THE VOLUMETRIC TITRATIONS OF SIMPLE OXYGENATED ORGANIC MOLECULES WITH CERIUM (IV) IN GLACIAL ACETIC ACID

By

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A THESIS

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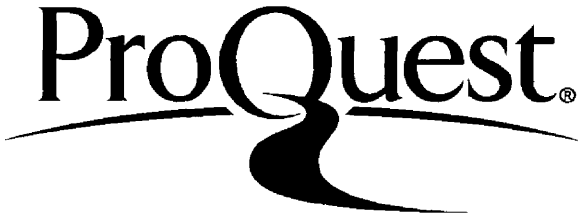

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ABSTRACT

While investigating the feasibility of applying acetic acid solutions of cerium (IV) to oxidimetric determinations, the following observations were noted.

(1) Because of the higher concentration of oxidant obtainable through its use, ammonium hexanitratocerate (IV) is employed in the preparation of acetic acid solutions of cerium (IV).

(2) An amperometric method employing two active electrodes provides an excellent means for obtaining the end points of the titrations.

(3) Cerium (IV) in acetic acid is reasonably stable in the absence of light or mineral acids.

(4) Sodium oxalate is an excellent reagent for use in the standardization of the cerium (IV) solutions. Because of the interference of nitrate, iron (II) perchlorate cannot be used for analyzing cerium (IV) solutions prepared from ammonium hexanitratocerate (IV); but this reagent provides a means for obtaining good results in the standardization of acetic acid solutions of sodium permanganate or chromium trioxide.

(5) Sodium oxalate and sodium mesoxalate are determinable in the presence of a wide variety of oxygenated molecules. Since an empirical method must be used in detecting the end point, the results are less satisfactory for the titration of malonic acid or citric acid; but reproducible results can be obtained.

(6) Carbon dioxide is the only volatile product detected in the oxidations. An apparent stoichiometric reaction between the solvent and reductant is demonstrated by the use of 1-carbon-14 acetic acid in the solvent. The ratios of total moles of carbon dioxide to moles of carbon dioxide derived from the solvent are: sodium oxalate, 2:1; sodium mesoxalate, 3:1; malonic acid, 2:2; and citric acid, 3:3.

(7) The variation of the redox potential of the cerium system under various conditions of acidity suggests complex formation in the acetic acid.

These accomplishments serve to illustrate partial fulfillment of the broad objectives established at the beginning of the investigation.

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INTRODUCTION

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Recently non-aqueous solvents have been receiving a great deal of attention in their application to acid base titrations (24,25), acetic acid being the solvent studied most extensively in these investigations. The acidic character of this solvent makes it possible to titrate, directly, very weak bases dissolved in this medium with acetic acid solutions of standardized perchloric acid. Its physical and chemical properties coupled with the availability makes this reagent particularly adaptable to studies of this type.

While non-aqueous solvents have been investigated extensively in their application to acidimetry, titrations involving the use of oxidants have been investigated only superficially (33,34). A variety of reasons may explain this lack of study: (1) insolubility of the usual inorganic oxidants in organic solvents, (2) instability of the reagent in ordinary solvents, and (3) the excessive cost of the solvent.

Glacial acetic acid because of its relative stability and solvent properties has served as a solvent for oxidation studies in theoretical and preparative organic chemical studies (4,13,16,19, 26,31,32). In many cases utilization of acetic acid as a solvent permits the use of an homogeneous solution of reactants and contributes to stability and selectivity of the oxidant. By the

utilization of the proper oxidant, advantage may be taken of these properties to extend the scope of direct organic determinations using oxidimetry.

Cerium (IV) has received a great deal of attention in organic oxidimetry (17,27,28,29) and since it exhibits a reasonable degree of selectivity in aqueous media, it seemed to be particularly well suited for a study of organic oxidations in glacial acetic acid.

The ultimate objective of this work was to demonstrate the application of cerium (IV) in glacial acetic acid to the direct determination of simple organic molecules. In addition, data were to be collected which would aid in the elucidation of the mechanism by which oxidations take place in this medium with cerium (IV) as the oxidant.

HISTORY

HISTORY

The concept of oxidation in organic chemistry is rather difficult to define. It is possible to increase the apparent oxidation number of an organic molecule in a variety of ways: (1) dehydrogenation, (2) direct addition of oxygen to the molecule, or (3) substitution. By careful examination of the oxidized molecules, it is possible to group all of these examples into the oxidation concept employed in inorganic chemistry, the loss of electrons. In general organic oxidations proceed with the ultimate loss of an even number of electrons.

Since all of these definitions exist covering organic oxidations, one might expect that there would be at least an equal number of oxidant classes which would cause the diversified reactions. In this work only ionic oxidizing agents, a classification used by Waters (13), were employed. These oxidants may be regarded essentially as electron abstractors as opposed to dehydrogenating agents. Included in this class of oxidants are iron (III), ferricyanide, silver (II) diammine, and cerium (IV); all of these reagents undergo a single electron change. It may be noted that these reagents attack only molecules which contain elements such as nitrogen or oxygen on which there is at least one pair of unshared electrons. It has been proposed (6) that oxidation of such molecules with ionic oxidants

proceeds by the initial removal of a single electron resulting in a free radical. The remaining unpaired electron is very labile and is abstracted more easily, resulting in an irreversible process. Because of the irreversibility of the second step in the oxidation, it is impossible to obtain an accurate measurement of the potential necessary to produce an oxidation of the organic molecule.

Several reagents exhibit a reasonable degree of selectivity in the oxidations they perform. When used in the oxidation of oxygenated organic molecules, cerium (IV) in aqueous media is such an oxidant. A set of rules governing the quantitative oxidation of organic molecules has been presented (28) and reference to them will indicate, to some degree, the selectivity of cerium (IV) in organic oxidations which are applicable to analytical determinations:

(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.

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

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

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

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

(7) Formaldehyde is rapidly hydrated and the hydrate is rapidly oxidized to formic acid. This is a specific property of cerate oxidations as distinct from periodate oxidations.

These rules hold only for aqueous media and it might be expected that different results would be obtained when the oxidations are done in another solvent. One would expect that the solvate formed in a non-aqueous solvent would differ in reactivity from that of the corresponding hydrate.

Glacial acetic acid has been employed extensively as a solvent in preparative and theoretical organic oxidations (4,13,16,19,26,31, 32), especially for those oxidations involving the per acids, lead tetra-acetate, and chromic acid. Its utilization as a solvent in direct volumetric oxidation has been limited to a series of papers by Tomecek and co-workers (33,34). These investigations concerned themselves with the study of various oxidants which were soluble in glacial acetic acid by using them in the titration of inorganic reductants and a few organic substances.

The progress of the reaction and detection of equivalence point were determined potentiometrically. The cell used in the potentiometric measurements was a saturated calomel electrode as the reference electrode and platinum as the indicator electrode.

Bromine was the reagent receiving the most attention. Chromic acid, sodium permanganate, lead tetra-acetate, iodine, iodine monochloride, iodine monobromide, and hydrogen peroxide received less attention. Hydrogen peroxide, iodine, and iodine monobromide showed

no promise. Since iodine monochloride underwent the same reactions as bromine, although less effectively, it received little study. Bromine in acetic acid was the system which received the most consideration. By adding sodium acetate to the solution being titrated, it was possible to titrate some molecules directly to a potentiometric end point. Among the substances which were found to be determinable in this way were: N-dimethylaniline, aniline, benzylmercaptan, hydroquinone, and ascorbic acid. One immediate and obvious difficulty involved in the employment of bromine is that in addition to oxidation, substitution and addition reactions must be considered. If possibilities exist for more than one of the reactions to occur, the results may well be erratic.

By careful purification of the solvent, stable solutions of sodium permanganate and chromic acid were reportedly obtained. Among the oxidants studied, only these two ionic reagents were investigated. The titrations conducted with these were principally of inorganic reductants; however, a few organic oxidations were reported. Diphenylamine, p-aminophenol, and hydroquinone were found to be directly titratable with acetic acid solutions of chromic acid while sodium permanganate was used only in the titration of hydroquinone. Solutions of lead tetra-acetate were found to be quite stable; and although the equilibration of the potential was slow throughout the titration, they reported that measurements of ascorbic acid, mandelic acid, and benzyl mercaptan were satisfactory by a direct titration with this reagent.

All of the titrations were conducted on a semi-micro scale with a volume of about two ml. being used in most titrations. The data given by the authors concerning their work were too limited to evaluate the applicability of the systems to quantitative organic analysis.

EXPERIMENTAL

EXPERIMENTAL

A. Reagents

Merck "Reagent Grade" and Baker's "Analyzed" Acetic Acid were both used as solvents. In the titrations with Ce(IV) further purification of the acetic acid was found to be unnecessary; however, in the studies concerning stability, precautions were taken to eliminate oxidizable impurities. Purification was accomplished by one distillation from chromium trioxide followed by a second distillation from potassium permanganate.

The iron (II) perchlorate, 70% perchloric acid, and cerium (IV) salts were obtained from the G. Frederick Smith Chemical Company. Merck "Reagent" primary standard purity sodium oxalate, Baker's "Analyzed" chromium trioxide, and Fisher Scientific Company "CP Grade" sodium permanganate were used. Merck "Reagent Grade" citric acid was employed. Dow Chemical Company malonic acid was further purified by recrystallizations from water followed by recrystallization from ether. The final product was found to be 99.7% pure by titration with standard sodium hydroxide. Eastman Kodak Company "White Label" acetic anhydride was used. The other reagents were prepared by accepted procedures.

The studies involving carbon-14 acetic acid were carried out with 0.1 millicurie (ca. 8 mg.) sodium acetate with the carboxyl

group tagged obtained from Chem Rad Division, Nuclear Instrument and Chemical Company.

B. Apparatus

A Fisher Elecdropode (sens. = 0.025 micro amp per scale division) equipped with 2 cm. 18 gauge platinum wire electrodes and a Sargent Potentiometer (4 volt span) were used for the detection of equivalence points. A magnetic stirrer was used and provisions were made for introducing a stream of nitrogen into the solution being titrated. In the radio-isotope studies a Nuclear Scaling Unit Model 163 in conjunction with a Tracerlab Windowless Flow Counter, S C 16, fed with Matheson Geiger Flow Gas (Helium-isobutane) was used for the counting.

The light sensitivity of the solution of Ce (IV) required the use of amber burets for the titrations. A Fisher Orsat Type gas analyzer was used in the attempt to detect combustible gases evolved from the oxidation.

C. Preparation of Solutions

1. Ammonium hexanitratocerate (IV)

Ammonium hexanitratocerate (IV) hexahydrate was dried at 105°C, powdered, and added in large excess to glacial acetic acid. The occasionally stirred suspension was heated to 60°C and held at this temperature for a minimum of four hours. The mixture was allowed to cool slowly by standing in the dark overnight, and was filtered

through a sintered glass filter of M porosity. The solution was standardized by titrating sodium oxalate dissolved in glacial acetic acid made 1 N with respect to perchloric acid. The end point was detected amperometrically with two active electrodes.

2. Sodium Permanganate

Sodium permanganate was used in preference to the corresponding potassium salt because of its much greater solubility in acetic acid. The permanganate solutions were prepared by dissolving the approximate weight of sodium permanganate in enough purified acetic acid to make the desired concentration. The actual concentration of the permanganate solution prepared in this way was found by titrating a weighed amount of primary standard sodium oxalate. The sodium oxalate was dissolved and titrated in an aqueous medium made acid to the extent of 2 ml. sulfuric acid per 25 ml. water. The end point was taken at the point where the permanganate color persisted for 45 seconds. The fading of the color at the end point made the detection of the equivalence point rather indefinite; however, fairly reproducible, and apparently reliable, results are obtained under these circumstances.

3. Chromium Trioxide

These solutions were prepared by dissolving the approximate weight of chromium trioxide in the desired volume of purified acetic acid. The chromium trioxide solution was then standardized by adding

a measured volume to an excess of 10% aqueous potassium iodide in a glass stoppered flask. The reaction mixture was left in the dark for thirty minutes. At the end of this time, the liberated iodine was titrated to a starch end point with aqueous standard sodium thiosulfate (33).

4. Iron (II) Perchlorate

Acetic anhydride in slight excess over that necessary to react with the water present in the reagent was added to the measured amount of glacial acetic acid. After flushing the acetic acid with nitrogen, the approximate weight of iron (II) perchlorate, to make the desired concentration, was added. This solution was left under a nitrogen atmosphere for a minimum of two hours, but frequently for much longer. To determine the actual concentration, a measured volume of the iron (II) solution was added to a solution of 5 ml. 85% phosphoric acid in 20 ml. water. The resultant solution was titrated to a diphenylamine end point with a standard dichromate solution prepared from primary standard potassium dichromate.

5. Lead Tetra-acetate

The reagent was prepared by adding dry red lead slowly with efficient stirring to a solution of acetic acid and acetic anhydride which was held at 80°C (11). The lead tetra-acetate separates as a solid on cooling the solution. After recrystallizing the solid from acetic acid and drying under vacuum over sodium hydroxide, an

approximate weight was added to enough acetic acid to give the desired concentration. The solution was standardized iodometrically in the same manner as the chromium trioxide solutions (33).

The solutions prepared according to these procedures were used in various places throughout the work.

D. Solubility of Cerium (IV) Salts in Glacial Acetic Acid

The limited solubility of most cerium (IV) salts in acetic acid required an investigation to ascertain which salt of this oxidant could be employed to the greatest advantage in this medium. Before determinations involving the oxidizing ability of this reagent could be studied, reasonable solubility must be attained.

The salts used were commercially available ceric sulfate, ammonium tetrasulfato cerate (IV), and ammonium hexanitratocerate (IV) obtained from the G. F. Smith Chemical Company. Cerium (IV) hydroxide was prepared by the precipitation of cerium (IV) from an aqueous solution of ammonium hexanitratocerate (IV) with aqueous ammonia. The precipitate was collected by filtration; and after washing with water, it was dried by washing with acetone and leaving it exposed to air.

For saturating the acetic acid with the cerium (IV) salt, the salt was powdered and added in excess to acetic acid. The suspension was heated to approximately 60°C and shaken occasionally. This heating was maintained for a minimum of four hours. After this time, the suspension was placed in the dark and allowed to cool for at least twelve hours, and then filtered through a sintered glass funnel of

medium porosity. A cerium (IV) determination was made by using a suitable reductant according to procedures given in later sections. With the exception of the nitratocerate solutions all cerium (IV) determinations were made with standardized acetic acid solution of iron (II) perchlorate serving as the reducing agent. In the absence of the nitrate, iron (II) solutions are more convenient to use since the approach to the end point is more apparent. This factor is of particular importance in the determination of cerium (IV) when present in very small concentration. In the titration, a measured volume of the standard iron (II) solution was added to the titration vessel under a nitrogen atmosphere. Two ml. of 70% perchloric acid were added, and the titration conducted to an amperometric end point. In this titration the current flow passes through a maximum, proceeds to zero and then increases sharply with the first excess of cerium (IV). Since nitrates interfere with determinations involving iron (II) perchlorate in acetic acid, the concentrations of cerium (IV) solution were determined by the oxalate procedure when ammonium hexanitratocerate (IV) was used. A complete description of this procedure is given in the section entitled "Standardization".

Table I lists the approximate cerium (IV) concentration when an excess of the particular cerium (IV) salt is placed in contact with the acetic acid using the prescribed procedure.

These data show that the most favorable solubility is obtained through the use of ammonium hexanitratocerate (IV). The higher

TABLE I

SATURATED Ce (IV) CONCENTRATIONS IN ACETIC ACID

Cerium (IV) Salt	Approximate Normality
$Ce(SO_4)_2$	< 0.005
$(NH_4)_2\ Ce(SO_4)_2$	0.005
$Ce(OH)_4$	0.01
$(NH_4)_2\ Ce(NO_3)_6$	> 0.04

solubility obtained with this reagent indicates a wider range of applicability. For that reason, ammonium hexanitratocerate (IV) was used almost exclusively in preparation of the oxidizing solutions which were used in studying possible analytical applications to which acetic acid solutions of cerium (IV) could be applied.

When a mineral acid such as sulfuric, nitric, or perchloric acid was used to wet the cerium hydroxide and the resultant product was put in acetic acid, the color intensity of the solution indicated much greater cerium (IV) solubility. This increase in solubility was offset by the much greater rate of decomposition of the resulting solution. Complete loss of color and simultaneous loss of oxidizing power occurred in a few hours.

The information collected in these investigations indicated that the most promising salt to study was ammonium hexanitrotocerate (IV).

E. Detection of Equivalence Point

The high color developed in some of the oxidations and the insolubility of the usual cerium (IV) indicators in acetic acid solutions of perchloric acid made an electrometric technique necessary for following the progress of the titration.

1. Potentiometric Titration

The use of a cell consisting of a saturated calomel reference electrode and a platinum electrode was satisfactory for detecting the end point; however, the magnitude of the observed potentials varied. The unreliability of the observed potential can be attributed to the instability of the saturated calomel reference electrode. Instability of the electrode might be expected since a large and uncertain liquid junction potential would be developed at the interface of the two solutions, acetic acid and aqueous potassium chloride. The magnitude of this liquid-liquid junction potential would vary as diffusion takes place and the solvent characteristics change. In addition to the liquid junction potential, diffusion of the acetic acid into the calomel cell would probably cause a variation in the activity of the potassium chloride and as a consequence cause instability of the potential of the reference electrode.

To minimize these effects and improve the reproducibility of the observed potential, a silver-silver chloride reference electrode was used in preference to the calomel electrode. The silver-silver

chloride reference electrode was prepared by making a silver wire the anode with a platinum cathode and passing a current through an hydrochloric acid solution (14).

Using silver-silver chloride and platinum electrodes the potentials observed during a potentiometric titration in glacial acetic acid were reproducible. A reproducible change of about 500 mv was observed at the end point of an iron (II) or sodium oxalate titration with acetic acid solutions of cerium (IV) in the presence of perchloric acid.

While the change in potential is sharp and of large magnitude, a certain amount of precaution is necessary to maintain the silver chloride film when this reference electrode is used.

