spectrophotometer. The concentration of ferrous ion was determined from a standard absorbance versus concentration plot (Fig. 7).

Log concentration of ferrous ion and log absorbance of carbon dioxide were plotted as a function of time to determine if their formations were of first order. Both plots gave straight lines with identical slopes (Fig. 10).

A pure potassium bromide disk was prepared in the usual way and irradiated with ultraviolet light for 15 minutes to determine if the radiation initiated carbon dioxide absorption from the atmosphere. Another disk containing 2.0 mg. di-sodium EDTA in 600 mg. disk was irradiated for 15 minutes to determine if the EDTA ligand was decomposed in the absence of an oxidising agent. No carbon dioxide absorption was observed in either case.

Attempted Removal of Carbon Dioxide from Potassium Bromide Disk

A 600 mg. disk containing 2.0 mg. of HFe(III)EDTA was irradiated for 60 minutes before the spectrum was recorded. The disk was reground, placed in the die under vacuum for 15 minutes and pressed under vacuum at 7,000 p.s.i. for 10 minutes in an attempt to remove the trapped carbon dioxide. The spectrum was again recorded and compared to the spectrum before regrinding (Fig. 8). The absorption peak at 4.2 microns was greatly reduced.

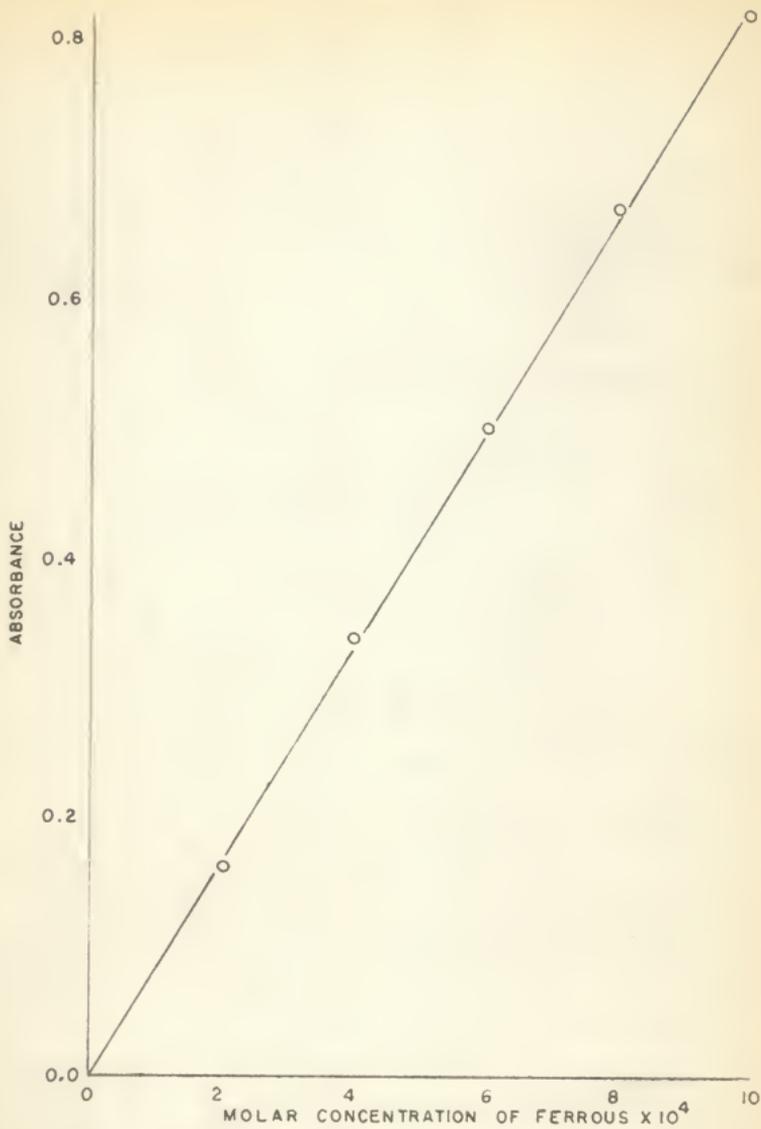


Figure 7. Standard ferrous-bipyridyl curve.

