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# A kinetic investigation of the reaction of ethylenedinitrilotetraacetic acid (EDTA) and cerium (IV) in acid solution

Sahmia K. Al-Hashimi

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# A KINETIC INVESTIGATION OF THE REACTION OF ETHYLENEDINITRILOTETRAACETIC ACID (EDTA) AND CERIUM (IV) IN ACID SOLUTION

BY

SAHMIA K. AL-HASHIMI, 1939

A

THESIS

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Approved by

Sami S. Hanna (advisor) Wm H. Webb

M. E. Finley

# ABSTRACT

The reaction between Ce(IV) salt solutions and EDTA solution was followed titrimetrically and spectrophotometrically and found to occur in stages. Four equivalents of Ce(IV) are reduced per mole of EDTA almost instantaneously at room temperature or even lower. With increasing temperature and reaction time an ultimate of about 14 equivalents of Ce(IV) is consumed per mole of EDTA. Formaldehyde, carbon dioxide, and other unidentified compounds are the products of oxidation of EDTA with Ce(IV). The kinetics of the reaction in aqueous sulfuric acid (0.09 - 2.95 M) was studied over the temperature range 11.7-40° by a spectrophotometric technique. In the region of concentrations workable in UV spectrophotometry ($10^{-5}$ -- $10^{-4}$ M Ce(IV)), and where one mole of EDTA reduces four moles of Ce(IV), the reaction is first order in each reactant and shows variable dependence on the concentration of hydrogen ions. The reaction rate is a maximum at about 1 M $[H^+]$ and decreases on either side. Only below unit molar concentration of $H^+$ a Ce(IV)-EDTA complex is observed to form and decay. The observed rates can be described by the rate expression

$$-\frac{d[Ce(IV)]}{dt} = k[H^+]^n [Ce(IV)][EDTA]$$

where n varies from about +2.5 to -2.5. The experimental energy of activation over a 30° range in 6 M $[H^+]$ is 17.6 ± 0.2 k cal/mole.

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# Chapter I

# INTRODUCTION

The study of Ce(IV) oxidations of organic compounds has become increasingly important in the past few years. However, there are only a few reports in the literature on the oxidation of amino or polyaminocarboxylic acids by Ce(IV) or by other oxidizing agents. We have, therefore, initiated an extensive program to study the kinetics and mechanisms of oxidation of polyaminocarboxylic acids commonly used as chelating agents. This work is primarily devoted to an investigation of the Ce(IV)-EDTA (ethylenedinitrilotetraacetic acid) system. Preliminary observations with permanganate and with other chelating agents are also reported.

EDTA is known to form complexes with trivalent lanthanides, and such complexes have been the subject of detailed investigations[1-3]. On the other hand, very little is known about complexes with Ce(IV). It was observed in this laboratory, four years ago[4], that Ce(IV)

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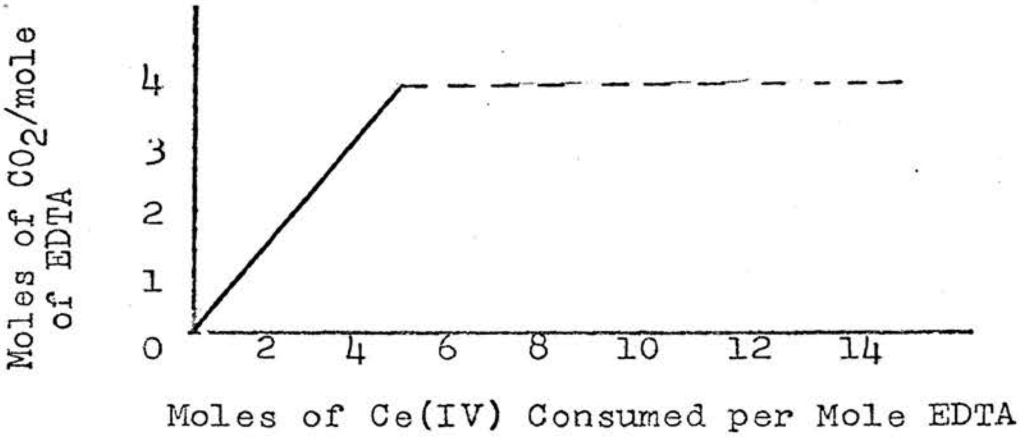
[1] R.C. Vickery, J. Chem. Soc., 1895 (1952).

[2] E.G. Wheelwright, F.H. Speeding and G. Schwarzenbach, J. Am. Chem. Soc., 75, 4196 (1953).

[3] G. Schwarzenbach, R. Gut, and G. Anderegg, Helv. Chim. Acta, 37, 937 (1954).

[4] R.D. Mitchell, M.S. Thesis in Chemistry, U.M.R. (1964).

was reduced rather than complexed by EDTA which observation prompted the present investigation. In 1965, the literature contains a report on a Ce(IV)-EDTA complex[5], which was found to be unstable, and to decompose within a few minutes after its formation to give Ce(III) and unidentified oxidation products. Earlier, Palei and Udaltsova[6], reported on the reductive ability of EDTA which was found to react with Mn(VII) in 1-2 N $H_2SO_4$ solutions in the ratio of 1 mole of EDTA:8 equivalents of potassium permanganate. With Ce(IV), such a ratio was observed only on heating[6]. The fate of EDTA in such oxidations was not revealed and the workers simply reported that the molecule of EDTA is destroyed in acid medium, liberating four molecules of carbon dioxide. The relationship between the Ce(IV) consumed, the EDTA destroyed, and the $CO_2$ liberated in the oxidation-reduction reaction is shown in the diagram.



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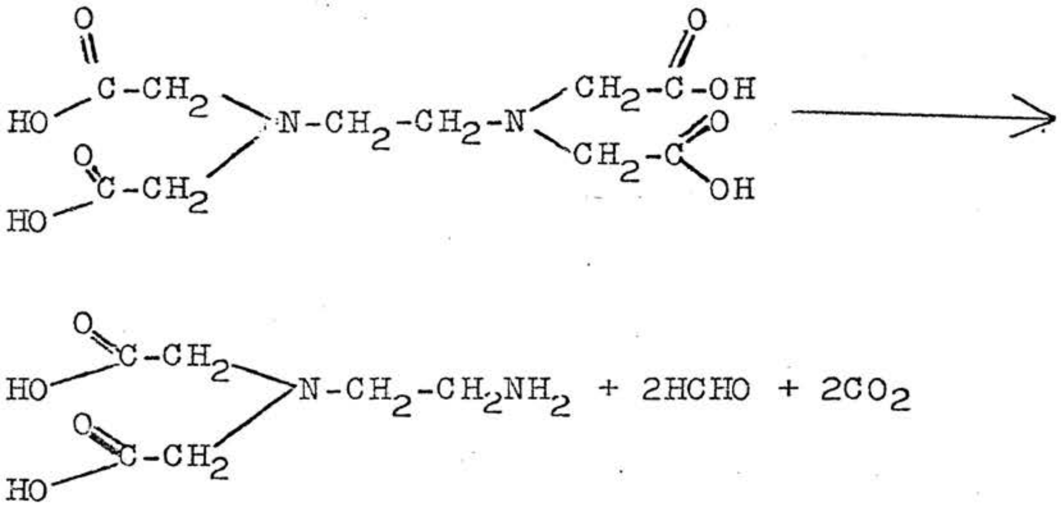
[5] T.R. Bhat and R. Radhamma, Ind. J. Chem., 3, 151 (1965)

[6] P.N. Palei and N.I. Udaltsova, Zhur. Anal. Khim. (J. Anal. Chem. USSR), 15, 668 (1960)

Recently[7], a study of the stoichiometry of the reaction between EDTA and Ce(IV), in acid medium, revealed that 4 equivalents of Ce(IV) are consumed per mole of the chelating agent, liberating about 2.5 moles of $CO_2$. The formation of N,N'-dimethylethylenediamine, $CH_3\text{-}\overset{H}{N}\text{-}CH_2\text{-}CH_2\text{-}\overset{H}{N}\text{-}CH_3$ was reported as a reaction product, but the yield was not specified[7]. On the other hand, the anodic oxidation of EDTA at a potential difference of 4-6 V between shiny platinum electrodes at a current strength of 80 milliamps was reported to give the following products after 30-60 minutes[8]:



Oxidation of EDTA with hydrogen peroxide at pH 3-12 has also been reported[9]. Initial products are iminodiacetic acid and glyoxal; formaldehyde, carbon dioxide, glycine, glyoxalic acid, formic acid and ammonia were also reported as degradation products from EDTA.

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[7] H. Holzapfel and K. Dittrich, Talanta, 13, 309 (1966)
[8] L. Kopecka, Chem. Listy, 50, 1084 (1956)
[9] J. Alary and A. Coeur, Bull. Soc. Chim. France, 2453 (1965)

In alkaline medium, the rates of oxidation of a number of chelating agents by alkaline ferricyanide, $[Fe(CN)_6]^{3-}$, were reported recently[10]. The ratio of moles of ferricyanide consumed per mole of EDTA, calculated from absorbance at 420 mμ was 4.0 after six half-lives (EDTA in excess, comsumption of $Fe(CN)_6{}^{3-}$ followed spectrophotometrically), and increased slowly thereafter. The observed rate law was $-d[Fe(CN)_6]^{3-}/dt = k_2[Y^{4-}][Fe(CN)_6]^{3-}$ where $Y^{4-}$ denotes the species resulting from EDTA in an alkaline medium. The organic products were reported, by inference from earlier work[9], to be iminodiacetic acid and glycollic acid.

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[10] D.G. Lambert and M.M. Jones, J. Am. Chem. Soc., 88, 4615 (1966).

# Chapter II

# EXPERIMENTAL SECTION

## A. Materials

Ceric ammonium hexanitrate $(NH_4)_2Ce(NO_3)_6$, ceric ammonium tetrasulfate $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$, the disodium salt of ethylenedinitrilotetraacetic acid dihydrate (EDTA) and the inorganic acids and salts used were reagent grade and were used without further purification. Solutions of the Ce(IV) salts were prepared by direct weighing, and for the very dilute solutions, by dilution of standardized solutions; the primary standard used was reagent-grade ferrous ammonium sulfate (Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$) and the indicator was o-phenanthroline prepared according to standard procedures.

## B. Stoichiometry

Known volumes of standardized solutions of Ce(IV) were allowed to react with EDTA solutions under a variety of conditions. The concentrations of reactants and acids were varied, and the effects of such variations were studied. The temperature was varied from 10° C to about 100° C (boiling solution) and the reactions were observed for periods of time ranging from a few seconds to a few days. The number of moles of Ce(IV) consumed per mole of EDTA was determined by titration with standard Fe(II) solution using o-phenanthroline as indicator. In some experiments, the reaction between EDTA and Ce(IV) was quenched by the addition of a known excess of Fe(II) solution and back titrated with Ce(IV) solution. Where the concentrations allowed, the stoichiometry was evaluated from absorbance measurements. In a few cases, the stoichiometry was determined for the reaction between ~1 M ceric ammonium hexanitrate solution in water and solid EDTA at room temperature. This reaction is quite vigorous; actually, it resembles the reaction of carbonates with acids in that $CO_2$ effervesces abundantly. The amount of $CO_2$ evolved during such reactions was measured volumetrically using the apparatus shown in Figure I-A. At temperatures higher than ambient, the apparatus shown in Figure I-B was preferably used.

## C. Kinetics

The rates of reaction were followed spectrophotometrically at 316 mμ where Ce(IV), but not EDTA, the medium, or the products, absorbs very strongly (Fig. 2). The absorbances were recorded automatically by a time-drive attachment on a Beckmann DK-2A spectrophotometer. The cells were placed in a thermostated cell-holder, and the temperature was regulated by a circulating Lauda Ultrathermostat, and was maintained at the desired temperature at better than ± 0.05° C. The reference cell contained EDTA in $H_2SO_4$ of the same molarity as

Figure 1A. Diagram of Apparatus for Measuring the Extent of Decarboxylation of Solid EDTA with $\sim$ 1 $\underline{M}$ Ceric Ammonium Hexanitrate at Room Temperature.

