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A STUDY OF THE DECOMPOSITION OF AMMONIUM HEXANITRATOCERATE (IV) IN GLACIAL ACETIC ACID

Thesis for the Degree of Ph. D.

MICHIGAN STATE UNIVERSITY
Leo H. Bowman

1961

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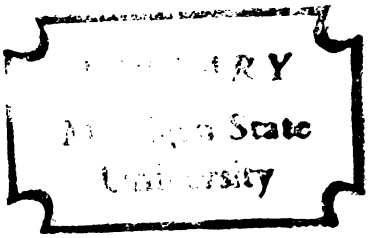

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ABSTRACT

A STUDY OF THE DECOMPOSITION OF AMMONIUM HEXANITRATOCERATE(IV) IN GLACIAL ACETIC ACID

by Leo H. Bowman

In the course of using acetic acid solutions of ammonium hexanitratocerate(IV), as an oxidizing agent for the determination of organic functional groups, it has been observed that this reagent is somewhat unstable when exposed to light, that relatively rapid decomposition occurs upon the addition of mineral acids, and that at no time has there been any evidence of gaseous products produced during this decomposition.

Efforts to define the observations above were complicated by the complexity of the system, ammonium hexanitratocerate(IV) in a solution of perchloric acid and water in glacial acetic acid. Physical-chemical techniques, however, have provided some insight into the solvolytic reactions occurring, eliminated free radical mechanisms from consideration, and suggested that the enol form of acetic acid might be the reductant responsible for decomposition of the cerium(IV) state.

The reaction kinetics have also been determined. The reaction appears to follow the rather simple kinetics of:

$$-\frac{d[Ce(IV)]}{dt} = k\frac{[Ce(IV)][HClO_4]^2[HOAc]^n}{H_2O}$$

The instability of the reagent in the presence of mineral acids circumvents the use of excess reagent followed by back titration of the

unreacted cerium(IV). This limitation severely narrows the scope of the utility of this solution as an analytical reagent by requiring that an oxidation be very rapid, so that a direct titration can be employed. Attempts to determine glycolic acid and acetoxyacetic acid were unsuccessful due to the slowness of the oxidation, succinic acid was not attacked by the reagent, and acetoacetic ester and sodium glyoxylate were rapidly oxidized.

A STUDY OF THE DECOMPOSITION OF AMMONIUM HEXANITRATOCERATE(IV) IN GLACIAL ACETIC ACID

By

Leo H. Bowman

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1961

G 22662
9/27/62

ACKNOWLEDGMENT

The author would like to express his sincere gratitude to the Michigan State University Department of Chemistry and its staff for providing the opportunity of pursuing graduate training in chemistry. I am especially grateful for the supervision, guidance, and counsel provided by Dr. K. G. Stone and the analytical staff throughout my work.

My family and I also wish to express our appreciation to the Socony Mobil Oil Co., the Dow Chemical Company, and the Archer Daniels Midland Co. for their financial assistance during the course of this endeavor. Additional thanks are extended to the Dow Chemical Company and Roland Gohlke for their mass spectrometry assistance.

A special acknowledgment is extended to the author's family for their encouragement and cheerful endurement of the deprivations required of them during both my undergraduate and graduate studies.

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
EXPERIMENTAL	8
Organizational Guide	9
I. Reagents	11
II. Apparatus	12
III. Preparation of Solutions	13
IV. Experimental Data and Procedures	14
A. Initial Observations Concerning the Reagent Solution Under Investigation	14
B. Reaction Kinetics	20
C. Tests for Free Radicals	23
D. Efforts to Identify the Reaction Products	24
E. Oxidation of Some Organic Molecules	30
V. Graphic and Spectral Curves	31
DISCUSSION OF RESULTS	49
LITERATURE CITED	61
APPENDIXES	67

LIST OF TABLES

TABLE Page

I. Electrode Potentials with Reference to the Normal Hydrogen Electrode 2

II. The Influence of Light on the Stability of the Cerate Reagent 1N in Perchloric Acid 15

III. Summary of Conductance Titration Data 18

IV. Potentiometric Titration of 0.023N Ce(IV) Reagent with 0.4435 N $HClO_4$ 18

V. Change in $[HClO_4]$ in the Course of Cerate Decomposition 22

VI. Comparison of Decomposition Rate With $[HClO_4]$. . . 22

VII. Compilation of Data Derived from the Tetrabutyl-ammonium Hydroxide Titrations 29

LIST OF FIGURES

FIGURE Page

1. Spectra of Perchloric Acid Acidified Reagent with Time 32
2. Conductometric and Potentiometric Titration of Cerate Reagent with Perchloric-Acetic Acid Solution . . 33
3. Conductometric Titration of Ammonium Nitrate Spiked Cerate Reagent with Perchloric-Acetic Acid Solution 34
4. Effect of Water on Decomposition of Cerate Reagent with Time 35
5. Effect of Water on Rate of Decomposition of Cerate Reagent 36
6. Effect of Perchloric Acid on Decomposition of Cerate Reagent with Time 37
7. Effect of Perchloric Acid on Rate of Decomposition of Cerate Reagent 38
8. Comparison of Reaction Rate with Varying Perchloric Acid 39
9. Spectra of Vacuum Distillation Residual Solutions . . 40
10. Spectra of Residual Solutions Remaining After Evaporation 41
11. Near Infrared Spectra of the Solvent System 42
12. Infrared Spectrum of Unknown Yellow Oil 43
13. Potentiometric Titration of Benzoic Acid with Tetrabutylammonium Hydroxide 44
14. Potentiometric Titration of Decomposed Reagent with Tetrabutylammonium Hydroxide 45

LIST OF FIGURES - Continued

FIGURE Page

15. Potentiometric Titration of Nitric Acid Spiked, Decomposed Reagent with Tetrabutylammonium Hydroxide 46

16. Potentiometric Titration of Undecomposed Reagent with Tetrabutylammonium Hydroxide. 47

17. Potentiometric Titration of Nitric Acid Spiked, Undecomposed Reagent with Tetrabutylammonium Hydroxide 48

INTRODUCTION

The element cerium is said to have been discovered by Berzelius and Hinsinger in 1803 (81), but it was 1861 before any attempt was made to use it as a volumetric oxidizing agent (50). Little was done on this subject, however, until Bermath and Ruland published their investigation: "Uber die Oxydations Wirking von Cerisulfat" in 1920 (4). These workers are sometimes referred to as the originators of modern ceratimetry, although it remained for the almost simultaneous efforts of professors H. H. Willard (83) of the University of Michigan and N. Howell Furman (26) of Princeton in 1928 to systematically study this system and lay a stable foundation from which the field has grown to a position of great importance in modern technology.

Cerium(IV), however, has received a great deal of attention in the past thirty years as a powerful and versatile oxidizing agent. Its versatility stems from the wide variation of redox potential that can be obtained. This is apparently due to the ability of cerium to complex with various mineral acids, as illustrated in Table I for aqueous systems. As a consequence, it is possible to vary the reduction potential from 1.28 to 1.87 volts simply by selecting the desired acid and its concentration.

Table I. Electrode Potentials with Reference to the Normal Hydrogen Electrode (70)

Acid Conc. N.	$HClO_4$	HNO_3	H_2SO_4	HCl
1	1.70	1.61	1.44	1.28
2	1.71	1.62	1.44	--
4	1.75	1.61	1.43	--
6	1.82	--	--	--
8	1.87	1.56	1.42	--

Cerium(IV) also has the desirable characteristic of specificity in the reactions it will undergo. Perchlorato-ceric acid has evolved as one of the most desirable oxidants for organic compounds, and its characteristics have been reasonably well defined (69):

(1) Only those compounds, the electronic configuration of which is capable of rearrangement to a stable form by the removal of two electrons and two protons, are oxidized.

(2) The carbonyl group must hydrate to a glycol form before it can be oxidized.

(3) Compounds containing an active methylene group are oxidized.

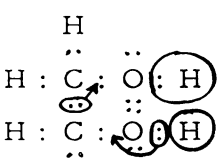
(4) Compounds yielding aldehydes or ketones, unsubstituted by oxygen in the alpha position, as end products are not quantitatively oxidized and give empirical results.

(5) End products are fatty acids, ketones, aldehydes (other than formaldehyde), and carbon dioxide.

(6) Formaldehyde is rapidly hydrated and the hydrate is rapidly oxidized to formic acid. This is a specific property of cerate oxidations.

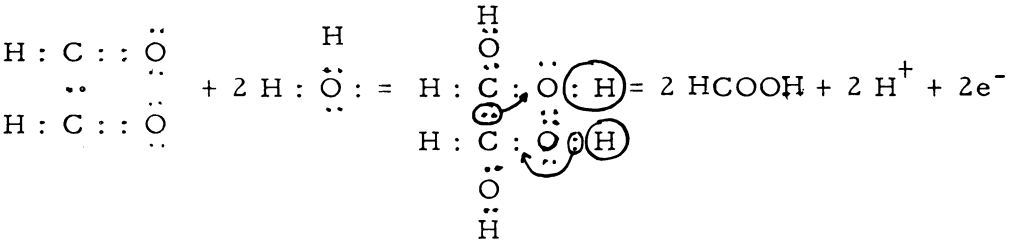
These principles can be illustrated by the following mechanistic examples:

(1) Oxidation of a 1, 2 glycol.

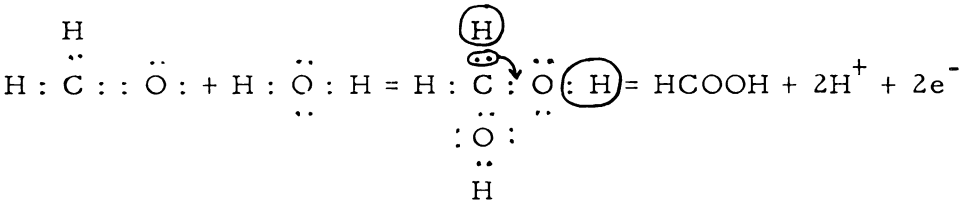


$= 2HCHO + 2H^{+} + 2e^{-}$

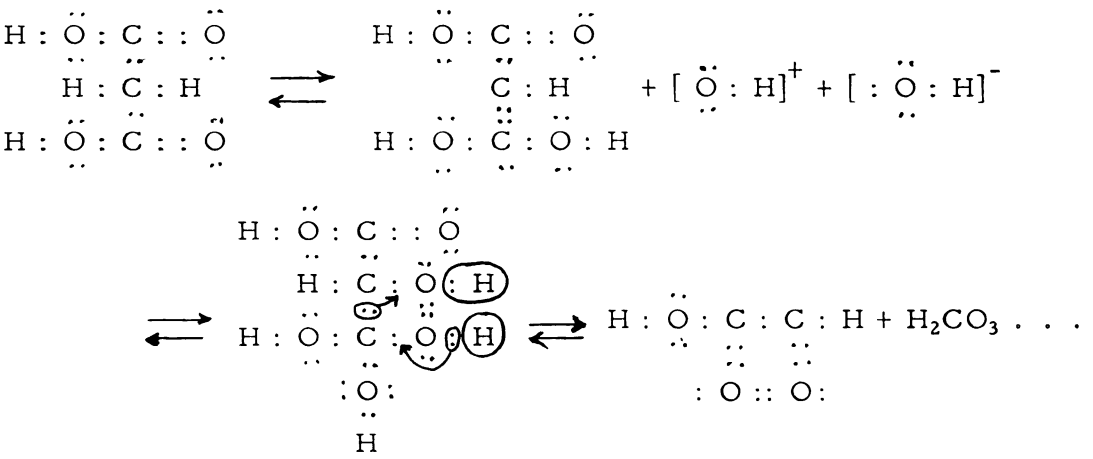
(2) Oxidation of a carbonyl compound.



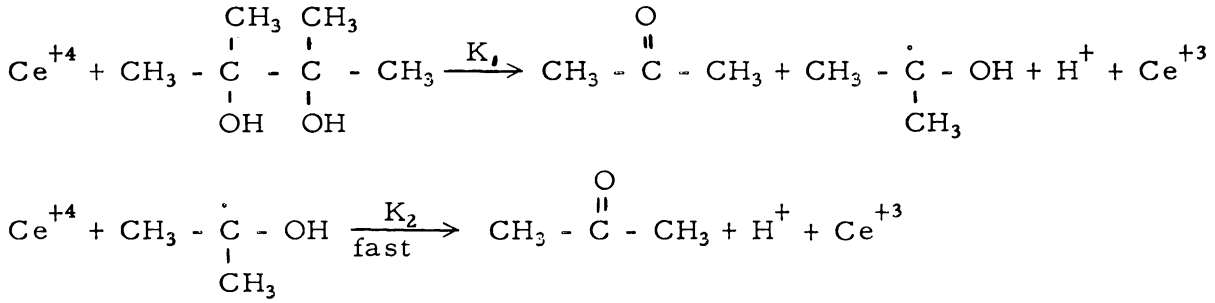
(3) Oxidation of formaldehyde.



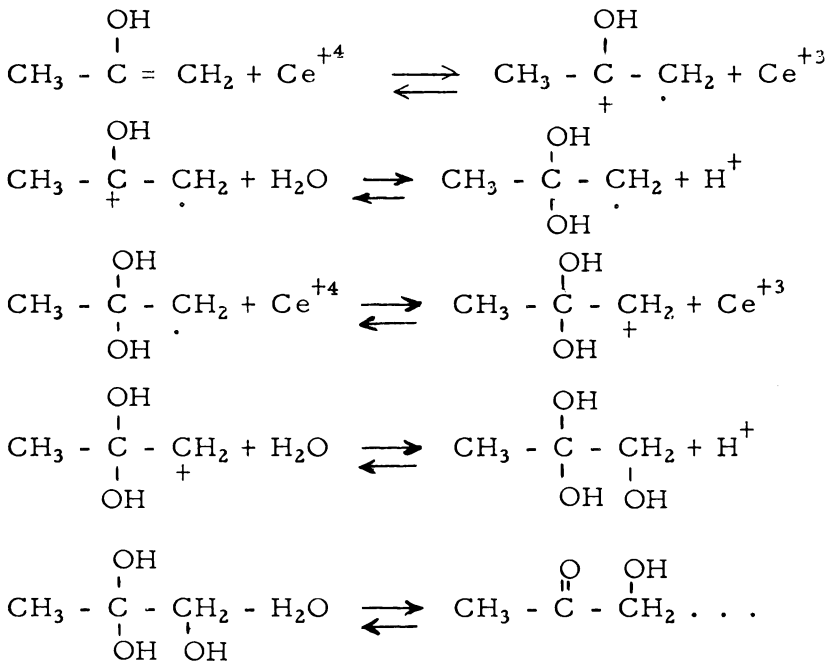
(4) Oxidation of an active methylene group.



Although the above work has undoubtedly contributed to the use of perchlorato-ceric acid as an oxidizing agent, the mechanistic routes are still somewhat in question, as illustrated by the number of kinetic studies that continue to appear in the literature (13, 34, 63, 64). For example; Mino, Kaizerman, and Rasmussen (53) found first order kinetics for both the oxidant and the reductant in the oxidation of pinacol which lead them to postulate the following free radical mechanism:



Shorter and Hinshelwood (63) investigated the oxidation of acetone and pointed out the importance of enolization and hydration to oxidation but postulated a somewhat different mechanism from that of Smith and Duke:



Regardless of the limitations involved, cerium(IV) solutions have found wide use in the volumetric analysis of inorganic ions (1, 6, 30, 55, 83, 84, 85, 86, 88) as well as in organic chemistry and biological chemistry. In the latter fields cerium, as well as other oxidizing agents, has been used extensively as a selective oxidant for preparative purposes (27, 49, 71, 72, 73), structural studies (41, 42), qualitative analysis (15), and quantitative analysis (13, 38, 49, 53, 67, 68). Still, applications of most oxidizing agents are based primarily on empirical rules and the

investigator's experience. Waters (28) has summarized the characteristics of many of the common oxidizing agents in tabular form for the purpose of organic preparations, not including cerium(IV).