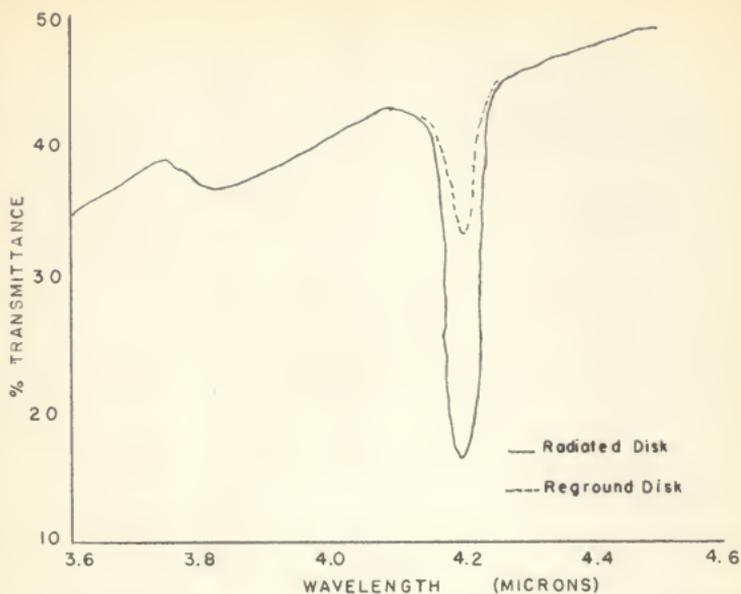


Figure 8. Absorption of CO₂ before and after regrinding and repressing.

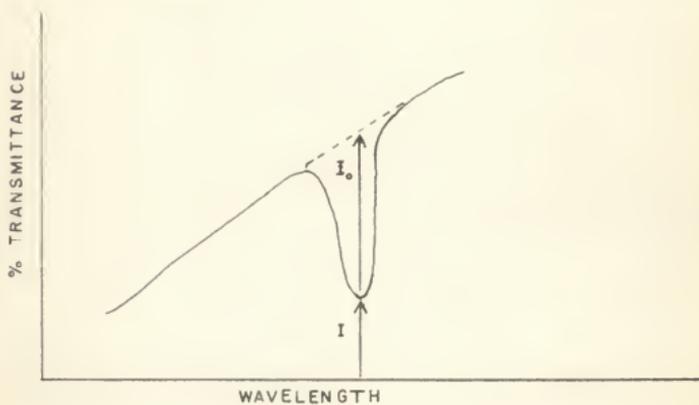


Figure 9. Baseline method of obtaining I_0/I .