A - part of reaction flask containing Ce(IV) solid solution
B - part of reaction flask containing EDTA
C - condenser
D - leveling burette
E - gas burette
F - manometer
G - stopcock
H - three-way stopcock

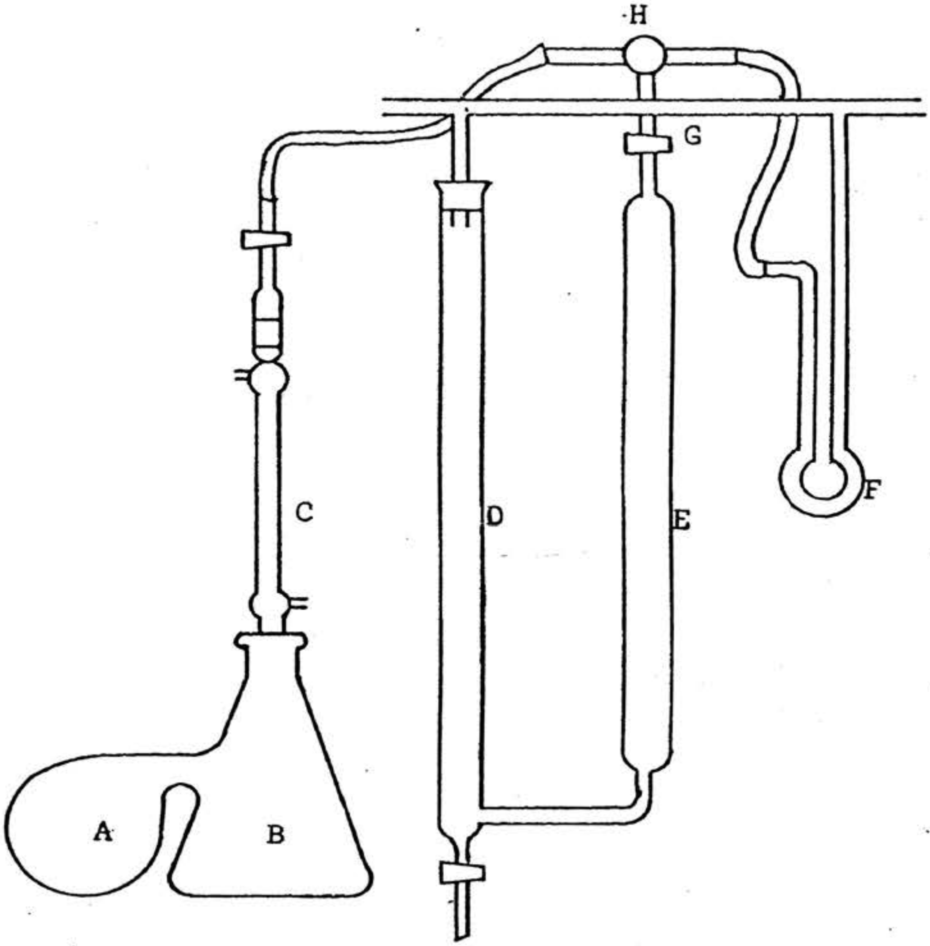


Figure 1A

Figure 1B. Diagram of Apparatus for Measuring the Extent of Decarboxylation of EDTA and of Other Polyaminocarboxylic Acids with $\sim$0.1 M Ceric Ammonium Hexanitrate at Different Temperatures.

A - constant temperature bath
B - reaction flask
C - magnetic stirrer
D - condenser
E - gas burette
F - manometer
G - leveling burette
H - stopcock
I - three-way stopcock
J - cup containing EDTA solution

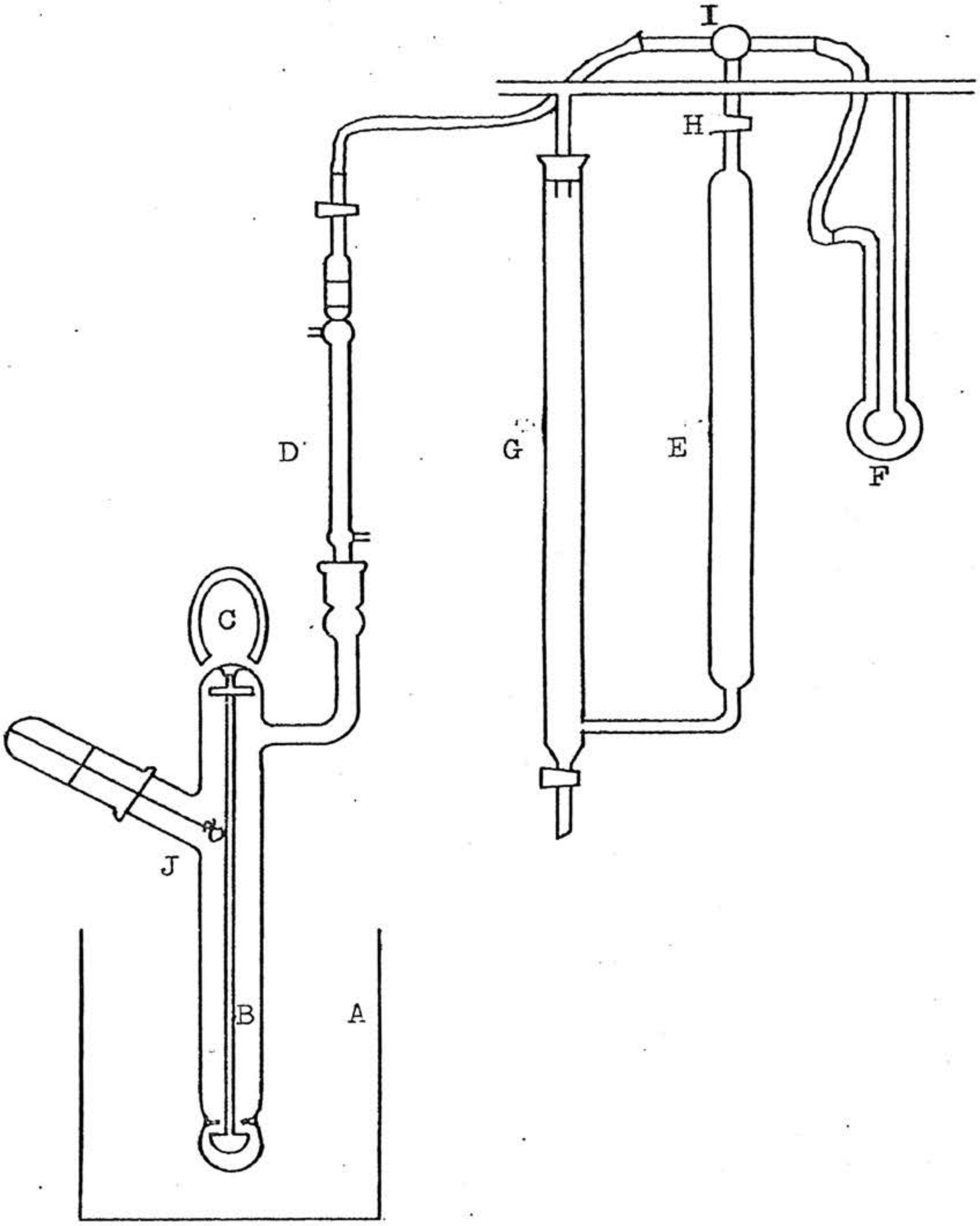


Figure 1B

Figure 2. Spectrum of Ce(IV) in Acid Solution at 25°C. Lower Curve Represents Absorbance Scale from 1-2.

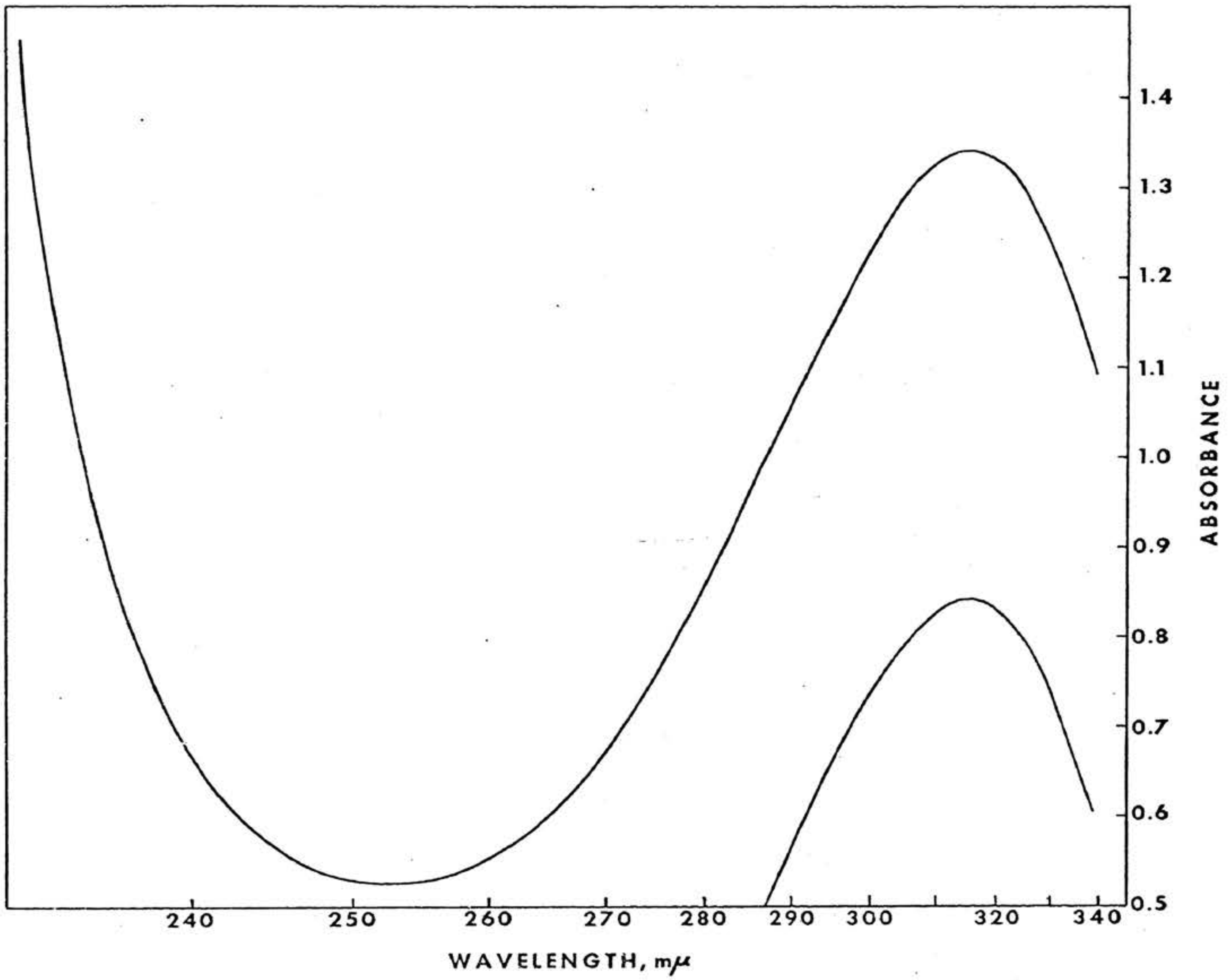

1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
ABSORBANCE
240
250
260
270
280
290
300
320
340
WAVELENGTH, mμ

Figure 2

the reaction mixture. The reaction cell contained 3 ml of Ce(IV) solution of a predetermined molarity in $H_2SO_4$ or $H_2SO_4$-salt mixture of known concentrations. To start a run, the time-drive attachment was switched on at the appropriate speed (usually 1 inch per minute), and 50 µl of an aqueous EDTA solution of a known concentration were injected in the Ce(IV) solution which was already thermostated in the cell compartment. The plunger of the delivering microliter syringe was worked up and down a few times to ensure quick and thorough mixing. Separate trials with a solution of a colored indicator showed that mixing was efficient within one to two seconds from injection time. In cases of moderately fast reactions, the recording pen was pulled across the chart by a constant speed constant tork motor. Uniform speeds of about one inch per second were easily achieved by this improvised device.

The absorbance of the reaction mixture at 316 mµ was automatically recorded with time, and within a few minutes reached zero (Fig. 3). The percentage reaction was easily calculated from the graph, and when the values were plotted <u>versus</u> time on one-cycle semi-log graph paper, Figure 4, straight lines were obtained over two to three half-lives for Ce(IV). The half-lives were read at the 50% line and the first-order rate constants were computed from the equation:

Figure 3. The Change of Absorbance of a Ce(IV)-EDTA Solution with Time at 20.7°C at 316 mμ.