2. Amperometric Technique with Two Active Electrodes

In order to circumvent the inherent difficulties of end point detection by potentiometric means, an attempt was made to utilize an amperometric method with two active electrodes (30) for following the progress of the titration.

This method of end point detection proved to be adaptable to most of the systems considered in this work and was the principal means of detection used throughout the determinations.

A Fisher Elecdropode was used as the source of potential applied across the two platinum electrodes (18 gauge platinum wire 2 cm. long). The exact potential applied varied with the system and the particular potential is given in the individual determinations.

In general the potential which was applied was determined in the following manner. A titration of the particular system under consideration was carried out. At the end point the applied potential was varied; and with each addition of titrant, the current flow at a given potential was noted. The minimum potential at which there was a maximum change in galvanometer reading for each addition of reagent was chosen as the value which would be used in all determinations involving the particular reagent.

When this method of end point detection was applicable to the determination, the values obtained for the titrations were reliable and reproducible as was demonstrated in subsequent work.

F. Standardization of Oxidants

The choice of reagent suitable for use in the determination of the concentration of a particular oxidant dissolved in acetic acid is made complex by the instability or insolubility in this solvent of the common reductants ordinarily employed for this purpose. The choice of reductant which would be suitable for standardization of the oxidant is governed by the following considerations: (1) The reductant when dissolved in glacial acetic acid must react rapidly and in a stoichiometric manner with a glacial acetic acid solution of the oxidant under consideration. (2) The reductant must be appreciably soluble in glacial acetic acid. (3) It must be stable in the acetic acid. (4) Its concentration must be determinable by an independent procedure.

In the process of searching for reductants suitable for standardization procedures several reagents were investigated:

1. Arsenious oxide

This primary standard proved to be too insoluble to be applicable to standardization procedures. The same difficulty was encountered in an attempt to use sodium arsenite.

2. Stannous Chloride

This common reductant was too insoluble, and cloudiness developing in a saturated solution on standing, indicated instability in this medium.

3. Sodium nitrite

This reagent is appreciably soluble and a glacial acetic acid solution of it is oxidized rapidly by Ce (IV) solutions. The salt, however, is too unstable in this medium to be feasibly employed. It decomposes with a visible evolution of a colorless gas.

4. Hydroquinone

Hydroquinone was the principal standard employed by Tomecek (33,34) in his work; and for that reason, deserves some attention. This easily oxidized material is soluble and stable in acetic acid; however, uncertainties regarding purity and indications leading to the conclusion of non-stoichiometric reactions forced the rejection of this substance for standardization purposes.

5. Iron (II) salts

With one exception, described in the following section, these salts proved to be too insoluble in acetic acid to act as reagents for standardization. Investigated in this category were iron (II) sulfate, ammonium iron (II) sulfate, Oesper's salt (Ferrous ethylenediamine sulfate tetrahydrate), iron (II) chloride, and iron (II) perchlorate. Only iron (II) perchlorate exhibited any promise as a possible reductant in this medium.

Iron (II) perchlorate conformed to nearly all of the prescribed qualifications necessary for the purpose of standardization of oxidants in acetic acid. It possessed good solubility properties since 0.1 N solutions of iron (II) perchlorate in acetic acid are readily prepared. It reacts stoichiometrically and rapidly with the oxidants investigated. When stored under a nitrogen atmosphere, glacial acetic acid solutions of iron (II) perchlorate are quite stable; and solutions of iron (II) perchlorate are easily standardized by titration with aqueous solutions of primary standard potassium dichromate to a diphenylamine end point. To demonstrate the coincidence of the color change with the equivalence point, a potentiometric titration was made with the indicator present. The result of such a titration is shown in Fig. 1.

While solutions of this reagent reacted rapidly and quantitatively with glacial acetic acid solutions of cerium (IV), nitrate was found to offer a serious interference in this medium. The results obtained

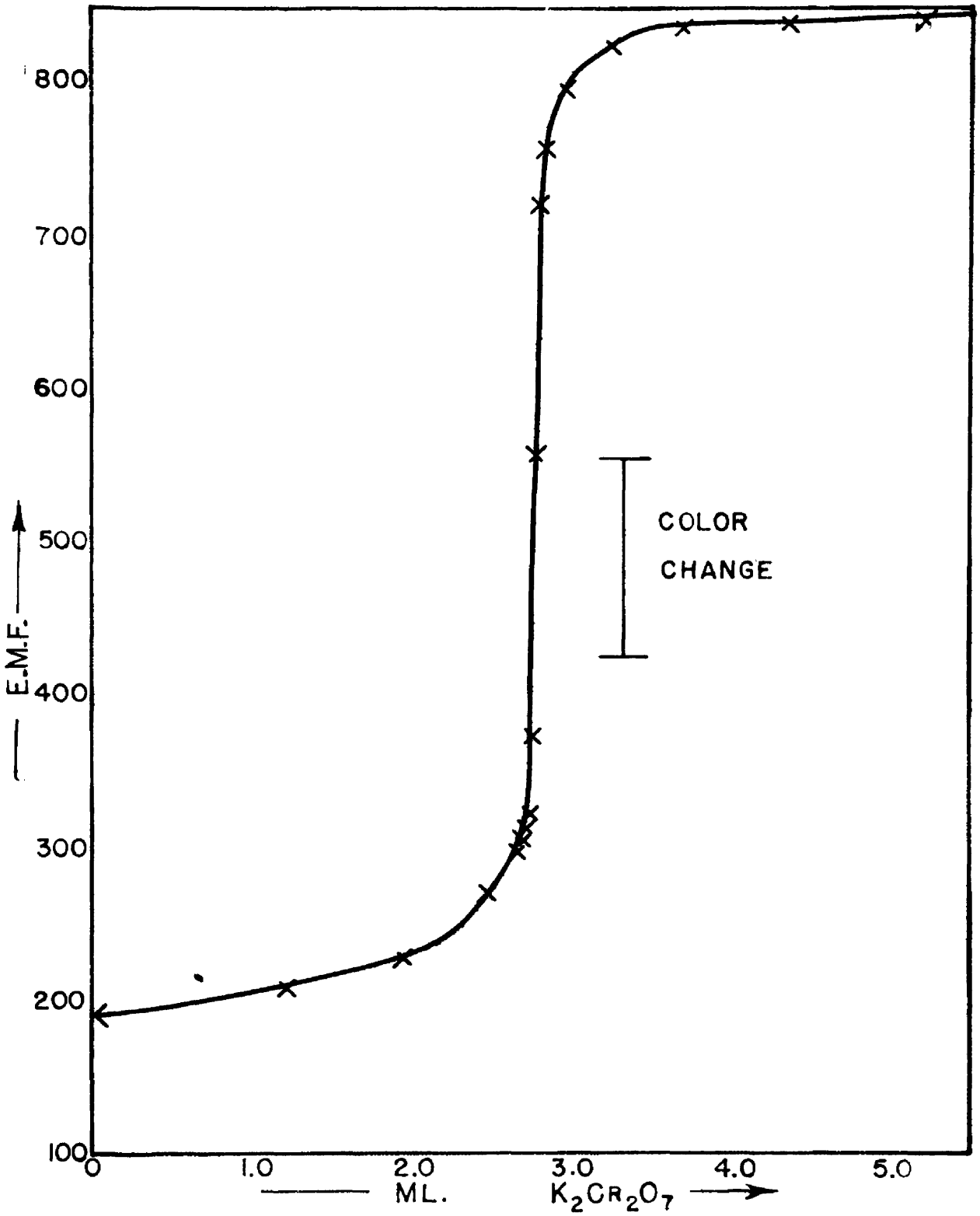


FIG. I POTENTIOMETRIC CURVE DEMONSTRATING COINCIDENCE OF EQUIVALENCE POINT AND DIPHENYLAMINE COLOR CHANGE.

by titration of the iron (II) solutions with acetic acid solutions of ammonium hexanitratocerate (IV) varied depending on the length of time taken to perform the titration. To substantiate the statement regarding nitrate interference, acetic acid solutions of calcium nitrate were reduced by iron (II). When the iron (II) perchlorate was added to a solution of calcium nitrate in glacial acetic acid, made 1 M with respect to perchloric acid, oxidation took place at an appreciable rate. This effect was noted by adding the iron (II) to the calcium nitrate solution in which the electrodes, across which 150 mv. were applied from the Electropode, were dipping. On addition of the iron (II) solution, there was an immediate and large increase in current flow. The galvanometer reading then dropped off at an appreciable rate to the original reading of zero. This falling off of current is attributable to the depletion of the iron (II) so that the iron (II), iron (III) couple is no longer present. This rate of oxidation of iron (II) by nitrate is too slow to afford a means for a direct nitrate determination; but it does serve to show the incompatibility of iron (II) and nitrate in this medium.

Since ammonium hexanitratocerate (IV) was the cerium (IV) salt found to have the best solubility properties in glacial acetic acid, iron (II) perchlorate was discarded as a reagent for the standardization of the cerium (IV) solutions.

s. Standardization of Acetic Acid Solutions of Chromium Trioxide or Sodium Permanganate by Iron (II) Perchlorate: Even though

iron (II) perchlorate solutions cannot be employed in the standardization of glacial acetic acid solutions of cerium (IV) from ammonium hexanitratocerate (IV), it does possess certain qualities which make it desirable as a reductant to be used in acetic acid. It must be recognized that, with the exception of being susceptible to oxidation by nitrate, this salt conforms to the requirements prescribed for a reductant which may be employed in the standardization of a particular oxidant dissolved in glacial acetic acid. In order to demonstrate the applicability of this reagent as a reductant, sodium permanganate and chromium trioxide were determined by standard solutions of iron (II) perchlorate.

Sodium permanganate is quite soluble in acetic acid and seems to offer some possibilities as an oxidant for organic molecules. Chromium trioxide in this medium has been used for some time as an oxidant in structural determinations and theoretical considerations in organic chemistry (4,13,16,19,26,31,32). Iron (II) perchlorate in acetic acid provides a solution suitable for the determination of either oxidant without introducing aqueous reagents into the oxidation reaction.

Acetic acid solutions of iron (II) perchlorate, sodium permanganate, and chromium trioxide were prepared and standardized by the methods described in a previous section.

If no precautions are taken, iron (II) perchlorate solutions are slowly oxidized by air. Evidence for this instability toward

air oxidation of acetic acid solutions of iron (II) perchlorate is presented in Table II. The data found in this table were collected by titrating measured volumes of the iron (II) solution with aqueous standard potassium dichromate at the listed times.

TABLE II

STABILITY OF IRON (II) PERCHLORATE SOLUTIONS

Days	N Under Air	N Under N_2
0	0.0265	0.0265
1	0.0258	0.0264
3	0.0240	0.0265

The values show that when the acetic acid is flushed with nitrogen prior to dissolving of the iron (II) perchlorate; and if the solution is stored under nitrogen, no appreciable decomposition takes place in three days. These values are compared to the values obtained when no precautions are taken to exclude air from the solution, here appreciable oxidation has occurred. By passing a stream of nitrogen through the solution being titrated, air oxidation of iron (II) is minimized and sharp and reproducible end points are obtained by the amperometric technique.

b. Detection of Iron (II) System End Point: During the titration of iron (II) perchlorate, the solutions become too highly colored to

permit the use of redox indicators, the color presumably being due to the iron (III) formed in the particular oxidation. Non-reproducibility of potential measurements employing a calomel reference electrode, and the difficulties encountered in employing a silver-silver chloride electrode made the use of a potentiometric method impractical for detection of an equivalence point. Fortunately, the iron (II), iron (III) system was adaptable to an amperometric technique employing two active electrodes. To increase the sensitivity of the measurement, about 0.5 ml. 70% perchloric acid is added to the solution being titrated. Applying 150 mv. across the electrodes and passing nitrogen through the stirred solution being titrated permits attainment of reliable and reproducible end points. The value of 150 mv. was obtained experimentally by the method described previously from the data found in Table III.

Sulfuric acid and 85% phosphoric acid were tried in lieu of the perchloric acid. These acids proved to give unsatisfactory results. When sulfuric acid was used, a precipitate of iron (II) sulfate was formed. With the formation of this precipitate, the oxidation became somewhat sluggish and the final results were inaccurate. Resorting to the use of 85% phosphoric acid, a clear solution was maintained throughout the titration; however, the values for the oxidant concentration were variable and low, relative to the accepted standardization procedures.

TABLE III

SENSITIVITY OF AMPEROMETRIC END POINT: $Fe(ClO_4)_2$ TITRATED WITH $NaMnO_4$*

Potential in mv.	$\frac{\Delta i}{\Delta ml.}$	$\frac{\Delta amp.}{\Delta ml.}$
50	-1.2	
75	-3.6	
100	-5.5	
125	-7.9	
150	-10.2	
175	-10.4	
200	-10.5	

*50 ml. 0.0102 N $Fe(ClO_4)_2$ titrated with 25.20 ml. 0.0194 N $NaMnO_4$

c. Determinations With Acetic Acid Solutions of Iron (II)

Perchlorate: Sodium permanganate in glacial acetic acid was determined by titrating a measured volume of the standardized iron (II) solution with the permanganate solution or by adding an excess of standard iron (II) solution and back titrating the excess iron (II). It was necessary to adopt this procedure in preference to the direct titration of permanganate with the iron (II) solution since the addition of perchloric acid to acetic acid solutions of sodium permanganate accelerated the decomposition of the permanganate solution appreciably.

A desired volume of the standardized iron (II) perchlorate solution is pipetted into the titration beaker through which nitrogen is being passed. The final solution volume is such that the electrodes are covered. To this solution, 0.5 ml. 70% $HClO_4$ is added. Nitrogen is continually passed through the solution throughout the course of the titration. The acetic acid solution of sodium permanganage is then used to titrate the iron (II) solution. The titration is conducted by adding the titrant rapidly at first and dropwise as the end point is approached. The approach of the end point is indicated by the magnitude of the decrease in the galvanometer reading with each addition of permanganate solution. In the course of the titration the current flow reaches a maximum and then decreases, slowly at first and rapidly near the end point. The galvanometer reading is zero at the end point corresponding to the disappearance of the iron (II).

The values shown in Table IV illustrate the accuracy and reproducibility of the method. Within the limits of error the comparisons between the two methods of determination are in good agreement.

The two values listed for titrations of the same solution of permanganate are indicative of the stability of acetic acid solutions of sodium permanganate. In spite of the precautions taken in purifying the solvent, appreciable permanganate decomposition takes place in a relatively short time. This decomposition indicates the necessity for standardization of the permanganate immediately prior to its use.

TABLE IV

COMPARISON BETWEEN $Na_2C_2O_4$ AND $Fe(ClO_4)_2$ DETERMINATIONS OF $NaMnO_4$

N of $Fe(ClO_4)_2$ Solution	Time Elapsed (days)	N of $Na(MnO_4)$ vs $Fe(ClO_4)_2$	N of $Na\ MnO_4$ vs. Oxalate
0.1103	0	0.0901	0.0897
0.1103	0	0.0900	0.0903
0.1103	1.5	0.0637	0.0635
0.1103	1.5	0.0636	0.0637

Table V represents the results obtained in the analysis of the chromium trioxide solution. These data demonstrate the feasibility of performing a direct titration of the chromium trioxide solution with the known iron (II) perchlorate solution as well as titrating an iron (II) solution with a chromium trioxide solution. The results obtained using the acetic acid solutions of iron (II) perchlorate agree favorably with those found iodometrically.

The titrations made in the determination of chromium trioxide are made in essentially the same manner as the permanganate titrations. A measured volume of the solution to be titrated is added to the titration beaker while a stream of nitrogen is passing through the solution being stirred by a magnetic stirrer. To this solution is added about 0.5 ml. 70% perchloric acid and the titration is conducted in a nitrogen atmosphere to an amperometric end point.

TABLE V

COMPARISON BETWEEN KI AND $Fe(ClO_4)_2$ DETERMINATIONS OF CrO_3

N of $Fe(ClO_4)_2$	N of CrO_3 vs. $Fe(ClO_4)_2$	N of CrO_3 vs. KI
	Titration of Standard $Fe(ClO_4)_2$ with CrO_3	
0.0679	0.1087	0.1089
0.0679	0.1088	0.1089
0.0679	0.1087	0.1089
0.0710	0.0683	0.0684
0.0710	0.0684	0.0684
	Titration of CrO_3 with Standard $Fe(ClO_4)_2$	
0.0710	0.0685	0.0684
0.0710	0.0684	0.0684
0.0710	0.0683	0.0684
0.0710	0.1087	0.1089
0.0510	0.1159	0.1161
0.0510	0.1158	0.1161

When the standardized iron (II) perchlorate solution is being titrated, the galvanometer behaves in much the same manner as the equivalent titration done using permanganate. The current flow passes through a large maximum and falls off to zero at the end point. In the reverse procedure, the titration of chromium trioxide solutions, the current passes through a small maximum and proceeds

to zero at the end point. The next addition of iron (II) results in a large increase in the galvanometer reading.

While iron (II) perchlorate in acetic acid is unsatisfactory for the titration of oxidants in the presence of nitrate, it serves as a very satisfactory reagent for the titration of some oxidants in the absence of this serious interference.

6. Sodium Oxalate

Sodium oxalate has been employed as a reagent for standardization of aqueous perchloric acid solutions of cerium (IV) (28,29).

Oxalic acid, dissolved in glacial acetic acid, is oxidized very sluggishly by ammonium hexanitratocerate (IV) in this medium; however, when the acetic acid solution of oxalate is made 1 N with respect to perchloric acid, oxidation proceeds rapidly to a reproducible end point. The end point is determinable either potentiometrically or amperometrically.

In order to establish the stoichiometry of the oxalate oxidation with cerium (IV), the following experiments were designed: (1) A comparison between determination of cerium (IV) by titrating a measured amount of the solution of cerium (IV) added to water with standard aqueous iron (II) sulfate to the value obtained by sodium oxalate titration. (2) Reduction of a weighed amount of known purity ammonium hexanitratocerate (IV) with an excess of oxalate and back titrating the excess with a cerium (IV) solution which had been standardized previously against sodium oxalate.