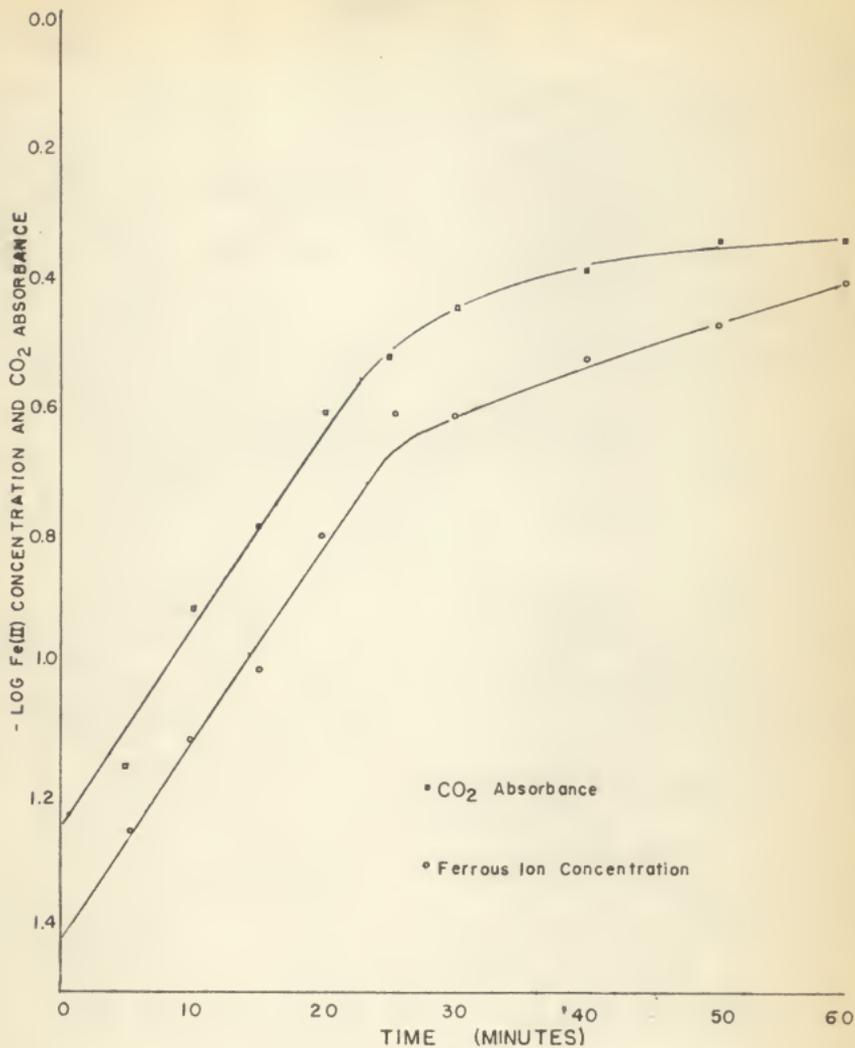


Figure 10. Rate of formation of ferrous ion and CO₂.

DISCUSSION

Structure of HFe(III)EDTA and $\text{NH}_4\text{Fe(III)EDTA}$

HFe(III)EDTA has a magnetic susceptibility very similar to that of iron(III) sulfate indicating that the structure is ionic. Klemm (9) has reported a value of 5.91 Bohr magnetons for the magnetic moment of $\text{NH}_4\text{Fe(III)EDTA}\cdot\text{H}_2\text{O}$ which also indicates that the structure is ionic.

The molecular weight of HFe(III)EDTA determined from the titration with standard sodium hydroxide is 361. This suggests that the complex contains one molecule of water, since such a structure would have a molecular weight of 363. A structure containing one molecule of water has been proposed by Klemm (9).

Two acid equivalents per $\text{HFe(III)EDTA}\cdot\text{H}_2\text{O}$ were observed during the pH titration (Fig. 4). The second equivalent was very similar in acid strength to the two remaining acid equivalents of di-sodium EDTA (Fig. 6). If all the acetate groups of the EDTA were chelated, only one acid equivalent would be expected.

According to the infrared spectrum of $\text{HFe(III)EDTA}\cdot\text{H}_2\text{O}$ (Fig. 1) there was an unionized carboxyl group absorption at 5.7 microns. This indicates that all acetate groups were not bound to the Fe(III).

In the infrared spectrum of $\text{NH}_4\text{Fe(III)EDTA}\cdot\text{H}_2\text{O}$ (Fig. 2) no unionized carboxyl group absorption was observed at 5.7 microns. The solid crystalline compound apparently exists as the ammonium salt of the unchelated acetate group.

Effects of Radiation of HFe(III)EDTA

A steady increase in the absorption peak at 4.2 microns was observed when the single disk was irradiated. It is assumed that this absorption was due to carbon dioxide formed during irradiation. A plot of log absorbance versus time gave a straight line for the first 25 minutes indicating that the formation was of first order (Fig. 10). After 25 minutes radiation the ratio I_0/I approached a constant value. The disk apparently became saturated with carbon dioxide at this point and the excess carbon dioxide was lost to the atmosphere.

A plot of log concentration of ferrous ion formed by photodecomposition versus time also gave a straight line for the first 25 minutes. After 25 minutes radiation the rate of formation of ferrous ion decreased rapidly. For the first 25 minutes of radiation the slope of the plot of log absorbance of carbon dioxide versus time is nearly identical to the slope of the plot of log concentration of ferrous ion versus time indicating that there is a one to one relationship between the formation of carbon dioxide and the formation of ferrous ion and that the formation was of first order. The rate constant is $2.08 \times 10^{-3} \text{ sec.}^{-1}$. After 25 minutes irradiation there were approximately 4×10^{-4} moles of ferrous ion formed or approximately 9 ml. of carbon dioxide formed. This 9 ml. of carbon dioxide was confined to a volume of approximately 0.2 cc. This means that nearly 50 atmospheres of pressure was exerted by the carbon dioxide on the potassium bromide lattice. It is not unreasonable to assume that this pressure was sufficient to rupture the potassium bromide lattice causing much scattering of the ultraviolet rays resulting in the decrease in rate of formation of ferrous ion.