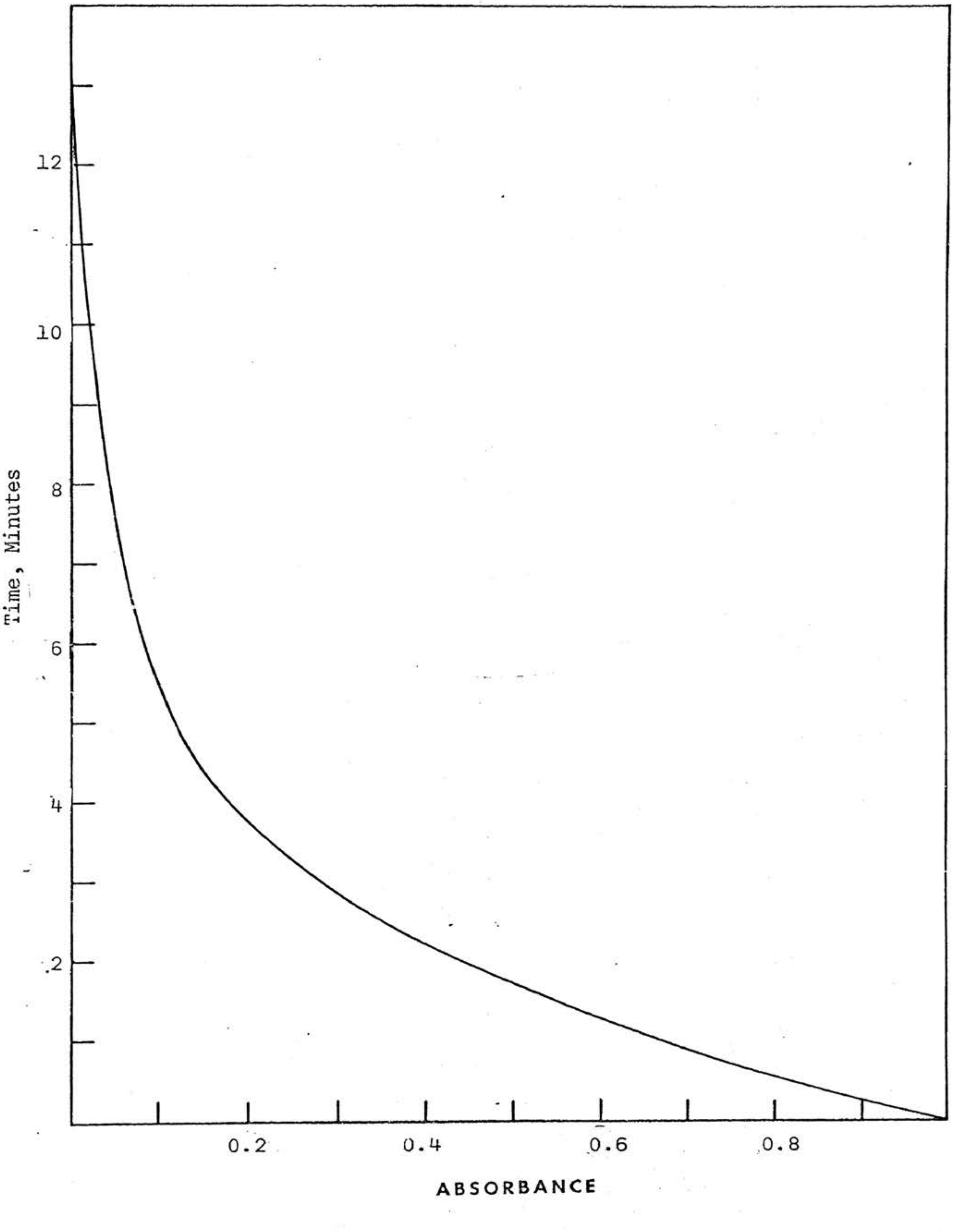


Figure 3

Figure 4. Semi-log Plot of Percentage Reaction (Consumption of Ce(IV)) *versus* Time.

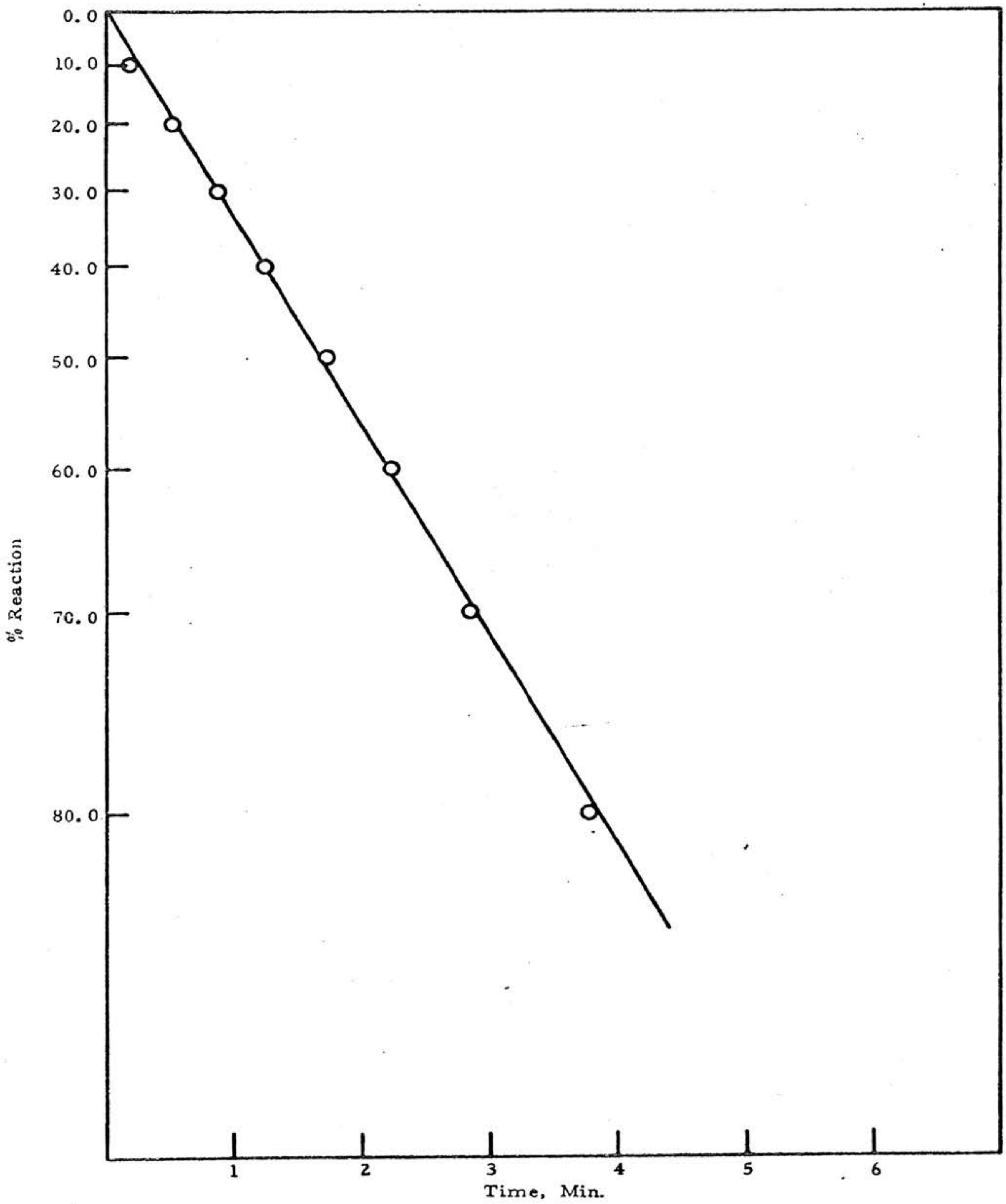


Figure 4

$$k_1 = 0.693/t_{0.5}$$

The EDTA was always in such an excess that its concentration did not vary by more than 1-2% at most when the Ce(IV) was already half-consumed, and the second-order rate constants, $k_2$, were obtained by dividing $k_1$ by the concentration of EDTA in any particular run. Rate constants were reproducible to better than ± 6%.

# Chapter III

# RESULTS AND DISCUSSION

## A. Stoichiometry

The reaction between Ce(IV) salt solutions and EDTA proceeds in stages. The extent of reaction was determined at moderate concentration ranges ($\sim$0.1 M) by direct titration of EDTA with Ce(IV) or by adding excess Ce(IV) and back titrating with Fe(II) using o -phenanthroline as indicator. In either case, it was observed that 4-5 equivalents of Ce(IV) per mole of EDTA were consumed almost instantaneously at room temperature. An additional 4 equivalents were consumed by warming to about 60° C for a few minutes. After the reactants were boiled for 30 minutes, a total of about 14 equivalents of Ce(IV) per mole of EDTA were consumed. Table IA shows the variation in the equivalence between the two reactants as a function of the acidity of the medium, while Tables IB and IC show the effects of temperature and time respectively on the stoichiometry of the reaction under investigation.

The reaction between Ce(IV) and EDTA leads to decarboxylation (at least partial) as evidenced by the evolution of $CO_2$ gas in measurable quantities. The reaction between an aqueous solution of 1 M ceric ammonium hexanitrate and solid EDTA is as vigorous as the reaction of acids with carbonates or bicarbonates. It was noted consistently, in this work, that although about 4 equivalents of Ce(IV)

## TABLE I-A

## (STOICHIOMETRY OF EDTA-Ce(IV) REACTION - EFFECT OF $[H^+]$)

The Reaction Between 25 ml Ceric Ammonium Hexanitrate (0.0993 M) and 1 ml EDTA (0.1 M) in Solutions of Different Acid Concentrations

Temperature: 25° C

| $[H^+]$ | Number of Equivalents of Ce(IV) Consumed per Mole of EDTA |
|---|---|
| 1 | 5.15 |
| 2 | 4.75 |
| 3 | 4.50 |
| 4 | 4.45 |
| 5 | 4.20 |
| 6 | 4.20, 4.1, 4.25,<br>4.19, 4.23, 4.27 |

## TABLE I-B

## (STOICHIOMETRY OF EDTA-Ce(IV) REACTION - EFFECT OF TEMPERATURE)

The Influence of Temperature on the Reaction Between Excess Ceric Ammonium Hexanitrate (0.0993 M) and EDTA (1 ml, 0.1 M) in 6 N $H_2SO_4$

| Temperature, °C | Number of Equivalents of Ce(IV) Consumed per Mole of EDTA* |
|---|---|
| 25 | 4.4 |
| 60 | 9.3 |
| 100 | 13.9 |

* Equivalents calculated from back-titration with Fe(II) after about 0.5 hr reaction at the specified temperature.

## TABLE I-C

## (STOICHIOMETRY OF EDTA-Ce(IV) REACTION - EFFECT OF TIME)

Progress of the Reaction Between Ceric Ammonium Hexanitrate (25 ml, 0.098 M) and EDTA (L ml, 0.1 M) in 1 N $H_2SO_4$. Equivalents Calculated from Back-Titration with Fe(II) at Specified Times

Temperature: 25° C

| Time, Minutes | Number of Equivalents of Ce(IV) Consumed per Mole of EDTA |
|---|---|
| 0.25 | (4.10, 4.25, 4.19)* |
| 1 | 5.00 |
| 5 | 5.10 |
| 15 | 5.30 |
| 30 | 5.60 |
| 60 | 6.10 |
| 120 | 6.10 |
| 240 | 7.10 |
| 3 days | 12.10 |
| 30 minutes at boiling temperature | 13.10 |

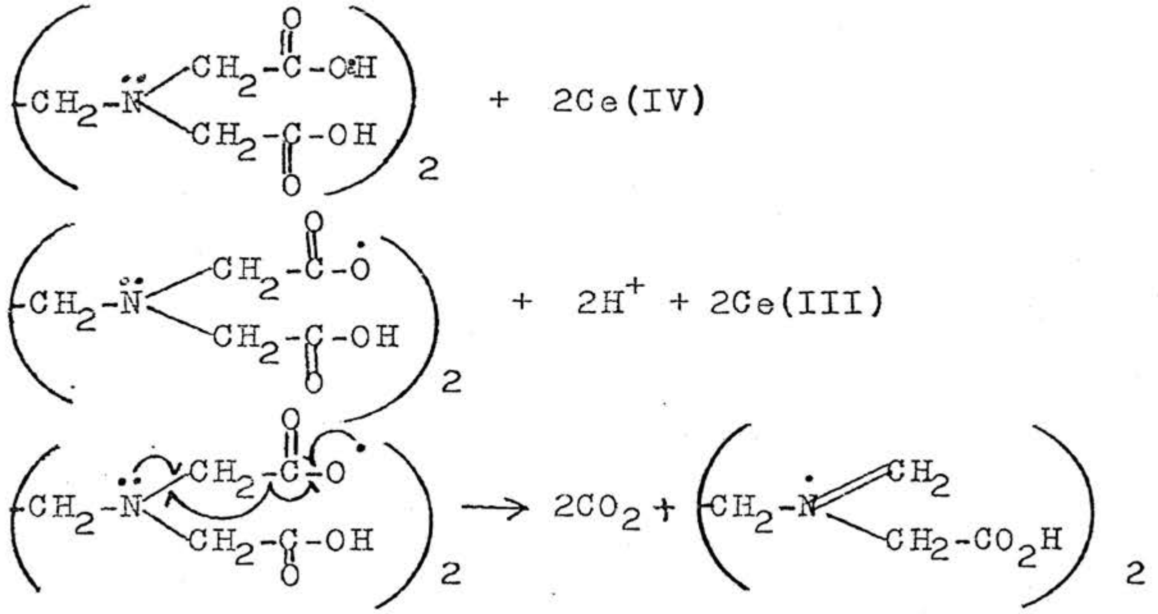
* These determinations were carried out by fast mixing of reactants by injection, immediate quenching with Fe(II) solution, and back-titration with Ce(IV).