This ignorance and empiricism in the field of organic oxidations is primarily due to three factors: the concept of oxidation itself is frequently difficult to define, the definitions of oxidative processes mechanistically are often troublesome to study, and most reactions are not thermodynamically reversible.

The latter factor thwarts efforts to establish an oxidation-reduction scale that is so helpful in comparing the oxidizing power of inorganic systems. This is understandable when one considers that reversible systems have mobile electrons while the electrons of nonreversible covalent linkage are very firmly bound; and thus require a considerable amount of activation energy or "overpotential" to sever such linkages. As a consequence, anomalous values result for the electrode processes and make a tabulation analogous to the inorganic situation nearly worthless.

The concept of oxidation in organic chemistry is much more varied than in inorganic chemistry. In inorganic oxidations one simply observes a transfer of electrons; whereas in organic oxidations it is possible to increase the apparent oxidation number of an atom by dehydrogenation, direct addition, or substitution. Upon closer inspection, however, it is apparent that these three processes can be rationalized on the same basis as those of inorganic oxidations, a transfer of electrons.

Nearly all of the oxidimetry work up to the present time has been carried out in aqueous solutions. This is somewhat surprising since nonaqueous solvents have received a great deal of attention in their uses as leveling and differentiating solvents for the determination of acids and bases over the entire acidity scale (9, 11, 24, 25, 54, 56, 75). Acetic acid has been one of the foremost solvents to be investigated in this capacity (2, 10, 12, 31, 37, 57, 62). Furthermore, acetic acid has also

been one of the few solvents to be investigated at all as a medium for oxidation reactions. It has been used on a number of occasions for theoretical and preparative organic oxidation reactions (5, 8, 27, 29, 33, 46, 58, 74, 77, 78), but its use as a solvent for analytical redox determinations, to the best of my knowledge, has been limited to the work of Tomicek (79, 80); Stone (35, 39); Erdey (17); and co-workers.

Tomicek and his associates (79, 80) studied various oxidants soluble in glacial acetic acid. Bromine, chromic acid, sodium permanganate, lead tetraacetate, iodine, iodine monochloride, iodine monobromide, and hydrogen peroxide were given varied amounts of attention. Several of these reagents showed promise for both inorganic and organic analysis.

Hinsvark and Stone (39) studied several aspects of the cerium(IV)-acetic acid system i.e., the solubility of cerium salts in glacial acetic acid, the detection of the redox equivalence point, the standardization of the cerium(IV) reagent, the relative redox potentials of the cerium system in acetic acid solutions of perchloric acid and sulfuric acid, and numerous random oxidations of oxygenated organic compounds.

Stone and Harris (35) investigated the oxidation of sodium azide and hydrazine with cerium(IV) in acetic-perchloric acid solution.

The latter two investigations, coupled with the generally desirable characteristics of both cerium(IV) and acetic acid in their respective capacities, suggested further study of this system. It is to this task that this dissertation is directed. More specifically, our ultimate goal was to elucidate the mechanism of the decomposition of ammonium hexanitratocerate(IV) in an acetic-perchloric acid solution. It was anticipated that the realization of this goal would not only aid one in the application of the cerate reagent to organic analysis but also shed light on oxidation reactions in general.

EXPERIMENTAL

ORGANIZATIONAL GUIDE

I. Reagents.

II. Apparatus.

III. Preparation of solutions.

IV. Experimental data and procedures.

A. Initial observations concerning the reagent solution under investigation.

a. Reagent stability.
(1) Influence of light.
(2) Influence of perchloric acid.
b. Absence of gaseous products.
c. Investigation of the color change produced by the addition of perchloric acid.
(1) Photometric titration.
(2) Ionic migration.
(3) Influence of mineral acids.
(4) Ion exchange chromatography.
(5) Conductometric titrations.
d. Formation of a white precipitate.
(1) Qualitative and quantitative analysis.
e. Decrease in oxidizing power.
(1) Reduction of ability to oxidize the oxalate ion.
(2) Oxidation of the iodide and chloride ions.
f. Propionic acid substitution for acetic acid.
g. Qualitative nature of the precipitate recovered from the reagent after long standing.

B. Reaction Kinetics.

a. Water and cerium dependence
b. Perchloric acid dependence.
c. Influence of ammonium ion.
d. Influence of perchlorate, nitrate, and acetic acid.

C. Tests for free radicals.

a. Electron paramagnetic resonance spectra.
b. Free radical scavengers.
c. Influence of oxygen and light on the reaction rate.

D. Efforts to identify reaction products.

a. Isolation and qualitative analysis techniques.

(1) Distillation techniques.
(2) Evaporation.
(3) Steam distillation.
(4) Extraction techniques.
(5) Precipitation.
(6) Absorption spectra (ultraviolet, visible, infrared, and near infrared).
(7) Chemical qualitative analysis.
(8) Nuclear magnetic resonance analysis.
(9) Polarography.
(10) Acid-base titrations.
(11) Mass spectroscopy.

E. Oxidation of some organic molecules.

V. Graphic and spectral curves.

I. REAGENTS

Fisher and DuPont "Reagent Grade" and Baker's "Analyzed" acetic acid were used as the solvent for this study. Early in this investigation the solvent was distilled from chromium trioxide and followed by a second distillation from potassium permanganate to assure the absence of possible reducing impurities. No effort was made to protect the solvent from the atmosphere. Both of the above distillations were preceded by a refluxing period of three to five hours. This procedure was eventually eliminated after a comparison of the spectra and reaction characteristics of the purified and nonpurified solvents gave no indication of undesirable impurities in the commercial solvents. Mallinckrodt Analytical Reagent potassium permanganate and chromium trioxide were used.

Baker "Analyzed" 70% perchloric acid was used.

Merck "Reagent" primary standard purity sodium oxalate, Baker "Analyzed" sodium acetate, and The G. Fredrick Smith Chemical Company ceric ammonium nitrate [ammonium hexanitratocerate(IV)] were also used.

Eastman Kodak Company "White Label" acetic anhydride was distilled before using.

Acid impurities present in Matheson, Coleman, and Bell methyl isobutyl ketone were removed by passing the solvent through a column of Fisher adsorption alumina (9). Matheson, Coleman, and Bell tetra-n-butylammonium iodide and Mallinckrodt purified silver oxide were utilized in the preparation of tetrabutylammonium hydroxide.

II. APPARATUS

A Sargent "model III" manual polarograph equipped with a Beckman number 19031 twin inlay platinum electrode was used for the detection of the redox equivalence points. A magnetic stirrer and an amber buret were used for the titrations. The latter was required by the instability of the ammonium hexanitratocerate(IV) in glacial acetic acid when exposed to light.

The conductometric titrations were carried out using a Arthur H. Thomas Company Serfass Conductance Bridge, Model RCM15, and 1 $cm.^2$ platinum electrodes plated with platinum black.

A Beckman Zeromatic pH meter was used to observe the potential changes during the tetrabutylammonium hydroxide titrations. A glass electrode was used as the active electrode and a sleeve-type calomel electrode was utilized as the reference electrode. A magnetic stirrer was again used to agitate the solutions.

A Beckman DK-2 recording spectrophotometer was applied extensively in the investigation of ultraviolet and visible absorption spectra of numerous samples. One cm. silica cells were used.

Other instruments that were applied less frequently included the following: Beckman GC-2 Gas Chromatograph; Varian Associates Nuclear Magnetic Resonance equipment; Sargent Polarograph, Model XXI; Perkin Elmer Recording Infrared Spectrophotometer, Model 21; electron paramagnetic resonance equipment in the Michigan State University Department of Physics; and a magnetic scanning, 90° sector type mass spectrometer.

III. PREPARATION OF SOLUTIONS

The reagent, ammonium hexanitratocerate(IV) in acetic acid, was prepared by saturating glacial acetic acid with the dried salt at 60°C. This was carried out by heating the acetic acid to 60°C., adding a large excess of dried ammonium hexanitratocerate(IV) salt, and stirring for approximately four hours. The resulting solution was allowed to stand overnight before filtering through a medium porosity sintered glass filter (38).

The above procedure was eventually modified in that sufficient water was added to give an approximately 1 M solution of water in the acetic acid solvent. This addition had the twofold purpose of increasing the solubility of the cerate salt, which tended to precipitate upon standing, and also to increase the stability of the cerium(IV) state.

The reagent solution was standardized against a standard solution of sodium oxalate in glacial acetic acid with sufficient 70% perchloric acid present to prevent the final perchloric acid concentration going below 0.5 N. The end point was detected amperometrically (38, 76).

Tetrabutylammonium hydroxide was prepared by the method of Cundiff and Markunas (11). The tetrabutylammonium hydroxide was not passed through a strongly basic anion exchange column, however. The reagent was standardized against Baker "Analyzed" benzoic acid in methyl isobutyl ketone to a potentiometric end point using a glass indicating electrode and a sleeve-type calomel reference electrode.

Karl Fischer reagents were prepared in the usual manner (21, 60). The reagent was standardized visually with weighed water samples.

IV. EXPERIMENTAL DATA AND PROCEDURES

A. Initial Observations Concerning the Reagent Solution Under Investigation

(a) Reagent Stability.

Ammonium hexanitratocerate(IV) has sufficient solubility and stability in glacial acetic acid to merit investigation as an analytical redox reagent.

It has been observed that the aforementioned reagent was somewhat unstable, and that this instability was increased by exposure to light and also by the addition of perchloric acid. The effect of the former was studied quantitatively by Harris and Stone (38). The latter was investigated in the course of this work.

Four 175 ml. samples of approximately 1.2 N perchloric acid and 7.8×10^{-3} N cerium(IV) in acetic acid were prepared by identical techniques. All of the samples were held at $25^{\circ}C. \pm 0.5^{\circ}C.$ in volumetric flasks. Two flasks, however, were heavily taped with black insulation tape to protect the samples from exposure to the light. Twenty-five ml. aliquots were removed at recorded time intervals and pipetted into an excess of sodium oxalate in 1N perchloric-acetic acid solution. The excess oxalate was back titrated with standard cerate reagent. The average results of the two samples for both the clear and dark flasks are recorded in Table II.

This light sensitivity made it necessary to store the reagent solution in darkened containers. The instability of the reagent toward perchloric acid precluded the possibility of using a perchloric-acetic acid solution directly or using an excess reagent-back titration technique.

Table II. The Influence of Light on the Stability of the Cerate Reagent 1N in Perchloric Acid

Time (mins.)	N of Ce(IV) Solutions x 10^{+3}	
	Clear Flask	Dark Flask
0	7.8	7.8
33	3.7	4.0
60	2.2	2.4
105	0.9	1.0
135	0.6	0.7
165	0.4	0.5
195	0.2	0.4

(b) Absence of Gaseous Products.

Another rather startling observation of the decomposition was the lack of gaseous products in the reduction process. Experiments were carried out with relatively large quantities of the decomposing reagent solution in a closed system consisting of a round-bottomed, single-necked flask and an attached U-tube. The apparatus and a portion of reagent was allowed to equilibrate in a constant temperature bath at 25°C. Sufficient perchloric acid was added to the flask to give an approximately one molar solution when the reservoir was filled. As much cerate reagent as possible was added in order to minimize the dead space in the reservoir. Complete decomposition at 25°C. failed to indicate the presence of gaseous decomposition products.

(c) Investigation of the Color Change Produced by the Addition of Perchloric Acid.

The cerate reagent had the characteristic orange color of the cerium(IV) ion. The addition of 70% perchloric acid brought about a deepening of the color to an orange-red hue (Figure 1). The addition

of water prior to the perchloric acid treatment seemed to lessen the degree of color change. Several attempts to define this color change gave only inconclusive results.

Ion migration experiments with platinum electrodes immersed in the reagent solution in opposite arms of a U-tube packed with glass beads failed to indicate the charge of the species; instead, the yellow-orange color depleted approximately two inches below the negative electrode and then appeared to disappear uniformly throughout the solution. A rapid evolution of gas was noted at the negative electrode and a smaller amount at the positive electrode.

The use of different mineral acids had a pronounced effect on the appearance of the solution. Perchloric acid, as was stated previously, produced a very noticeable color change, and the decomposition proceeded at such a rate as to be detected visually. A white precipitate also formed. Nitric and hydrochloric acids, on the other hand, did not seem to effect the stability of the reagent to any great degree. The hydrochloric acid did deepen the color somewhat, however.

A photometric titration with perchloric acid was attempted in order to investigate possible stoichiometric relationships between the acid, the ammonium hexanitratocerate(IV), and the color. This technique proved to be of little value, since the production of the white precipitate mentioned in the preceding paragraph continued to come out of solution even after centrifuging.

Attempts to determine the charge of the cerium(IV) species by ion exchange chromatography also proved fruitless. Columns of Dowex-50 in the sodium form and Dowex-2 in the chloride form were conditioned by repeated treatments with aqueous hydrochloric acid and aqueous sodium acetate solutions respectively. These treatments were continued until the former gave no indication of the sodium ion

and the latter no indication of the chloride ion in their effluent streams. The columns were further conditioned by thorough washings with glacial acetic acid. Passing a solution of the reagent 1N in perchloric acid through the columns failed to give any indication of exchange of the colored cerium species in either case.

Fifty ml. samples of undecomposed cerate reagent were titrated with dilute perchloric-acetic acid solution conductometrically. A maximum and a minimum were observed on every occasion. The maximum seemed to correspond to the initiation of precipitation of the white solid. An analogous titration was carried out simultaneously but was followed potentiometrically (Figure 2). The apparatus used in the latter procedure was identical with that used for the tetrabutylammonium hydroxide titrations to be described later.

Addition of a known amount of ammonium nitrate did not alter the slope of the conductivity curve (Figure 3). The data derived from these conductometric titrations is summarized in Table III.

The potentiometric perchloric acid titration did not give a well defined curve. Upon more acute observation, however, it was possible to detect four points of slope inflection; although their authenticity might well be questioned (Figure 2, Table IV).

(d) Formation of a White Precipitate.

The white precipitate formed upon the addition of perchloric acid to the reagent was filtered on a medium porosity sintered glass filter and dried in a vacuum desiccator over calcium chloride and potassium hydroxide pellets. Qualitative analysis indicated the presence of ammonium and perchlorate ions. The melting points of the precipitates prepared from samples of perchloric acid, magnesium perchlorate, and the unknown with nitron were all sharp and fell between 247 and 250°C. Quantitative determination of the perchlorate ion gravimetrically using

Table III. Summary of Conductometric Titration Data.

Sample	[Ce(IV)] When Titrated	Ratio of meq. H^+/meq. Ce(IV) Observed Minimum	Observed Maximum	Corrected Minimum†
Reagent	0.023	3.34	0.52	2.12
Reagent	0.023	3.25	0.53	1.92
Reagent	0.026	3.15	0.38	2.27
Reagent	0.030	2.75	0.45	2.30
Reagent	0.030	2.63	0.53	2.10
Reagent + NH_4NO_3	0.030	2.59*	0.53	2.06

*The value so designated was corrected for the ammonium nitrate added.