After regrinding and repressing, the concentration of carbon dioxide in the potassium bromide lattice was greatly reduced (Fig. 10).

Irradiation of the pure potassium bromide disk and the di-sodium EDTA in a potassium bromide disk gave no measureable formation of carbon dioxide indicating that the formation of carbon dioxide is dependent on the presence of an ion such as Fe(III), which in the Fe(III)EDTA⁻ ion acts as an electron sink.

An increase of absorption was observed in the 7.1 micron or 1460-1430 cm⁻¹ region. This is the characteristic absorption for the deformation mode of the CH₃ group attached to a nitrogen atom (2). It is assumed that this is the remainder of the acetate group after decarboxylation.

SUMMARY AND CONCLUSIONS

Pure HFe(III)EDTA was prepared by the reaction of ferric hydroxide and H₄EDTA. The ammonium salt, NH₄Fe(III)EDTA, was prepared by titrating the HFe(III)EDTA to the first equivalence point with ammonium hydroxide.

The structure of HFe(III)EDTA was determined by means of pH titrations and infrared analysis. The experimentally determined molecular weight of HFe(III)EDTA is 361 which suggests that the structure contains one molecule of water. Klemm reports one water molecule in NH₄Fe(III)EDTA·H₂O (9). Two acid equivalents were observed per HFe(III)EDTA·H₂O, the second being very similar in acid strength to the acid equivalents of di-sodium EDTA. The infrared spectrum of HFe(III)EDTA·H₂O indicates that all of the acetate groups of the EDTA are not bound to the iron.

The experimental data indicate that only three of the acetate groups of the EDTA are chelated, the fourth remaining unionized. The vacant coordination site on the iron is apparently occupied by a water molecule.

The infrared spectrum of $\text{NH}_4\text{Fe(III)EDTA}\cdot\text{H}_2\text{O}$ indicates that all of the acetate groups of the EDTA in this compound are ionized. It is assumed that this compound exists as the ammonium salt of the unchelated acetate group.

At the first equivalence point of the pH titrations the coordinated water molecule was apparently replaced by a hydroxyl ion. The second equivalence point was then due to the unionized acetate group. The $\text{NH}_4\text{Fe(III)EDTA}\cdot\text{H}_2\text{O}$ seems to have rearranged on drying from the hydroxy compound containing an unionized acetate group to the water coordinated compound containing the ammonium salt of the acetate group.

Carbon dioxide was formed as a decomposition product when $\text{HFe(III)EDTA}\cdot\text{H}_2\text{O}$ was irradiated with ultraviolet light. The Fe(III) was reduced to Fe(II) during the radiation. The formation of carbon dioxide and ferrous ion occurred by first-order kinetics with a one to one relationship for the first 25 minutes of radiation. The rate constant was $2.08 \times 10^{-3} \text{ sec.}^{-1}$. After 25 minutes of radiation the rate of formation of ferrous ion was greatly reduced and the concentration of carbon dioxide in the potassium bromide disk approached a constant value. It is assumed that the nearly 50 atmospheres of pressure exerted by carbon dioxide on the potassium bromide lattice ruptured the lattice causing much scattering of the ultraviolet radiation which resulted in the decreased rate of formation of the ferrous ion.

The infrared spectrum of $\text{HFe(III)EDTA}\cdot\text{H}_2\text{O}$ after 60 minutes of radiation showed a strong increase of absorption in the 7.1 micron region. It is assumed that this absorption was due to the CH_3 deformation mode of the NCH_3 group which remained after decarboxylation.

The initial step in the photoreduction is assumed to be the transfer of an electron from a chelated acetate group to the ferric ion forming a carboxylate radical. The radical then decomposes to give carbon dioxide and a $\text{CH}_2\cdot$ radical. A similar sequence has been proposed for the photodecomposition of other organic acids (16). The $\text{CH}_2\cdot$ radical can then react with a water molecule to form the CH_3 group and a $\text{HO}\cdot$ radical. Two $\text{HO}\cdot$ radicals may combine to form HOCH which is decomposed by ultraviolet radiation to H_2O and O_2 . The proposed mechanism is shown in Fig. 11.