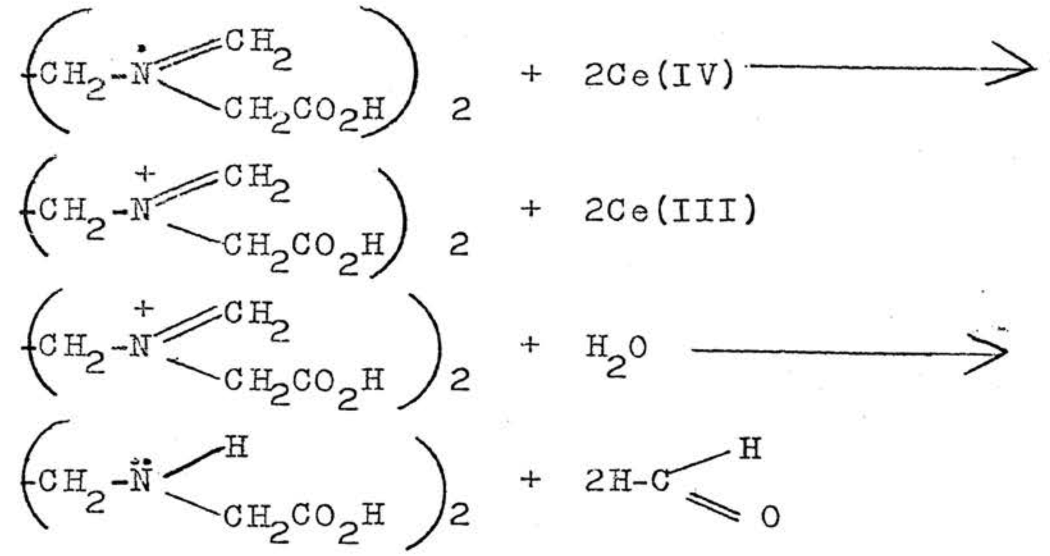
are consumed per mole EDTA almost instantaneously at room temperature, only slightly over 2 equivalents of $CO_2$ are produced simultaneously (Table II-A). In other words, the stoichiometry of the almost instantaneous reaction of Ce(IV) with EDTA can be summarized as follows:

EDTA : Ce(IV) : $CO_2$
1 4 2

Even under the conditions where more than 4 equivalents of Ce(IV) are reduced per mole of EDTA, the number of equivalents of $CO_2$ gas evolved per mole of Ce(IV) consumed seldom exceeds 0.56 (Table II-B).

This could probably be accounted for by the following scheme of reactions which shows that the oxidizing power of Ce(IV) touches on centers other than the carboxylic groups in the EDTA molecule.





The overall reaction can be rewritten:

EDTA + 4Ce(IV) $\longrightarrow$ 2$CO_2$ + Organic Oxidation Products

At slightly elevated temperatures (60° C), and after one hour reaction time between EDTA and excess Ce(IV) the number of equivalents of $CO_2$ produced per mole of EDTA reached a maximum of 3.4-3.5 as shown in Table II-A.

For comparison, the results obtained under similar conditions for a variety of chelating agents are shown in Table III.

It is interesting to note that the addition of 4 equivalents of Ce(IV) (as ceric ammonium hexanitrate in $D_2O$) to EDTA had resulted in complete disappearance of the sharp and simple NMR peaks characteristic of EDTA (Fig. 5).

## B. Kinetics

Guided by the variation in the stoichiometry of the EDTA-Ce(IV) reaction with time and with temperature (cf.

## TABLE II-A

## (EFFECT OF $[H^+]$ ON THE DECARBOXYLATION OF EDTA BY Ce(IV))

The Reaction Between Ceric Ammonium Hexanitrate (25 ml, 0.0988 M) and EDTA (1 ml, 0.1 M) in Acid Solution at 60° C .

| $[H^+]$ | Number of Equivalents of $CO_2$/mole of EDTA |
|---|---|
| 1 N | 2.29 |
| 2 N | 2.67 |
| 3 N | 3.13 |
| 5 N | 3.29 |
| 6 N | 3.40 |

## TABLE II-B

## (STOICHIOMETRY OF THE DECARBOXYLATION OF EDTA BY Ce(IV))

The Reaction Between Solid EDTA and Ceric Ammonium Hexanitrate (~1 M) Solution at Room Temperature

| EDTA millimole | Ce(IV) millimole | $CO_2$ millimole | $CO_2$/EDTA | $CO_2$/Ce(IV) |
|---|---|---|---|---|
| 0.537 | 1.01 | 0.566 | 1.05 | 0.56 |
| 0.537 | 2.02 | 1.129 | 2.10 | 0.56 |
| 0.537 | 3.03 | 1.750 | 3.26 | 0.57 |
| 0.537 | 2.02 | 1.129 | 2.10 | 0.56 |
| 0.806 | 2.02 | 1.450 | 1.45 | 0.58 |
| 1.074 | 2.02 | 1.088 | 1.08 | 0.57 |
| 1.343 | 2.02 | 0.864 | 0.86 | 0.57 |

## TABLE III

### (STOICHIOMETRY OF Ce(IV)-CHELATING AGENTS REACTIONS)

The Reaction Between Different Chelating Agents (1 ml, 0.1 M) and Excess Ceric Ammonium Nitrate (25 ml, 0.1 M in Acid Solution (6 N $H_2SO_4$) at 60° C; Titrimetrically.

| Chelating Agent* | Equivalents Ce(IV) Consumed/Mole Chelating Agent | Equivalents $CO_2$ Produced/Mole Chelating Agent |
|---|---|---|
| DM | 6.3 | 2.1 |
| DTPA | 11.1 | 4.4 |
| EDTA | 9.3 | 3.5 |
| ME | 9.2 | 3.1 |
| NTA | 7.3 | 2.1 |

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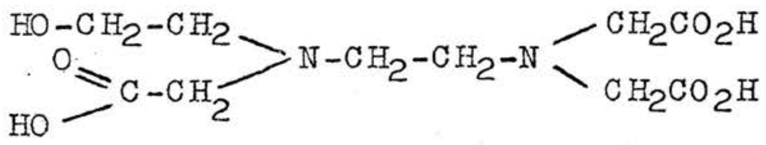
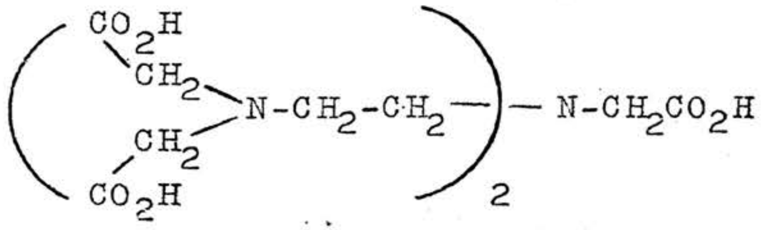
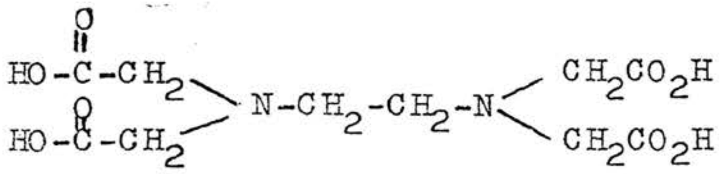
* DM acid: hydroxyethylethylenediamine triacetic acid



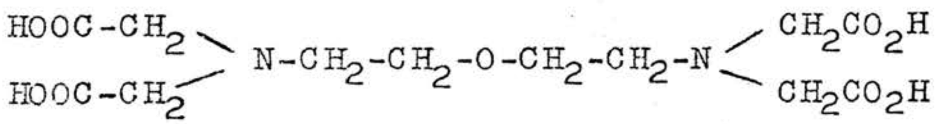
DTPA: ethylene triamine pentaacetic acid



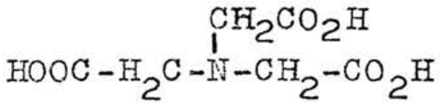
EDTA: ethylenedinitrilotetraacetic acid



ME: diaminoethylether tetraacetic acid



NTA: nitrilotriacetic acid



$$HOOC-H_2C-\overset{CH_2CO_2H}{\overset{|}{N}}-CH_2-CO_2H$$

Figure 5. NMR Spectra of

(1) 1 M Ceric Ammonium Hexanitrate in $D_2O$

(2) 1.5 M EDTA (disodium salt) in $D_2O$

(3) Reaction product from reacting 1 ml of ~1 M Ceric ammonium hexanitrate in $D_2O$ with 0.5 g EDTA (disodium salt)

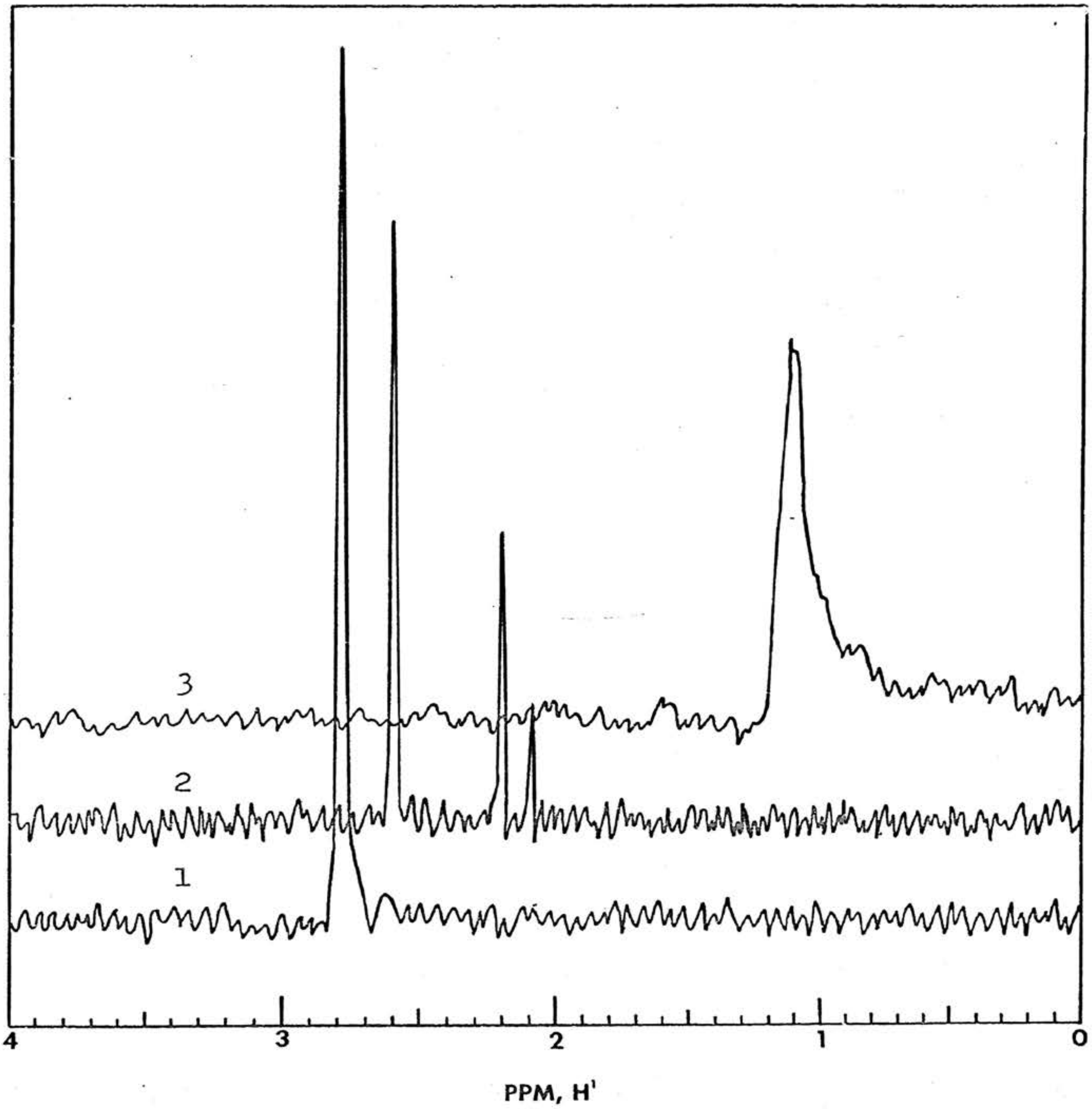


Figure 5

Tables I-B and I-C), it was decided to look into the kinetics of this system. Except for the initial stages of the reaction, the rate of disappearance of Ce(IV) is quite slow as shown in Table I-C. Accordingly, and since a product study of the reaction involving 1 mole of EDTA with 4 equivalents of Ce(IV) has already been reported, it was necessary to investigate the kinetics of the first moderately fast stage of reaction. At 0.1 M concentrations for reactants, the reaction was too fast to measure by any of the available equipment. Fortunately, however, Ce(IV) is known to absorb rather strongly at 316 mμ such that a $10^{-4}$M solution in a 1-cm path cell shows an absorbance of about one. It was even more fortunate to realize that a reaction between ~$10^{-4}$M Ce(IV) and ~$10^{-3}$M EDTA proceeds at such a rate that it could be conveniently studied, at room temperature, by following the decrease in absorbance at 316 mμ, automatically recorded, with time. In this way, sampling was avoided, and half-lives as small as 4-5 seconds could be recorded. But, first, it was necessary to insure that in the low region of concentrations, the stoichiometry of studied reaction was still 1EDTA:4 Ce(IV). When 5 equivalents of Ce(IV) were mixed with one mmol EDTA in the concentration range allowable in the UV, the absorbance of the reaction mixture, a few minutes later, pointed to the consumption of only 4 equivalents of Ce(IV).