†The heading entitled "Corrected Minimum" refers to the corrections required to compensate for the titrant necessary to reach the maximum and also to compensate for the ammonium ion present in the solution from the slow decomposition of the cerate reagent. The initial saturated cerium solutions were approximately 0.03 N in cerium(IV), but the titrated solutions had decomposed to varying degrees; thus reducing the denominator of the ratio and increasing the numerator by virtue of the ammonium ion liberated, but unaccounted for by titrating the cerium(IV) ion (Appendix II). The latter corrections were based on 0.03 N as the initial concentration, since the reagent was not standardized immediately after preparation but just prior to use. This shortsightedness most certainly introduced an error in the corrections but sufficed to indicate that there were apparently two equivalents of acid consumed per cerium.

Table IV. Potentiometric Titration of 0.023N Ce(IV) Reagent with 0.4435N $HClO_4$.

Equivalence Point	Ml./Break	Ratio of $[HClO_4]/[Ce(IV)]$
1.75 ml.	1.75	0.68
4.70 ml.	2.95	1.1
7.85 ml.	3.15	1.2
11.05 ml.	3.20	1.2

nitron as the precipitant (22, 82) gave an average value of 84.68% perchlorate in the white solid. The theoretical value for perchlorate based on ammonium perchlorate is 84.65%. It was therefore concluded that the white solid was indeed ammonium perchlorate.

(e) Decrease in Oxidizing Power.

Accompanying the above observations was the obvious decrease in oxidizing power relative to the oxalate ion. The solution after complete decomposition, however, still had quite strong oxidizing properties: chloride was oxidized to chlorine and iodide to iodine. This property was apparently due to liberated nitric acid. Blanks containing the nitrate ion, added nitric acid or inorganic nitrates, acted similarly.

(f) Propionic Acid Substitution for Acetic Acid.

Propionic acid was substituted for acetic acid, and their differences qualitatively observed. The ammonium hexanitratocerate(IV) salt appeared to be somewhat less soluble in the propionic acid. Other than that, the propionic acid solution displayed the same characteristics as observed for acetic acid: orange solution going to red upon the addition of perchloric acid, reduced stability in the presence of perchloric acid, and no gaseous decomposition products.

(g) Qualitative Nature of the Precipitate Recovered from the Reagent After Long Standing.

The reagent containing only glacial acetic acid as the solvent precipitated an orange solid when stored in a reservoir protected from the light and atmospheric moisture. A sample of the finely divided orange solid was dried over potassium hydroxide and calcium chloride for several days in a vacuum desiccator. The sample was then subjected to further drying for twenty-four hours in an Abderhalden apparatus containing potassium hydroxide and calcium chloride under reduced

pressure as the desiccant and at boiling acetic acid temperature. The infrared absorption spectrum of a Nujol mull of the dried orange solid was nearly identical with the spectrum of ammonium hexanitratocerate(IV).

The addition of sufficient water to bring the final concentration up to approximately 1M prevented the precipitation of the orange solid and also increased the stability of the reagent.

B. Reaction Kinetics

(a) Water and Cerium(IV) Dependence.

The water dependence on the reaction rate was determined in the following manner. Six 135 ml. solutions of varying water concentrations in acetic, perchloric acid were prepared: 100 ml. of approximately 1.5N perchloric acid in acetic acid was pipetted into each of six 200 ml. volumetric flasks, and varying amounts of acetic anhydride and complementary volumes of acetic acid sufficient to bring the total volume to 135 ml. were added. These solutions were stoppered and allowed to equilibrate overnight in a constant temperature bath at $25^{\circ}C. \pm 0.5^{\circ}C.$

The following day 10 ml. of each was removed by pipet, and the water content determined by the Karl Fischer method on portions of these samples.

Fifty ml. of the cerate reagent, also at $25^{\circ}C.$, was added to each of the samples at recorded times. Twenty-five ml. samples were removed from the well mixed solutions at recorded intervals by pipet and transferred into beakers containing 15 ml. of approximately 0.04N sodium oxalate in acetic acid. One ml. of perchloric acid was then added, and the excess oxalate back titrated with the standardized cerate reagent to an amperometric end point.

A plot of the logarithm of the cerium(IV) concentration against time gave a family of straight lines (Figure 4). The slopes of these

lines, d[Ce]/dt, plotted against the reciprocal water concentration also gave a straight line (Figure 5).

(b) Perchloric Acid Dependence.

The effect of perchloric acid concentration on the decomposition rate was determined in an analogous manner. One hundred and fifty ml. solutions of acetic acid, varied amounts of 70% perchloric acid, and calculated amounts of acetic anhydride to give a final water concentration of 1.2M were prepared. These solutions were allowed to remain in the constant temperature bath at 25°C. ± 0.5°C. for at least forty-eight hours. The water concentration was then determined with Karl Fischer reagent and adjusted to 1.2M by the addition of acetic anhydride or water. The perchloric acid concentration was determined by a visual titration with a standard solution of sodium acetate in glacial acetic acid to a crystal-violet blue-green end point.

One hundred and twenty-five ml. of the solutions of nearly constant water concentrations and varied, but known, perchloric acid concentrations were pipetted into volumetric flasks. Fifty ml. of cerate reagent at 25°C. was added to each at recorded times. Determination of the cerium(IV) at various time intervals was carried out as described for the water dependence study.

Figures 6 and 7 summarized the results from this study.

Titration of the perchloric acid before and after decomposition indicated that its concentration was depleted in the course of the reaction (Table V). As a consequence of this phenomena, an attempt was made to more thoroughly investigate the lower acid concentrations in an effort to detect a break in the perchloric acid dependence. It was believed that perhaps a point would be reached where the ratio of the amount of acid added to the amount of acid consumed would become such that the presumably acid catalyzed oxidation would not exhibit a linear

Table V. Change in $HClO_4$ in the Course of Cerate Decomposition.

N Before Decomposition	N After Decomposition	Change in N
1.174	1.092	-0.082
1.034	0.939	-0.095
0.801	0.706	-0.095
0.548	0.554	+0.006
0.318	0.277	-0.041
0.189	0.144	-0.045

acceleration proportional to the perchloric acid added. This objective was only partially met due to the difficulties of working with the numerous variables at the concentration ranges desired. Table VI and Figure 8, however, show the results of two experiments which seemed to indicate a diminishing decomposition rate with decreased perchloric acid concentrations.

Table VI. Comparison of Decomposition Rate with $[HClO_4]$.

N $HClO_4$	Time Required to Reach 0.06M Ce(IV)	Ce(IV) Initially
0.029	44 hr.	0.00874
0.42	29 min.	0.00868
0.86	6 min.	0.00860
1.33	3 min.	0.00860
1.71	2 min.	0.00860
0.0078	44 hr.	0.00772
0.011	37 hr.	0.0772
0.10	6 hr.	0.0735
0.22	70 min.	0.0736

(c) Influence of the Ammonium Ion.

The addition of ammonium nitrate to the cerate-perchlorate solution seemed to decrease the rate of cerium reduction. When sufficient perchloric acid was added to neutralize the additional ammonium nitrate, however, no significant alteration in the rate was noted. Four samples with 0.0394 g., 0.0612 g., 0.1264 g., and 0.2504 g. of ammonium nitrate and the calculated amount of perchloric acid in 50 ml. of cerate reagent 1N in perchloric acid were used.

The ammonium ion was quantitatively recovered to further substantiate the above observation. The ammonia was determined with a micro Kjeldahl apparatus. A few drops of 1-octanol was added to the sample container to prevent foaming. The ammonia was steam distilled into saturated boric acid. The BO_2^- was titrated with 0.0777N hydrochloric acid to a freshly prepared methyl red end point. Samples were run on a cerate reagent blank and on both the filtrate and precipitate of a filtered, decomposed reagent solution.

(d) Influence of Perchlorate, Nitrate, and Acetic Acid.

The nitrate or perchlorate ions did not greatly effect the rate of decomposition.

It was not possible to check the influence of the acetic acid. An attempt was made to find a mutually satisfactory solvent for both the ammonium hexanitratocerate(IV) salt and the acetic acid, but no such solvent was discovered.

C. Tests for Free Radicals

Cerium(IV) oxidations are sometimes explained on the basis of free radical processes (53, 63). Therefore, the following experiments were run to qualitatively eliminate or prove the existence of free radicals in this situation.

(a) Electron Paramagnetic Resonance Spectra.

Samples were run on the electro paramagnetic resonance equipment of the physics department of Michigan State University. No free radicals were indicated.

(b) Free Radical Scavengers.

The use of chemical scavengers also gave no indication of the presence of radicals. Styrene, acrylonitrile, methyl methacrylate, and methylacrylate were all used. A blank of lead tetraacetate decomposing in glacial acetic acid at 115°C. gave positive tests in all four cases (3, 46). 1, 1-Diphenyl-2-picrylhydrazine also gave negative results with the decomposing cerate solution (51). None of the latter reagent was available to run with the lead tetraacetate blank, however.

(c) Influence of Oxygen and Light on the Reaction Rate.

Purging the cerate solution with nitrogen or oxygen prior to the addition of the perchloric acid did not visually influence the reaction.

There was a noticeable light dependence on the decomposition rate of the cerate reagent solution. Similarly, there was a small but detectable light dependence on the solution containing perchloric acid (Table II).

D. Efforts to Identify the Reaction Products

(a) Isolation and Qualitative Analysis Techniques.

Ultraviolet or visible spectra failed to give any characteristic absorption, due to the complexity of the resulting solution.

All efforts to utilize distillation techniques were also to no avail. Attempts to isolate the oxidation products were made at both atmospheric and reduced pressures. In all cases one seemed to isolate only acetic acid; a yellow fraction as the last distillate cut; and a

residual solution of strong acids, nitric and perchloric. The yellow color in the one fraction seemed to be due to nitrogen dioxide. The ultraviolet spectra of the residual solution, when diluted considerably with water, displayed absorbency maxima at 239 mμ. and 252 mμ. (Figure 9).

A sample placed in a closed train of absorption towers was hooked to an aspirator and bubbled with dry air for almost two weeks in an effort to pull off all the liquids at room temperature. Once again only a heavy viscous solution remained. The inorganic salts had previously been precipitated out by pouring the solution into a large excess of ether. The ultraviolet spectra of the viscous solution gave an absorption peak at 295 mμ. (Figure 10).

Steam distillation was also tried on a neutralized solution of the decomposed solution. This solution was then saturated with carbon dioxide and again distilled. Qualitative organic analysis on the two distillates failed to indicate any organics present. Included in the qualitative tests were tests for enols (52), carbonyls (65), formaldehyde and formic acid (16), and dioxo and oxomethylene (43) groups.

The above tests along with others were run on appropriate blanks as well as other decomposed and decomposing samples. The haloform reaction (66) and the nitroprusside test (7, 44) for methyl ketones gave negative results. Feigl's succinic acid test was also negative (19). No indication of the presence of peroxides was observed based on the oxidation of reduced phenolphthalein (18, 59).

The test for enol, however, deserves further mention. The test was based on the addition of bromine to the alkene linkage with subsequent loss of hydrogen bromide to give a monobromide derivative. The liberation of iodine by the latter upon the addition of iodide to an acid solution indicated enolization. The excess bromine was removed with sulfur dioxide. All the samples tested (acetoacetic ester,

decomposed reagent, a solution of 1N perchloric acid and 0.18N nitric acid in acetic acid, and a solution of 1N perchloric acid in acetic acid) gave evidence of the liberation of iodine. A blank of 1N perchloric acid in acetic acid did not liberate iodine upon the addition of aqueous potassium iodide. In addition, the solution of acetic acid 1N in perchloric acid reduced 2% potassium permanganate. The near infrared spectra of acetic acid was altered appreciably by the addition of perchloric acid (20). A blank of perchloric acid did not absorb in the region in question (20) (Figure 11).

Extraction procedures using such solvents as benzene, carbon tetrachloride, and ether did not prove applicable. These extractions were carried out at various pHs during the neutralization of the decomposed solution. In all cases only inorganic salts remained after evaporation of the solvents at room temperature.

Extractions were also carried out on the bicarbonate solution remaining from the steam distillation procedure. Ether, benzene, carbon tetrachloride, hexane, and n-butyl acetate were used. A few colorless needles formed from the latter two extractants. These crystals melted at 107-109°C. to a yellow oil. Ammonium bicarbonate melts at 107°C. and could be present at this point.

A procedure utilizing both precipitation and extraction gave prospects of isolation. It was noted in all instances, where a decomposed reagent solution was allowed to stand for considerable time, that the solution took on a yellow cast. This procedure made it possible to isolate a very small amount of yellow-brown oil. The oil gave a characteristic infrared absorption spectrum, when measured on a Perkin Elmer Recording Infrared Spectrophotometer, Model 21, and boiled at approximately 95°C., as determined by the micro technique of Shriner and Fuson (65) (Figure 12). The isolation procedure was as follows: The white precipitate, ammonium perchlorate, was removed

by filtration through a medium porosity sintered glass filter. The solution was then made anhydrous by the addition of acetic anhydride and an excess of potassium acetate was added. The solids were again removed by filtration. Treatment of the filtrate with a four to five-fold excess of dry ether gave still more solid which was filtered off. The solids removed were dried in a vacuum desiccator over calcium chloride and potassium hydroxide pellets and then transferred to a Soxhlet extraction apparatus where they were extracted for twelve to twenty-four hours with dry benzene. The benzene was evaporated at room temperature leaving a small amount of yellowish-brown oil. An effort was made to increase the production of this yellowish oil, and hence the isolation yield, by continued addition of solid ammonium hexanitratocerate(IV) and perchloric acid to a decomposed reagent solution. Such efforts were not successful, however, causing one to doubt the existence of the oil as a product and or casting doubt on the efficiency of the isolation technique. Evaporation of an equal quantity of commercial benzene did not give the oil.

Some qualitative organic analyses were run on minute samples of the oil without any positive identification of functional groups.

Attempts to crystallize the oil from numerous solvents was also unsuccessful. As a result of these attempts, however, it was found that the oil was soluble in hexane.

The infrared spectrum gave a well defined pattern but seemed to display only carbon, hydrogen absorption (Figure 12). There was a small peak at 5.9 and 3.1 μ. but not sufficient to suspect the carbonyl or carboxyl groups as the principal absorbing species, but rather, perhaps only as minute impurities.

The yellow oil in hexane was subjected to vapor phase chromatography on a Beckman GC-2 Chromatograph. Only one compound was observed. The apparatus was operated at 70^{o}C., gas pressure of 30 p.s.i. attenuator 1, and 250 m.a.

The nuclear magnetic resonance spectra of a sample of the decomposed reagent solution and an appropriate blank were recorded. The spectra gave no indication of the presence of absorbing species other than the system itself.

Polarographic analysis was attempted in anticipation of detecting any readily reducible compounds in solution. A Sargent Polarograph, Model XXI, was used. This technique proved useless for the decomposed solutions, however, apparently due to the presence of nitric acid, which could not be removed without further contamination or destruction of the sample. A very small amount of the yellow oil in acetic-perchloric acid seemed to give an oxidizing wave.

A number of acid-base titrations were carried out with tetrabutylammonium hydroxide (11) as the titrant and acid free methyl isobutyl ketone (9) as the differentiating solvent for the acid mixtures. The reagent was standardized against benzoic acid to a potentiometric end point using a sleeve-type calomel electrode in conjunction with a glass electrode on a Beckman Zeromatic pH Meter. A typical standardization curve is illustrated by Figure 13.

Several samples of decomposed reagent were titrated. Three distinct breaks were observed on all occasions. A representative titration curve is shown by Figure 14. Since nitric acid was suspected as one of the acids present, samples were titrated with a known amount of dilute nitric acid added (Figure 15).