For comparison purposes a weighed quantity of primary standard sodium oxalate was added to acetic acid made 1 N with respect to perchloric acid. The solution was then titrated to an amperometric end point with the cerium (IV) solution and the concentration of cerium (IV) calculated.

The values for cerium (IV) concentration obtained from the oxalate titration were compared against those obtained from a titration employing aqueous standardized iron (II) sulfate. A measured volume of the cerium (IV) solution was pipetted into an equal volume of water. The resultant solution was made acid by adding 2 ml. 70% perchloric acid and the concentration of cerium (IV) determined with an aqueous iron (II) sulfate solution which had been standardized against potassium dichromate. The titration was carried out to an amperometric end point with an applied potential of 150 mv. The values found by this comparison are found in Table VI.

TABLE VI

COMPARISON OF Ce(IV) DETERMINATIONS: $Na_2C_2O_4$ vs. AQUEOUS $FeSO_4$

Oxalate Titration			Iron (II) Sulfate Titration		
Mg. $Na_2C_2O_4$	Ml. Ce(IV) Soln.	Calc'd. Ce(IV) N	Ml. Ce(IV) Soln.	Ml. 0.0777 N	Calc'd. Ce(IV) N
39.6	20.67	0.0287	20.00	7.51	0.0291
49.6	25.56	0.0290	50.00	18.70	0.0291
54.2	28.19	0.0289	50.00	18.67	0.0290

The comparisons are in good agreement and the values help to demonstrate the stoichiometry. As further proof of stoichiometry the second experiment was designed.

The ammonium hexanitratocerate was dried at 110°C. for two hours and its purity determined by titrating an aqueous solution of a weighed quantity with iron (II) sulfate. The average value for the purity was found to be 92.60%, with a range of 92.51 to 92.73.

A weighed sample of the analyzed cerium (IV) salt was added to a solution of excess primary standard sodium oxalate in acetic acid 1 N with respect to perchloric acid. The excess sodium oxalate was titrated to an amperometric end point with an acetic acid solution of ammonium hexanitratocerate (IV) which had been standardized against sodium oxalate. The results obtained are shown in Table VII.

TABLE VII

DETERMINATION OF $Na_2C_2O_4$ WITH KNOWN PURITY $(NH_4)_2Ce(NO_3)_6$

Purity of $(NH_4)_2Ce(NO_3)_6$	Grams $(NH_4)_2Ce(NO_3)_6$	Mg. $Na_2C_2O_4$ Taken	Ml. 0.0410 N Ce(IV) Soln. for Excess $Na_2C_2O_4$	Mg. $Na_2C_2O_4$ Found
92.60	0.6401	80.2	2.63	79.9
92.60	0.7949	158.8	24.90	158.5

These data serve to supplement those obtained in the previous check on the stoichiometry of the reaction. The close agreement found between the weights of sodium oxalate taken and found help to

show completeness and stoichiometry of oxalate oxidation with acetic acid solutions of cerium (IV).

When sodium oxalate is used, it is possible to titrate with cerium (IV) solutions directly, providing the perchloric acid concentration in the solution exceeds 0.5 N. The oxidation proceeds slightly faster in 1 N perchloric acid but becomes sluggish at perchloric acid concentrations less than 0.5 N. The end point is detected, as in the iron (II) perchlorate titrations, amperometrically with two active electrodes. The potential applied across the electrodes was set at 275 mv. This value was obtained experimentally from the data in Table VIII.

TABLE VIII

SENSITIVITY OF AMPEROMETRIC END POINT: NaC_2O_4 TITRATED WITH Ce(IV)*

Applied Potential (mv.)	200	225	250	275	300
μ amp./ml. Ce(IV) Soln. at end point	8.13	8.75	9.75	10.5	10.3

* 39.6 mg. $Na_2C_2O_4$ titrated with 20.67 ml. 0.0290 N Ce(IV) Solution

The value of 275 mv. is the lowest applied potential which gives the maximum galvanometer deflection at the end point when the cerium (IV) solution is added dropwise into 50 ml. of the sodium oxalate solution 1 N with respect to perchloric acid.

During the course of the titration of sodium oxalate with the cerium (III), the current increases to a very slight maximum, falls off to zero, and at the end point increases sharply. The cerium (IV) solution is added rapidly at first and dropwise at the end point. The approach to the end point is easily observed by noting the slight decrease of current flow with each addition or better, by observing the persistance of color of the cerium (IV) solution. As the equivalence point is approached, the faint yellow color of the cerium (IV) solution persists for an increasingly greater length of time. The galvanometer reading becomes constant within a thirty second period regardless of the point in the titration. The first excess of cerium (IV) results in a sharp increase in the galvanometer reading and a curve like that shown in Fig. 2 is obtained. When employing this technique in the titration of oxalate by acetic acid solution of ammonium hexanitratocerate (IV), results shown in Table IX are obtained.

TABLE IX

REPRODUCIBILITY OF DETERMINATION OF ACETIC ACID SOLUTIONS OF Ce(IV) WITH $Na_2C_2O_4$

Ce (IV) Solution	Normality of $Na_2C_2O_4$ Ce (IV) Found By Different Titrations		
	Trial		
	1	2	3
1	0.0261	0.0259	0.0260
2	0.0426	0.0426	0.0425
3	0.00913	0.00914	

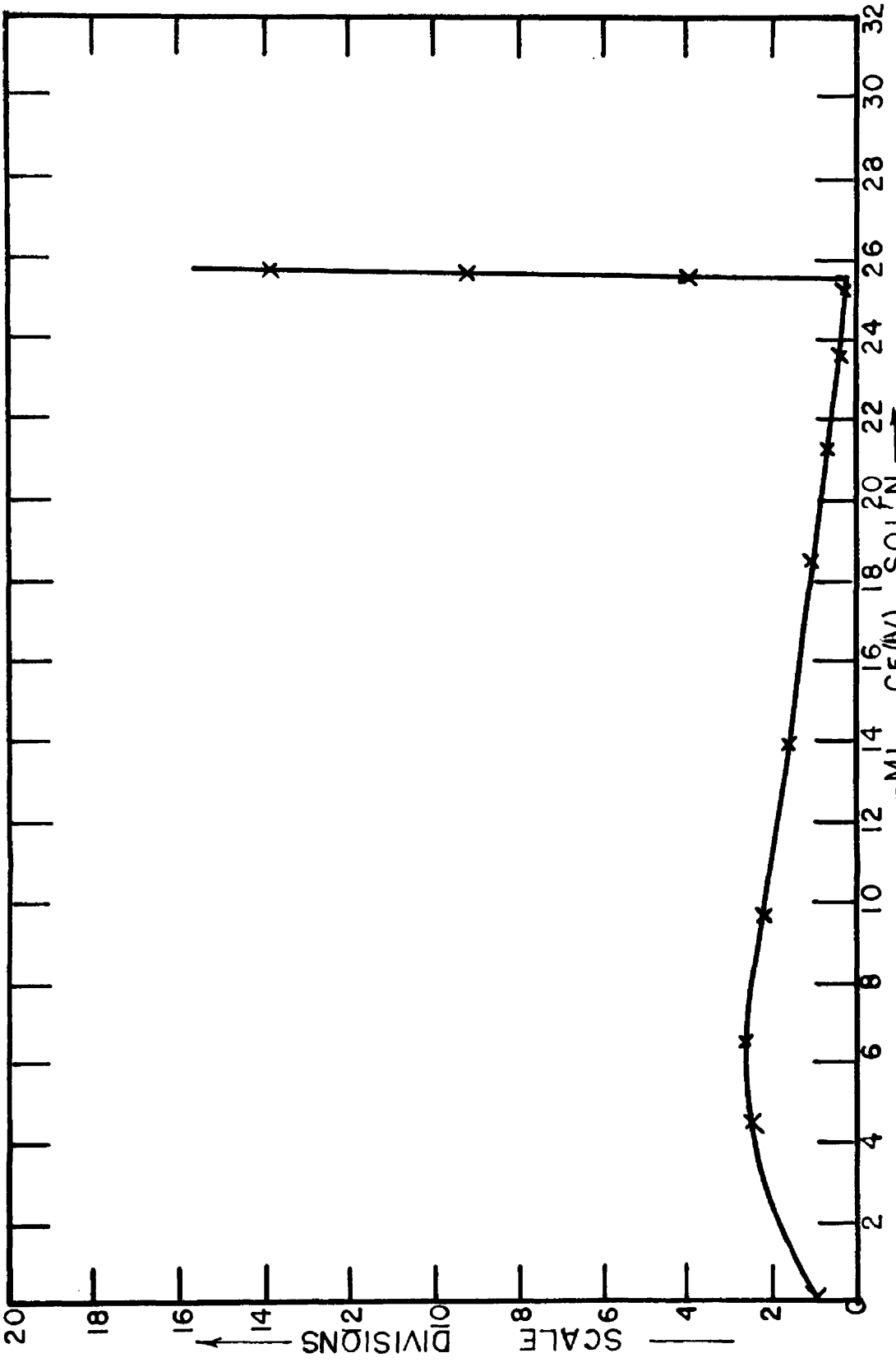


FIG. 2 TYPICAL AMPEROMETRIC TITRATION CURVE: 49.6 MG $Na_2C_2O_4$ WITH 0.0287 N Ce(IV) SOLUTION.

These results show the reproducibility that is possible when sodium oxalate is employed in the standardization of ammonium hexanitratocerate (IV) dissolved in glacial acetic acid.

This reagent conforms to all of the requirements adapted as being necessary in the standardization of this oxidant: (1) It is stable. (2) Simply through weighing, known concentrations of reductant are obtained. (3) It has appreciable solubility in the solvent. (4) It reacts rapidly and stoichiometrically with the oxidant. Since it does conform completely, sodium oxalate was adopted as the reagent to be used in standardization of all cerium (IV) solutions.

G. Stability of Acetic Acid Solutions of Ammonium Hexanitratocerate (IV)

On the bases of the slow oxidation of acetic acid by cerium (IV) in aqueous media (12,19,28) one might expect that acetic acid solutions of cerium (IV) would be somewhat less stable than the corresponding aqueous solution. Before this system could be investigated for analytical applications, it was necessary to determine cerium (IV) stability in an acetic acid medium.

1. Photosensitivity of Cerium (IV) Solutions

By analogy to the light sensitivity of some cerium (IV) salts in aqueous media (28), it would be expected that light would have some effect on the stability of cerium (IV) in acetic acid.

To demonstrate the relative stability of acetic acid solutions of ammonium hexanitratocerate (IV) stored in light and dark, a solution, prepared by the method previously described, was divided into two portions. The acetic acid had been carefully purified by distillation from chromium trioxide followed by a distillation away from potassium permanganate. The two portions of the cerium (IV) solution were placed in glass stoppered flasks, one of which was clear and the other completely protected from light. The two flasks were stored side by side on the desk top and exposed to the normal laboratory radiation. At the time intervals listed, the respective cerium (IV) solution was used to titrate a weighed sample of sodium oxalate in the manner previously described. The concentrations of the two solutions are given in Table X.

TABLE X

LIGHT SENSITIVITY OF ACETIC ACID SOLUTIONS OF Ce (IV)

Time (Days)	Light	Dark
0	0.0260	0.0260
1	0.0241	0.0255
2	0.0230	0.0253
3	0.0185	0.0248
5	0.0134	0.0221

All titrations were made from an amber buret, and the results indicate the advisability of protecting the cerium (IV) solution from light in order to minimize decomposition. When protected from light, the cerium (IV) solutions are reasonably stable; and only in very accurate work is it necessary to restandardize the cerium (IV) solution in a given work period.

2. Stability of Acetic Acid Solutions of Cerium in the Presence of Perchloric Acid

As has been indicated in previous sections, the rate of decomposition of cerium (IV) is accelerated by the presence of perchloric acid. The data in Table XI serves as evidence to support these indications.

The values for the cerium (IV) concentration were obtained in the following way: to 50 ml. of a standardized cerium (IV) solution enough perchloric acid was added to make the desired concentration. Periodically 10 ml. of this solution was pipetted into an acetic acid solution containing a weighed excess of sodium oxalate and made 1 N with respect to perchloric acid. The excess sodium oxalate was determined by titration to an amperometric end point with the standard cerium (IV) solution. The decomposition took place in the dark in amber flasks while the temperature was held at 27°C. The results obtained from these determinations are listed in Table XI.

One might expect results such as these by making an analogy to aqueous solutions of Ce (IV). In aqueous solutions of perchloric acid, cerium (IV) exhibits its greatest oxidizing power.

TABLE XI

STABILITY OF ACETIC ACID SOLUTION OF Ce (IV) CONTAINING $HClO_4$

Elapsed Time (Min.)	Normality $HClO_4$	Normality of Ce (IV) Solutions 0.5	0.75	1.0
0		0.0405	0.0318	0.0306
20		0.0385	0.0272	0.0254
50		0.0360	0.0244	0.0186
110		0.0304	0.0190	0.0146

3. Employment of Back Titration Technique

The accelerated decomposition of cerium (IV) in acetic acid solutions containing perchloric acid would indicate that an excess technique cannot be employed. Since this technique, adding an excess of oxidant to the solution being analyzed and back titrating the excess oxidant after an elapsed period of time, is employed extensively in cerium (IV) oxidations, further investigation was necessary. If it could be assumed that a cerium (IV) blank, i.e., a solution containing everything but the reductant to be determined, would decompose at the same rate as the excess cerium (IV) in the sample, then an excess technique could be employed.

To test the validity of this assumption, sodium oxalate was used. To a weighed sample of sodium oxalate, dissolved in acetic acid in the presence of enough perchloric acid to make the final solution about 0.5 N, 50 ml. of a standard cerium (IV) solution was added.

The solution was then placed in the dark for 60 minutes. After the elapsed time, a weighed amount of sodium oxalate in excess over the remaining cerium (IV) was added to the solution. The excess sodium oxalate was determined by titration with a standard cerium (IV) solution to an amperometric end point. The same procedure was carried out on a blank, the decomposition of which was used to calculate the decomposition of the excess cerium (IV) in the sample. The procedure was employed on two samples and two blanks and the results are listed in Table XII.

TABLE XII

EXCESS TECHNIQUE FOR DETERMINATION OF $Na_2C_2O_4$

Mg. $Na_2C_2O_4$ Taken	Mg. $Na_2C_2O_4$ Found Using Blank Calculation	Mg. $Na_2C_2O_4$ Found Neglecting Decomposition of Excess Ce (IV)
48.6	45.2	48.9
39.3	36.9	41.7

These values indicate the inability to apply a back titration technique to cerium (IV) oxidations. This imposes a serious limitation on the applicability of cerium (IV) solutions to organic determinations, only reductants oxidizable by direct titration are determinable with reliability.

H. Comparison of the Cerium System Redox Potentials in Acetic Acid Solutions of Perchloric Acid and Sulfuric Acid

In aqueous media the oxidation-reduction potential of the cerium (III), cerium (IV) couple is greatly affected by (1) the acid concentration and (2) the particular acid present in solution (28,29). In water the cerium (IV) apparently forms a complex with the anion of the acid; the different anionic complexes formed in this manner differ considerably in their redox potentials. In aqueous solutions made 1 N with respect to the various acids the cerium couple potentials vary in the following manner: perchloric acid, 1.70; nitric acid, 1.61; sulfuric acid, 1.44; and hydrochloric acid, 1.28. Considering only perchloric acid, the potentials vary depending on the acid concentration: 1 N, 1.70; 2 N, 1.71; 4 N, 1.75; 6 N, 1.82; and 8 N, 1.87.

The variation of the cerium system potentials in aqueous solutions of the different acids and the effect of the acid concentration suggests a comparison between the two media, water and acetic acid, with perchloric acid and sulfuric acid present in the system being oxidized. Nitric acid is not considered because of the difficulties encountered in the presence of nitrates in acetic acid media. Hydrochloric acid was not considered since it undergoes reaction with the cerium (IV) in acetic acid to form chlorine; the formation of chlorine is made evident by the distinct odor of chlorine from the reaction mixture.

As has been stated previously, the use of a calomel reference electrode produces unreliable and non-reproducible results. The variability of results can be attributed to the large and uncertain liquid junction potential which exists at the interface of the two solutions, and also with changes in the activity ratio of the electrolyte as diffusion of the acetic acid occurs.

In recent years the silver-silver chloride electrode has been employed extensively as a reference electrode, thereby eliminating a liquid junction potential (14). In an attempt to avoid the errors of measurement caused by having the two media, water and acetic acid, in contact, a cell consisting of a silver-silver chloride reference electrode and a platinum indicator electrode was used.

While the standard electrode potential of this reference electrode is known very accurately in aqueous media, it is impossible to compare this value to the one obtained in acetic acid for the following reason. In order to assign a single electrode potential to a particular half cell it is necessary to have a standard. In aqueous solutions the standard is the hydrogen electrode to which the value of zero is arbitrarily assigned. This standard value in water may be entirely different from that obtained in the non-aqueous solvent, and at present there is no satisfactory method available for a direct comparison between the two media. The potentials measured in each medium are comparable with one another but a quantitative comparison between the values obtained in the different solvents has no significance (14).

While it is impossible to assign a definite value to the silver-silver chloride reference electrode in acetic acid, the values obtained through its use clearly demonstrate the effect of different acids and acid concentrations on the redox potential of the cerium couple in this medium.

Since the actual position of the potential break at the equivalence point was not of interest (only the magnitude of the potential of the cerium (III), cerium (IV) system was the measurement involved in the study), iron (II) perchlorate solutions were titrated with the cerium (IV) solutions. Using this reductant one would not expect the end point to be reproducible since the presence of nitrate would present a serious interference.

In the actual measurements, 10 ml. 0.0410 N iron (II) perchlorate is introduced into a beaker containing 50 ml. of acetic acid made to the desired concentration with the acid under consideration. The iron (II) solution is then titrated with the acetic acid solution of cerium (IV) past the end point to the cerium (IV) concentration where the observed potential becomes constant. This point of constancy is approximately, but greater than, two times the amount of cerium (IV) necessary to reach the equivalence point of the titration. This constant value is taken as the redox potential of the cerium couple in this medium.