In this kinetic study the initial concentrations of both reactants were varied, but to simplify the calculations of rate constants the EDTA was always in such great excess that its concentration would have changed by 1-2% at most after one-half of the Ce(IV) was consumed (See Appendix I). Table IV shows a summary of the results which point to a second-order reaction overall, first order in each component. Thus,

$$-d\left[Ce(IV)\right]/dt = k_2\left[Ce(IV)\right]\left[EDTA\right]$$

Since the EDTA is in great excess, the above expression reduces to

$$-d\left[Ce(IV)\right]/dt = k_1\left[Ce(IV)\right]$$

where $k_1 = k_2\left[EDTA\right]$

Integrating, we have

$$-\ln\left[Ce(IV)\right] = k_1 t + \text{const.}$$

or

$$-\ln\left[Ce(IV)\right]_o/\left[Ce(IV)\right]_t = k_1 t$$

which is a first-order equation. Accordingly, one expects a straight line relationship between time and the concentration of Ce(IV) plotted on a semi-log graph paper. Figure 4 depicts the results of run number 1 . The half-life, $t_{0.5}$, read at the 50% reaction line is converted into $k_1$ through the use of the relationship

$$k_1 = 0.693/t_{0.5}$$

The second-order rate constant, $k_2$, is in turn calculated from $k_1$.

## TABLE IV

## (EFFECT OF CHANGING THE INITIAL CONCENTRATIONS ON THE EDTA-Ce(IV) REACTION)

Half-lives and Reaction Rate Constants for the Reaction Between Ce(IV) and EDTA in 6 N $H_2SO_4$; Spectrophotometrically at 316 mu

| $[Ce(IV)]_o$ $10^4M$ | $[EDTA]_o$ $10^3$ M | $t_{0.5}$ sec | $k_2$, $M^{-1}sec^{-1}$ |
|---|---|---|---|
| 1.64 | 1.64 | 53 | 79.6 |
| 1.06 | 1.64 | 55 | 76.8 |
| 0.53 | 1.64 | 54 | 78.34 |
| 1.64 | 0.82 | 96 | 87.9 |
| 1.64 | 1.64 | 50 | 84.45 |
| 1.64 | 3.28 | 37 | 82.31 |
| | | Average....... | 81.6 ± 5.4 |

## C. Influence of Variation of Acid Concentration

Earlier work on the oxidation of oxalic acid with Ce(IV) prompted a study of the effect of changing the concentration of the acid ($H_2SO_4$) in the reaction medium. Since most of the preliminary work, performed titrimetrically, was best accomplished in 6 N $H_2SO_4$ acid solution the same medium was used as a starting point. On lowering the acid concentration to the vicinity of 1 N $H_2SO_4$, the reaction rates became progressively faster. This was puzzling since a recent report in the literature[5], claimed that the rate of the reaction was directly proportional to the concentration of hydrogen ions in solution. However, a closer look revealed that the work already reported was performed at concentrations below 1 N acid. The work for this investigation was repeated and extended from ~6 N down to 0.2 N $H_2SO_4$. The results are summarized in Table V and shown in Figure 6. From the figure, it is obvious that an inflexion point occurs at just about 1 N acid, with the rate decreasing as we increase the acid concentration to ~6 N or as we decrease it to 0.2 N.

The rate equation which summarizes and accomodates the above information can, therefore, be written as

$$-d\left[Ce(IV)\right]/dt = k_2\left[H^+\right]^n\left[Ce(IV)\right]\left[EDTA\right]$$

where n varies from about +2.5 to -2.5.

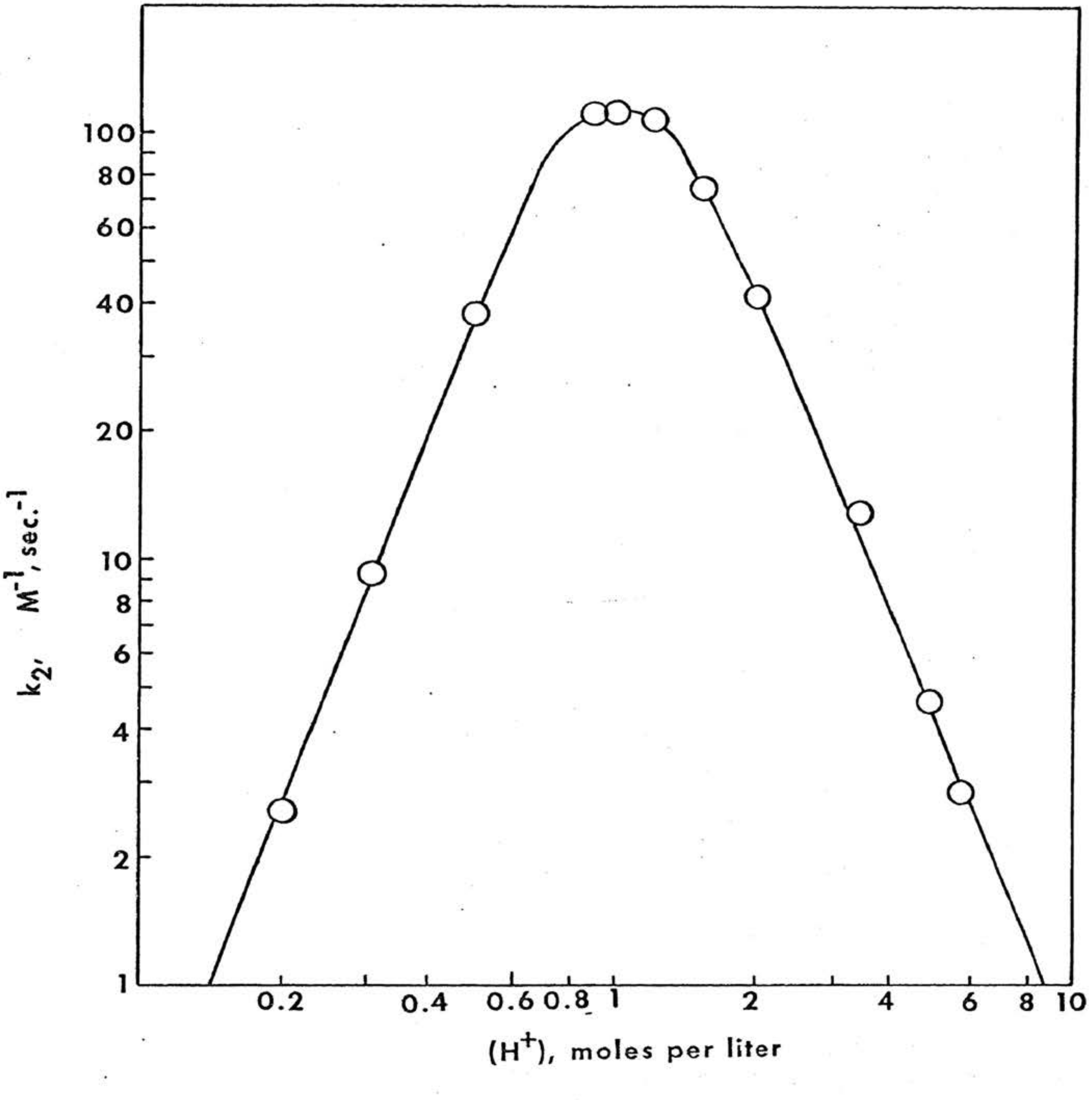
## TABLE V

## (EFFECT OF $\left[H^+\right]$ ON THE RATE OF EDTA-Ce(IV) REACTION)

The Reaction Between Ceric Ammonium Sulfate ($1.64 \times 10^{-4}$ M) and EDTA ($1.64 \times 10^{-3}$ M) at Different Acid Concentrations at 20.7°C, Spectrophotometrically at 316 mµ

| $\left[H^+\right]$ | $t_{0.5}$, sec | $10^3 k_1$, sec$^{-1}$ | $k_2$, M$^{-1}$sec$^{-1}$ |
|---|---|---|---|
| 0.2 | 165.0 | 4.2 | 2.56 |
| 0.3 | 46.5 | 14.9 | 9.085 |
| 0.5 | 11.2 | 61.76 | 37.65 |
| 0.9 | 3.75 | 184.8 | 112.68 |
| 1.0 | 3.72 | 186.29 | 113.59 |
| 1.2 | 3.9 | 177.69 | 108.3 |
| 1.5 | 5.7 | 121.57 | 74.12 |
| 1.7 | 7.68 | 90.23 | 55.01 |
| 2.0 | 10.30 | 67.28 | 41.02 |
| 3.0 | 15.0 | 46.2 | 28.17 |
| 3.5 | 32.4 | 21.38 | 13.03 |
| 3.6 | 33.9 | 20.52 | 12.51 |
| 5.0 | 92.76 | 7.47 | 4.55 |
| 5.49 | 122.7 | 5.64 | 3.439 |
| 5.85 | 150.0 | 4.62 | 2.817 |

Figure 6. The Variation in the Rate Constants for the EDTA-Ce(IV) Reaction with Hydrogen Ion Concentration.



100
80
60
40
20
10
8
6
4
2
1
0.2
0.4
0.6
0.8
1
2
4
6
8
10
$k_2$, $M^{-1}$, sec.$^{-1}$
($H^+$), moles per liter

Figure 6

The sameness of the slope on both sides may not be meaningful and therefore no interpretations will be made on the observation until further studies are conducted.

A number of points should be clarified before indulging in a discussion of the influence of acid concentration on the reductive ability of EDTA when mixed with Ce(IV). First: EDTA is an $\alpha$-amino acid and the two nitrogens are basic enough to become protonated to different degrees in different acid media. The formation constants for the species $H_5EDTA^+$ and $H_6EDTA^{+2}$ have been determined recently[11] in solutions of unit ionic strength ($NaClO_4$) and found to be 25.1 and 0.76 respectively. In a solution which is 6 M in $H^+$, the fraction of EDTA present in the forms $H_5EDTA^+$ and $H_6EDTA^{+2}$ is expected to be substantial. In such species, the reductive ability is reduced drastically if not totally inhibited. Second: If complexation between Ce(IV) and $H_4EDTA$ takes place as a first step towards the oxidation-reduction reaction which is observed, one would expect the concentration of the complex to decrease with increasing $[H^+]$ in the medium, since

$$H_4EDTA + Ce(IV)^{+4} \rightleftharpoons [EDTA\text{-}Ce(IV)] + 4H^+$$

Actually, one would expect an inverse proportionality between the concentration of such a complex and the 4th power of the $H^+$ ion concentration in the medium. The

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[11] G. Anderegg, Helv. Chim. Acta, 50, 2333 (1967).

formation of a 1:1 complex between Ce(IV) and EDTA has been reported[5], and has been confirmed in this work. Its momentary build-up (at 295 mµ) and decay was observed but only in solutions of low acidity ($\approx$pH2). If the reaction which leads finally to Ce(III) and oxidation products of EDTA takes place in 2 steps: complexation followed by electron transfer, and if the second step is catalyzed by $H^+$, one can see a possible explanation for the variable dependence on $H^+$ ion concentration depicted in Figure 6. Third: The oxidative power of Ce(IV) depends on the medium[12], particularly the acidity of the medium[13]. The formal potentials, $E^{\circ}$, of Ce(IV)-Ce(III) couple versus saturated hydrogen electrode vary from 1.44 to 1.42 volts as the normality of $H_2SO_4$ is changed from 1 to 8[13]. Furthermore, Ce(IV) is known to exist in different forms in acidic solutions[14]. For example, it was estimated that in 2 M perchloric acid, 28% of the Ce(IV) is present as aquated $Ce^{4+}$, the remainder predominantly as $Ce(OH)^{3+}$ and as a dimer such as $(CeOCe)^{6+}$ or $(CeOCeOH)^{5+}$.[15] From electrical migration experiments, in 0.5 to 20 N $H_2SO_4$, Ce(IV) was shown to exist in the

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[12] H.A. Laitinen, "Chemical Analysis", McGraw-Hill Book Co., Inc., New York, N.Y., 1960, p. 378-382.