Samples of undecomposed cerate reagent were also titrated. Only two breaks were observed in these titrations prior to decomposition (Figure 16). A nitric acid "spiked" sample was also titrated (Figure 17).

A summary of the data compiled as a result of these titrations is tabulated in Table VII.

Table VII. Compilation of Data Derived from the Tetrabutylammonium Hydroxide Titrations.

Sample	Normality of T.B.A.H.	Equivalence Points (ml.)	Volumes/ Eq. Point (-HNO_3)	Ratio of Meq. H^+/Meq. Ce(IV)	Millivolts at Eq. Point
D-0.25*	0.083	2.05	2.05		387
		3.23	1.05	3.23	233
		4.28	1.18	3.62	137
D-0.25	0.077	1.87	1.87		372
		3.08	1.21	3.45	187
		4.15	1.07	3.05	85
D-0.25 + 0.1N HNO_3	0.077	1.87	1.87		392
		4.34	1.50	4.66	223
		5.81	1.47	4.52	121
D-0.25 + 0.1N HNO_3	0.073	1.94	1.94		382
		4.22	1.26	3.14	217
		5.38	1.16	3.41	123
2 ml. of Reagent	0.083	0.83	0.83		214
		2.93	2.10	3.34	142
4 ml. Reagent + 0.1N HNO_3	0.083	2.32	2.32		---
		6.96	4.64	3.38	---

*D-0.25 designated decomposed reagent solution 0.25N in perchloric acid. One ml. of D-0.25 and 1 ml. of D-0.25 plus 1 ml. of the nitric acid solution were titrated. Similarly 1 ml. of 0.1N nitric acid was added to the volumes of undecomposed cerium(IV) indicated.

The potential values at the equivalence points varied considerably; therefore, it would seem that the qualitative nature of the acids present could not be based on this data.

All other attempts to isolate the reaction products having failed, a request was made to The Dow Chemical Company for the use of their mass spectrometer equipment. The request was graciously granted, and samples of the decomposed solution, the yellow-brown oily substance, and appropriate blanks were analyzed.

The instrument utilized was of the magnetic scanning, ninety degree sector type. Samples were run at various temperatures ranging from room temperatures up to 250°C. The analyzer tube pressure was 10^{-9} to 10^{-10} mm. of mercury and the sample inlet system about 10^{-1} to 10^{-2} mm. of mercury with the sample introduced. The instrument had a mass range of one to seven hundred and required approximately three minutes to scan one hundred mass units. The only materials in contact with the sample were glass, platinum, and Teflon.

The oil gave only a small amount of an unidentifiable compound, or compounds, with sufficient vapor pressure to be observed.

Solution samples containing perchloric acid were not analyzable. The perchloric acid apparently attacked the glass, giving rise to a multitude of silicon containing fragments that made spectra interpretation impossible.

E. Oxidation of Some Organic Molecules

Several compounds previously isolated by other investigators from the oxidation of acetic acid or compounds that might be proposed on the basis of postulated mechanisms were subjected to oxidation with the reagent under investigation. Acetoacetic ester and the sodium salt of glyoxylic acid were rapidly oxidized. Glycolic and acetoxyacetic acids were oxidized but far too slowly to be considered for direct analysis. Succinic acid was not oxidized.

V. GRAPHIC AND SPECTRAL CURVES

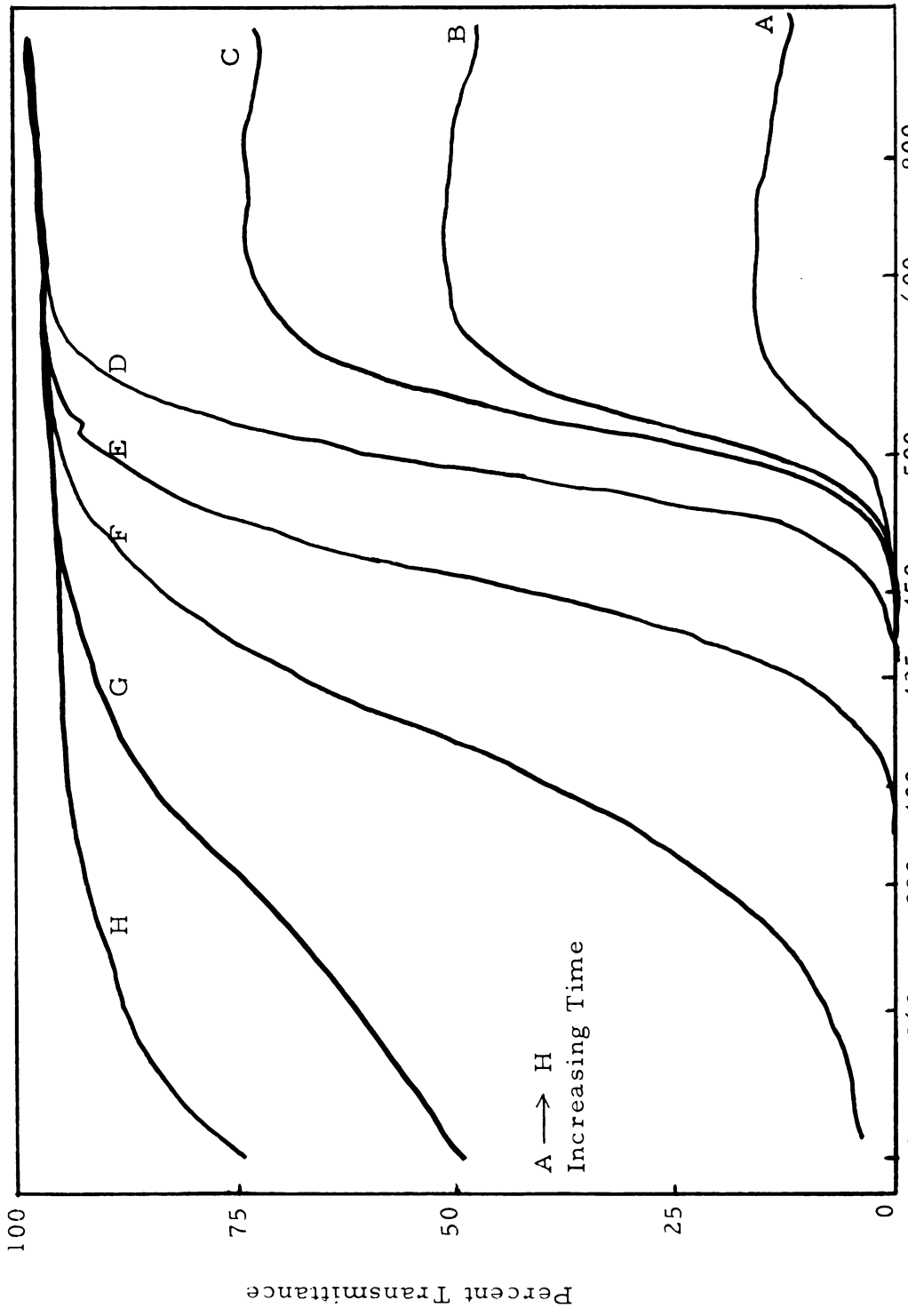


Figure 1. Spectra of Perchloric Acid Acidified Reagent with Time.

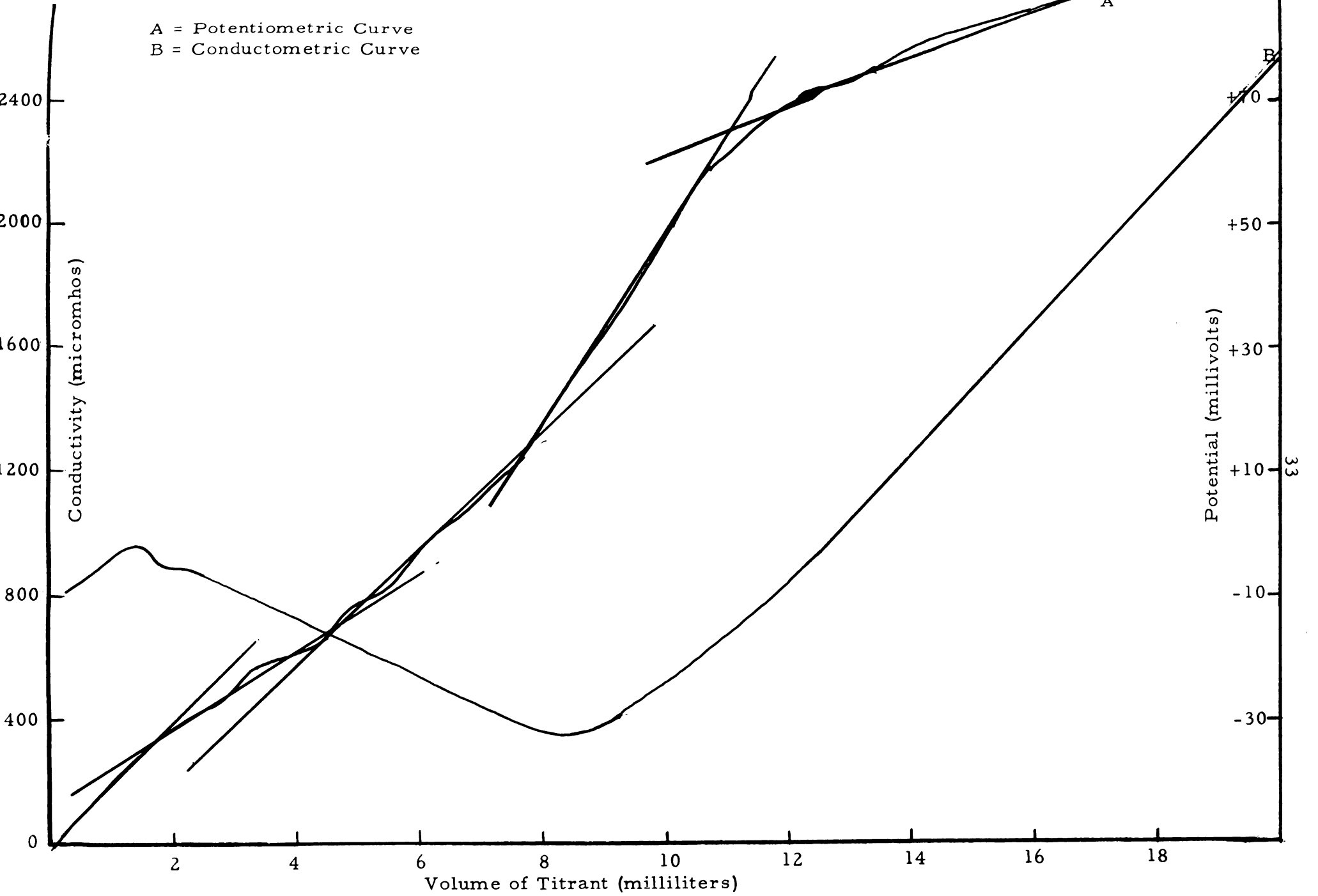


Figure 2. Conductometric and Potentiometric Titration of Cerate Reagent with Perchloric-Acetic Acid Solution.

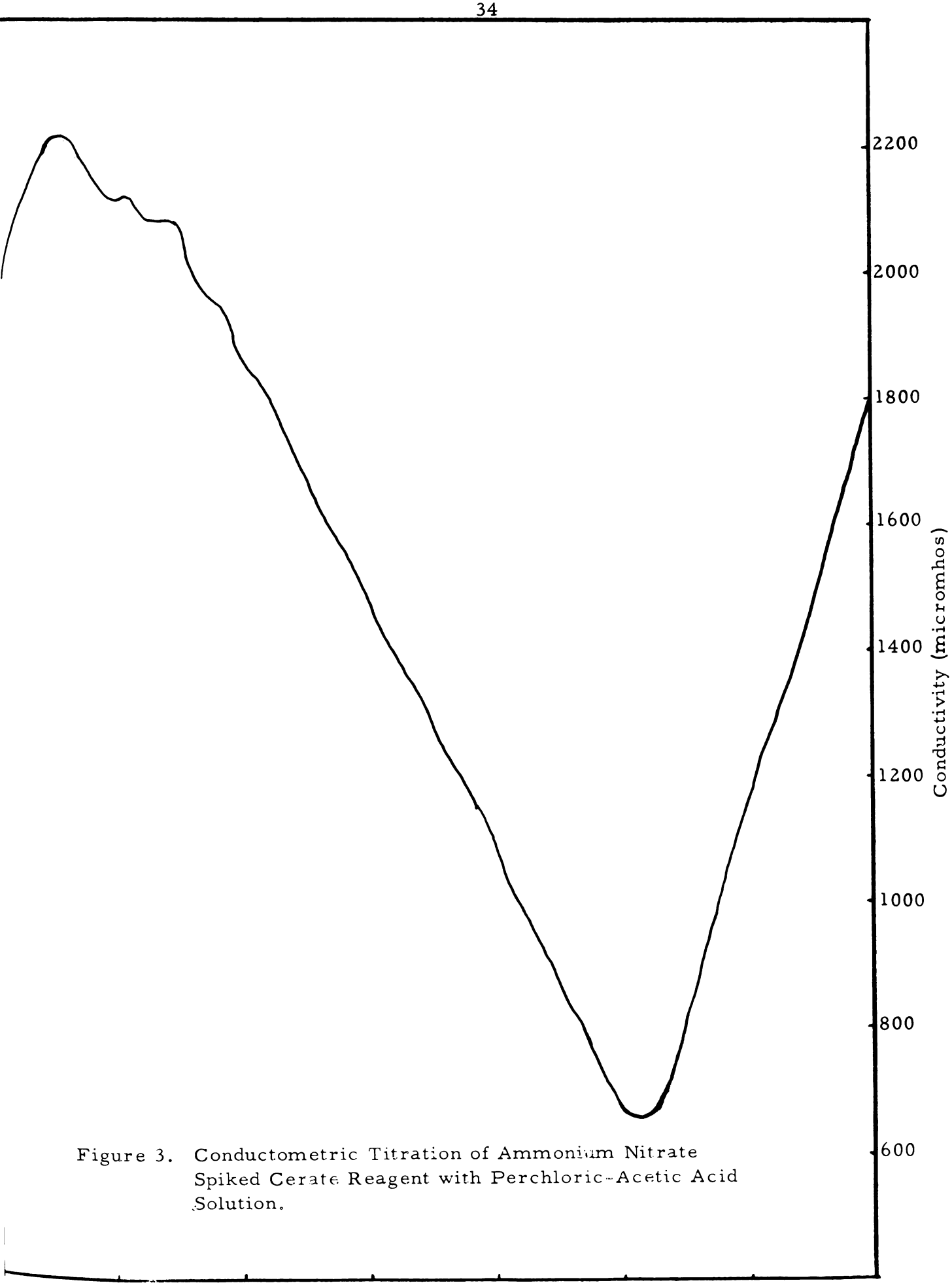
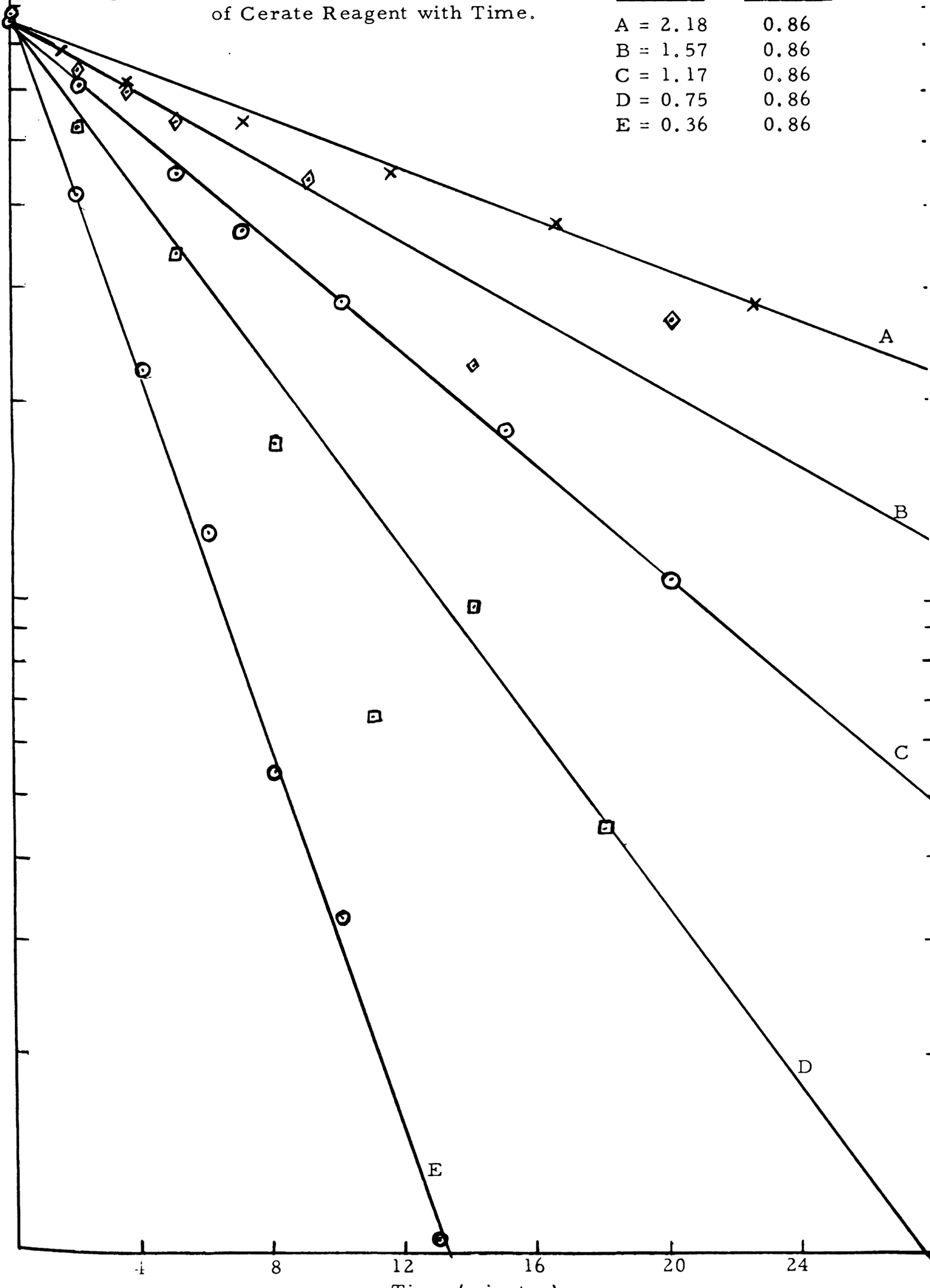


