

CERATE OXIDIMETRY OF ALPHA-HYDROXY
ACIDS AND RELATED MOLECULES
IN ACETIC ACID

Thesis for the Degree of Ph. D.
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John Thomas Gatto
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ABSTRACT

CERATE OXIDIMETRY OF ALPHA-HYDROXY ACIDS AND RELATED MOLECULES IN ACETIC ACID

by John Thomas Gatto

The applicability of ammonium hexanitratocerate (IV) in acetic acid as a general reagent for the oxidation of alpha-hydroxy and alpha-keto carboxylic acids, as well as some other oxygenated organic molecules, was investigated.

It was readily apparent that organic molecules with common functional groups were oxidized at radically different rates by the reagent. The feasibility of utilizing either a direct or an excess method can not be reliably predicted by examining the structure of the molecule or by visualization of the probable products.

Direct titrations were possible for mandelic acid and phenylcyclopentylglycolic acid. The excess method was successful for pyruvic acid and benzoylformic acid.

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CERATE OXIDIMETRY OF ALPHA-HYDROXY ACIDS AND
RELATED MOLECULES IN ACETIC ACID

By

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INTRODUCTION

The use of cerium (IV) in strong mineral acid solution as an oxidative reagent for the determination of organic compounds was presented by G. F. Smith (36) and G. F. Smith and F. R. Duke (37). More recently, W. Petzold (29) has thoroughly summarized the extensive analytical uses of cerium. Thus far, to the best of my knowledge, the use of cerium as an oxidative reagent for the determination of organic compounds in non-aqueous solvents has been limited to acetic acid and acetonitrile (30). O. Hinsvark (19) initially examined the feasibility of using ammonium hexanitratocerate (IV) in glacial acetic acid and established a standardization procedure utilizing perchloric acid, sodium oxalate as the primary standard, and a biamperometric end point detection. W. Harris (17) investigated the oxidation of sodium azide and hydrazine acetate with cerium in an acetic-perchloric acid medium. L. Bowman (7) in attempting to ascertain the cerium species present in solution did determine a kinetic expression for the decomposition of the reagent in the presence of perchloric acid. R. Aufuldish (4), using cerium as a titrant, established methods for determining some oxygenated compounds and, using carbon disulfide as an extractant, established a method for recovering some of the reaction products.

The work presented here was concerned with further investigation of the use of cerium as a reagent for specific types of organic compounds. In addition, it was concerned with the manner in which the organic compounds were oxidized and possible identification of the cerium species involved in the oxidation.

EXPERIMENTAL

I. Reagents

J. T. Baker "Baker Analyzed" REAGENT Glacial Acetic Acid. Contrary to Bowman's conclusions (7) it was found necessary to distill the acetic acid from chromic oxide before use. Baker distributes two grades of "Baker Analyzed" Glacial Acetic Acid: one that conforms to a dichromate test (31) and one, which is used in this laboratory, that does not. As a result it was found that the use of some undistilled batches of acetic acid to prepare the cerium reagent resulted in titres being about 0.03N rather than 0.05N which, based on the addition of weighed amounts of ammonium hexanitratocerate, should have been the value found.

Baker 70% perchloric acid, hydrochloric acid, nitric acid, sulfuric acid, sodium hydroxide, barium hydroxide, ammonium nitrate, citric acid, tartaric acid, malonic acid, calcium acetate, disodium tartrate, formaldehyde, acetic anhydride, acetonitrile and sodium oxalate; all reagent grade.

G. Fredrick Smith ammonium hexanitratocerate, ceric sulfate, ammonium tetrasulfatocerate, and ceric hydroxide.

Merck carbon disulfide.

Fisher lactic acid.

Mallinckrodt sodium carbonate, primary standard.

Matheson, Coleman and Bell propanediol, pyruvic acid, ascorbic acid, ethyl mandelate, phenyl hydrazine, and 30% glyoxal solution.

Eastman acetylacetone and chromotropic acid.

S. B. Penick alpha-phenylcyclopentylglycolic acid, benzoylformic acid, benzoyl formamide, and methyl benzoyl formate.

Nitron M.P. 186-188° C., (lit. 189°C.). (12)

Glycolic Acid M.P. 80°C., (lit. 80°C). (16)

Mandelic Acid recrystallized from benzene M.P. 118°C. (lit. 118-119°C). (16)

Samples of flavonol and benzoylacetic acid were obtained through the courtesy of F. Urbach (personal preparations).