[13] G.F. Smith and C.A. Getz, Ind. Eng. Chem., Anal. Ed., **10**, 191 (1938).

[14] L.J. Heidt and M.E. Smith, J. Am. Chem. Soc., **70**, 2476 (1948).

[15] T.J. Hardwick and E. Robertson, Can. J. Chem., **29**, 818, 828 (1951).

form of anionic complexes which were believed to be $Ce(OH)(SO_4)_3^{3-}$ largely[16]. In the lower acidity regions, conditions are complicated by the hydrolysis of Ce(IV) to $Ce(OH)^{3+}$ which is known to have less oxidizing power than $CeCl^{3+}$ for example[17].

From the previous discussion it becomes apparent that in changing the medium from ~0.2 to ~6 N $H_2SO_4$ the reacting species and their concentrations undergo drastic changes, the combination of which could result in the observed maximum rate at ~1 N acid.

So far, an attempt has been made to show the complexity of the system. However, it would be unfair not to present a simple, even naive explanation for maximum reaction rate at ~1 N $H_2SO_4$. One possible explanation for the reversal in the dependence of rate on $[H^+]$ is that the reaction proceeds in two steps consecutively,

$$\underset{\text{EDTA + Ce(IV)}}{A + B} \rightleftharpoons \underset{\text{Complex}}{C} \longrightarrow \underset{\text{Products}}{P}$$

The concentration of the "complex" C would be inversely proportional to the hydrogen ion concentration raised to some power, 2, 3 or 4, depending on the EDTA species. If reaction is between Ce(IV) and $H_4EDTA$, $H_3EDTA^{1-}$, or $H_2EDTA^{2-}$, the concentration of the complex should be inversely proportional to $[H^+]^4$, $[H^+]^3$, and $[H^+]^2$ respectively. For values of $H^+ < 1$, the higher terms

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[16] E.G. Jones and F.G. Soper, J. Chem. Soc., 802 (1935).

[17] F.R. Duke and C.E. Borchers, J. Am. Chem. Soc., 75, 5186 (1955).

would be even much smaller. For example for $[H^+]=0.2$, $[H^+]^4=1.6\times10^{-3}$. On the other hand, for $[H^+]=2$, $[H^+]^4=16$. So, one can see a reversal in the trend as we pass by $[H^+]=1$. We recognize, however, that the explanation is naive, since we have not taken into account the concentrations of the species $H_4EDTA$, $H_3EDTA^{1-}$, and $H_2EDTA^{2-}$ is the different acid media.

## D. The Influence of Salts

Studies of the effect of changing ionic strength, $\mu$, on rates of ionic reactions are very important in formulating reaction mechanisms[18]. In this study, rather high concentrations ($>1$ M) of salts had to be used since the media were already rich in ions (1-6 N $H_2SO_4$). Under such conditions the classical application of the Bronsted-Bjerrum equation, $k=k_o10^{z_Az_B\sqrt{\mu}}$, where $k_o$ denotes the rate constant at zero ionic strength ($\mu=0$) and $z_A$, $z_B$ the formal charges on reacting species A and B, is not justified[19]. Nevertheless, we conducted a few experiments in which the conditions were kept the same except for variations in the salt concentrations. The results are summarized in Table VI, and depicted in Figure 7 which shows a negative slope of $\sim2$ for the log k *versus* $\sqrt{\mu}$

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[18] S.W. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill Book Co., Inc., New York, N.Y., 1960, p. 525.

[19] C.W. Davies in "Progress in Reaction Kinetics", Ed. G. Porter, Pergamon Press, London, 1960, vol. 1.

## TABLE VI

## (EFFECT OF IONIC STRENGTH ON THE EDTA-Ce(IV) REACTION)

The Reaction Between Ceric Ammonium Sulfate ($1.64\times10^{-4}$ M) and EDTA ($1.64\times10^{-3}$ M) in Acid Solutions of Different Ionic Strengths (0.5 M $H_2SO_4$ + X M $NaClO_4$) at 21.0 C; Spectrophotometrically at $\lambda = 316$ mu

| $NaClO_4$ Mol/lit | Half-life, sec | $k_2$, $M^{-1}sec^{-1}$ |
|---|---|---|
| --- | 3.5 | 120.7 |
| 0.5 | 7.3 | 57.7 |
| 1.0 | 13.0 | 32.4 |
| 1.5 | 18.9 | 22.3 |
| 2.0 | 30.0 | 14.1 |
| 2.5 | 45.0 | 9.4 |

Figure 7. The Influence of Ionic Strength on the EDTA - Ce(IV) Reaction.

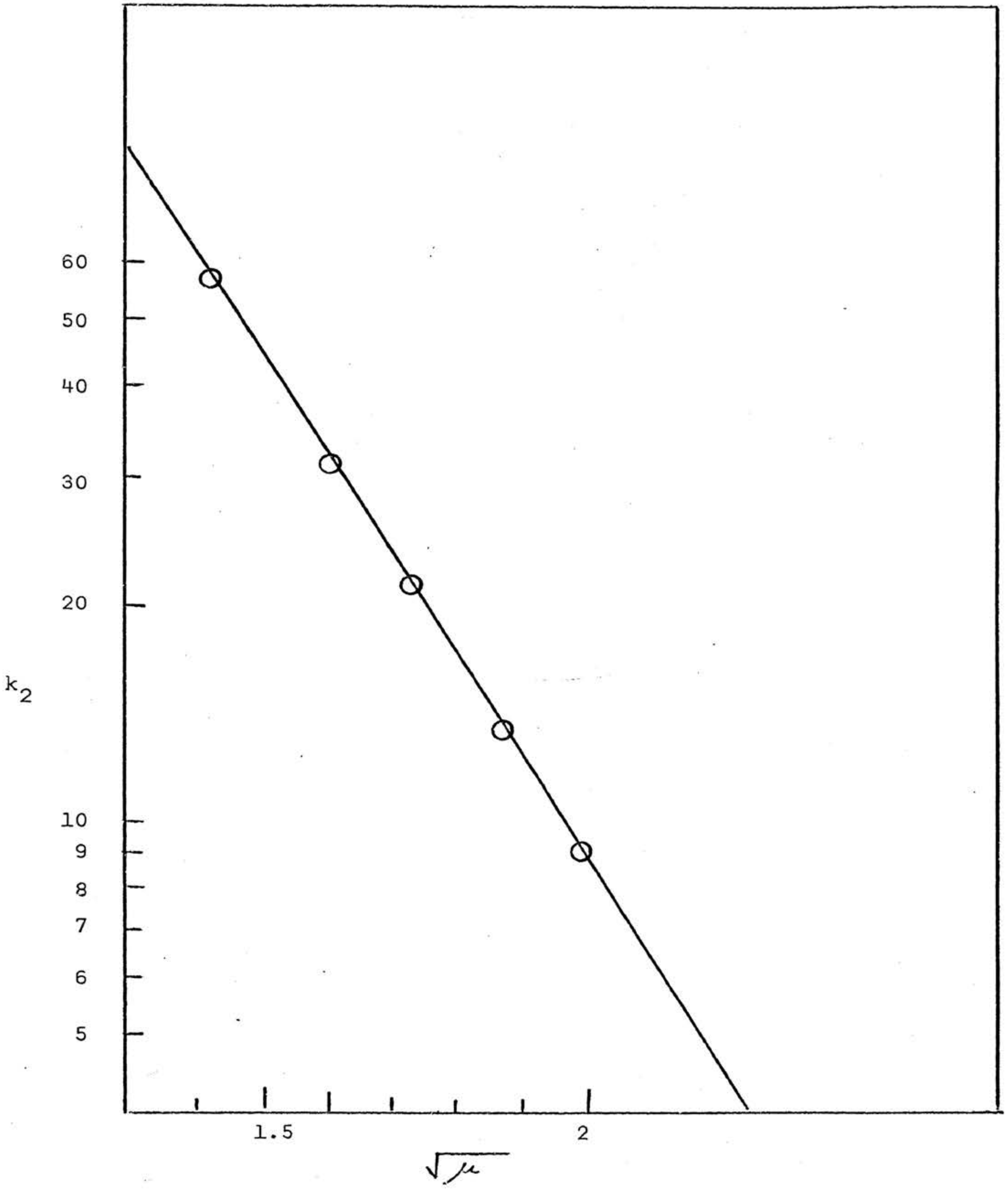

Figure 7

plot for $H_2SO_4$-$NaClO_4$ solutions. This result, if meaningful, may be taken to imply that the reaction between EDTA and Ce(IV) in that acid region ($\sim$1 N) is a reaction between two oppositely charged ions ($z_A z_B$ negative). If the Ce(IV) reactive species is positively charged, the negative slope may indicate a negatively charged EDTA reactive species. In any event, the outcome of the plot in Figure 7 should not be taken too seriously. At this concentration range existing theories are not adequately substantiated or simply not justified because of the assumptions involved.

There is reason to believe, however, that the changes in $k_2$ for the Ce(IV)-EDTA reaction can be adequately explained on the basis of changes in the protonating power of the medium as the concentration of salt is changed. Earlier work on the Hammett acidity functions, $H_o$, has shown that the acidity of a medium increases with increasing concentration of added neutral salts[20]. We confirmed this observation in our work by measuring the intensity of absorption of a colored indicator, p -nitroaniline, the protonated form of which is colorless, as a function of increasing salt concentrations. Figures 8 and 9 show the absorbance of p-nitroaniline in $H_2SO_4$

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[20] M.A. Paul, J. Am. Chem. Soc. 76, 3236 (1954).

Figure 8. Absorbance Curves of p-nitroaniline in $H_2SO_4$ Solution of Different Concentrations.

(1) 0.5 N $H_2SO_4$

(2) 1 N $H_2SO_4$

(3) 2 N $H_2SO_4$

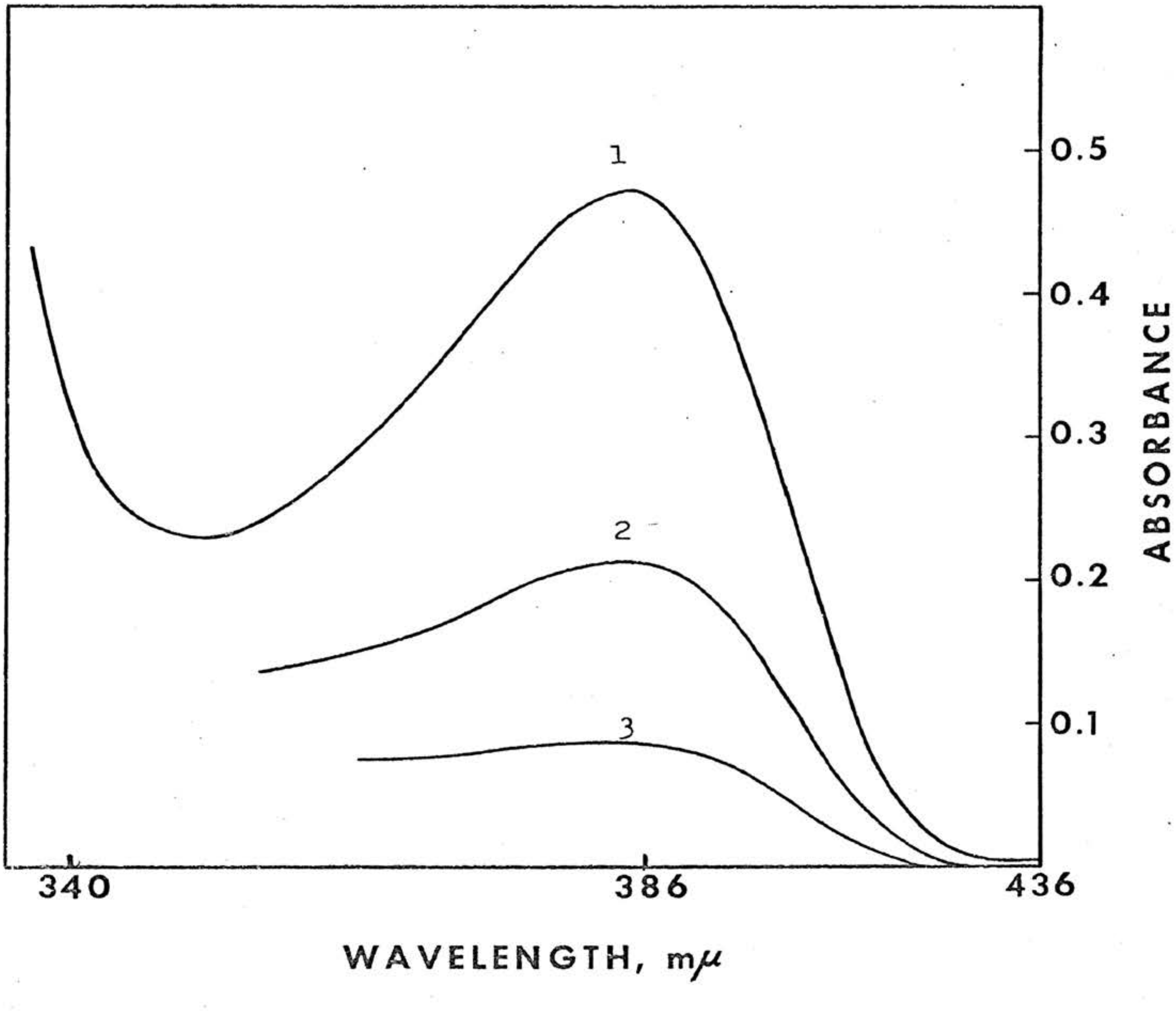


Figure 8

Figure 9. Absorbance Curves for p-nitroaniline in $H_2SO_4$ Solutions of Different Concentrations.