Figure 3. Conductometric Titration of Ammonium Nitrate Spiked Cerate Reagent with Perchloric-Acetic Acid Solution.

Figure 4. Effect of Water on Decomposition of Cerate Reagent with Time.

	$[H_2O]$	$[HClO_4]$
A	2.18	0.86
B	1.57	0.86
C	1.17	0.86
D	0.75	0.86
E	0.36	0.86



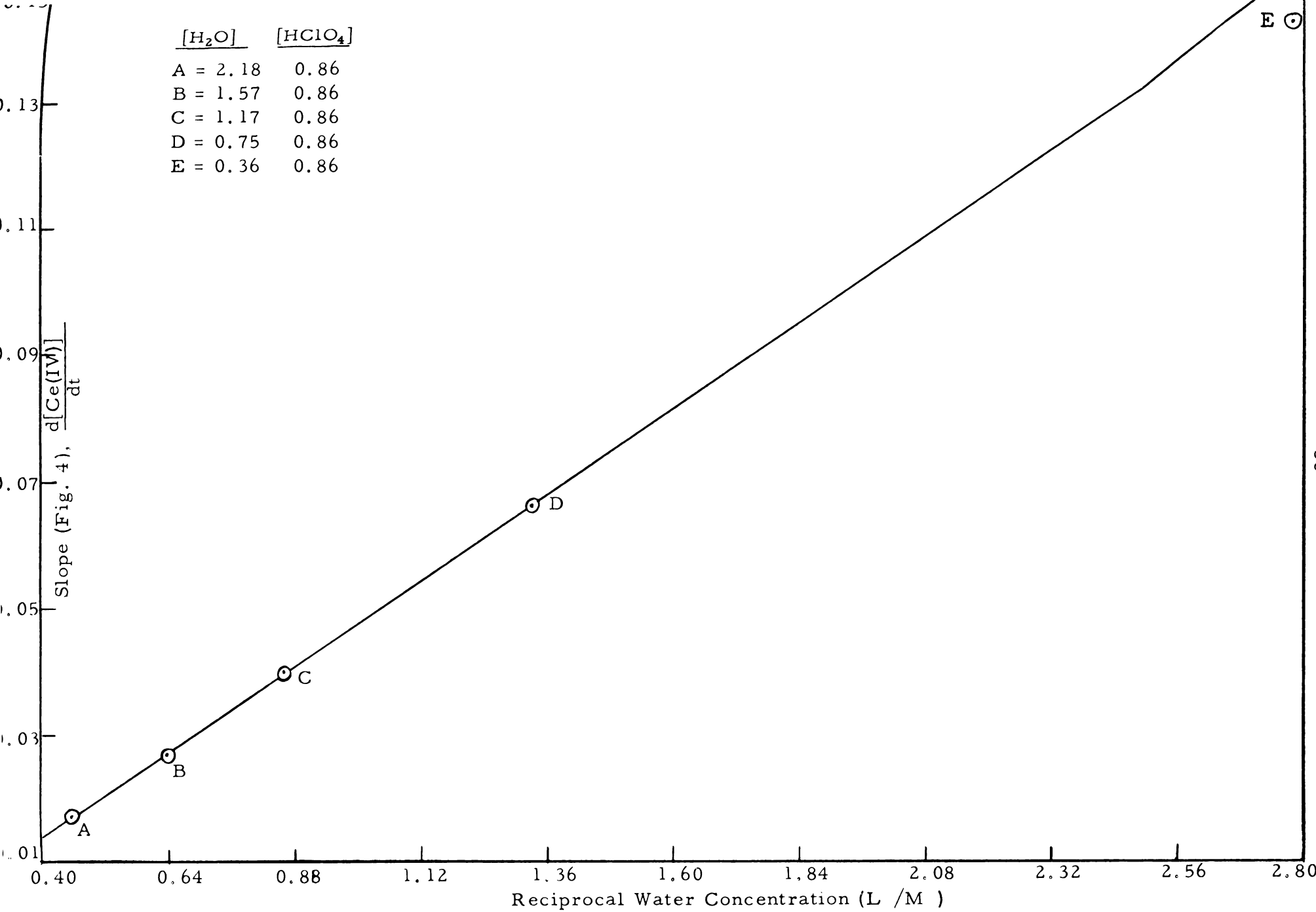


Figure 5. Effect of Water on Rate of Decomposition of Cerate Reagent.

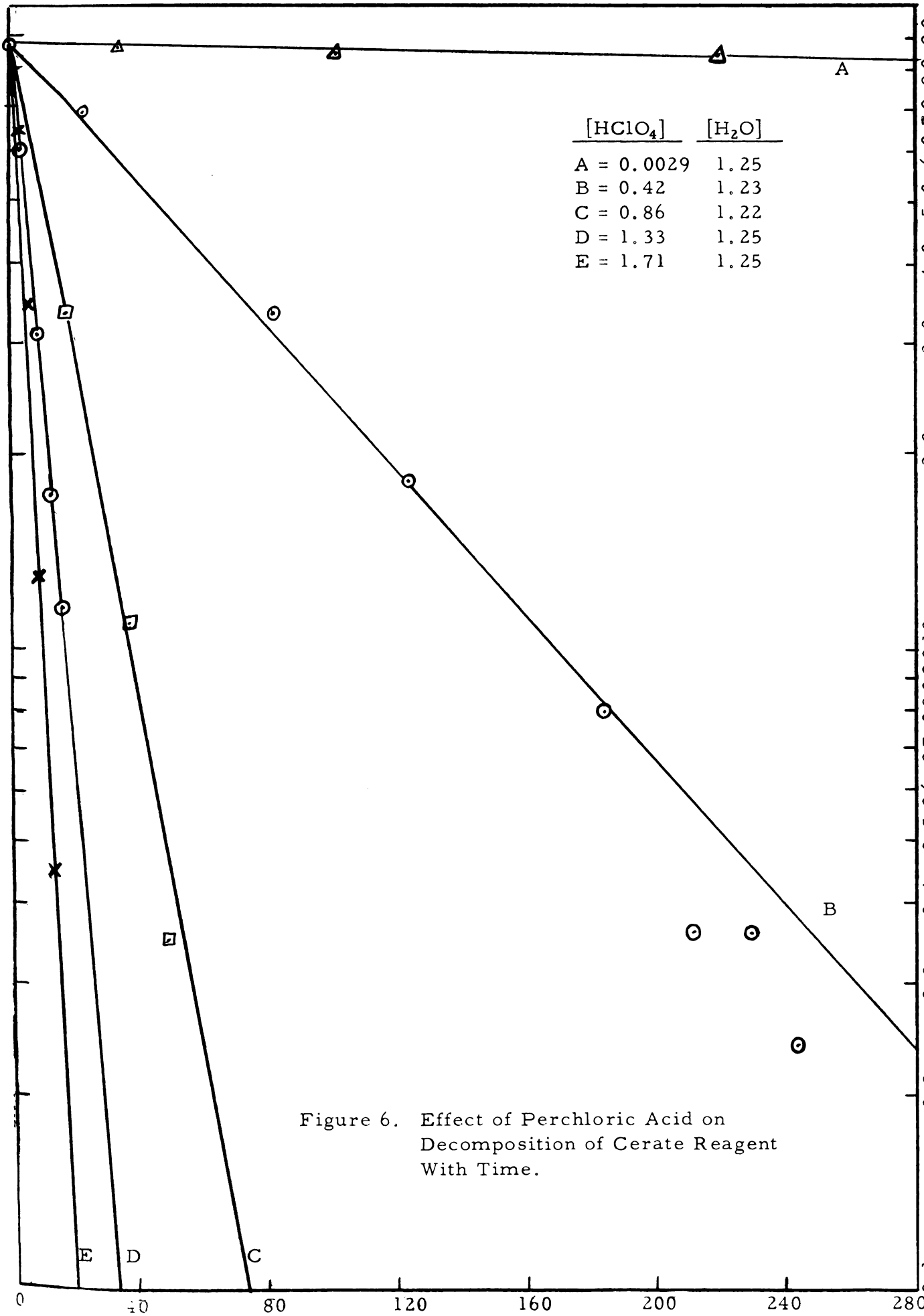


Figure 6. Effect of Perchloric Acid on Decomposition of Cerate Reagent With Time.

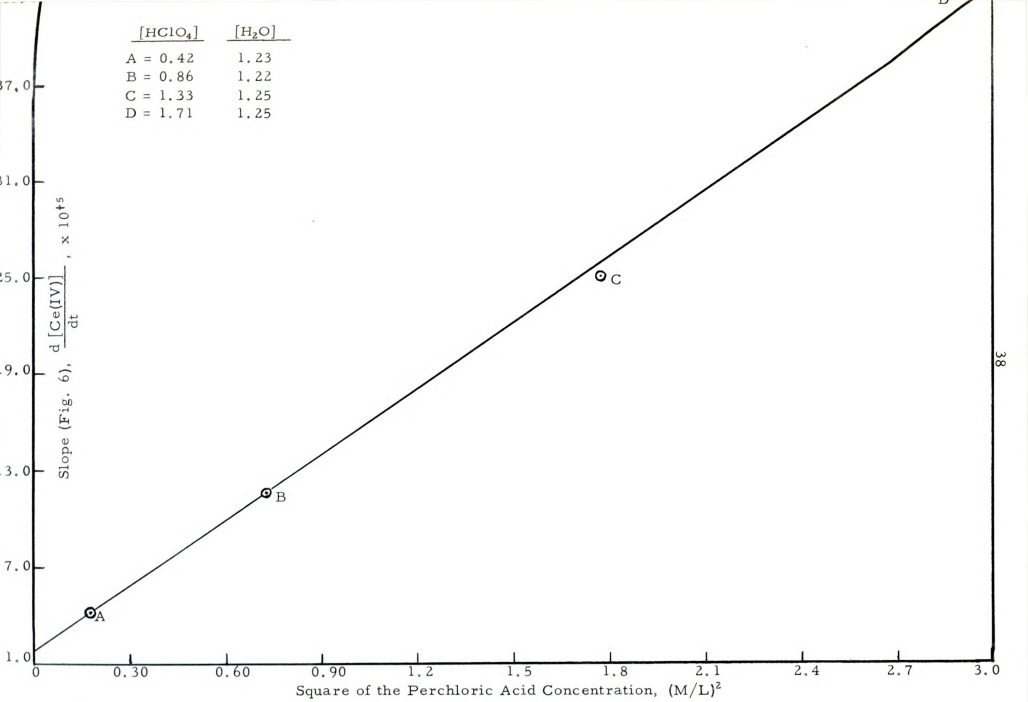
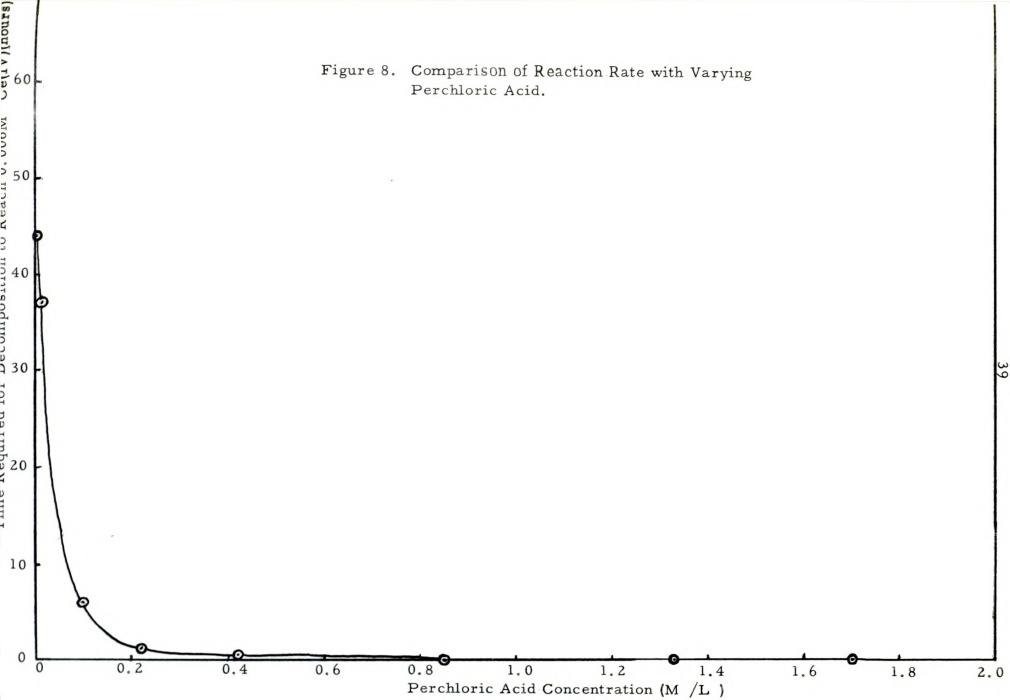


Figure 7. Effect of Perchloric Acid on Rate of Decomposition of Cerate Reagent.