Samples of mesitoylformic acid and mesitoic acid were obtained through the courtesy of J. Janssen (personal preparations).

Ceric hydroxide was prepared according to the method suggested by H. Laitinen (24). Ceric oxide was prepared by igniting ceric hydroxide for two hours at 900°C.

Benzoin, benzoin oxime, benzil, benzilic acid, benzohydroxamic acid, diphenylglyoxime and diphenylfuroxan were the same samples used by R. Aufuldish.

II. APPARATUS

A Sargent "Model III" manual polarograph equipped with platinum-platinum electrodes was used for the biamperometric detection of the endpoint. A magnetic stirrer and an amber buret were used for all cerium titrations.

A Beckman model DB recording spectrophotometer was used for obtaining ultra-violet spectra.

A Beckman DK-2 recording spectrophotometer was used for obtaining near infra-red spectra.

A Beckman IR-5 recording spectrophotometer was used for obtaining infra-red spectra. The samples were mounted in the form of KBr discs.

A Beckman DU spectrophotometer was used for obtaining spectra in the visible region.

III. SOLUTIONS

The cerium reagent was prepared by heating 950 ml of acetic acid made 1M in water to 60°C. in a one liter two-necked round-bottom flask and adding 26 grams of ammonium hexanitratocerate ($(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$). After allowing the solution to stand for one hour at this temperature with constant stirring, it was allowed to cool to room temperature. It was not necessary to filter the solution before it was transferred to a one liter amber bottle for storage. Solutions thus prepared in the morning were ready for use in the afternoon. During the preparation and transfer of the cerium solution it is advisable to work in a minimum of light. Initial titres were about 0.05N, and even though they rarely changed more than one part per thousand within several days they were checked daily. The reagent was standardized against 0.0700N sodium oxalate in glacial acetic acid made 1M in perchloric acid. The standard oxalate solutions were not used whenever the ambient temperatures varied by more than 1°C. from the temperature at which the solutions were prepared.

The ceric hydroxide-nitric acid reagent was prepared by refluxing 5 grams of ceric hydroxide with 25 ml of concentrated nitric acid until the solution was a deep cherry-red. The solution was filtered after it had been allowed to cool to room temperature. Five ml of this concentrate

were added to one liter of glacial acetic acid. The standardization procedure was the same as for the ammonium hexanitratocerate reagent.

Carbonate free barium hydroxide was prepared by filtering a saturated solution of barium hydroxide thru a cotton plug into a polyethylene bottle. The bottle was then fitted with a siphon and a drying tube filled with ascarite.

Standard solutions of 0.1N hydrochloric acid were prepared by adding 17 ml of concentrated acid to two liters of water and standardizing the solution against sodium carbonate, using methyl orange as the indicator.

Carbonate free solutions of sodium hydroxide were prepared by adding 5 ml of the clear supernatant of a saturated solution of sodium hydroxide to one liter of water. The resultant solution was standardized against potassium acid phthalate using phenolphthalein as the indicator.

IV. PROCEDURES

Direct titrations with the cerium reagent were performed by dissolving the organic sample in glacial acetic acid, adding enough perchloric acid calculated to make the final solution (including the added titrant) 1M in perchloric acid, and titrating to a biamperometric end point.

Indirect titrations were performed by adding an excess of cerium reagent estimated to be about twice the amount needed to react with the organic sample which was dissolved in glacial acetic acid. If possible, enough perchloric acid needed to make the solution 1M was added

immediately, and the excess cerium was titrated with a standard solution of sodium oxalate. Where necessary the reaction mixture was allowed to stand for longer periods, well protected from light, and the perchloric acid added just before the back titration with sodium oxalate.