The titration is clean cut when perchloric acid is used; however, a precipitate is formed when sulfuric acid is employed.

The formation of this precipitate, presumably consisting of iron (II) and iron (III) sulfates, causes sluggishness of the reaction and an unsatisfactory titration.

The actual titration curves are illustrated in Fig. 3 while Table XIII lists the values observed as the redox potentials of the cerium systems.

TABLE XIII

EFFECT OF ACID ON THE POTENTIAL OF THE Ce (III), Ce (IV) COUPLE IN ACETIC ACID MEDIA

Acid	Acid Concentration	Potential** in mv.
$HClO_4$*	0.25	988
$HClO_4$	0.50	999
$HClO_4$	1.0	1024
$HClO_4$	1.5	1041
$HClO_4$	2.5	1059
H_2SO_4	2.5	806

* When sulfuric acid is added in excess after the potential has become established the observed value drops to one slightly above that observed with sulfuric acid alone.

** Referred to a silver-silver chloride electrode.

As in aqueous solutions, the redox potential of the cerium system in acetic acid varies with (1) the acid concentration and (2) the particular acid present. While it is impossible to compare the

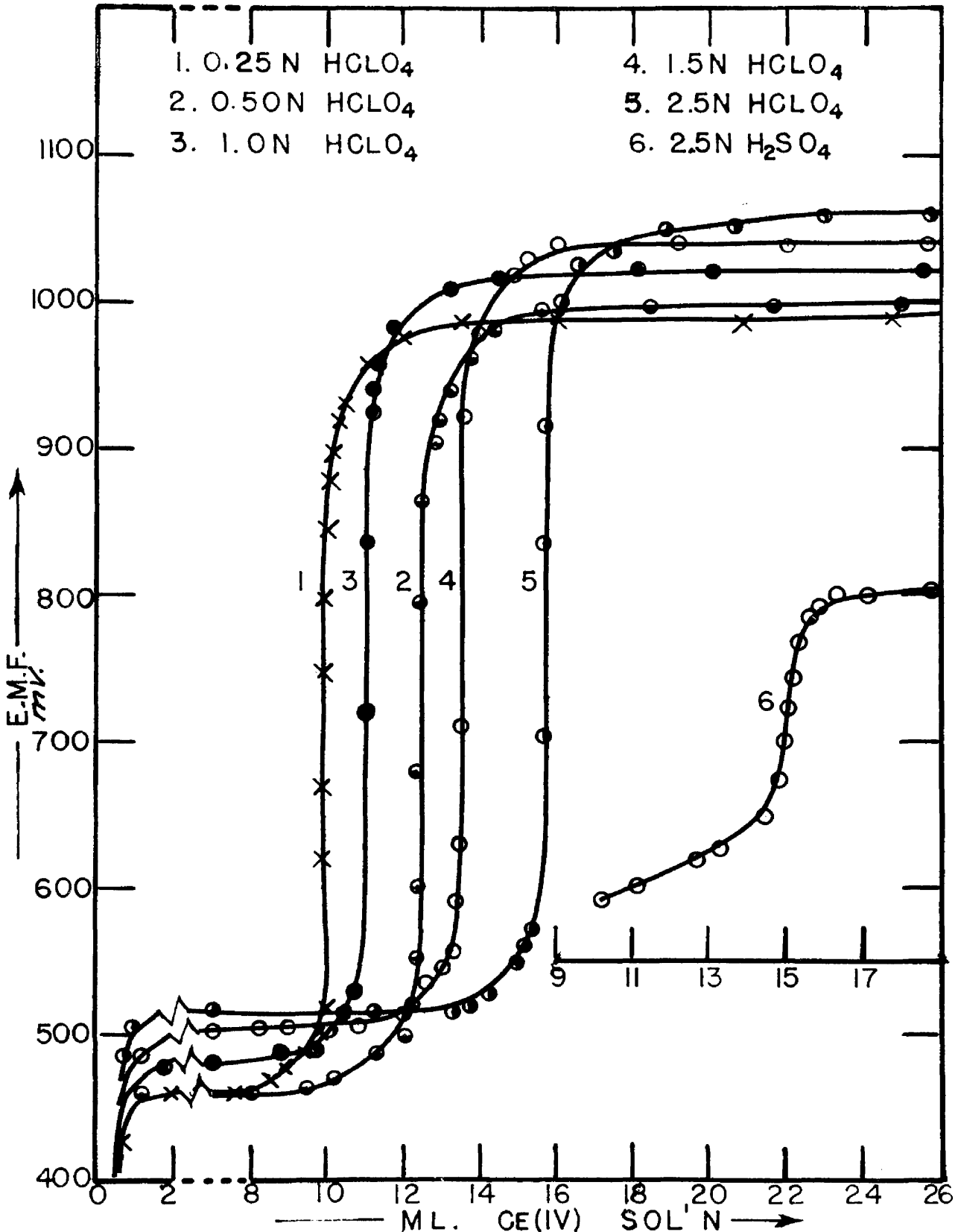


FIG. 3. POTENTIOMETRIC TITRATION CURVES UNDER VARIOUS CONDITIONS OF ACIDITY.

observed values obtained in aqueous and acetic acid media, it is possible to compare the values in each medium. When this is done, one can observe that the differences in redox potentials between solutions of sulfuric and perchloric acids is in the same order of magnitude regardless of whether the solvent is water or acetic acid. Comparing the effect of varying acid concentrations one can see that the increase in potential accompanying an increase in acidity is about the same regardless of the solvent employed.

It is possible to explain the variation of redox potentials for the cerium system in acetic acid solutions of different mineral acids at various concentrations by drawing an analogy to the explanation offered for the same effect in aqueous media. It seems probable that, in the presence of different mineral acids, various anionic complexes are formed. The particular complex present in solution will determine the potential which is observed.

By referring to the actual titration curves in Fig. 3, it is possible to obtain additional evidence substantiating the statements regarding nitrate interference. The same amount of iron (II) was added to each solution, only the rate of titration varied. The different rates of titration caused variations in the length of time for the nitrate and iron (II) to react. The large differences in location of end points only help to illustrate the necessity of excluding nitrate in titrations involving acetic acid solutions of iron (II) perchlorate.

I. Determination of Carbon Dioxide Evolution

Qualitative Detection of Carbon Dioxide: Utilization of an Orsat type gas analyzer for the analysis of the evolved gases from the oxidation mixtures resulted only in the qualitative detection of carbon dioxide.

In this experiment the reaction vessel containing the substance to be oxidized was connected to the gas inlet tube of the analyzer with rubber tubing. To this solution a calculated slight excess of cerium (IV) was added while a slight vacuum was applied to the system. After the addition of cerium (IV) was complete the vacuum was increased by lowering the mercury level in the gas buret. When the reaction was complete, there was a decrease in gas volume when the gas was passed through the potassium hydroxide. Subsequent attempted combustion in an oxygen atmosphere resulted in the formation of no gas which was taken out by potassium hydroxide. This information indicated that carbon dioxide was the only volatile substance which was formed in the oxidative reaction.

Before conclusions could be drawn concerning carbon dioxide evolution and stoichiometry of the reactions, the actual amount of carbon dioxide evolution had to be determined. This measurement was conducted with an apparatus schematically illustrated in Fig. 4.

Acetic acid containing the reductant in the reaction vessel was first saturated with carbon dioxide. Nitrogen was then forced through the system for two hours, or until no more carbon dioxide

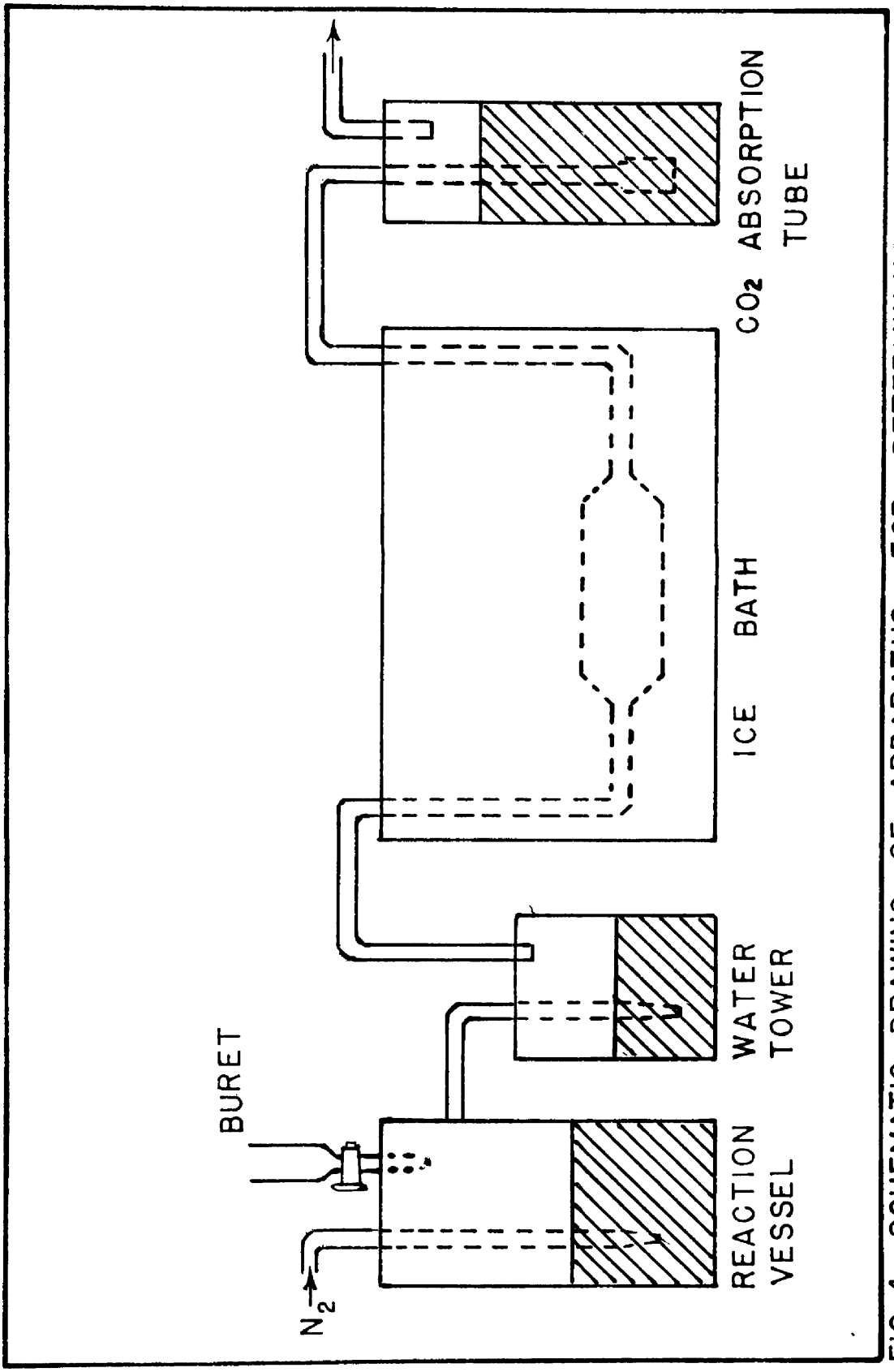


FIG. 4. SCHEMATIC DRAWING OF APPARATUS FOR DETERMINING EVOLVED CARBON DIOXIDE.

was detectable in the absorption tube containing barium hydroxide. When the carbon dioxide had been swept from the system, a measured volume of about 0.2 N standard barium hydroxide was introduced into the absorption tube. A calculated quantity of the cerium (IV) solution was introduced into the reaction vessel and the nitrogen was then turned on to sweep the evolved carbon dioxide into the absorption tube. After 2.5 hours of sweeping with nitrogen, at a slow rate to eliminate mechanical entrainment of acetic acid, the absorption tube was disconnected from the train and the barium carbonate removed by filtration. The excess standard barium hydroxide was titrated with a standard hydrochloric acid solution to phenolphthalein end point. This information was then employed to calculate the millimoles of carbon dioxide evolved per millimole reductant. The data found in Table XIV illustrate the results found by these measurements.

TABLE XIV

CO_2 FORMATION IN THE OXIDATION OF VARIOUS REDUCTANTS

Substance Oxidized	Trial	Millimoles CO_2 / Millimole Reductant	Millimoles Ce (IV) / Millimole CO_2
Sodium oxalate	1	2.08	1.01
	2	1.96	1.03
	3	2.03	0.99
Sodium mesoxalate	1	3.21	1.25
	2	3.08	1.36
	3	3.03	1.30
Citric acid	1	2.96	3.08
	2	2.59	3.18
	3	2.93	2.85
Malonic acid	1	2.05	2.24
	2	1.99	2.28
	3	1.91	2.19

J. Radioactivity Measurements on Evolved Carbon Dioxide

Some of the reactions involving the organic oxidations of cerium (IV) in acetic acid suggested participation of the solvent in the oxidation process. Unlike water, with this reagent it is possible to obtain a measure of the degree of involvement easily and accurately through the utilization of the carbon-14 isotope. A quantity, 0.1 millicurie, about 8 mg., of sodium acetate with the carboxyl group tagged with carbon-14 was obtained. (See appendix for calculations.) The previous work indicated the necessity for conducting the measurement on the four reductants, oxalic acid, mesoxalic acid, malonic acid, and citric acid. For the study, the sodium acetate was dissolved in 20 ml. acetic acid, 1.0 ml. of this stock solution was added to an acetic acid solution of a weighed quantity of substance under investigation. The same amount of the stock solution was added to 50 ml. of a standard acetic acid solution of ammonium hexanitratocerate (IV). By making both solutions the same concentration with respect to the tagged acetic acid, complications due to dilution of the isotope on addition of the oxidant would be eliminated. The collection of carbon-14 dioxide was made in a manner identical to that described in the section concerned with measurement of carbon dioxide. The barium carbonate was collected by filtering through a sintered porcelain crucible, dried and weighed. A weighed quantity of the total barium carbonate, about 50 mg., was taken and placed in an aluminum counting dish with a diameter of 2 cm.

By taking approximately equal sample sizes, errors due to geometry and self-absorbtion of the sample were minimized. The known fraction enabled calculation of the total radioactivity of the collected sample. For comparison purposes, weighed samples of the acetic acid solvent were combusted in a micro carbon-hydrogen combustion train. The evolved carbon dioxide was passed into barium hydroxide solutions and the precipitated barium carbonate prepared for counting in the same way as with the barium carbonate collected from the cerium (IV) oxidations of the desired reductant.

After collecting the samples of barium carbonate, the degree of participation of the solvent was determined by comparing the count data obtained from the cerium (IV) oxidation to that obtained from the combustion of the acetic acid. The direct proportionality of the counts per minute to the concentration of carbon-14 makes this a simple calculation. To eliminate any question regarding exchange of the carbon-14 isotope between the reductant and acetic acid, sodium oxalate was dissolved in a large excess of the tagged acetic acid solvent under the same conditions found in the oxidation reaction with the exception that the cerium was present in the reduced form. This solution stood for four days and was concentrated under vacuum. The residue was taken up in water, made basic with dilute ammonium hydroxide, and filtered. To the filtrate, a solution of calcium chloride was added; and the precipitated calcium oxalate was filtered, dried and counted. The count showed no significant

difference from the background as can be seen from the average values: Background = 42.3 counts/minute, calcium oxalate = 41.8 counts/minute. These values demonstrated that any effect of exchange of carbon-14 could be eliminated as a possible factor in the radioactivity measurement.

The results of the radioactivity measurements are shown in Table XV.

TABLE XV

DEGREE OF SOLVENT PARTICIPATION USING $CH_3C^{14}O_2H$

Sample	Counts/Minute / millimole reductant	Counts/Minute/Millimole CO_2 From Reductant / Counts/Minute/Millimole CO_2 From Acetic Acid
Acetic acid-1	1900	
Acetic acid-2	2020	
Sodium oxalate-1	2000	1.02
Sodium oxalate-2	2130	1.08
Malonic acid-1	4380	2.24
Malonic acid-2	3860	1.97
Citric acid-1	5930	3.02
Citric acid-2	6500	3.32
Mesoxalic acid-1	2130	1.08
Mesoxalic acid-2	2065	1.05

K. Indication of Peroxide Formation During Cerium (IV) Oxidation

It is conceivable that oxidation with cerium (IV) in this medium proceeds by way of formation of peroxides as intermediates. Usual qualitative tests for peroxides are not applicable in the presence of an oxidant like cerium (IV). The following observations support the proposal of peroxide intermediate formation.

In the analysis of a mixture of hydrogen peroxide, peroxyacetic acid, and acetyl peroxide (15), the hydrogen peroxide is determined by titration with a standard sodium permanganate solution. The peroxyacetic acid is determined by taking advantage of the difference in reaction rates between it and acetyl peroxide in the oxidation of potassium iodide. With peroxyacetic acid, potassium iodide is oxidized immediately. The total peroxide value is determined by allowing the solution to stand in contact with potassium iodide until all peroxides have reacted. In both iodide oxidations the released iodine is titrated with sodium thiosulfate.

Interference with the permanagnate end point detection in the presence of peroxyacetic acid forms the bases for this test. It is reported that the presence of peroxyacetic acid obscures the end point of the permanganate oxidation of hydrogen peroxide by forming a pinkish red color. The formation of the red color is attributed to the reoxidation of manganese (II) to a higher oxidation state by the peroxyacetic acid. After a solution of cerium (IV) in glacial acetic acid made two normal with respect to perchloric acid has been

in the process of decomposition for one hour, the excess cerium (IV) is precipitated with phosphoric acid. The solution is then filtered and the filtrate divided into two portions. To one portion, a solution of manganese (II) is added. When this is done, a pinkish red color is developed, indicating the presence of peroxyacetic acid. A less definite but nevertheless positive test is the immediate appearance of iodine on the addition of a potassium iodide solution to the second portion. Nitric acid causes a slower oxidation of iodide made evident by a blank.

These tests are purely qualitative and are not stated as conclusive evidence. The tests, however, serve to indicate the possible formation of a peroxide intermediate in the decomposition of acetic acid solutions of cerium (IV). When the tests were applied to solutions containing the more easily oxidized materials, oxalic acid, malonic acid, mesoxalic acid, and citric acid they were negative.