Figure 8. Comparison of Reaction Rate with Varying Perchloric Acid.



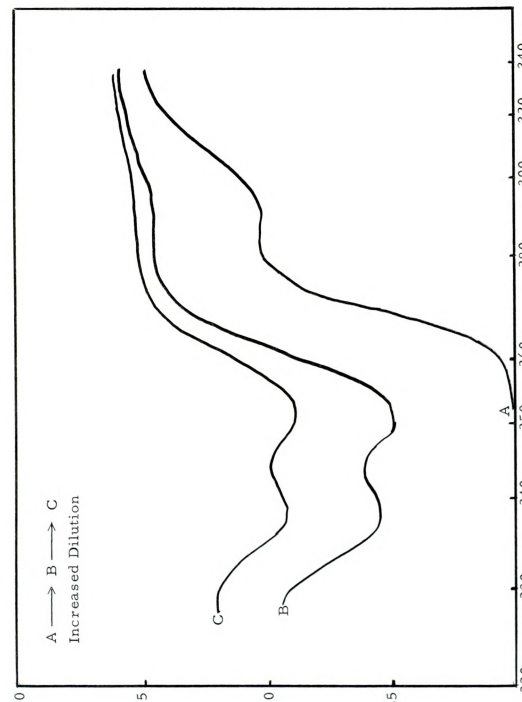


Figure 9. Spectra of Vacuum Distillation Residual Solutions.

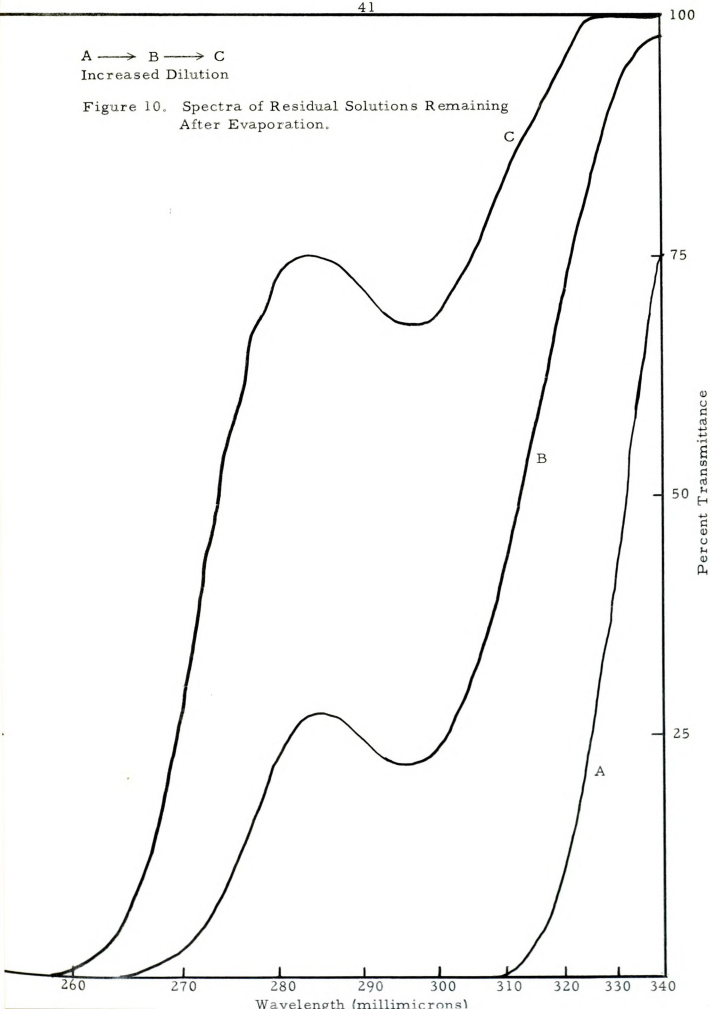


Figure 10. Spectra of Residual Solutions Remaining After Evaporation.

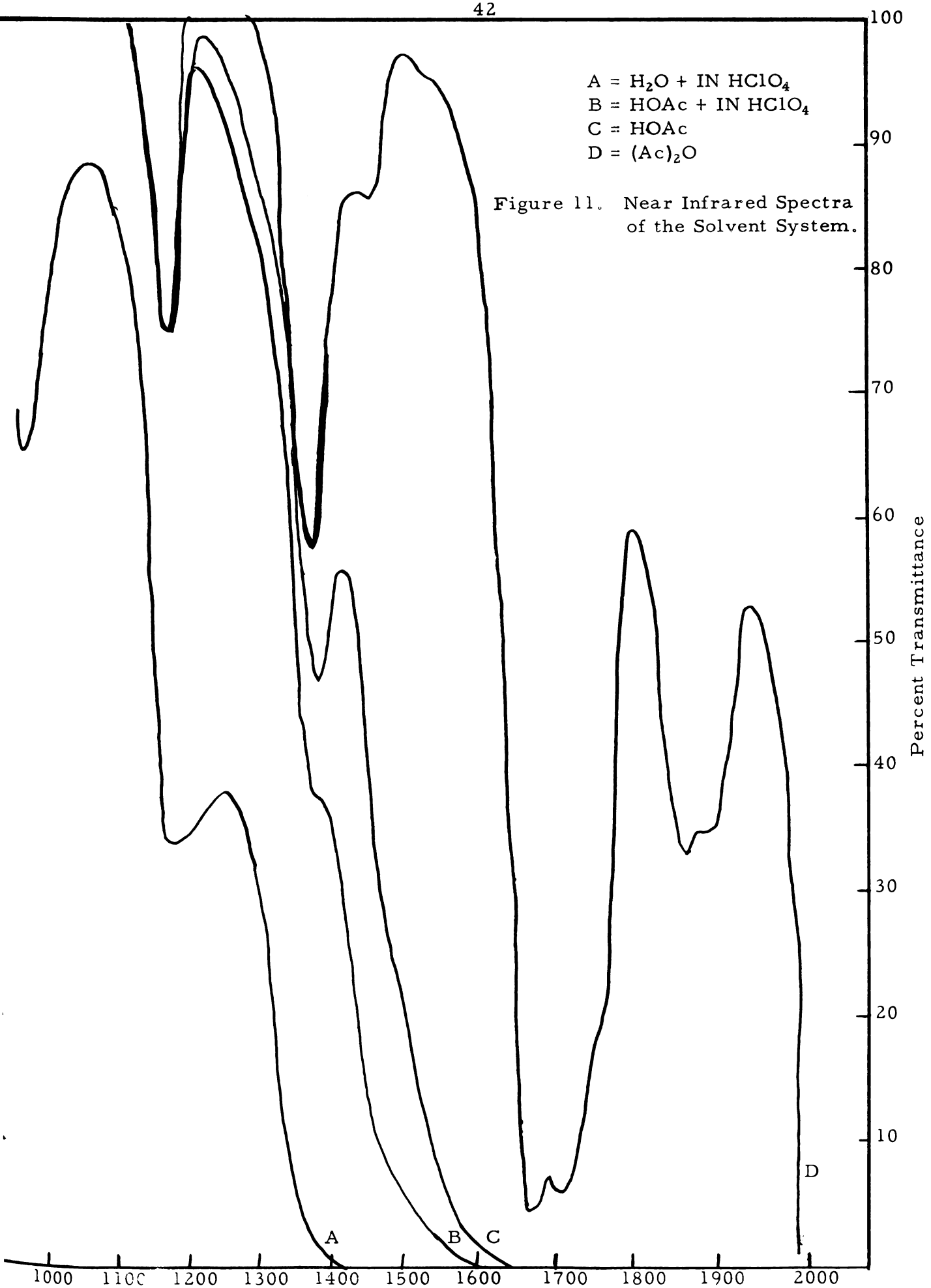


Figure 11. Near Infrared Spectra of the Solvent System.

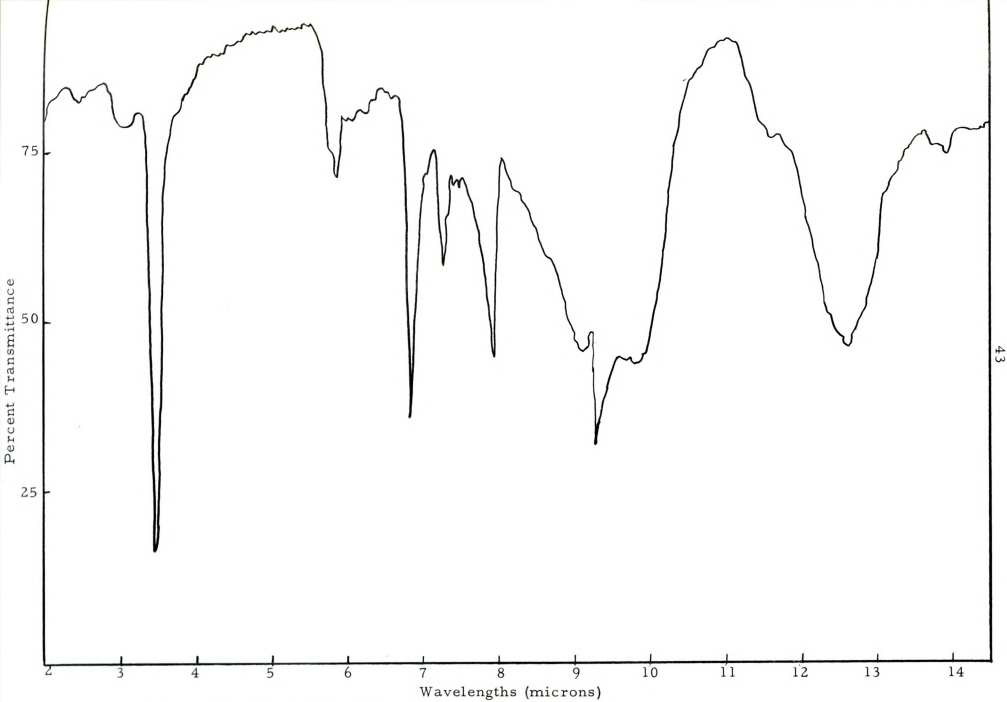


Figure 12. Infrared Spectrum of Unknown Yellow Oil.

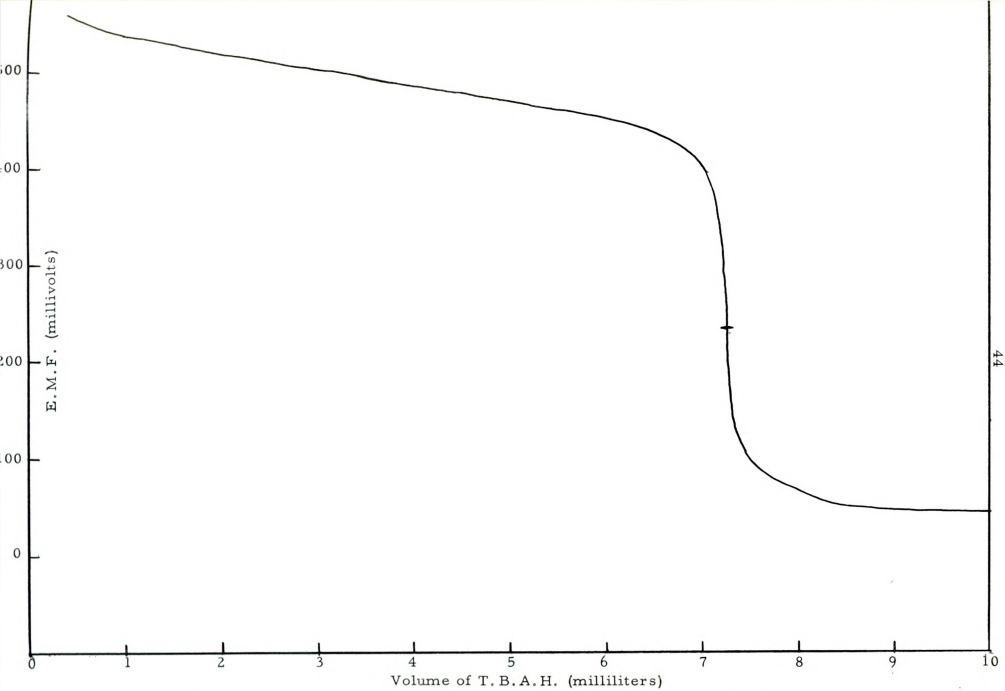


Figure 13. Titration of Benzoic Acid with Tetrabutylammonium Hydroxide.

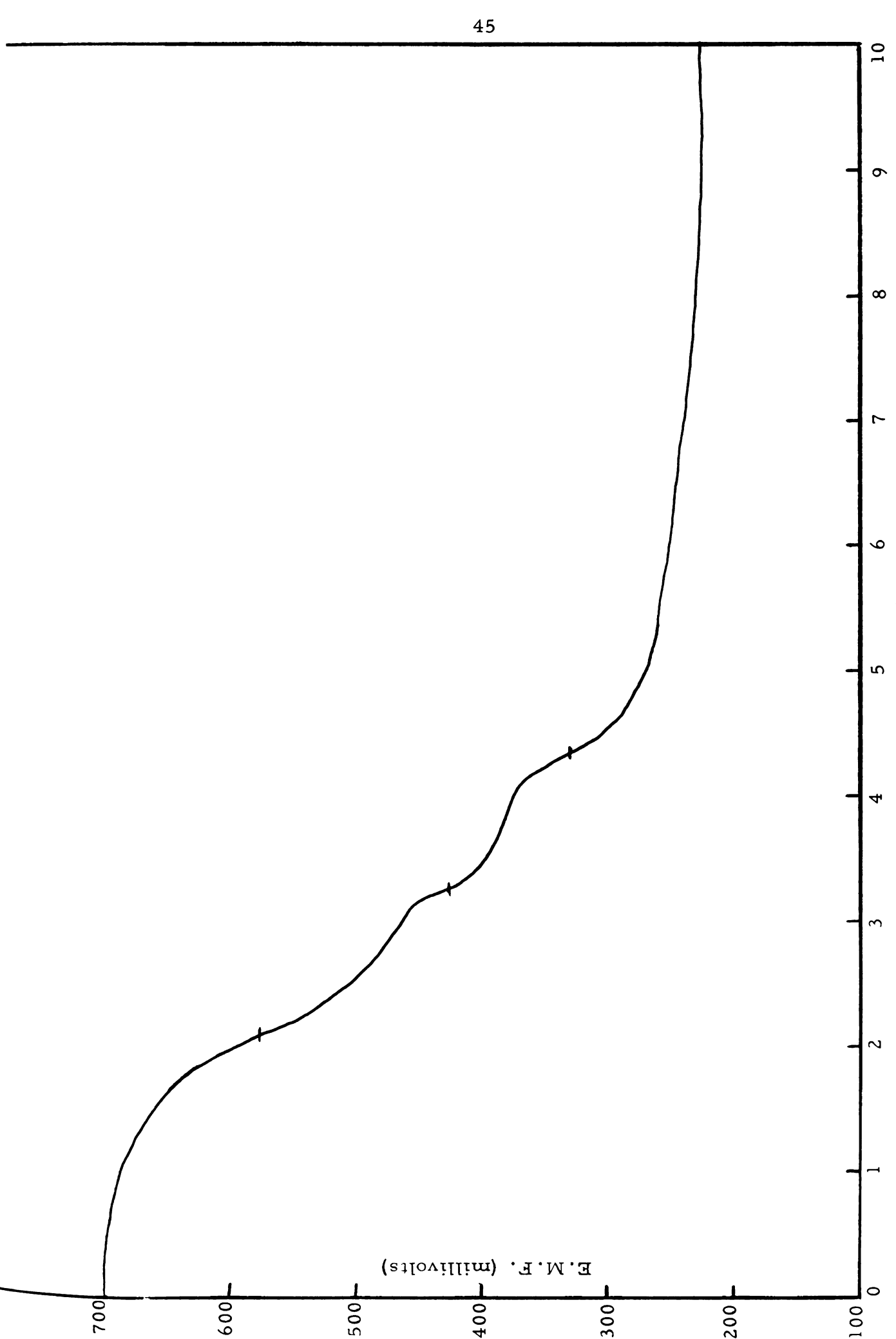


Figure 14. Potentiometric Titration of Decomposed Reagent with Tetrabutylammonium Hydroxide.