Whenever the entire volume of the cerium reagent was added at one time to a solution of the organic sample, a 300 ml gas washing tower was used as the reaction vessel for the recovery of carbon dioxide from the reaction mixtures. Nitrogen was used as the carrier gas. Before it entered the reaction vessel it was passed through a washing tower containing a solution of barium hydroxide. The gaseous oxidation products were swept out of the reaction vessel by the nitrogen and through a trap in a dry ice-acetone bath where any entrained vapors such as acetic acid would be condensed. The carrier gas then passed through two 500 ml gas washing towers containing standard solutions of barium hydroxide. The exit tube of the system was protected by a drying tube containing ascarite. The system was purged with nitrogen before the cerium reagent was added. It was found that from one to two hours were required for the complete recovery of carbon dioxide if the bubble rate in the first washing tower was one to two bubbles per second. The excess barium hydroxide was determined by titration with standard hydrochloric acid using phenolphthalein as the indicator. In cases where it was desired to simulate the conditions of a titration by controlling the rate of addition of the cerium reagent, a 125 ml three-necked flask was used as the reaction vessel. A 50 ml buret fitted with a ground glass joint was positioned in the center neck for

the addition of the reagent, and the entrance and exit tubes for the carrier gas occupied the other two necks.



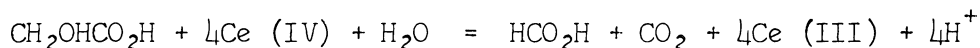
RESULTS AND DISCUSSION

I. Alpha-Hydroxy Carboxylic Acids with an Alpha-Hydrogen.

Early work by Smith and Duke (37) on alpha-hydroxy acids showed that aqueous solutions $4M$ in perchloric acid, excess reagent, and often elevated temperatures and extended reaction times were required for complete oxidation of the organic compound to carbon dioxide and formic acid. In the study by Aufuldish of the oxidation of benzoin, one of the compounds examined was benzilic acid, which was readily determined by direct titration at room temperature with the final solution being $1M$ in perchloric acid. One of the objects of the present study was to ascertain the applicability of the reagent to the determination of other alpha-hydroxy acids. Those acids examined were glycolic, lactic, mandelic, beta-phenyl lactic, phenylcyclopentylglycolic, tartaric and citric.

A. Glycolic Acid.

Bowman, although he reported that the oxidation of glycolic acid (CH_2OHCO_2H) was slow, made no mention of the products or of the stoichiometry. Smith reported that in aqueous sulfuric acid medium 3.95 equivalents of Ce (IV) per mole were used, the reaction presumably being:



Glycolic acid cannot be determined by direct titration. One millimole of organic sample consumed only a few tenths of a milliliter of $0.03N$ cerium reagent. If no perchloric acid is present a yellow-orange

precipitate is formed as the first few drops of titrant are added and as more titrant is added it redissolves. The precipitate does not decompose upon standing in solution for at least several hours, nor does it appear to decompose after being stored in a weighing bottle in a dried condition for four months. The precipitate was recovered by filtration using a sintered glass funnel and dried in a vacuum desiccator until the odor of acetic acid was gone. The precipitate is not readily soluble in water, ethanol or sulfuric acid, but is readily decomposed by hydrochloric or perchloric acids. Treatment with concentrated sodium hydroxide produces a deep blue color. A drop of 30% hydrogen peroxide produces a brown-red color. An old qualitative test for cerium (40) consisted of treating the sample with sodium hydroxide and hydrogen peroxide to produce, supposedly, a peroxy cerium (IV) salt of a brown-red color. Since this color is formed by the precipitate with the addition of only the hydrogen peroxide, it can be presumed that both the cerium and the basicity in the form of an hydroxyl group is present.

The cerium content was established by igniting the precipitate at 900°C. for one hour in order to obtain the oxide (41).

Table I. Cerium content of cerium-glycolate precipitate.

Sample, mg.	CeO ₂ , mg.	% Cerium
126.8	60.4	38.8
104.0	47.6	38.8
108.6	49.1	40.0

Nitron (12) was used as the reagent for the determination of the nitrate content. The cerium-glycolate precipitate was treated with sodium carbonate solution; the presumption being that if a Ce-NO_3 bond were present it would be hydrolyzed to Ce-OH with the formation of free soluble nitrate.

Table II. Nitrate content of cerium-glycolate precipitate.

Sample, mg.	Nitrate, mg.	% Nitrate
A. 39.7	5.54	14.0
39.7	5.56	14.0
39.7	5.48	13.8
B. 39.5	5.37	13.6
39.5	5.47	13.9
39.5	5.42	13.7

Assuming that there is one atom of cerium per molecule of precipitate the molecular weight would be 361, and there would be 0.80 nitrate per atom of cerium.