It is impossible to apply this procedure to a quantitative measurement of peroxide since, in the presence of nitrate, iodide is oxidized at a slow yet appreciable rate in acetic acid.

OXIDATIONS

OXIDATIONS

Although many oxygenated organic substances were subjected to oxidation with acetic acid solutions of ammonium hexanitratocerate (IV), very few were oxidized at a rate fast enough to make the material determinable with this oxidant. The accelerated rate of decomposition of cerium (IV) in glacial acetic acid solutions, 1 N with respect to perchloric acid, prevents the utilization of an excess technique and imposes a limitation on oxidimetric determinations. Only those oxidations which take place at a rate permitting a direct titration can be utilized with sufficient accuracy to constitute a determination.

Some of the oxidations considered in this section have been mentioned previously but now they will be discussed in greater detail.

A. Hydroquinone

The extensive attention given to this reagent in the oxidation studies by Tomecek (33,34) suggested that it would be appropriate to investigate the oxidation of hydroquinone by acetic acid solution of cerium (IV). Since the quinone-hydroquinone system is one of the few reversible organic oxidation-reduction reactions (6), certain advantages may be found by employing this reagent in further study. That the reversible system is formed during the titration of hydroquinone with cerium (IV) is indicated by the behavior of the

galvanometer during the titration and the appearance of the typical yellow quinone color. The amperometric titration curve is shown in Fig. 5. The appearance of the large maximum prior to the first excess of cerium (IV) indicates the formation of an easily reversible oxidation reduction system (30).

The hydroquinone was prepared for the determinations by recrystallizing the crude material twice from water. The recrystallized material was dried under vacuum over Anhydrone; and weighed samples, dissolved in acetic acid, were titrated with the cerium (IV) solutions which had been standardized against primary standard sodium oxalate.

When perchloric acid is present in the hydroquinone solution being titrated, there is no appearance of a definite equivalence point. A possible reason for this could be because the increased oxidizing power of cerium (IV) makes it capable of oxidizing the quinone. In the absence of perchloric acid the reaction proceeds rapidly and smoothly with the consumption of two meq. cerium (IV) per millimole hydroquinone. Using this information the data in Table XVI were obtained.

TABLE XVI

HYDROQUINONE TITRATION WITH Ce (IV)

Determination Number	Mg. Hydroquinone Taken	Mg. Hydroquinone Found
1	21.9	21.7
2	74.7	74.4

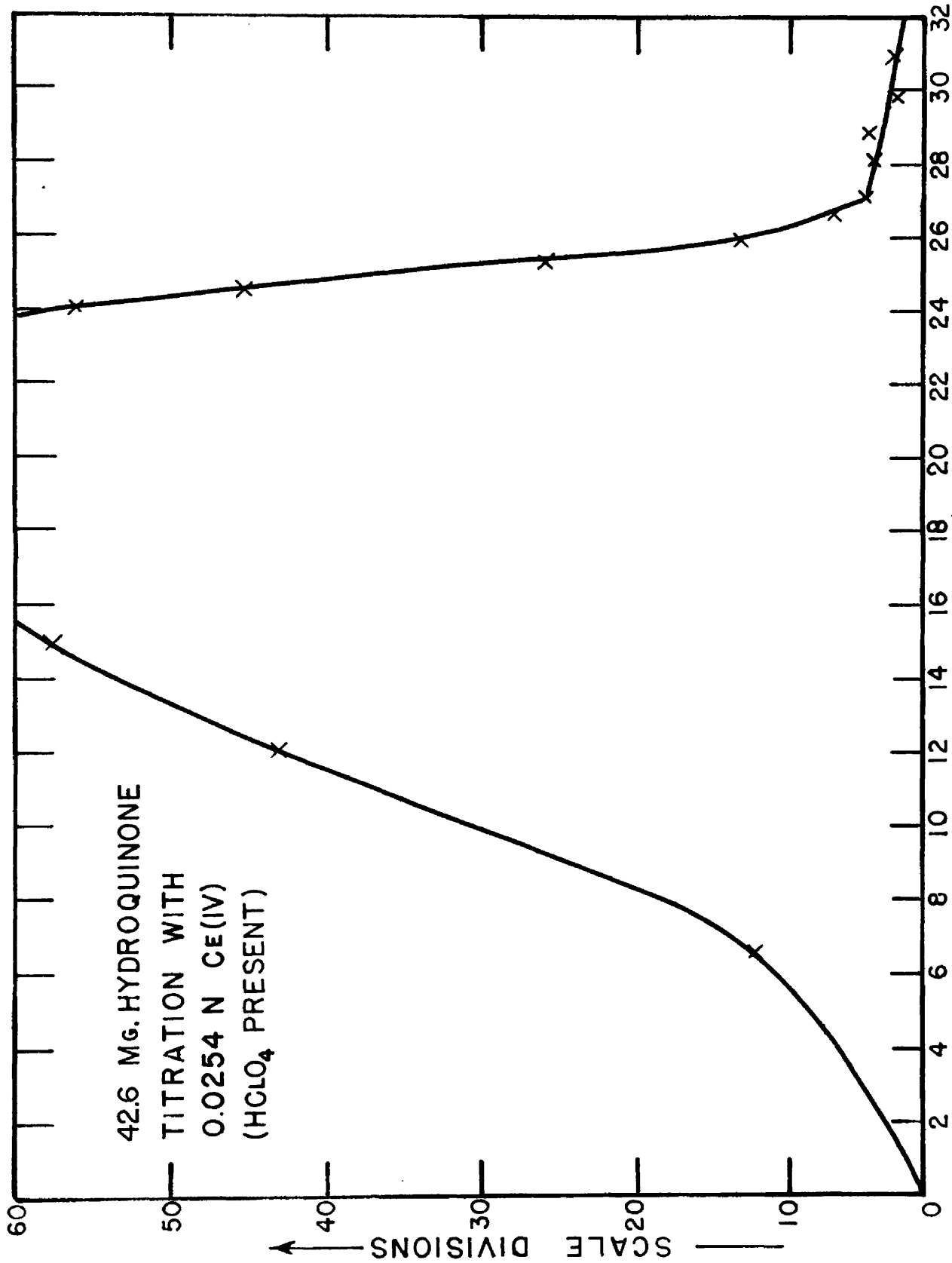


FIG. 5. AMPEROMETRIC TITRATION CURVE OF HYDROQUINONE.

This procedure may be employed for the determination of easily oxidized aromatic molecules like hydroquinone; but it is unsatisfactory when molecules like phenol, aniline, p-aminobenzoic acid, or fluorene are titrated. The oxidation is slow and indefinite when these substances are subjected to the conditions employed in these oxidimetric procedures.

Since most of the development in cerate oxidimetry has come from investigations of the oxidation of aliphatic substances (17,28,29,37), simple aliphatic materials received the principal amount of attention in this study concerning oxidation by cerium (IV) in acetic acid.

B. Sodium Oxalate

Sodium oxalate oxidations are considered in some detail in previous sections; but so far, little reference has been made to the actual determination. The oxidation proceeds smoothly and stoichiometrically over a wide range of concentration, and the titrations are conducted to a reliable and reproducible amperometric end point. The reaction involves the evolution of two millimoles of carbon dioxide per millimole of oxalate, but one millimole of carbon dioxide apparently is derived from the acetic acid. In the oxidation process, two meq. of cerium (IV) are consumed for every millimole of oxalate present. The perchloric acid concentration is not critical providing it is in excess of 0.5 N. Below this concentration the oxidation becomes somewhat sluggish.

Since the reaction between cerium (IV) and oxalate in this solvent proceeds at a very rapid rate, it seemed possible that oxalate might be determinable in a solution containing other oxygenated materials susceptible to attack by cerium (IV), if their oxidation proceeds at a sufficiently slow rate. Working on this assumption, weighed quantities of sodium oxalate were added to acetic acid, 1 N with respect to perchloric acid, containing a wide variety of oxygenated materials. Titrations were performed on these solutions with standard acetic acid solutions of cerium (IV) in the manner described previously. The results of the titrations made under these conditions are shown in Table XVII.

With a few exceptions these results show increased selectivity of cerium (IV) oxidations in glacial acetic acid. Most of the results obtained are within experimental error and exceed the accuracy which might be expected. Apparently under the conditions which have proved reliable in the determination of sodium oxalate, the compounds added as possible interferences are oxidized too slowly to seriously affect the results. All of the substances which were added are known to be oxidized by cerium (IV); but by comparison to oxalate, they react at a negligible rate. If, as in the case of glycerol and ethylene glycol, a free polyol is present, oxidation of the free material takes place at an appreciable rate. When this mixture is treated with an excess of acetic anhydride at room temperature for 15 minutes, the free polyol is sufficiently acetylated so that its rate of oxidation is slowed; and a direct titration of oxalate is made possible.

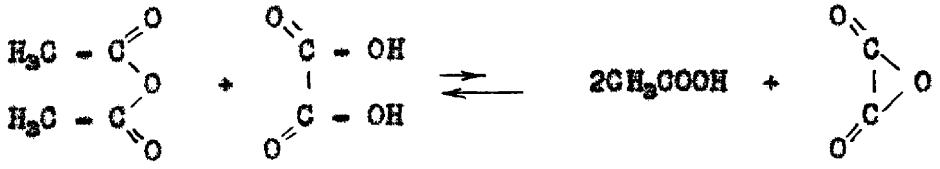
TABLE XVII

EFFECT OF OXYGENATED IMPURITIES ON THE OXIDIMETRIC TITRATIONS OF $Na_2C_2O_4$

Added Impurity	Amount of Impurity	Mg. $Na_2C_2O_4$ Taken	Found
Sodium formate (1)	50 mg.	74.4	74.6
Sodium formate (2)	50 mg.	59.3	59.3
Acetic anhydride (1)	3.0 ml.	53.9	53.9
Acetic anhydride (2)	3.0 ml.	66.5	66.6
Ethyl alcohol plus acetic anhydride (1)	1.0 ml. 3.0 ml.	38.9	36.9
Ethyl alcohol plus acetic anhydride (2)	1.0 ml. 3.0 ml.	52.6	50.4
Ethyl alcohol (1)	2.0 ml.	51.7	51.6
Ethyl alcohol (2)	2.0 ml.	36.7	36.9
Isopropyl alcohol (1)	2.0 ml.	41.7	41.6
Isopropyl alcohol (2)	2.0 ml.	42.6	42.5
Formaldehyde (1)	50 mg. $(CH_2O)_3$	55.6	55.9
Formaldehyde (2)	50 mg. $(CH_2O)_3$	36.7	36.8
Benzaldehyde (1)	0.5 ml.	No end point	
Benzaldehyde (2)	0.2 ml.	35.1	34.9
Benzaldehyde (3)	0.2 ml.	50.1	50.3
Acetone (1)	2.0 ml.	48.5	48.3
Acetone (2)	2.0 ml.	53.7	53.6
Glycerol	0.5 ml.	No end point	
Glycerol plus acetic anhydride (1)	0.5 ml. 3.0 ml.	45.4	45.6
Glycerol plus acetic anhydride (2)	0.5 ml. 3.0 ml.	74.4	74.9
Ethylene glycol	0.5 ml.	No end point	
Ethylene glycol plus acetic anhydride (1)	0.5 ml. 3.0 ml.	53.8	54.2
Ethylene glycol plus acetic anhydride (2)	0.5 ml. 3.0 ml.	38.1	38.7
Sucrose (1)	100 mg.	No end point	
Sucrose (2)	50 mg.	No end point	
Sucrose plus acetic anhydride	50 mg. 3.0 ml.	No end point	
Tartaric acid	50 mg.	No end point	
Tartaric acid plus acetic anhydride	50 mg. 3.0 ml.	No end point	

Other polyols, such as sucrose or tartaric acid, present an interference whether acetic anhydride is present or absent. In these cases it is believed that insufficient acetylation has occurred to slow the oxidation enough to prevent the interference. If an attempt is made to increase the amount of acetylation by heating the solution in the presence of acetic anhydride and letting the solution stand at an elevated temperature for an hour, there is still no end point. Apparently steric hinderance of the molecules is sufficient to prevent adequate acetylation which would make the determination practical.

In the light of the observations noted for polyols, it is difficult to reconcile the effect caused by the action of ethanol in a medium containing acetic anhydride. It seems possible that in the presence of acetic anhydride an ethyl ester of oxalic acid is formed. The behavior of the galvanometer during titration supports this speculation. Oxidation proceeds rapidly at the beginning of the titration and slows to an almost negligible rate. If the solution stands, however, the next addition of cerium (IV) is consumed rapidly, indicating transesterification. Possibly an equilibrium reaction of this type may be established:



Either anhydride now could react with the ethyl alcohol to form an ester. An alternative suggestion might be the disproportionation of

oxalic anhydride with the formation of carbon monoxide and carbon dioxide (10). This suggestion is discredited by the value obtained for oxalate in the other determinations in the presence of acetic anhydride.

Fortunately, the reaction of cerium (IV) with ethyl alcohol proceeds sufficiently slowly to permit a direct titration of oxalate in the presence of acetic acid without the necessity of acetylation of the alcohol. The results obtained in this titration are excellent.

In general the results obtained for the determination of sodium oxalate in the presence of a wide variety of oxygenated substances are good. On the basis of the values, it would seem justifiable to state that the selectivity of cerium (IV) oxidations are improved in the acetic acid medium over those in aqueous media.

C. Sodium Mesoxalate

Sodium mesoxalate (Sodium dihydroxymalonate) has received brief consideration in the studies concerning carbon dioxide evolution; but this section is devoted to a detailed discussion of the direct titration of sodium mesoxalate with acetic acid solutions of cerium (IV). Under the conditions employed in the titrations, this reagent is one of the more satisfactory chemicals determinable by the oxidimetric technique.

Sodium mesoxalate is easily prepared by alkaline hydrolysis of dibromomalonic acid (9). Dibromomalonic acid is prepared by adding a

stoichiometric amount of bromine, dropwise, into a solution of malonic acid in dilute hydrochloric acid. The addition of bromine must be done while maintaining the malonic acid solution at ice bath temperature in order to prevent decarboxylation. After about half of the bromine has been added, the dibromomalonic acid precipitates. The crystalline precipitate is separated by filtration and stored in a vacuum over sodium hydroxide until all the hydrogen bromide is removed. Sodium mesoxalate is prepared by gradually adding the dibromomalonic acid to a stirred, cold, 25% solution of sodium hydroxide. After addition is complete, the alkaline solution is heated on a steam bath for two to three hours. When the solution is cooled, sodium mesoxalate precipitates. The precipitate is washed with a small quantity of water and recrystallized from water. The salt is dried at 100°C. and stored in a dessicator over Anhydrone until ready for use. By combusting a weighed quantity of the salt in sulfuric acid and weighing the sodium sulfate residue, the reagent was found to be 98.7% pure.

The conditions for the oxidimetric titration of sodium mesoxalate are identical with those employed in the titration of sodium oxalate. Weighed samples of the analyzed sodium mesoxalate are placed in about 25 ml. acetic acid which has been made approximately 1 N with respect to perchloric acid. After dissolution of the sample is complete, it is titrated to an amperometric end point with an acetic acid solution of cerium (IV) which has been standardized against sodium oxalate. The oxidation appears to proceed at a somewhat slower rate than the corresponding reaction with oxalate; however, it proceeds rapidly and

there is no question concerning the position of the equivalence point of the reaction.

To check on the stoichiometry, a number of titrations were conducted to determine the number of meq. of cerium (IV) consumed per millimole sodium mesoxalate. The data derived from these titrations are listed in Table XVIII. Theoretically four meq. of cerium (IV) would be required to oxidize sodium mesoxalate completely to carbon dioxide.

TABLE XVIII

STOICHIOMETRY OF SODIUM MESOXALATE OXIDATIONS

Millimoles Sodium Mesoxalate	Meq. Ce (IV)	Meq. Ce (IV) / Mmole Sodium Mesoxalate
0.159	0.635	3.98
0.201	0.803	4.00
0.194	0.777	4.01
0.279	1.107	3.97

These data coupled with the information derived from the measurements concerning carbon dioxide evolution, three millimoles carbon dioxide (one of which comes from the solvent) are evolved per millimole sodium mesoxalate, indicate that the reaction is stoichiometric; but that carbon dioxide is not the sole product.

Since the oxidation of this reagent proceeds smoothly and very rapidly, a study, comparable to that in the oxalate determination, was

started. It would be interesting to know what effect added impurities would have on the direct titration of sodium mesoxalate with a standard cerium (IV) solutions. The same oxidizable impurities which were employed in the oxalate interference studies were added to solutions of sodium mesoxalate which were to be titrated with the standard cerium (IV) solutions. When the titrations were conducted and the results calculated on the basis of 98.7% sodium mesoxalate, the data in Table XIX were obtained.

The increased number of interferences in the determination of sodium mesoxalate tends to illustrate the somewhat slower reaction rate of cerium (IV) oxidation of this reagent relative to the corresponding reaction of oxalate.