(1) 0.1 M $H_2SO_4$
(2) 0.15 M $H_2SO_4$
(3) 0.25 M $H_2SO_4$
(4) 0.35 M $H_2SO_4$
(5) 0.45 M $H_2SO_4$
(6) 0.6 M $H_2SO_4$
(7) 0.75 M $H_2SO_4$

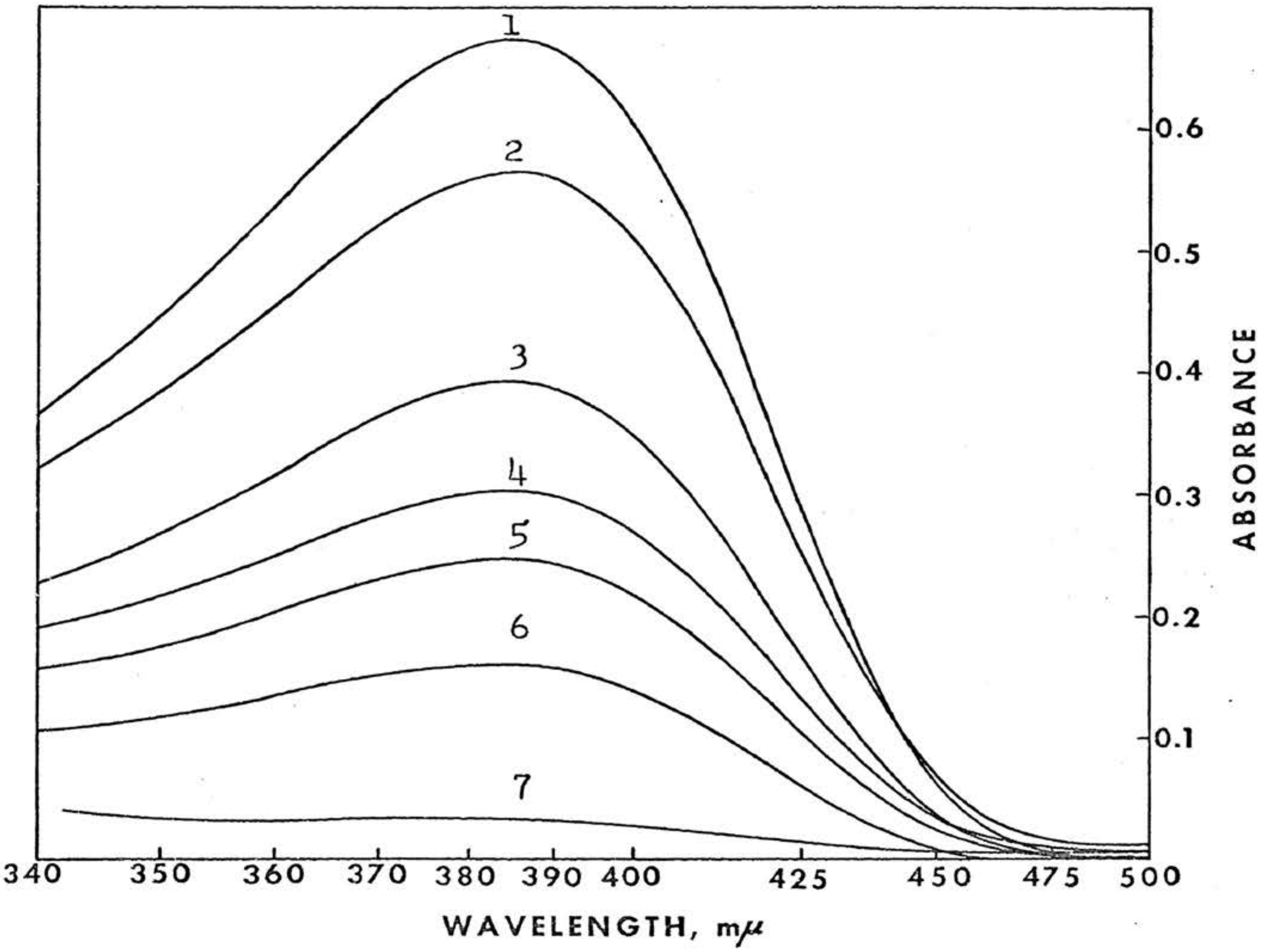
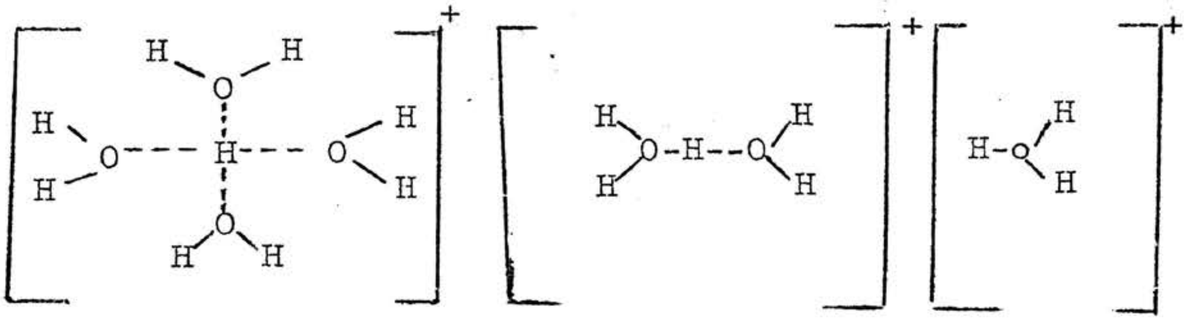

1
2
3
4
5
6
7
0.6
0.5
0.4
0.3
0.2
0.1
ABSORBANCE
340
350
360
370
380
390
400
425
450
475
500
WAVELENGTH, mμ

Figure 9

solutions of different strengths. Figure 10 depicts absorbances for the indicator in 0.5 N $H_2SO_4$ alone (middle curve), in 0.5 N $H_2SO_4$ + 2 M $NaClO_4$ (lower curve), and in 0.5 N $H_2SO_4$ + 2 M $(NH_4)_2SO_4$ (upper curve). It is obvious that the addition of $NaClO_4$ increases the protonating power of the medium. Similar results were obtained with NaCl, KCl, $KNO_3$ and $LiClO_4$. This could be interpreted as a result of a decrease in the amount of solvation of protons in the medium due to clustering of the water molecules around the added salt. Schematically, one would expect the protonating power to increase steadily as you move from I$\longrightarrow$III.



I II III

The results obtained with $H_2SO_4$-$(NH)_2SO_4$ media can also be interpreted by the decrease in the acidity of the medium observed when $(NH_4)_2SO_4$ is the added salt. Figure 10 shows absorbance curves for p-nitroaniline in $H_2SO_4$-$(NH_4)_2SO_4$ solution mixtures of a constant ionic strength. It is interesting to note (Figures 10 and 11) that $(NH_4)_2SO_4$ actually decreases the acidity of the medium despite the fact that it itself is a slightly

Figure 10. Absorbance Curves for p-nitroaniline in

(1) $H_2SO_4$-$(NH_4)_2SO_4$

(2) $H_2SO_4$

(3) $H_2SO_4$ + $NaClO_4$

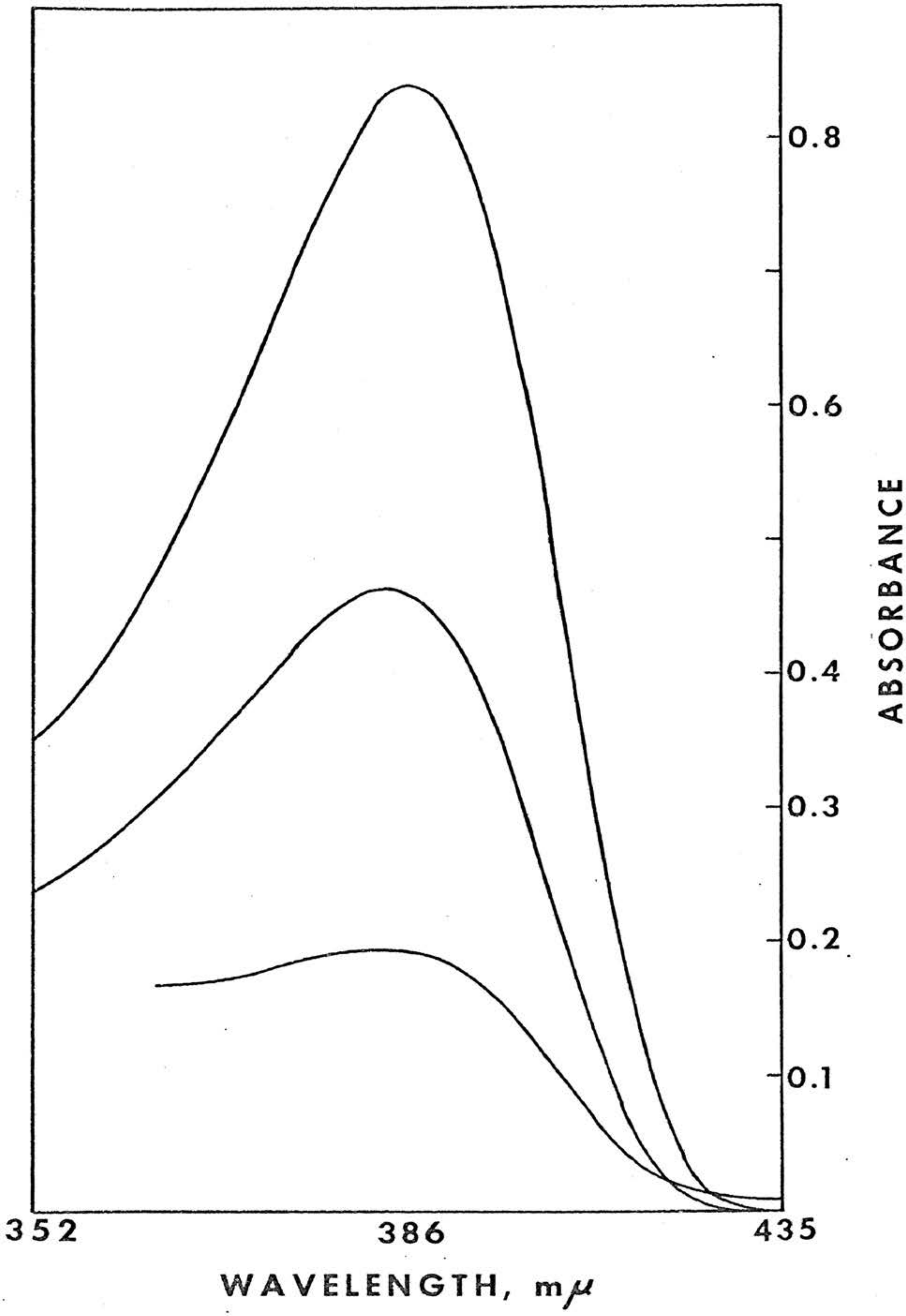


Figure 10

acidic salt. There is no interpretation for this fact at this time.

## E. Influence of Temperature

The results of varying the temperature from 11° to 40° C on the rates of the reaction in question are summarized in Table VII and an Arrhenius plot is depicted in Figure 12. The Arrhenius activation energy was calculated to be 17.6 ± 0.2 k cal/mole.

Figure 11. Absorbance Curves for p-Nitroaniline in $H_2SO_4$-$(NH_4)_2SO_4$ Solution Mixtures of Constant Ionic Strength.