The glycolate content was determined by treating the precipitate with concentrated sulfuric acid which would cleave the organic molecule to carbon dioxide and formaldehyde, the latter being determined spectrophotometrically with chromotropic acid according to the method described in Stone (38). There appears to be 1.2 molecules of glycolate per atom of cerium.

Table III. Glycolate content of cerium-glycolate precipitate.

Sample, mg.	Glycolate, mg.	% Glycolate
A. 17.2	3.80	22.1
17.2	4.38	25.5
17.2	4.77	27.7
B. 16.5	3.52	21.3
16.5	3.91	23.1
16.5	4.12	24.9

The simple test adding strong base to the precipitate and suspending a piece of moist litmus paper above it initially produced a positive test for ammonium ion; however, this result was not duplicated with any other sample.

Examination of the infra-red spectra of the precipitate indicates the presence of nitrate, carboxyl, primary alcohol, carbonyl, hydroxyl and possibly ammonium ion (Figure 1a and 1b) (5). The infra-red spectra of glycolic acid itself (Figure 2a and 2b) shows a primary alcohol band at 1080 cm^{-1} , where the precipitate shows this band at 1064 cm^{-1} . Goulden (14) in his studies of the infra-red spectra of metal glycolates and glycolate esters found this band at 1092 cm^{-1} in the ester and at 1067 cm^{-1} in zinc glycolate. This decrease in frequency indicates the chelation of the cation through the alcoholic oxygen, and supports the idea that the same kind of bonding exists in the cerium-glycolate precipitate. The non-integral stoichiometry found for the precipitate would indicate that it is not a pure salt; since cerium (IV) can readily accomodate six ligands there could be various combinations of nitrate, chelated glycolate, hydroxyl and possible acetate which would provide odd values.

After a few days a curdy white precipitate settles out of the reaction mixture after the precipitate has been removed. Qualitative examination of the infra-red spectrum of this material indicates that it is a mixture of ammonium nitrate and cerous glycolate. (5)

In an attempt to ascertain the role of the solvent in the formation of the precipitate, the same procedure was tried in redistilled acetonitrile of very low water content. A precipitate did form, much in appearance like that from acetic acid. It was separated by filtration and remained only a short time on the funnel before being put in a desiccator. Within several minutes the solid had taken on a wet appearance, and though placed in a sealed container it soon degenerated into a white precipitate with a very viscous clear supernatant. No analyses were performed on it.

The indirect method, the addition of excess cerium reagent to the organic sample and subsequent back titration with a solution of standard oxalate, was then tried. One solution contained equimolar concentrations of cerium (IV) and glycolic acid. At the end of 22 hours 98% of the cerium had been consumed. Another solution contained four equivalents of Ce (IV) per mole of glycolic acid. At the end of 22 hours 53% of cerium had been consumed. A more precise time study was attempted by following Ce(IV) consumption as a function of time. For one series the Ce (IV) concentration was measured by adding perchloric acid and titrating with sodium oxalate. Plots of various simple functions of concentration versus time showed no linear relationships. The difficulty here could be that the addition of the perchloric acid accelerated the rate of reaction and changed the concentration of Ce (IV)

at the time of measurement.

Table IV. Stoichiometry of glycolic acid oxidations by an excess method.

Organic m mole	Reaction Time hours	Mequiv. Ce (IV)/ Organic m mole
0.500	4.8	1.12
0.500	9.0	1.53
0.500	12.0	1.91
0.500	22.0	2.08

In another series the Ce(IV) concentration was measured spectrophotometrically. Here again plots of various simple functions of concentration versus time showed no linear relationships. At this point it could be said that the rate law would be complicated since there are two oxidations possibly occurring; the glycolic acid being oxidized to formaldehyde and the formaldehyde being oxidized to formic acid. Accordingly the rate of oxidation of formaldehyde was estimated. After 70 hours, a solution which was initially 0.047N in Ce (IV) and 0.0325M in formaldehyde showed a 52% decrease in Ce (IV) concentration. Thus the apparent rate of oxidation of formaldehyde is only about three or four times slower than that of glycolic acid.

Table V. Carbon dioxide recoveries from glycolic acid oxidations.

Reaction Time hours	Sweep Time hours	Organic m moles	CO ₂ m moles	Recovery %
16	2	2.00	1.71	85.5
54	2	2.00	1.79	89.5

Since the consumption of cerium (IV) by glycolic acid by direct titration is negligible, and since the excess method does not provide decent stoichiometry within a reasonable time, it can readily be concluded that glycolic acid is not amenable to analysis with the cerium reagent.