As in the oxalate titrations in the presence of ethanol and acetic anhydride, ethyl alcohol exerts an unexpected influence. Unlike the results of the oxalate titrations, however, the values are low regardless of the presence or absence of acetic anhydride. The behavior of the current flow in the course of the titration indicates esterification. An apparent end point is obtained, that is, there is a large deflection of the galvanometer recorded with each addition. Continued oxidation does take place, however, at a slower rate; and if the solution stands for some time and more oxidant is added, the first addition of cerium (IV) is consumed at a rapid rate. This behavior can be explained on the basis of a transesterification equilibrium reaction; and on standing, more free mesoxalic acid is liberated which will react rapidly with the oxidant. As the concentration of ethyl alcohol is

TABLE XIX

EFFECT OF OXYGENATED IMPURITIES ON THE OXIDIMETRIC TITRATION OF SODIUM MESOXALATE

Added Impurity	Amount of Impurity	Mg. Sodium Mesoxalate Taken	Found
None		27.6	27.5
None		48.5	48.3
Sodium formate (1)	50 mg.	40.4	40.4
Sodium formate (2)	50 mg.	48.5	48.3
Acetic anhydride (1)	3.0 ml.	43.6	43.8
Acetic anhydride (2)	3.0 ml.	49.1	48.7
Ethyl alcohol plus acetic anhydride (1)	1.0 ml. 3.0 ml.	57.2	54.9
Ethyl alcohol plus acetic anhydride (2)	1.0 ml. 3.0 ml.	48.6	42.5
Ethyl alcohol (1)	2.0 ml.	23.8	22.8
Ethyl alcohol (2)	1.0 ml.	31.0	29.3
Ethyl alcohol (3)	0.2 ml.	43.8	43.1
Ethyl alcohol (4)	0.1 ml.	26.7	26.9
Ethyl alcohol (5)	0.1 ml.	43.1	43.6
Isopropyl alcohol (1)	1.0 ml.	43.6	43.7
Isopropyl alcohol (2)	1.0 ml.	36.5	36.9
Formaldehyde	50 mg. $(CH_2O)_3$	No end point	
Formaldehyde plus acetic anhydride	50 mg. $(CH_2O)_3$ 3.0 ml.	No end point	
Benzaldehyde	0.1 ml.	No end point	
Acetone (1)	1.0 ml.	46.7	46.5
Acetone (2)	1.0 ml.	23.1	23.2
Glycerol	0.5 ml.	No end point	
Glycerol plus acetic anhydride	0.5 ml. 3.0 ml.	Unsatisfactory (Reaction too slow)	
Glycerol plus acetic anhydride	0.2 ml. 3.0 ml.	27.6	27.2
Glycerol plus acetic anhydride	0.2 ml. 3.0 ml.	50.8	51.3
Ethylene glycol	0.5 ml.	No end point	
Ethylene glycol plus acetic anhydride (1)	0.5 ml. 3.0 ml.	Unsatisfactory (Reaction too slow)	
Ethylene glycol plus acetic anhydride (2)	0.2 ml. 3.0 ml.	39.5	39.0
Ethylene glycol plus acetic anhydride (3)	0.2 ml. 3.0 ml.	51.7	50.9
Sucrose	50 mg.	No end point	
Sucrose plus acetic anhydride	50 mg. 3.0 ml.	No end point	
Tartaric acid	50 mg.	No end point	
Tartaric acid plus acetic anhydride	50 mg. 3.0 ml.	No end point	

decreased the difference between the values taken and found diminishes. When the mole ratio between sodium mesoxalate and ethyl alcohol becomes less than 1 to 16, results approaching experimental error are obtained.

The same sort of an explanation would serve to explain the peculiarity of the results found in the determination of mesoxalate with either ethylene glycol or glycerol present. Expected results are obtained when either is present by itself, i.e., no end point is obtained. When acetic anhydride is added, the galvanometer acts as in the titration in the presence of ethanol. Values much too low are obtained. Apparently esterification of mesoxalic acid with the polyol takes place when the polyol and acetic anhydride are both present. Unlike the oxalate titration the oxidation slows to such an extent that false and unreliable equivalence points are obtained.

An alternative explanation can be offered to explain the low results obtained in the presence of these alcohols in the presence of acetic anhydride. A partial acetylation of the mesoxalic acid could explain the observations equally as well providing these were the only data. Since good results are obtained with only acetic anhydride present, this proposal can be discredited.

Formaldehyde and benzaldehyde both interfere by preventing attainment of an end point. Near the equivalence point the oxidation of these aldehydes becomes apparent, and the oxidation of the reagent at this low concentration occurs at about the same rate as either aldehyde alone. It was thought that an excess of acetic anhydride when added to the solution containing formaldehyde might result in the formation

of methylene diacetate which would be oxidized at a slower rate. This might permit realization of a definite end point. This was not the case and no end point was obtained.

While the results of the mesoxalate titrations are not as good as those obtained with oxalate, they do indicate increased selectivity of cerium (IV) oxidations in acetic acid as compared to aqueous reactions. Acetylation of an easily oxidized material or a sufficiently large difference in rate of reaction permits the direct titration of mesoxalate in the presence of many substances which might be expected to interfere.

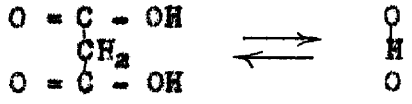
D. Malonic Acid

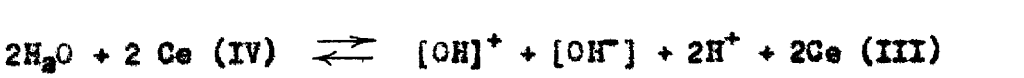
Compounds containing an active methylene group are among the aliphatic substances which are determinable by cerium (IV) oxidimetry in aqueous media (17,28,29,37). In a comparison of solvent effects on cerium (IV) oxidations, it is essential that a substance containing an active methylene group be investigated quite extensively. Malonic acid is such a reagent which can be conveniently applied to a study of this type.

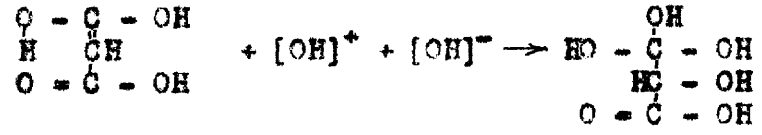
In aqueous media a standard solution of cerium (IV) must be added in excess to an acidified malonic acid solution. After standing the designated length of time, the excess cerium (IV) is determined by direct titration with a suitable reductant (29). The concentration of malonic acid is then calculated by knowing the stoichiometry of the oxidation.

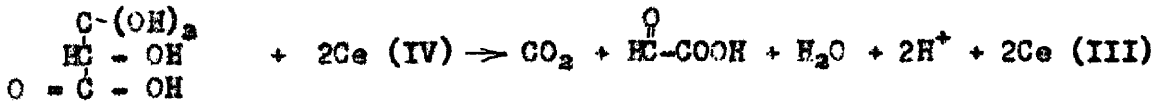
The particular acid employed in the aqueous oxidation is of prime importance (28). When the malonic acid solution is acidified with sulfuric acid the reaction is slow and not stoichiometric, 6.66 meq. cerium (IV) being consumed in the oxidation of each millimole of malonic acid (37). Using perchloric acid, the reaction time is diminished; and the reaction is apparently stoichiometric, 6 meq. cerium (IV) being required to oxidize each millimole of malonic acid (28,29).

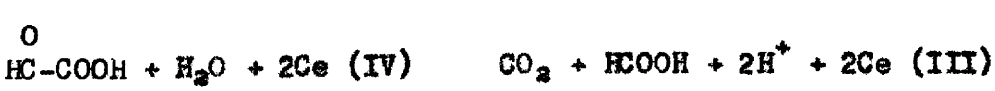
In the oxidative process, presumably the enol form of the tautomer is attacked, possibly by hydroxyl radicals, formed in the cerium (IV) oxidation (29). A mechanism which has been proposed to explain the oxidation is:











It is quite obvious that a mechanism such as this would be unsatisfactory in describing a cerium (IV) oxidation in acetic acid. A different mechanism of oxidation would very probably be accompanied by a different requirement in the amount of cerium (IV) needed to complete

the reaction. One might expect entirely different results in passing from an aqueous to an acetic acid medium.

For the purpose of investigation, the malonic acid was recrystallized twice from water and once from ether. A weighed amount of the recrystallized product, after being dried over Anhydrone, was titrated to a phenolphthalein end point with standard sodium hydroxide. The results of this analysis showed the material to be 99.7% malonic acid.

The unreliability of the excess technique in this medium imparts serious limitations on the thorough study of malonic acid oxidations. Only the results obtainable through direct titration procedures produce reliable measurements.

When titrated under the same conditions employed in the oxalate titrations, the oxidation of malonic acid proceeds rapidly at the start and slows as the titration progresses toward the end point. At the end point, oxidation is still taking place but at a much slower rate. Since oxidation is still occurring at the end point, some arbitrary means must be selected to determine at which point to stop the titration. In this case, since oxidation is still proceeding but at a slower rate, the end point is chosen at the point where the galvanometer reading remains constant for a period of ten seconds; and the next dropwise addition results in a galvanometer needle deflection comparable to that obtained at the end point in an oxalate oxidation. When this procedure is adopted, reproducible values in the malonic acid oxidation are obtained. Table XX lists a few typical determinations conducted

over a period of about six months, obtained by employing standard acetic acid solutions of cerium (IV), obtained from ammonium hexanitratocerate (IV), to titrate malonic acid.

TABLE XX

MALONIC ACID DETERMINATIONS WITH Ce (IV) IN GLACIAL ACETIC ACID

Date Performed	N Ce(IV) Solution	Ml. Ce(IV) Solution	Mmole Malonic Acid	Meq. Ce (IV) / Mmole Malonic Acid
Nov. 23, 1953	0.00927	9.26	0.0197	4.34
Nov. 24, 1953	0.00870	20.63	0.0394	4.55
Nov. 24, 1953	0.00870	10.30	0.0197	4.55
Dec. 9, 1953	0.00743	27.71	0.0456	4.52
Dec. 10, 1953	0.00716	30.37	0.0482	4.51
Mar. 11, 1954	0.0242	23.49	0.126	4.49
Mar. 12, 1954	0.0239	32.60	0.174	4.47

The uneven number of equivalents of cerium (IV) used in the oxidation indicates an incomplete reaction, a mixed reaction, or a polymerization reaction. Any of the mentioned alternatives can explain the continued oxidation after passing the end point; however, incompleteness of the oxidation seems to be discredited by the reproducibility of the values.

In order to obtain an end point of the type mentioned, it is necessary to titrate the malonic acid in an acetic acid solution less

than 2 N with respect to perchloric acid. Increasing the perchloric acid concentration to 2 N, prevents the attainment of an end point. This fact may be attributable to the increased oxidizing power of cerium (IV) in this medium, permitting a greater rate of reaction with the products.

Isolation of products, in general, resulted in failure. With the exception of carbon dioxide, no identifiable product could be isolated. The fact that the usual separation techniques resulted in the obtaining of small quantities of impure substances would indicate the formation of a mixture of products.

The separation of materials is made complex by a variety of factors. (1) Acetic acid possesses a relatively high boiling point; and in the presence of perchloric acid, it seems inadvisable to attempt a distillation of the final solution. (2) The relative insolubility of the cerium (IV) salts requireslarge volumes of solvent in order to maintain a homogeneous solution. (3) The product (or products) is probably highly oxygenated and possibly possess solubility properties similar to the large volume of cerium (III) and other inorganic salts present in the final solution. These factors, coupled with the complete ignorance concerning the type of compound involved, prevented the attainment of positive isolation results.

Several techniques were applied in the separation attempts: (1) Dilution of the reaction mixture with water before and after concentration under vacuum, followed by extraction with ether, benzene,

and carbon tetrachloride. Small quantities of residue were noted after evaporation of the ether solution. The quantities were too small to definitely determine, but they appeared to be inorganic.

(2) The paste resulting after removal of the acetic acid was subjected to extraction in a Soxhlet extractor with ether followed by extraction with alcohol. The acetic acid was removed by evaporation in a stream of air and evaporation in a vacuum. The residue found on evaporation of the ether extract was similar to that found above, however in larger quantity. The amount was still too small to be determinable but ignition indicated that a mixture of organic and inorganic substances was present. The extraction of the paste with alcohol resulted in the dissolution of large amounts of inorganic salts. The same results were obtained as above when the paste was made basic with ammonium hydroxide, only the quantity of inorganic salts dissolved in the alcohol or ether was diminished. The gelatinous precipitate would probably cause coprecipitation of the small quantity of product.

As has been mentioned in a previous section, carbon dioxide was the only volatile product detected through the use of an Orsat type gas analyzer. The method employed for the quantitative determination of evolved carbon dioxide has been described previously, and when applied to this system, two moles of carbon dioxide are evolved for each mole of malonic acid present at the beginning. This value is obtained by adding the calculated amount of cerium (IV) solution, in

the ratio 4.5 meq. cerium (IV) per millimole malonic acid, to a weighed amount of malonic acid in acetic acid made 1.5 N with respect to perchloric acid. The amount of carbon dioxide evolved in the oxidation is then determined by the described procedure. The amount of carbon dioxide evolved in the reaction conforms to the stoichiometry of the aqueous cerium (IV) oxidation; however, when 1-carbon-14 acetic acid is used, it is found that both moles of carbon dioxide are derived from the solvent.

This last observation illustrates the extensive participation of the solvent in this oxidation system. While the carbon-14 studies serve as an aid in establishing the stoichiometry of the reaction, it further confuses the problem of predicting final oxidation products. The involvement of the solvent in what appears to be a stoichiometric relationship, increases the number of possible products and makes it possible for the final products to be more complex. The studies serve to point out that the mechanism of oxidation in this medium must be different from that in aqueous media.

As a possible aid in further ellucidation of the reaction, lead tetra-acetate was employed. Lead tetra-acetate is an oxidant which is often employed in acetic acid and which exhibits a high degree of selectivity in its reactions (11,21). Formic acid and more complex organic substances which contain adjacent oxygenated groups are among the materials which undergo reaction with lead tetra-acetate, formic acid being the only known substance which will be rapidly oxidized to carbon

dioxide under the conditions employed in the determination (21,22).

The quantitative measurements employing lead tetra-acetate are performed in the following manner. The lead tetra-acetate solutions are prepared and standardized by the previously described procedure. An acetic acid solution of malonic acid is oxidized by adding the calculated amount of cerium (IV) solution, in the ratio of 4.5 meq. cerium (IV) for every millimole malonic acid. After oxidation is complete, enough sodium acetate is added so that after complete neutralization of the perchloric acid there is approximately 1 g. sodium acetate in excess. To this solution an excess of standard lead tetra-acetate is added. At the same time a blank is given the identical treatment, the blank being a solution which contains the same quantity of everything except the cerium solution and malonic acid. The solutions stand in the dark for the prescribed time and then an excess of 10% aqueous potassium iodide is added. After these solutions have stood in the dark for forty-five minutes, the liberated iodine is titrated to a starch end point with standard aqueous sodium thiosulfate. In order to ascribe significance to the above measurements, the effect of lead tetra-acetate on malonic acid must be ascertained. When a malonic acid solution is treated with lead tetra-acetate in the same way as described above, 99.7% of the added lead tetra-acetate remains unreacted. The results obtained by lead tetra-acetate oxidations on the cerium (IV) oxidation product of malonic acid are shown in Table XXI.

Apparently the reaction is complete at the end of two hours under these conditions with the utilization of 1.5 meq. lead tetra-acetate per

TABLE XXI

$Pb(OAc)_4$ OXIDATION OF Ce (IV) OXIDATION PRODUCT OF MALONIC ACID

Mmoles Malonic Acid*	Elapsed Time	Meq. $Pb(OAc)_4$ Consumed	Meq. $Pb(OAc)_4$ Mmole Malonic Acid
0.164	1 hr.	0.161	0.98
0.161	1 hr.	0.147	0.91
0.144	2 hr.	0.213	1.48
0.134	2 hr.	0.202	1.50
0.156	4 days	0.235	1.51
0.170	4 days	0.274	1.61

*Which were oxidized by the calculated quantity of cerium (IV).

millimole malonic acid. The length of time required to complete the reaction in itself indicates that formic acid is not present. Under these conditions with formic acid as the reductant the reaction is complete in 20 to 25 minutes (22). In addition to this observation, further evidence substantiating the absence of formic acid is acquired by utilizing the apparatus described in the carbon dioxide evolution studies. When the described procedure is used for the oxidation of the malonic acid oxidation product with lead tetra-acetate in the carbon dioxide apparatus, there is a negligible amount of carbon dioxide absorbed in the barium hydroxide. These observations lead to the elimination of formic acid as one of the possible oxidation products formed in the reaction between malonic acid and acetic acid solutions of cerium (IV).

The acetic acid solution of cerium (IV) contains another oxidant, nitrate, which may conceivably act as an interference under the conditions of the titration. This interference, if it were present, could explain the uneven number of electrons transferred per molecule of malonic acid in the oxidation process. In order to eliminate this point from consideration, two grams of lithium nitrate were added to the acetic acid solution of malonic acid made 1.5 N with respect to perchloric acid. This solution stood for two hours and then was titrated in the usual way. No difference was observed.

Very little interpretation of the results is possible because of the unreliability of the technique. Nevertheless an excess procedure was attempted in the determination of malonic acid. The procedure adopted was the same as that used in the oxalate titrations. The malonic acid solution containing the excess cerium (IV) stood for one hour and the excess cerium (IV) determined. When this procedure was used, the results shown in Table XXII were obtained.

Although uncertainties regarding the cerium (IV) decomposition prevent rigid interpretations of the results, this table of data helps to substantiate the statement that oxidation is still proceeding at the end point of the titration.

Because of the slowness of the reaction in the vicinity of the end point, any substance susceptible to attack by cerium (IV) acts as an interference in the titration of the substances investigated, an end point can be observed only in the presence of sodium formate and acetic anhydride.

TABLE XXII

EXCESS TECHNIQUE FOR THE DETERMINATION OF MALONIC ACID

Mmoles Malonic Acid	Meq. Ce(IV) Added	Meq. Ce (IV) / Mmole Malonic Acid	
		Neglecting Ce (IV) Decomposition	Using a Blank*
0.312	1.655	5.22	4.84
0.237	1.655	5.42	4.92
0.307	1.655	5.30	4.95

*Assuming the decomposition of excess cerium (IV) is the same in the sample solution as in a blank.

In summary it can be said that in the hands of an experienced man it is possible to titrate malonic acid, in glacial acetic acid made 1.5 N with respect to perchloric acid, directly to a reproducible amperometric end point by using acetic acid solutions of cerium (IV). The end point is difficult to see and is determined in an arbitrary manner. The perchloric acid concentration cannot exceed 2 N nor can any material be present which is susceptible to attack by cerium (IV). If either of these situations exist, no end point can be observed. In addition to the end point difficulties, the titration is slow; however, if no other method is available, this titration can produce satisfactory results.