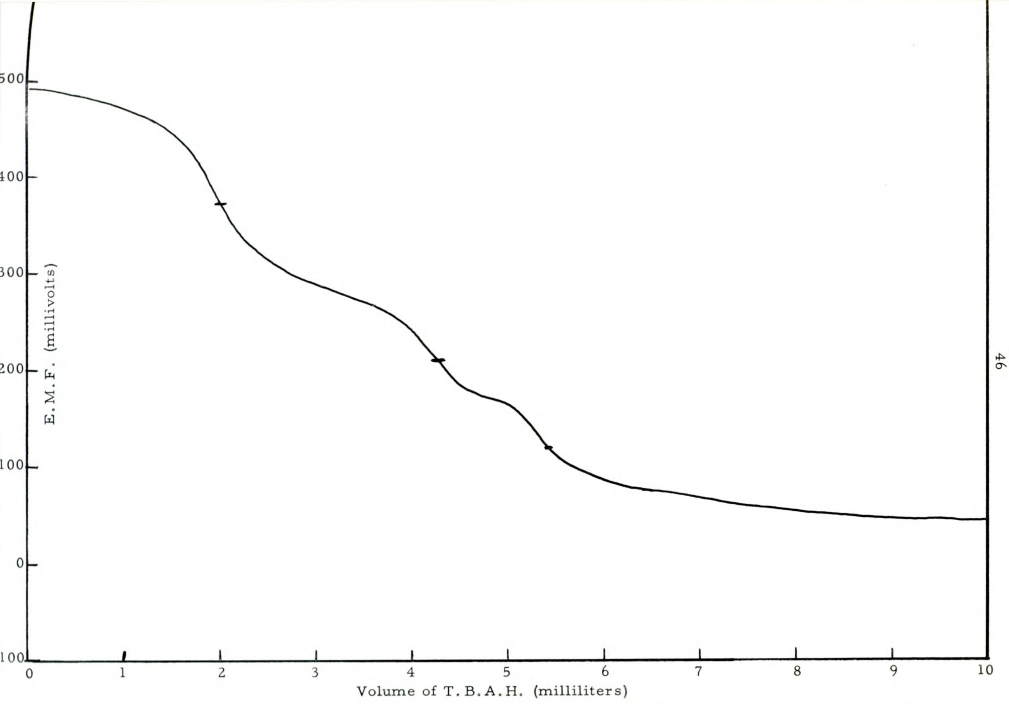


Figure 15. Potentiometric Titration of Nitric Acid Spiked, Decomposed Reagent with Tetrabutylammonium Hydroxide.

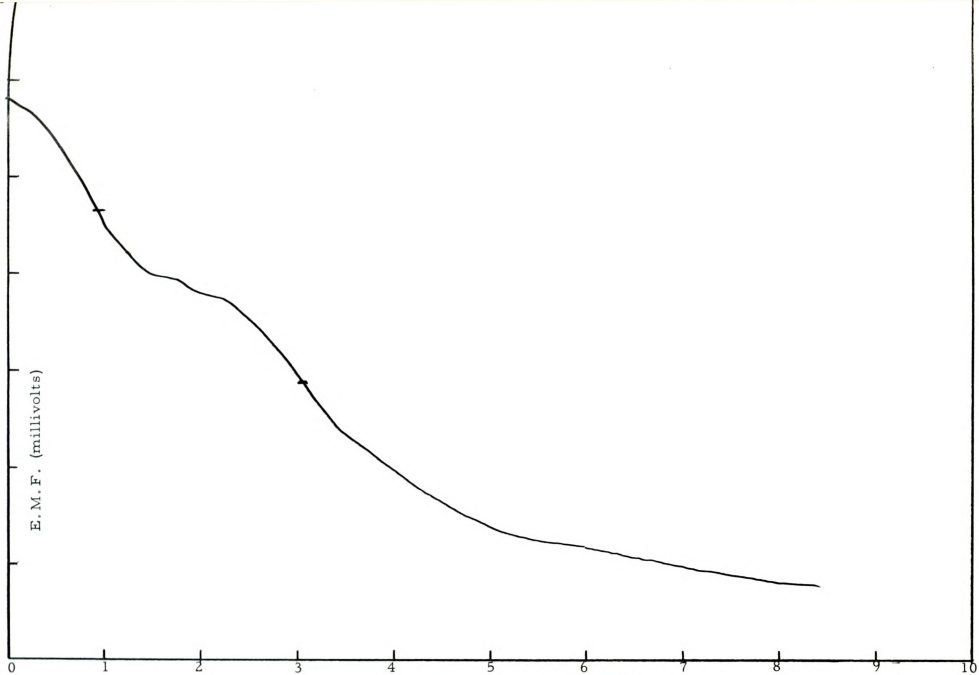


Figure 16. Potentiometric Titration of Undecomposed Reagent with Tetrabutylammonium Hydroxide.

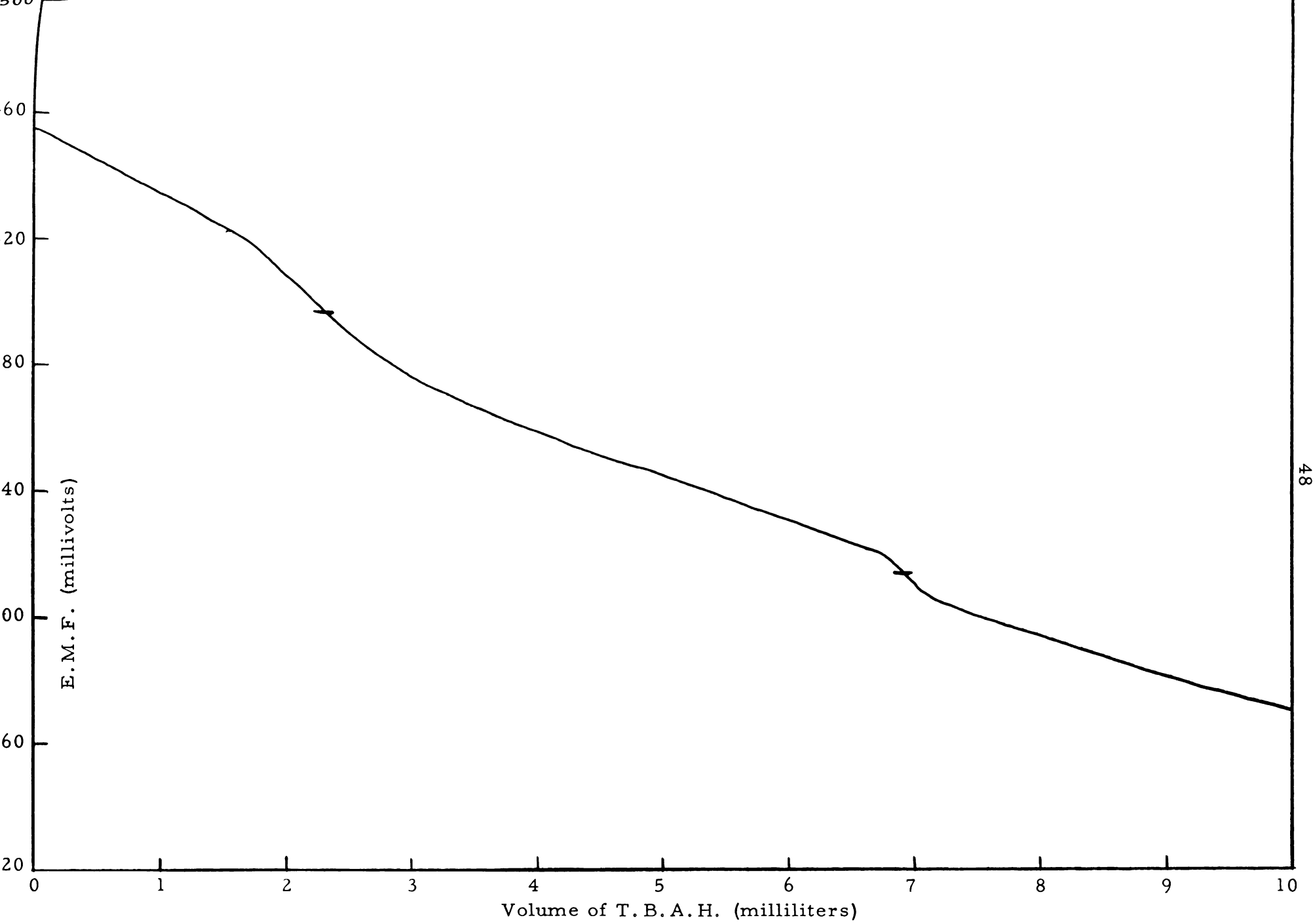


Figure 17. Potentiometric Titration of Nitric Acid Spiked, Undecomposed Reagent with Tetrabutylammonium Hydroxide.

DISCUSSION OF RESULTS

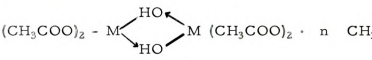
Earlier investigation (35, 38) with this cerate reagent used as a volumetric oxidizing agent indicated a lack of solution stability. The unstability of the reagent was favored by the presence of perchloric acid and by exposure to the light. It was the purpose of this study to investigate and, if possible, to define the phenomenon observed.

An investigation concerning a nonaqueous solvent alone presents many problems to the novice who has been primarily trained in terms of aqueous chemistry. In addition, the system being studied possessed a number of inherent experimental difficulties. The addition of highly corrosive and strongly oxidizing compounds such as perchloric acid, ammonium hexanitratocerate(IV), and nitric acid, multiplied the problems considerably. The presence of perchloric acid alone limits one's scope of operation tremendously. It stymied the use of micro-techniques such as vapor phase chromatography and mass spectrometry, it limited the usefulness of such techniques as distillations and extractions, and continually exposed the investigator to the dangers inherent with perchloric acid chemistry. The work was further complicated by the complexity of the overall system: perchloric acid, water, acetic acid, ammonium hexanitratocerate(IV) and its dissociation products, and reaction products of the cerium(IV) oxidation.

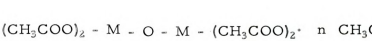
Since no oxidation products were ever isolated from this rather complex system, it was impossible to state with finality the processes that occurred. In the absence of such evidence, however, several physical-chemical techniques have provided sufficient evidence to allow one to speculate on the reactions operative during the cerium(IV) reduction.

First of all, one might anticipate that considerable solvolysis would have occurred in the solution process of the reagent preparation. The orange solid that was gradually precipitated upon standing indicated the possiblity of a solvolytic product of decreased solubility in the acetic

acid system. Impetus was added to this theory by the results of Audreith and co-workers (61) in which they isolated binuclear, crystalline hydroxo- and oxo-acetate complexes,

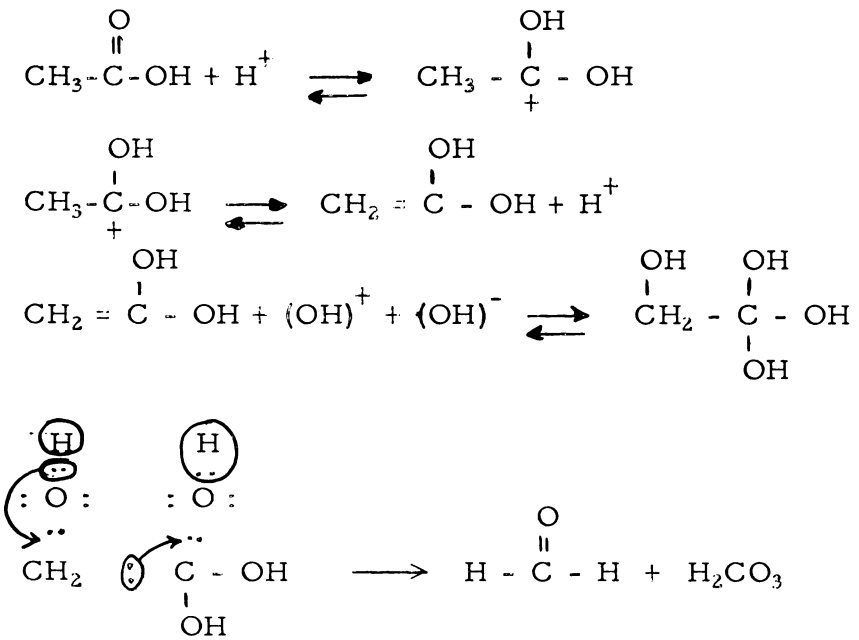


and



in their quest for a means of preparing anhydrous rare earth acetates from rare earth oxides in anhydrous acetic acid. In order to verify or disprove this theory, the orange solid was qualitatively investigated in anticipation of discovering displacement of the nitrate units from the coordination sphere of the cerium atom. It would appear, however, that only solvation or limited solvolysis occurred. There did not seem to be any extensive displacement reactions between the acetic acid or water and the salt. This conclusion was based on the observations that the color of the ammonium hexanitratocerate(IV) in acetic acid gave the orange color typical of the cerium(IV) ion; that the orange solid precipitated from the reagent had an infrared spectrum nearly identical to the original salt; and, as will be discussed later, that only one molecule of nitric acid was liberated per molecule of the salt.

Addition of perchloric acid or hydrochloric acid to the reagent solution altered the cerium species present, as indicated by an immediate deepening of the orange color to red. Nitric acid did not have this effect. The red coloration formed by the addition of perchloric acid rapidly depleted to colorless with a subsequent loss in oxidizing power. There was no evidence of gaseous products formed during this decomposition. This observation would seem to rule out the possibilities of oxidation of the ammonium ion, free radical oxidations, and oxidation of the acetic acid based on a mechanism analogous to an aqueous system:



The oxidation of the ammonium ion was further eliminated from consideration after quantitative recovery of the ammonia was carried out.

This lack of gaseous products, further discussed below, seemed to virtually eliminate free radical processes from consideration. Further experimentation was carried out to substantiate this theory, however, since some cerium(IV) oxidations have been postulated as proceeding by this route (53, 63).

Electron paramagnetic resonance and free radical scavengers gave no indication of intermediate radicals. Furthermore, in agreement with Kharasch and co-workers (46) in their investigation of the oxidation of acetic acid with lead tetracetate, one might anticipate that $\cdot CH_2COOH$ and $CH_3COO\cdot$ would be the primary radicals produced. The radical processes of disproportionation, recombination, etc., of these radicals were shown to produce carbon dioxide, methane, succinic acid, acetoxyacetic acid, methylene diacetate, and formaldehyde. Acetoxyacetic acid was the principal product. The absence of gaseous products,

the inability to isolate succinic acid, the absence of formaldehyde based on the qualitative test with chromotropic acid, and the fact that acetoxyacetic acid and methylene diacetate (40) were slowly oxidized by the reagent would seem to substantiate the theory that the decomposition did not proceed by a radical mechanism involving acetic acid.