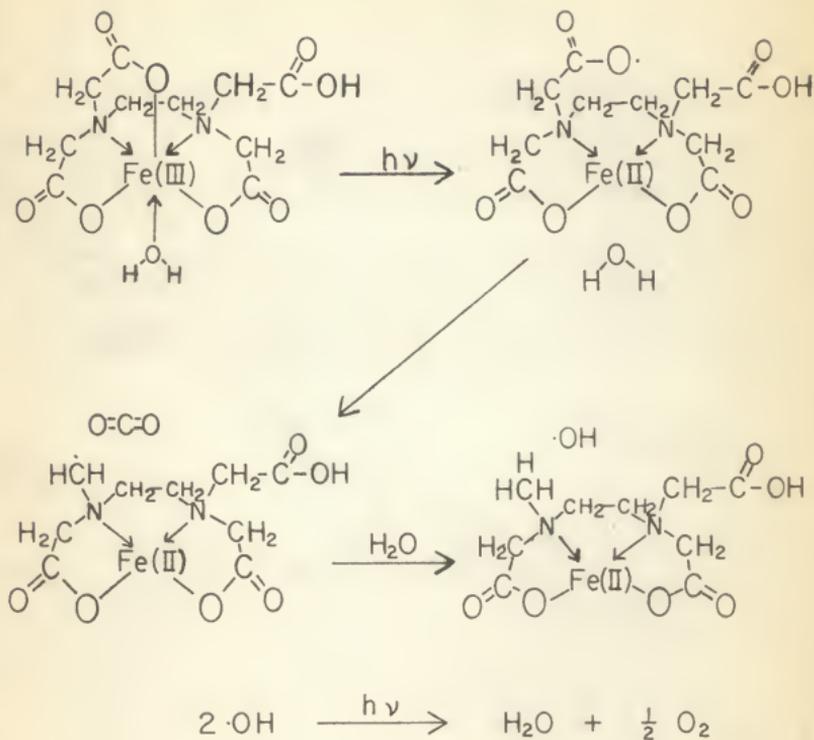


Figure 11. Proposed mechanism for photodecomposition of HFe(III)EDTA .

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AN ABSTRACT OF A THESIS

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1959

Relatively few publications concerning the photosensitivity of the ethylenediaminetetraacetatoferrate(III) ion, Fe(III)EDTA^- , appear in the literature. As yet no satisfactory mechanism for the photodecomposition of this ion has been proposed. However, the photosensitivity of the trioxalatoferrate(III) ion has received much attention. The mechanism for the photoreduction of this ion has been thoroughly investigated. Carbon dioxide is one of the photodecomposition products. Since both the trioxalatoferrate(III) ion and the Fe(III)EDTA^- ion have chelated carboxyl groups, carbon dioxide could also be a photodecomposition product of the Fe(III)EDTA^- ion. Carbon dioxide trapped in the lattice of a potassium bromide disk during the thermal decomposition of nitrocellulose has been observed by other workers.

In the present work $\text{KFe(III)EDTA}\cdot\text{H}_2\text{O}$ has been prepared and its structure has been determined by pH titrations and infrared analysis. The changes induced in this compound by ultraviolet irradiation in potassium bromide disks has been studied by observing the changes in the infrared spectrum. During the irradiation carbon dioxide was formed as a decomposition product and the Fe(III) was reduced to Fe(II) . The rate of formation of carbon dioxide was identical to the rate of formation of Fe(II) indicating a one to one relationship. The formation occurred by first-order kinetics for the first 25 minutes. After 25 minutes of radiation the pressure exerted by the trapped carbon dioxide apparently ruptured the lattice causing much scattering of the ultraviolet radiation which resulted in a decrease in rate of formation of ferrous ion and saturation of the potassium bromide disk with carbon dioxide.

A mechanism for the photoreduction has been proposed consistent with the observed data and with information obtained by other workers concerning the

photodecomposition of other organic acids. According to this proposed mechanism an electron is transferred from a chelated acetate group to the Fe(III) and a carboxylate radical is formed. The carboxylate radical then decomposes to give carbon dioxide and a terminal $\text{CH}_2\cdot$ radical which may further react with water to give a CH_3 group and an $\text{HO}\cdot$ radical. $\text{HO}\cdot$ radicals may further react to give water and oxygen.