On the basis of the information collected it is impossible to state that any one of three alternatives, (1) an incomplete reaction, (2) a mixed reaction, or (3) a polymerization reaction, is taking place to account for the uneven number of equivalents used in the oxidation.

One can only speculate, and even then any one of the observations could be construed to fit a given alternative.

Concerning the stoichiometry more definite information is available. The product or products formed must be oxidizable with lead tetraacetate, one of the products cannot be formic acid. In the oxidation two moles of carbon dioxide are evolved for each mole of malonic acid. Since both moles of carbon dioxide are apparently derived from the solvent, at least two moles of acetic acid must be actively engaged in the oxidation process.

A little more will be said later concerning stoichiometry and results; but now it is impossible to say more than that it is possible to oxidize malonic acid with cerium (IV) in a reproducible manner.

E. Citric Acid

Citric acid is another reagent which is commonly determined in aqueous media by cerium (IV) oxidations (17,28,29,37). The increasing complexity of the molecule might lead one to predict a more complex oxidation scheme and consequently a wider variety of side reactions than the corresponding oxidation of malonic acid. This appears to be the case since malonic acid is proposed as an intermediate in the oxidation mechanism of aqueous citric acid by 4 N perchloric acid solutions of cerium (IV) (28,29). Although the oxidative mechanisms in the two media are not comparable, the oxidation of citric acid in acetic acid might be expected to be quite complex. The same type of difficulties might be expected with this reagent as is encountered in the malonic acid oxidations.

In an aqueous medium, citric acid is determined by adding an excess of a standard cerium (IV) solution to an aqueous solution of citric acid acidified with perchloric acid (28,29). After standing for the designated time, the excess cerium (IV) is determined by back titration with a suitable reductant. When the reaction is carried out at room temperature, it goes to completion rapidly; but back titration leads to results which indicate undesired side reactions. By lowering the temperature and increasing the time of reaction, the side reactions are eliminated and the reaction proceeds as predicted. In the aqueous oxidation 14 equivalents of cerium (IV) are consumed per mole citric acid in forming two moles of formic acid and four moles of carbon dioxide.

Since the excess technique cannot be applied to oxidation using cerium (IV) as the oxidant in acetic acid solutions of perchloric acid, only a direct titration of citric acid can be made. The titration is conducted in much the same manner as in the corresponding malonic acid determination, and the oxidation process behaves in about the same way. A weighed quantity of citric acid is added to about 25 ml. acetic acid, 2 N with respect to perchloric acid. A standard cerium (IV) solution is then used to titrate the reagent to an amperometric end point. Initially, the cerium (IV) reacts immediately after addition; but as the titration proceeds, the rate of reaction decreases until at the end point the oxidation becomes very slow. Since oxidation is still in progress at the end point, it is necessary to adopt an arbitrary standard whereby it is possible to obtain reproducible end points.

The same procedure is adopted for the end point detection in this reaction as is employed in the determination of malonic acid. It is possible for an experienced operator to obtain an end point and measure citric acid concentrations to the extent of the values given in Table XXIII.

TABLE XXIII

CITRIC ACID DETERMINATIONS BY ACETIC ACID SOLUTIONS OF Ce (IV)

Date Performed	N Ce (IV)	Ml. Ce (IV) Used	Mmoles Citric Acid Titrated	Meq. Ce (IV) / Mmole Citric Acid
Nov. 25, '53	0.00549	17.32	0.0119	8.04
Dec. 2, '53	0.00475	20.05	0.0119	8.22
Mar. 5, '54	0.0204	32.30	0.0837	7.87
July 5, '54*	0.0262	19.88	0.0671	7.79
July 5, '54*	0.0262	33.60	0.112	7.87
July 5, '54*	0.0262	29.50	0.0965	8.02

*3 ml. acetic anhydride were added to the solution of citric acid.

An attempt was made in some of the titrations to improve the determination by adding acetic anhydride to some of the solutions. Reproducibility was not improved but stability of the galvanometer seemed to increase by adding the acetic anhydride.

The results indicate that a determination is possible, but the values obtained are neither as reproducible nor as reliable as those

found in the previous studies. The number of equivalents used in the oxidation approaches eight, and on this basis one might expect a stoichiometric reaction. This assumption does not appear to be justified. The inability to obtain more reproducible results in the titration, coupled with the results obtained from the measurements on carbon dioxide evolution, would indicate that extensive side reactions are taking place simultaneously with the principal reaction.

From the results of the carbon dioxide evolution studies it appears that there are three moles of carbon dioxide evolved for each mole of citric acid during the oxidation process. To further emphasize participation of the solvent in the oxidation, the carbon-14 studies show that apparently all of the carbon dioxide is derived from the solvent. When comparing the results obtained from citric acid to the others subjected to the same measurement, the reproducibility of the citric acid determinations differ significantly from the rest. A possible explanation for the lack of reproducibility can be attributed to the formation and subsequent slower reaction of initial oxidation products.

Attempts made to isolate identifiable quantities of reaction products produced negative results. Only in the case of carbon dioxide could a definite product be identified. The same procedures were used and the same difficulties were encountered with citric acid as in the malonic acid studies.

While isolation techniques were unsatisfactory, there are more concrete indications of products formed in this system.

Lead tetra-acetate solutions were used, in the same manner as previously described (22), on solutions containing the oxidation products formed from the reaction between cerium (IV) and citric acid. The results found in these measurements are shown in Table XXIV. Unfortunately no more tagged acetic acid was available and solvent participation is not known.

TABLE XXIV

LEAD TETRA-ACETATE OXIDATION OF Ce (IV) OXIDATION PRODUCT OF CITRIC ACID

Mmoles Citric Acid	Mmoles CO_2	Meq. $Pb(OAc)_4$	$\frac{\text{Meq. } Pb(OAc)_4}{\text{Mmole Citric Acid}}$	$\frac{\text{Mmole } CO_2}{\text{Mmole Acid}}$
0.0887	0.0912	0.182	2.05	1.03
0.101	0.109	0.209	2.07	1.08

These values were obtained by employing the lead tetra-acetate solution after a calculated amount of cerium (IV) had been added to a solution of citric acid in acetic acid 2 N with respect to perchloric acid. The calculated amount of cerium (IV) was in the ratio of eight milliequivalents cerium (IV) per millimole citric acid. The results of the measurement would indicate that a stoichiometric amount of formic acid is formed in the oxidation process.

In the titration with cerium (IV) the end point appears to be sharpened by the presence of acetic anhydride, that is, further oxidation of the solution is slowed at the end point. This indicates that some of

the products are reacting with acetic anhydride to form substances which are less susceptible to attack by cerium (IV). Previous work indicates that alcohols or simple aldehydes may be included in the possibilities.

Considerable doubt is cast on the validity of qualitative tests when done in this medium, even when neutralized, at such low concentrations; but indications of aldehydes were obtained by the Tollen's test. However, when attempts were made to precipitate the possible aldehydes with 2-4-dinitrophenylhydrazine or dimedone (5-5-dimethylcyclohexandione) the results were negative and the tests must be considered inconclusive.

In general one can say that in the hands of an experienced operator it is possible to obtain a satisfactory estimation of citric acid concentrations by employing acetic acid solutions of cerium (IV) in a direct titration. The results are not very reproducible and the titrations must be done slowly in order to avoid passing the end point. Unfortunately it is impossible to further elucidate the reaction by employing the excess technique and permit the reaction to go to completion; but on the basis of the whole, even number of electrons transferred one might expect a stoichiometric reaction. Subsequent work does not support this assumption and insbility to obtain reproducible values is attributed to side reactions.

Only carbon dioxide is positively identified as a product of the oxidation with all of the carbon dioxide being derived from the solvent. In addition to carbon dioxide there are good indications that formic acid is formed in a mole to mole ratio; and inconclusive results indicate the presence of some aldehydes.

F. Miscellaneous Oxidations

This section is devoted to the substances which received a superficial examination and which were found to be indeterminable by a direct titration with acetic acid solutions of cerium (IV) prepared from ammonium hexanitratocerate (IV). In choosing the compounds which were subjected to a cerium (IV) oxidation two different approaches were employed. (1) Those materials were selected which, when titrated with a cerium (IV) solution, might furnish an insight into the oxidation process through which the materials which received detailed attention pass. (2) A variety of substances were used so that a clearer picture of the selective action of cerium (IV) oxidations in this medium could be obtained.

All of the compounds were subjected to cerium (IV) oxidation under conditions identical with those employed for the titration of malonic acid, but none received as extensive an investigation.

1. Derivatives of Malonic Acid

In the study covering malonic acid, it was considered essential that esters of malonic acid and substituted malonic acid should receive attention for two reasons. First, it might be possible to work out a determination for these materials. Second, it might furnish information covering the cerium (IV) oxidation of malonic acid.

Potassium ethyl malonate (18) and methyl malonic acid (1) were prepared from redistilled diethylmalonate according to accepted procedures.

Both diethyl and monoethyl malonate are oxidized, but much more slowly than the acid. There were some indications that transesterification is taking place prior to oxidation. The methylmalonic acid also is oxidized slowly.

With the esters and the substituted malonic acid, the reaction takes place too slowly for a determination to be made by the direct titration with the cerium (IV) solution. These observations suggest that both carboxyl groups and the active methylene group must be free in order for oxidation to proceed at a favorable rate.

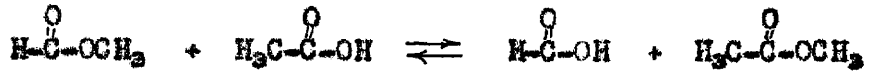
2. Methylene Diacetate, Methyl Formate, Methyl Acetate, and Ethyl Acetate

Any one of these esters could conceivably be formed in either the malonic acid or citric acid oxidation; and for that reason, an attempt was made to determine each with cerium (IV). The methyl formate, methyl acetate, and ethyl acetate were obtained commercially while methylene diacetate was prepared by the action of acetic anhydride on paraformaldehyde (20).

The methylene diacetate is oxidized much too slowly to be determined by a direct titration, while methyl formate, methyl acetate, and ethyl acetate appear to be stable in the medium.

In the investigation of methyl formate an interesting observation was made which is utilized later as a qualitative test for the identification of methyl formate. An acetic acid solution, 1 N with respect to perchloric acid, containing 57.3 mg. methyl formate is permitted to stand in a glass stoppered flask for 1.5 hours. At the end of this time enough sodium acetate is added to furnish an excess of about 1 g. over

that necessary to neutralize the perchloric acid. An excess of lead tetra-acetate is then added to the solution and the mixture left in the dark for 1 hour. After this reaction, the excess lead tetra-acetate is determined iodimetrically as described previously. This measurement showed that about 50% of the methyl formate had reacted. Presumably the lead tetra-acetate oxidation takes place on the formic acid produced in the reaction:



This reaction is offered here since it is used later. No claims are made concerning quantitative application but these observations are presented to show a method for the qualitative detection of methyl formate which is applicable in a medium of this type.

The attempts to use cerium (IV) in the oxidative determination of these esters resulted in failure. Using the results, however, these materials can be eliminated as possible intermediates or end products in a stoichiometric reaction of the compounds studied previously in greater detail.

3. Oxalacetic Acid and Pyruvic Acid

These reagents could conceivably be formed in the oxidative reaction of either malonic acid or sodium mesoxalate. In addition these materials serve to illustrate the reactions of α-keto acids with cerium (IV). When employed under the same conditions as used in the titration of malonic acid, these reagents are oxidized at a detectable rate, but the rates of

oxidation are not rapid enough to permit a direct titration. On this basis it seems justifiable to eliminate either reagent as an intermediate in the oxidative process of any of the determinable reductants.

4. Tartaric Acid

This reagent is another which cannot be determined by a direct titration with cerium (IV) in this medium. The reaction proceeds at a favorable rate at the beginning of the titration. However, as the titration progresses, the reaction slows. The point at which the rate becomes slow is not reproducible. Apparently partial acetylation takes place preventing the attainment of a reproducible end point.

5. Succinic Acid

This reagent deserves particular attention since it is one of the final products found in the decomposition of diacetyl peroxide which could conceivably be present in the oxidation medium. Succinic acid proved to be quite stable in the oxidizing medium.

6. Acetylacetone

This material was investigated to supplement the oxidation studies made on compounds containing active methylene groups. The reagent was obtained commercially; and during its titration, oxidation proceeds in much the same manner as in the corresponding malonic acid titration. The reaction proceeds quite rapidly at first and then slows. Unlike malonic acid, however, no reproducible end point can be obtained.

7. Formaldehyde and Benzaldehyde

According to work done in aqueous media, one of the factors which would require the use of empirical relationships in an oxidative determination with cerium (IV) is the formation of an aldehyde (28). Neither formaldehyde nor benzaldehyde is oxidized at a favorable rate regardless of the point in the titration. Both paraformaldehyde and aqueous formaldehyde, treated with an excess of acetic anhydride, were tried but there did not seem to be an appreciable difference in their rates of oxidation. Benzaldehyde is oxidized more rapidly than formaldehyde but still not at a rate favorable for a direct titration.

Results of the type described above would be expected by referring to the work involving the interferences in oxalic acid and mesoxalic acid titrations. As a rule, with the exception of oxalate, the formation of either aldehyde during an oxidation would be expected to yield empirical results in this medium as well as in aqueous media.

8. Glycolic Acid and Lactic Acid

As examples of α-hydroxy acids these reagents, obtained commercially, were investigated. As in the majority of cases in this section, the rates of oxidation were slow and did not permit a direct titration under the conditions employed.

9. Ethyl Alcohol and Methyl Alcohol

As would be expected from the studies on oxalate and mesoxalate interferences these simple alcohols are oxidized slowly. There is,

however, the characteristic orange red color formed during the addition of cerium (IV). This would indicate that a complex, similar to that formed in water during the qualitative test for simple alcohols, is obtained.

10. Sucrose, Glycerol, and Ethylene Glycol

In aqueous solutions these polyols react rapidly with cerium (IV), and they are determinable by a stoichiometric reaction when an excess cerium (IV) oxidimetry technique is employed.

In acetic acid, however, they are not oxidized at a rate permitting a direct titration. The behavior of these chemicals in the interference studies on oxalate and mesoxalate would indicate that partial acetylation occurs preventing the attainment of reproducible results.

11. Cinnamic Acid, Maleic Acid and Cyclohexene

These examples of two types of double bond unsaturation were investigated and found to be attacked by cerium (IV) solutions. Cinnamic acid received considerable attention. The oxidation of this chemical proceeds at a favorable rate at the start of a titration; but as its concentration is depleted the reaction slows so that an end point cannot be observed. During the titration, there appears to be a noticible change when approximately 4 meq. of cerium (IV) per millimole cinnamic acid have been added. There is no end point obtained however.

In order to obtain a clearer picture of the reaction after adding cerium (IV) in the ratio of 4 meq. cerium (IV) per millimole cinnamic acid, an ultra violet absorption spectrum was taken of each solution

under consideration. The measurements were made with a Beckman Model D. U. Spectrophotometer on solutions prepared in the following way. (1) A solution containing the cinnamic acid in acetic acid 2 N with respect to perchloric acid was measured against a blank containing only acetic acid and the same concentration of perchloric acid. (2) The same concentration of cinnamic acid was treated with enough cerium (IV) solution so that the mole ratio of oxidant to cinnamic acid was 4 to 1. The same amount of cerium (IV) solution was added to the same volume of acetic acid 2 N with respect to perchloric acid. After standing until the decomposition of cerium (IV) was complete, this solution was used as the blank to which the solution containing the oxidized cinnamic acid was compared. (3) Benzoic acid in the same molar concentration was prepared in acetic acid 2 N with respect to perchloric acid. This solution was measured against a blank containing only acetic acid made to 2 N with respect to perchloric acid.

The spectra obtained on the three described solutions are shown in Fig. 6.

A center which might be expected to be attacked during the oxidation of cinnamic acid with cerium (IV) is the double bond on the side chain. Attack of this double bond would lead to interference of resonance by decreasing the amount of conjugation. Concurrent with resonance interference would come the shifting of the absorption bands to a lower wave length.