These same arguments would also tend to exclude the formation of acetyl peroxide as an intermediate. Acetyl peroxide has been shown to oxidize acetic acid to methane, carbon dioxide, succinic acid, and a small amount of methyl acetate (46, 47).

Many postulated ionic mechanisms gave various organic acids as possible oxidation products of acetic acid. Therefore, acid-base titrations using tetrabutylammonium hydroxide as the titrant and methyl isobutyl ketone as the differentiating solvent were carried out in an effort to detect the presence of such constituents, and or aid in the clarification of the suspected solvolytic reactions involved between the solvent and the cerate salt. Comparing the titrations of undecomposed reagent and decomposed reagent, perchloric acid added, it was noted that the curves possessed an apparent resemblance when one ignored the initial perchloric acid break in the latter titration. Both the decomposed and undecomposed samples apparently contained nitric acid, as verified by the spiking technique, but the ratio of nitric acid after decomposition to the nitric acid present before decomposition appeared to be approximately three to one. The actual concentrations of nitric acid varied somewhat experimentally but always remained in the vicinity of one per cerium(IV) before decomposition and three per cerium(IV) after decomposition. This variation was not at all surprising considering the fact that the nitric acid liberated must certainly have been involved in an equilibrium step between the coordination sphere of the cerium(IV) atom and the displacing agent. Secondly, the fact that the cerium(IV) decomposed slowly, thus decreasing the cerium(IV)

concentration but not decreasing the nitric acid concentration proportionally, would also alter the ratio of nitric acid to cerium(IV).

Further evidence for the presence of nitric acid was the oxidation of the iodide and chloride ions to their respective halogens. Blanks containing free nitric acid or inorganic nitrates acted similarly.

The final break in both titration curves appeared to be due to the same acidic species. This acid required approximately three equivalents of base for each equivalent of cerium(IV). These values also fluctuated somewhat for apparently the same reason as described above.

The fact that the final titration break was present in both samples, decomposed and undecomposed reagent, would seem to imply that the acid was not an oxidation product but rather was a constituent inherent to the system itself.

The following equations, while not the only conceivable explanation, seemed to be the most satisfactory interpretation of the titration data presented.

The titration of undecomposed reagent:

(1) $(NH_4)_2\ Ce\ (NO_3)_6 + CH_3COOH \underset{\longleftarrow}{\overset{H_2O}{\longrightarrow}} (NH_4)_2\ Ce(NO_3)_5(OAc)_x$

$(OH)_y + HNO_3$

The fact that only one nitric acid was found per cerium(IV) in the tetrabutylammonium hydroxide titrations would require that this system acquire a stable equilibrium at the above conditions. $x + y = 1$

(2) $HNO_3 + (C_4H_9N)OH \longrightarrow (C_4H_9N)NO_3 + H_2O$

Titration of the nitric acid would give the first titration break and perhaps supply the thermodynamic driving force for equation (3) by removing the nitric acid.

(3) $(NH_4)_2\ Ce(NO_3)_5(OAc)_x(OH)_y + 3(C_4H_9N)OH \longrightarrow 3(C_4H_9N)NO_3 + 3H_2O + 2\ NH_4NO_3 + Ce(OH)_a(OAc)_b$

The ratio of three acid equivalents per equivalent of cerium(IV) corresponding to the second titration break would be accounted for by the fact that the ammonium ion would act as a stronger Lewis acid than the tetrabutylammonium ion in this medium and thus prevent the titration of the final two nitrate ions. a + b = 4.

The titration of decomposed reagent:

(4) Addition of perchloric acid to the products of reaction (1).

$2(NH_4)_2Ce(NO_3)_5(OAc)_x(OH)_y + 2HNO_3 + 4HClO_4 \longrightarrow (NO_3)_3$ Ce-O-$Ce(NO)_3$ $+ 4NH_4ClO_4 + 6HNO_3$

This reaction would account for the $3HNO_3/Ce(IV)$ ratio, the precipitation of ammonium perchlorate, and the formation of the red color by assuming the oxo dimer as the source.

(5) $6HNO_3 + 6(C_4H_9N)OH \longrightarrow 6(C_4H_9N)(NO_3) + 6H_2O$

(6) $(NO_3)_3Ce\text{-}O\text{-}Ce(NO_3)_3 + 6(C_4H_9N)OH \longrightarrow (OH_3)_3\ Ce\text{-}O\text{-}Ce(OH)_3 + 6(CEH_9N)(NO_3)$

This reaction would account for the final titration break with approximately $3H^+/Ce(IV)$.

While the above equations are not conclusive, they tend to corroborate the existence of dimeric species postulated by numerous investigators (14, 32, 36, 48, 61). The neutral dimeric species would also be compatable with the ion migration experimental observation that the cerium species did not seem to migrate to either electrode under the influence of a d.c. potential.

The postulated dimeric species, while not impossible on the basis of first order cerium(IV) kinetics, would seem to be somewhat less likely than an alternate explanation presented below, however:

(7) Addition of perchloric acid to the products of reaction (1).

$$(NH_4)_2Ce(NO_3)_5(OAc)_x(OH)_y + HNO_3 + 2HClO_4 \longrightarrow 2NH_4ClO_4 + 3HNO_3 + H_2Ce(NO_3)_3(OAc)_n(OH)_p$$

where $x + y = 1$ and $n + p = 3$.

This would satisfactorily account for the 3 H^+/Ce(IV) ratio and also for the color change if the acid species was red. Jones and Soper (45) investigated an analogous color change in aqueous-sulfuric acid solutions of ceric sulfate and showed that the color was due to a highly solvated species, $H_4Ce(SO_4)_4$. $H_2Ce(ClO_4)_6$ has also been said to be red. The fact that perchloric and hydrochloric acids produced the color change, while nitric acid did not, would seem to support this theory; since the former two acids are both stronger acids in acetic acid than nitric acid. Therefore, it would seem logical to speculate that the ceric acid species was responsible for the color change.

(8) $$H_2Ce(NO_3)_3(OAc)_n(OH)_p + 3(C_4H_9N)(OH) \longrightarrow 3(C_4H_9N)(NO_3) + Ce(OAc)_a(OH)_b$$

where $n + p = 3$ and $a + b = 4$.

Equation (8) would account for the final titration break corresponding to three acid units per cerium(IV).

The inability to define the colored intermediate as to its charge and composition by ionic migration, ion exchange chromatography, photometric titration, and absorption spectroscopy prompted us to

look at the conductivity characteristics of a sample of cerate reagent when titrated with an acetic acid solution of perchloric acid. The titrations gave reproducible and characteristic conductivity curves composed of a well defined maximum and minimum (Figure 2).

The initial increase in conductivity was believed to be due to the addition of hydrogen and perchlorate ions from the "super acid," perchloric acid. When sufficient perchloric acid had been added to exceed the solubility product of ammonium perchlorate, the conductivity began to decrease as precipitation began to occur. This phenomenon, of course, resulted in a conductivity maximum. The decrease in conductivity was attributed to the removal of ammonium ions by precipitation and by the elimination of the proton and nitrate ions through the formation of only slightly dissociated nitric acid. Spiking of a sample with ammonium nitrate did not alter the slope of the titration curve, thus verifying it as the substance being titrated.

The minimum in the titration occurred at approximately two equivalents of acid titrant per cerium(IV) ion present, when corrected for the amount of perchloric acid required to saturate the solution with ammonium perchlorate and for the amount of ammonium ion present from the slow decomposition of the cerate reagent (Appendix II). The increased conductivity beyond the minimum was due to excess perchloric acid added.

The actual oxidation-reduction step could not be definitely defined, since both physical and chemical methods failed to identify the oxidation products. We believe, however, that acetic acid must have been the species oxidized. Only two other possibilities existed, water and the ammonium ion. The former would seem to be eliminated on the basis of its kinetic order even though it is said to be oxidized very slowly in aqueous ceratimetry (48). The ammonium ion was eliminated on the basis of the lack of gaseous products, quantitative recovery of the

ammonia after decomposition, and the apparent lack of influence on the reaction rate with additional ammonium ion was added.

While acetic acid is generally viewed as a solvent very resistant to oxidative attack, it is not oxidized by ceric sulfate in aqueous sulfuric acid medium even when held at just below boiling for thirty to sixty minutes (87), its oxidation as glacial acetic acid has been reported on numerous occasions (3, 23, 46, 47). It is admittedly difficult to visualize such an oxidation occurring without the formation of gaseous products. Furthermore, many of the oxidation products of acetic acid reported by other investigators are oxidized by the cerium(IV) ion in one normal perchloric-acetic acid solution: methylene diacetate (40), glycolic acid, glyoxalic acid, acetoxyacetic acid, and formaldehyde.

On the other hand, Benson and co-workers have reported that the oxidation of acetic acid with plumbic acetate in the presence of additional acetate ion did not yield any gaseous products (3); and succinic acid, a compound generally isolated from all oxidations of acetic acid, is stable to this oxidant.

As was pointed out in the experimental section, no satisfactory means of determining the reaction order of acetic acid was found. The kinetics of the other components were determined, however, and indicated a surprisingly simple rate expression of:

$$\frac{d[Ce]}{dt} = \frac{[Ce^{(IV)}][HClO_4]^2}{[H_2O]}$$

with acetic acid, pseudo n^{th} order, assumed to be the reductant.

It is suggested that the enolization of the acetic acid in glacial acetic acid might have an important influence on its oxidizability at this concentration as compared to its stability in aqueous solutions. Evidence for the existence of the enol form was found experimentally and is supported by Foster and Payne's work on the osmium tetraoxide

catalyzed oxidation of acetic acid with hydrogen peroxide (23). Treatment with the peroxide in the absence of the catalyst showed only negligible oxidation after four hours at 100°C. The oxidation was accelerated and increased almost linearly with the quantity of osmium tetroxide added.

Since enolization is acid catalyzed, such a process might explain the retarding influence of water on the reaction rate i.e., water would have two competitive influences on enolization: one, it would increase the polarity of the solvent system; and two, it would compete with the acetic acid for the hydrogen ion.

In conclusion the following experimental facts and observations were apparent.

1. Ammonium hexanitratocerate(IV) is soluble in glacial acetic acid to the extent of approximately 0.03 M.

2. The cerate solution investigated has sufficient stability in the absence of light and mineral acids to require only daily standardization for most analytical purposes.

3. As a result of the factors indicated in item 2, only direct use of the reagent for volumetric analysis was found possible.

4. The addition of perchloric acid to the reagent produced a strongly oxidizing solution and a deep orange-red coloration which rapidly decomposed to yellow and eventually to colorless with a subsequent loss in oxidizing power. The absolute identity of this species was not clarified; although evidence has been presented to support either a dimeric oxo-cerium complex or a protonated cerium entity.

5. No gaseous products were observed during the cerium(IV) reduction.

6. Free radical mechanisms did not seem applicable.

7. The white precipitate formed during the decomposition in the presence of perchloric acid was identified as ammonium perchlorate.

8. Acetic acid appeared to be the reductant, water and ammonium ion were eliminated from consideration, and enolization was suggested as an important factor in its oxidation.

9. The reaction kinetics were:

$$-\frac{d[Ce(IV)]}{dt} = k\,\frac{[Ce(IV)][HClO_4]^2[HOAc]^n}{[H_2O]}$$

No experimental technique was found to determine the influence of the acetic acid. It was assumed to be pseudo n^{th}/order.

10. No experimental techniques were discovered to allow isolation or identification of the oxidation products.

11. The system, while of potential value in the analysis of organic compounds, was complicated by many factors that make a mechanistic study nearly impossible.

Since the nature of the reagent remains somewhat in doubt, yet its potential value is still apparent, the only future experimental alternative would seem to be a continuation of oxidations of a sufficient number of representative organic compounds to establish certain reaction trends. Eventually some very definite characteristics of the reagent's oxidizing properties should evolve and allow one to categorize its selectivity and applications in a manner analogous to that previously reproduced for aqueous systems.

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APPENDIXES

APPENDIX I

Kinetics Data

Water Dependence

Sample	Water	Sampling Interval (min.)	Titration (ml.)	Ce(IV) x 10^{+3}
A.	2.18	0.0	--	7.60
		1.5	16.17	6.84
		3.5	16.80	6.17
		7.0	17.60	5.32
		11.5	18.40	4.47
		16.5	19.10	3.73
		22.5	19.98	2.80
B.	1.57	0.0	--	7.60
		2.0	16.61	6.37
		3.5	17.02	5.94
		5.5	17.60	5.32
		9.0	18.53	4.34
		14.0	20.50	2.26
		20.0	20.11	2.66
C.	1.17	0.0	--	7.60
		2.0	16.92	6.04
		5.0	18.45	4.42
		7.0	19.20	3.63
		10.0	19.95	2.83
		15.0	20.91	1.81
		20.0	21.61	1.07
D.	0.75	0.0	--	7.60
		2.0	17.71	5.20
		5.0	19.45	3.36
		8.0*	21.00	1.72
		11.0	22.00	0.66
		14.0	21.71	0.97
		18.0	22.20	0.44
E.	0.36	0.0	--	7.78
		2.0	18.31	4.12
		4.0	20.05	2.23
		6.0	20.95	1.25
		8.0	21.60	0.54
		10.0	21.80	0.33
		13.0	22.00	0.10

*Aliquots of sample D taken at 8.0 and 11.0 were overtitrated, a slight excess was added to the aliquot at 8.0 minutes but an even larger error was made on the aliquot removed at 11.0 minutes.

Perchloric Acid Dependence

$HClO_4$	H_2O	Sampling Interval (mins.)	Titration ml.	Ce(IV) x 10^{+3}
0.0029	1.25	00	--	8.74
		32	13.22	8.59
		100	13.32	8.47
		229	13.40	8.37
		446	13.60	8.12
		1375	14.60	7.05
		1880	25.00	6.81
0.42	1.23	00	--	8.68
		21	14.78	6.83
		122	18.90	1.82
		183	19.75	0.79
		211	20.10	0.36
		229	20.10	0.36
		243	20.20	0.24
0.86	1.22	00	--	8.68
		16	27.88	3.31
		36	29.70	1.09
		48	30.31	0.35
		59	27.40	--
		68	28.00	--
		74	30.61	--
1.33	1.25	00	--	8.68
		3.0	25.90	5.98
		8.0	28.32	3.07
		12.0	29.43	1.73
		15.5	29.91	1.16
		18.5	29.21	--
		23.0	28.07	--
1.71	1.25	0.0	--	8.60
		3.0	25.55	6.41
		6.0	28.02	3.43
		9.0	29.80	1.29
		13.0	30.50	0.45
		16.0	30.53	--
		19.0	--	--

APPENDIX II

Determination of the Ratio of Acid Equivalents to Cerium(IV) Equivalents During the Conductivity Titration

$$\frac{(V_{min.} - V_{max.} - V_{NH_4^+})\,N}{V_{Ce}\,N_{Ce}} = \frac{\text{Equivalents of H}}{\text{Equivalents of CeIV}}$$

where:

$V_{Min.} \equiv$ the total volume of $HClO_4$ required to reach the minimum.

$V_{Max.} \equiv$ the volume of $HClO_4$ to reach the maximum.

$V_{NH_4^+} \equiv$ the volume of $HClO_4$ required to titrate the ammonium ion present as a result of the spontaneous, but slow, decomposition of the cerium(IV) to cerium(III).

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