(1) 0.1 M $H_2SO_4$ - 2.9 M $(NH_4)_2SO_4$
(2) 0.15 M $H_2SO_4$ - 2.85 M $(NH_4)_2SO_4$
(3) 0.25 M $H_2SO_4$ - 2.75 M $(NH_4)_2SO_4$
(4) 0.35 M $H_2SO_4$ - 2.65 M $(NH_4)_2SO_4$
(5) 0.45 M $H_2SO_4$ - 2.55 M $(NH_4)_2SO_4$
(6) 0.60 M $H_2SO_4$ - 2.4 M $(NH_4)_2SO_4$
(7) 3 M $H_2SO_4$ - 0 M $(NH_4)_2SO_4$

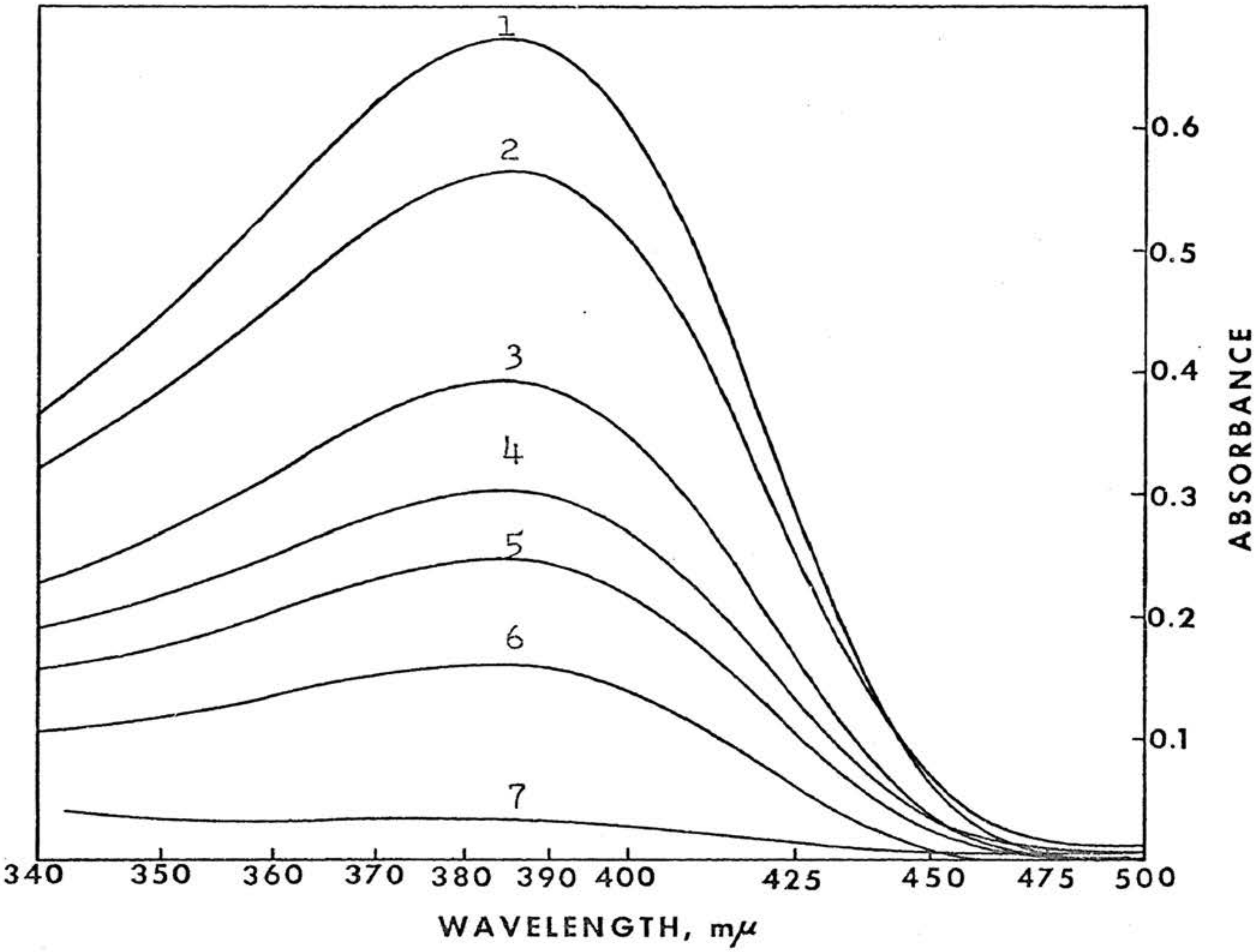

1
2
3
4
5
6
7
0.6
0.5
0.4
0.3
0.2
0.1
ABSORBANCE
340
350
360
370
380
390
400
425
450
475
500
WAVELENGTH, mμ

Figure 11

# TABLE VII

## (EFFECT OF TEMPERATURE ON THE EDTA-Ce(IV) REACTION)

The Reaction Between Ceric Ammonium Sulfate ($1.64 \times 10^{-4}$ M) and EDTA ($1.64 \times 10^{-3}$ M) in Acid Solution (5.85 N $H_2SO_4$) at Different Temperatures; Spectrophotometrically at $\lambda$ =316 mu

| Temperature °C | Half-life, sec | $k_2$, $M^{-1}sec^{-1}$ |
|---|---|---|
| 11.7 | 570.0 | 0.74 |
| 20.7 | 150.0 | 2.82 |
| 31.5 | 49.5 | 8.53 |
| 40.2 | 22.5 | 18.78 |

Figure 12. The Arrhenius Plot for the Ce(IV)-EDTA Reaction in 6 N $H_2SO_4$ Between 11° C and 40° C.

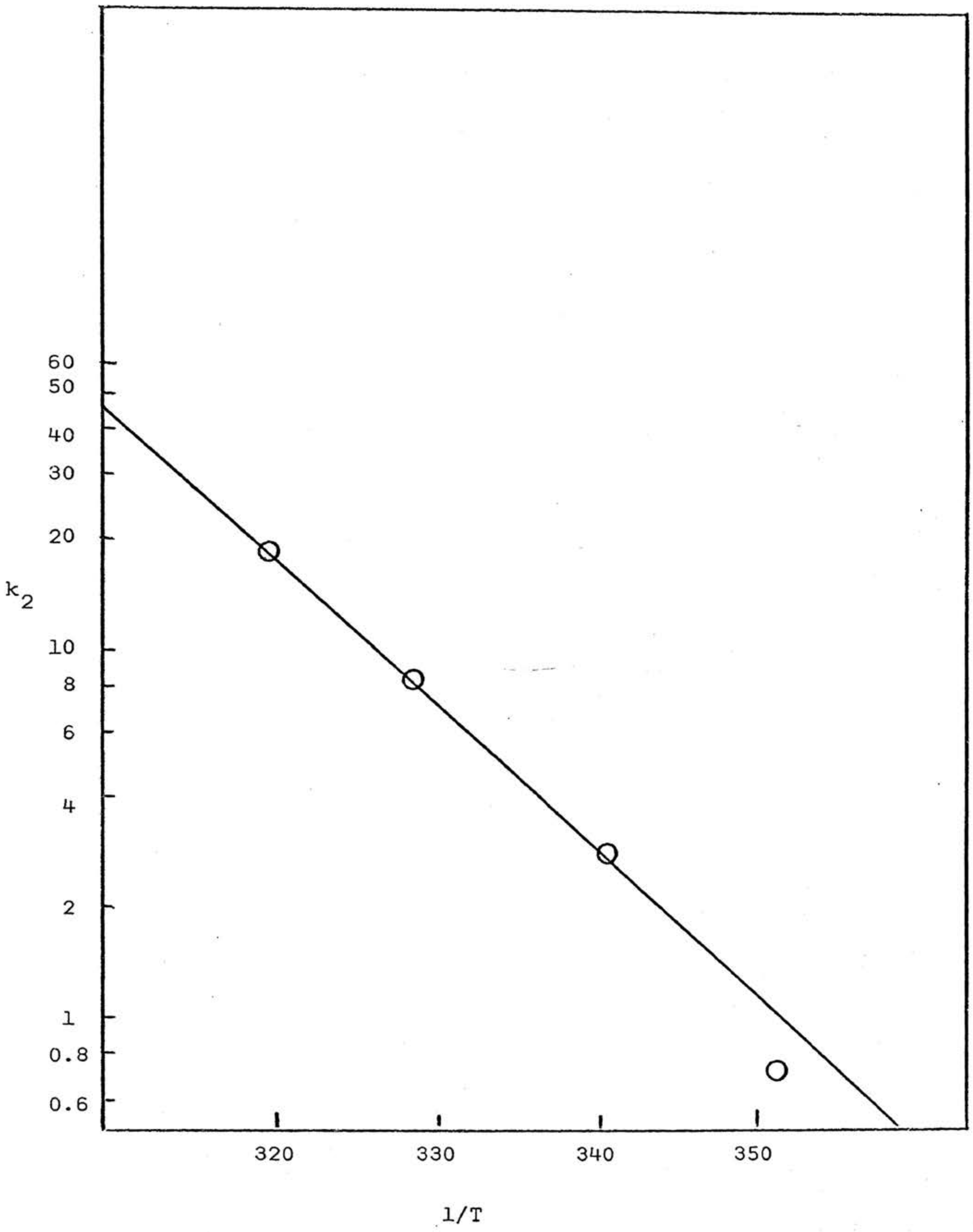


Figure 12

## Chapter IV

## SUMMARY AND CONCLUSIONS

Although quadrivalent cerium is reduced by ethylenedinitrilotetraacetic acid in acid medium, the reaction exhibits variable stoichiometry and is thus an undesirable reaction from the quantitative analytical point of view. The stoichiometry of the Ce(IV)-EDTA reaction shows a dependence on the acidity of the medium, the temperature, and the length of time the reactants are allowed to stay together. At boiling temperatures, almost 14 equivalents of Ce(IV) are reduced per mole of EDTA; at room temperature, only 4 equivalents are so reduced. Despite the variability in stoichiometry, the Ce(IV)-EDTA reaction offers great possibilities for physicochemical studies.

It is realized that the product analysis, reported in the literature, is not comprehensive enough to allow a translation of the kinetics presented in this work into a mechanism for the oxidation of EDTA by Ce(IV). It is therefore recommended that the following steps be carried out as a continuation of the effort started in this work:

1. A complete product analysis corresponding to the different stoichiometries of the EDTA-Ce(IV) reaction.
2. A corresponding study of the anodic oxidation of EDTA; the use of polarography would help in

determining whether the oxidation is a one- or two-electron process.

3. An extension of the present kinetic investigation to stages of the reaction where more than 4 equivalents of Ce(IV) are reduced per mole of EDTA.
4. An extension of the present study to the other polyaminocarboxylic acids, commonly used as chelating agents, to investigate the possibility of forming stable Ce(IV) complexes which could be used in quantitative separations.

# APPENDIX I

Calculation of percentage change in the concentration of EDTA in the rate measurements carried out spectrophotometrically

$[\mathrm{EDTA}]_{\mathrm{initial}} = 1.64 \times 10^{-3}$ $\underline{M}$

$[\mathrm{Ce(IV)}]_{0} = 10.6 \times 10^{-5}$ $\underline{M}$

At $t_{0.5}$, $[\mathrm{Ce(IV)}] = 5.3 \times 10^{-5}$ $\underline{M}$

Equivalent amount of EDTA consumed = $1.325 \times 10^{-5}$ $\underline{M}$

EDTA unconsumed = $1.627 \times 10^{-3}$ $\underline{M}$

% change in EDTA when half the $[\mathrm{Ce(IV)}]_{0}$ is consumed

= 0.81%

When $[\mathrm{Ce(IV)}]_{0} = 5.3 \times 10{-5}$ $\underline{M}$,

% change in EDTA when half the $[\mathrm{Ce(IV)}]_{0}$ is consumed

= 0.4%

When $[\mathrm{Ce(IV)}]_{0} = 1.6 \times 10^{-4}$ $\underline{M}$,

% change in EDTA when half the $[\mathrm{Ce(IV)}]_{0}$ is consumed

= 1.22%

## ACKNOWLEDGEMENTS

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# VITA

The author, Sahmia K. Al-Hashimi, was born July 1, 1939 at Mosoul, Iraq. She received her elementary and secondary education in Mosoul, and graduated from high school in June, 1953. She received her college education at the University of Baghdad and graduated with a B.S. in Chemistry in June, 1958. In January, 1959 she was appointed Instructor in the Chemistry Department of the Agricultural College until September 1966.

In Setpember 1966, she entered the University of Missouri - Rolla to study toward the M.S. degree in Chemistry. The M.S. degree in Chemistry was awarded in May, 1968.

During her stay in the United States, she received an educational scholarship from the Government of Iraq.