By making reference to the spectral curves, one can see that the absorption band of cinnamic acid is located at exactly the same wave

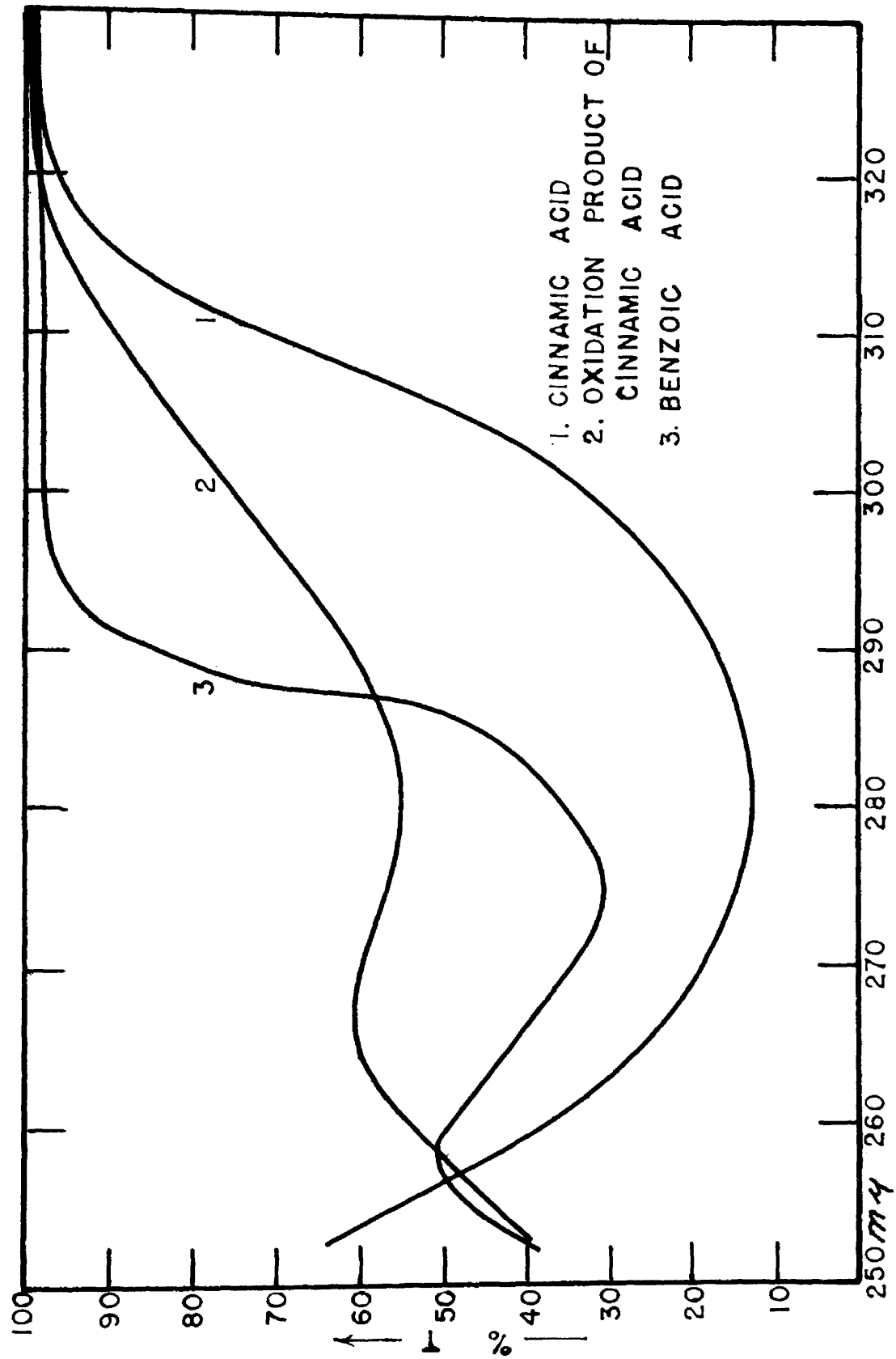


FIG. 6 ABSORPTION SPECTRA OF CINNAMIC ACID AND ITS CERIUM(IV) OXIDATION PRODUCT.

length as a lesser one of the oxidation system. On this basis it may be said that the oxidation of cinnamic acid is incomplete with the addition of four meq. cerium (IV) per millimole cinnamic acid. Attack of the double bond is indicated by the appearance of what seems to be a strong absorption band at about 254 mu. Below 252 mu the solutions become opaque and the exact location of this lower absorption band is unknown. If the oxidation process results in complete rupture of the double bond a product which might be expected is benzoic acid. It is quite obvious that benzoic acid is not a product formed in appreciable quantities when reference is made to the curve obtained with pure benzoic acid dissolved in the same medium as the oxidized cinnamic acid.

In the hope of being able to obtain a procedure which could be utilized in the direct oxidimetric titration of cinnamic acid, the perchloric acid concentration of the solutions being titrated were varied. Concentration ranges of from 1 to 4 N perchloric acid were employed but in no case was it possible to obtain an end point.

Cyclohexene and maleic acid are oxidized but at a slower rate throughout the titration than the corresponding oxidation of cinnamic acid.

While a determination of these unsaturated molecules was not realized, these observations show that double bond unsaturation is attacked by cerium (IV) at an appreciable rate in this medium.

12. 2,5-Dimethyl-3-Hexyne-2, 5-diol

This reagent, obtained commercially, appears to be quite stable in the oxidizing medium. This helps to illustrate the indication of greater

stability of triple bond unsaturations toward cerium (IV) oxidation than a double bond unsaturation in the acetic acid medium.

13. 2-Mercaptobenzthiazol

This mercaptan exhibited a surprisingly high degree of stability in the oxidation medium.

No attempt is made in these examinations to claim a thorough investigation of the oxidation possibilities of cerium (IV) in acetic acid; but a wide range of bond types received attention. In these studies none of the reagents were found to be determinable by the oxidation titration; but by the process of elimination some possible end products or intermediates are eliminated as possibilities in the oxidation scheme of the four chemicals investigated in detail.

DISCUSSION OF MECHANISM

DISCUSSION OF MECHANISM

The information collected in this work provides a basis for interesting speculation concerning the mechanism of cerium (IV) oxidations in this medium. For the mechanistic considerations a certain amount of information is available which is applicable to all of the reactions studied in detail. (1) The use of 1-carbon-14 acetic acid indicates extensive and stoichiometric participation of the solvent in the reactions. (2) Qualitative tests suggest the presence of peroxyacetic acid in the decomposing cerium (IV) solutions. (3) Only a limited number of compounds undergo reaction at a sufficiently rapid rate to permit a direct titration.

By reference to mechanistic studies in water, it is possible to derive information which may be applied to cerium (IV) oxidations in acetic acid. In aqueous media, it has been proposed that ionic oxidizing agents react in the following manner with oxygenated reductants (6,13). Using iron (III) as the oxidant acting on an organic molecule containing oxygen which has at least one pair of unshared electrons:

$$-C-O: + Fe^{+++} \rightleftharpoons -C-O\cdot + Fe^{++}$$

$$-C-O\cdot + Fe^{+++} \rightleftharpoons -C=O + Fe^{++}$$

The oxidation is probably preceded by an intermediate complex formation (7,8). The rate of oxidation is a function then of the oxidizing power of the oxidant and its ability to form the initial complex.

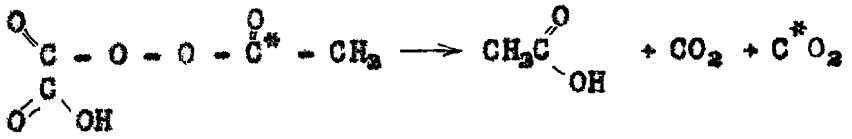
The evidence collected in this work is not sufficiently complete to propose a definite mechanism; but by referring to studies in aqueous media, it is possible to present a scheme which will explain the results found in this work.

A. Oxidation of Sodium Oxalate

Under the conditions employed in the determination of this reagent, the oxidation is essentially instantaneous. The reaction proceeds with the consumption of two meq. of cerium (IV) accompanied by the evolution of two millimoles of carbon dioxide per millimole oxalate. Only carbon dioxide could be detected as a product of the oxidation, and carbon-14 studies indicate extensive and apparently stoichiometric participation of the solvent. A measurement of carbon-14 dioxide indicates that the reaction proceeds involving acetic acid and oxalate in a mole for mole ratio.

In order to comply with these observations it would appear necessary that an unstable intermediate must be formed in the oxidation scheme which involves the solvent and the oxalate in equal molar proportions.

Definite proof is lacking but a reasonable explanation might be the formation of a mixed peroxide which would undergo further decomposition accompanied by an intramolecular rearrangement. This might be depicted in a scheme similar to the following:

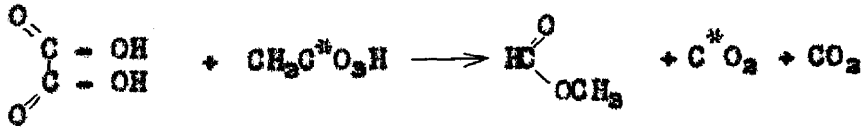


An intramolecular decomposition of this type would comply not only with the results obtained for cerium (IV) consumption and carbon dioxide evolution, but would also explain the inability to detect a combustible gas. If the decomposition of the proposed intermediate would proceed with the formation of a free methyl radical, methane would be expected as a product of the oxidation (19,23,35,36).

In addition to an intramolecular rearrangement of the type mentioned it would be conceivable that a modified Baeyer-Villiger reaction might explain the results (3).

A generalized Baeyer-Villiger Rearrangement is:

A Baeyer-Villiger Rearrangement modified to fit the oxalate system is:



If this type of a rearrangement were operative then methyl formate would be a reaction product. When applying the test for methyl formate, described previously, the results were negative. This indicates that if this reaction does take place, it is minor in extent.

While the evidence is not conclusive it seems possible that the proposed intermediate might be formed and that its decomposition proceeds in the manner shown.

B. Sodium Mesoxalate

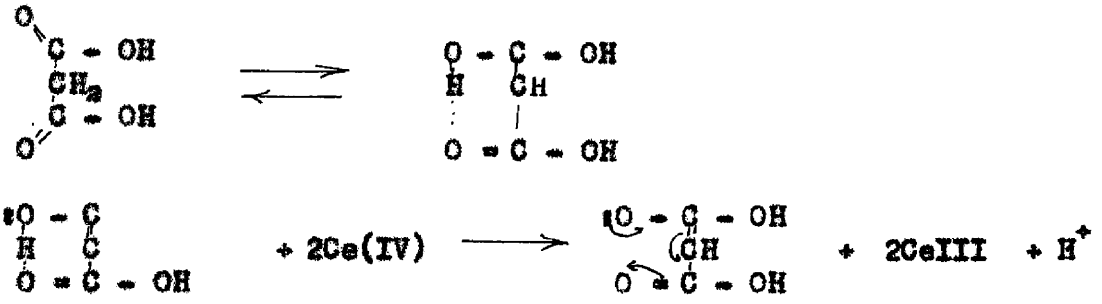
As in the titrations of oxalate, the oxidation of this reagent takes place essentially instaneously. The oxidation requires four milliequivalents cerium (IV) and is accompanied by the evolution of three millimoles of carbon dioxide. In the carbon dioxide evolution studies utilizing carbon-14, extensive participation of the solvent is indicated. Apparently acetic acid enters into the reaction in a stoichiometric manner. A molar ratio of one carbon dioxide derived from the solvent per one of mesoxalate oxidized is obtained through the use of this technique.

Again the evidence is too inconclusive to propose a definite mechanism; however, it would seem possible that the initial step in the oxidation step involves oxidative decarboxylation. If this takes place, the molecule remaining would be oxalic acid which could be oxidized as in the scheme mentioned previously.

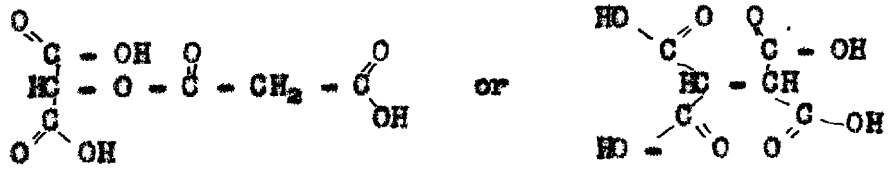
Clear cut evidence supporting this type of mechanism is lacking but employing an explanation such as this would comply with the observations: (1) No combustible gas is detected. (2) The reaction is somewhat slower than the corresponding oxalate oxidation. (3) The studies employing the carbon-14 tracer technique show that, in the oxidation process, the solvent participates in a stoichiometric manner with one mole of acetic acid being used per mole sodium mesoxalate oxidized. (4) The reproducibility and stoichiometry of the reaction are satisfied.

C. Citric Acid and Malonic Acid

The available data are not sufficient to offer a reasonable explanation for the oxidation of these materials. Apparently the reactions are quite complex. The complexity might be expected if the proposed mechanism in aqueous media mentioned previously takes place in the acetic acid medium. Using malonic acid as an example:



The resonance possibilities of the free radical may stabilize the radical sufficiently to permit polymerization. If this is the case one could expect two types of bonds to be formed preferentially in the polymer each of which has about the same bond energy:



These possibilities, if they exist, could explain the inability to isolate clear cut products and the fact that an end point is reached which corresponds to the transfer of an fractional number of equivalents. It does not explain the evolution of two millimoles of carbon dioxide both of which come from the solvent.

The lack of more information makes any more speculation pure guesswork.

What has been said concerning malonic acid could be repeated in the explanation concerning the oxidation of citric acid. The increased complexity of the molecule, however, would lead one to suspect an even wider variety of reactions. Because sufficient data are not available, it is impossible to draw conclusions other than those which would be exactly comparable to the speculation concerning malonic acid.

SUMMARY

SUMMARY

Initially this work was begun to investigate possible analytical applications for which acetic acid solutions of cerium (IV) could be used and to collect data which would aid in the elucidation of the oxidative mechanism through which the reactions proceed in this medium. In general, these objectives have been accomplished as is evidenced by the results produced in the investigation.

Acetic acid solutions of cerium (IV) were prepared from ammonium hexanitratocerate (IV) since investigation showed that higher concentrations of oxidant were obtainable in acetic acid through its use than with other salts. An amperometric technique employing two active electrodes was used almost exclusively in following the course of the titrations. This procedure for detecting the equivalence point was adopted in preference to potentiometric methods because of certain inherent difficulties encountered with the reference electrodes in this non-aqueous medium.

The following observations were noted in the investigation:

(1) Acetic acid solutions of cerium (IV) prepared from ammonium hexanitratocerate (IV) are reasonably stable if stored in the dark; only in very precise studies is it necessary to restandardize the solutions during a given work period. If the solutions are stored in light or if a mineral acid is present, the rate of decomposition of cerium (IV) is accelerated to an appreciable degree.

(2) It is possible to standardize cerium (IV) solutions with primary standard grade sodium oxalate. This reagent fulfills the requirements necessary for a standard reductant in this medium. In addition to sodium oxalate, iron (II) perchlorate exhibits the prescribed requirements for a standard reductant with one exception, nitrate presents a serious interference. Even though iron (II) perchlorate solutions can not be used for the determination of cerium (IV) in the presence of nitrate, they can be used to good advantage in the determination of other oxidants in the absence of nitrate. Evidence is offered demonstrating the feasibility of employing this reagent in the analysis of acetic acid solutions of sodium permanganate and chromium trioxide.

(3) Employing acetic acid solutions of cerium (IV), it is possible to determine sodium oxalate or sodium mesoxalate in the presence of a wide variety of oxygenated materials. On the basis of these results, it seems justifiable to claim increased selectivity of the oxidant in this medium. Malonic acid and citric acid are determinable by a direct oxidimetric titration. These last oxidations are not entirely satisfactory since empirical means must be employed in detecting the end point.

(4) In the oxidation process of these materials, carbon dioxide is evolved in a stoichiometric manner. Employing acetic acid which is tagged with carbon-14 in the carboxyl group, extensive solvent participation in the oxidation process is shown. Per mole of reductant, the values for total carbon dioxide evolution and amount of carbon dioxide

derived from the acetic acid for the individual reductants are: sodium oxalate, two and one; malonic acid, two and two; sodium mesoxalate, three and one; and citric acid, three and three.

(5) As in aqueous media the redox potential of the cerium couple in acetic acid is dependent on the type of mineral acid present and concentration of that acid. Perchloric acid provides the highest redox potential. The variation of the potential in the presence of different acids suggests that complexation takes place in this medium.

These accomplishments show partial fulfillment of the broad objectives established at the beginning of the investigation; however, during the course of the study, several other problems presented themselves:

(1) A more complete investigation of iron (II) perchlorate to realize its eventual possibilities in this medium.

(2) Further study concerning the employment of sodium permanganate in acetic acid.

(3) The extension of cerium (IV) oxidations to substances other than oxygenated materials.

(4) Utilization of other tagged molecules to further elucidate the oxidative mechanism.

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APPENDIXES

APPENDIX 1

Summary of Oxygenated Substances Subjected to Cerium (IV) Oxidations

Determinable by Direct Titration

Hydroquinone
Sodium Oxalate
Sodium Mesoxalate
Malonic Acid*
Citric Acid*

Reactions Proceeding Rapidly at First but Slowing Down During Titrations

Tartaric Acid
Ethylene Glycol
Glycerol
Acetylacetonate
Sucrose
Oxalacetic Acid
Pyruvic Acid

Reactions Proceeding Slowly Throughout the Titrations

Methylene Diacetate
Formaldehyde
Benzaldehyde
Ethyl Alcohol
Methyl Alcohol
Cinnamic Acid**
Malic Acid
Cyclohexene
2, 5-Dimethyl-3-Hexyne-2,5-Diol
2 Mercaptobenzthiazol
P-aminobenzoic acid and fluorene

Stable Materials

Methyl Formate
Methyl Acetate
Ethyl Acetate
Succinic Acid
Formic Acid
Benzoic Acid

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* Not very satisfactory
** Reacts at a rate approximating a favorable titration.

APPENDIX 2

Calculation Used for Estimating Minimum Amount of $CH_3C^{14}O_2H$ Needed

Requirements: In order to be statistically accurate the final count must be at least six times background or at least 240 counts per minute or 4.0 counts per second.

Assumptions: (1) Flow counter is 10% efficient. (2) The acetic acid and reductant react in a mole to mole ratio.

Calculations:

One millicurie (by definition) = 3.7×10^7 Disintegrations per second. At least 4.0 counts per second are necessary for accurate work. Assuming 10% efficiency of the counter, 40 disintegrations per second are necessary.

$\therefore \frac{40}{3.7 \times 10^7}$ millicuries are needed in each sample.

Sample sizes are in the order of 0.2 millimoles of reductant which are dissolved in 50 ml. or 875 millimoles of acetic acid.
Using the original assumption of a reaction involving mole to mole ratio of acetic acid to reductant this expression can be set up:

$$\frac{40}{3.7 \times 10^7} \text{ mc} \times \frac{875}{0.2} = 0.473 \times 10^{-2} \text{ mc/sample}$$

Since 20 samples are to be collected the minimum amount of material is about 0.1 mc.

APPENDIX 3

Sample Calculation for Determining the Involvement of Acetic Acid Using Carbon-14 Dioxide

Initial wt. sodium oxalate

52.6 mg. = 0.392 millimoles

Total wt. precipitated $BaCO_3$

154.0 mg.

Wt. $BaCO_3$ taken for counting

50.0 mg.

Net counts per minute on sample

273.5

Net counts per minute per millimole sodium oxalate

$$\frac{273.5}{} \times \frac{154}{50} \times \frac{1}{.392} = 2150 \ \frac{\text{counts per minute}}{\text{millimole oxalate}}$$

Going through the same procedure with the acetic acid solvent after combusting and collecting the carbon dioxide as $BaCl_3$

$$2020 \ \frac{\text{counts per minute}}{\text{millimole } CO_2 \text{ from acetic acid}}$$

$$\frac{2150}{2020} = \frac{1.06 \text{ millimoles } CO_2 \text{ from acetic acid}}{\text{Millimole oxalate oxidized}}$$