B. Lactic Acid

In the most recent review available (3) lactic acid ($\text{CH}_3\text{CHOHCO}_2\text{H}$) is not among those organics which have been determined by direct titration with Ce (IV). The percent purity of the lactic acid and the absence of specific impurities was established by methods given in Rosin(31). Even the excess method, after 57 hours, showed a consumption of Ce (IV), based on a two electron change, which varied from 85% to 130%. Carbon dioxide recoveries were run with the addition of two equivalents of Ce (IV) per mole of lactic acid in consideration of the following system:

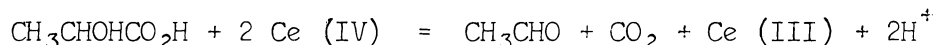


Table VI. Carbon dioxide recoveries from lactic acid oxidations.

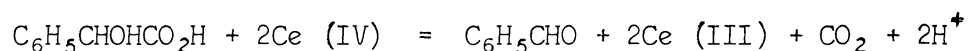
Reaction Time hrs.	Sweep Time hrs.	Organic m Moles	CO ₂ m Moles	Recovery %
64	2	1.24	0.885	70.5
72	2	1.24	0.885	70.5
93	2	5.04	3.64	72.3

From the above table it is apparent that only about 70% of the cerium (IV) is used in the primary oxidation of lactic acid to acetaldehyde. The remaining 30% is consumed by the acetaldehyde to produce acetic acid. Since lactic acid also consumes negligible amounts of

cerium reagent upon direct titration and, since it provides erratic results with the excess method, the same conclusions made about glycolic acid are also applicable.

C. Mandelic Acid

Mandelic acid ($\text{C}_6\text{H}_5\text{CHOHCO}_2\text{H}$) has been reported to be amenable to both direct, with the aid of a catalyst (30), and indirect, with the use of very high temperatures (39), methods of determination with Ce (IV) in aqueous mineral acid solution.



Mandelic acid which had been recrystallized from benzene and dried in a vacuum desiccator over magnesium perchlorate for 43 hours was used. Mandelic acid can be titrated directly with the Ce (IV) reagent to a biamperometric end point. Consistent results are obtained only if the electrode is cleaned by immersion in concentrated nitric acid for 10 minutes before each titration.

Table VII. Direct titration of mandelic acid.

Organic m Moles	Ce (IV) ml 0.04585 <u>N</u>	Ce (IV) meq. used
0.100	13.23	0.2033
0.100	13.25	0.2037
0.100	13.28	0.2043

Since the lines used to determine the end point are quite linear the 1 to 2% excess reagent consumed is probably due to its reacting with the product benzaldehyde. The mandelic acid can be quickly and accurately determined by the indirect method. About 4 milliequivalents of cerium

reagent per mole of organic are added to a solution of the sample. After 5 minutes, enough perchloric acid is added to make the solution 1M and the excess Ce (IV) is immediately titrated with standard oxalate. The end point is readily detected by the disappearance of the yellow color of the Ce (IV).

Table VIII. Mandelic acid stoichiometry.

Organic mg.	Organic m Moles	Meq. Ce (IV) Reagent Used	Meq. Ce (IV) Reagent/ m Moles Organic
30.4	0.200	0.398	1.99
65.2	0.429	0.862	2.01
72.2	0.475	0.941	1.99
73.3	0.476	0.953	2.01

The reaction mixture was extracted with carbon disulfide according to the method devised by Aufuldish. The carbon disulfide was evaporated and the residue taken up in ethanol and tested for benzaldehyde with 2,4-dinitrophenylhydrazine according to the method in Shriner and Fuson (35). The melting point of the precipitate was 153-155°C., and the melting point of an authentic derivative of benzaldehyde was 154-155.5°C.; the mixed melting point was 153-154.5°C.

Carbon dioxide recoveries were run immediately after the addition of the cerium reagent to the organic sample.

The direct method, even though more precise than the indirect, is accurate to only 2%; whereas the average value of the indirect determinations (2.00) corresponds exactly to the stoichiometry for the two electron oxidation.

Table IX. Carbon dioxide recoveries from mandelic acid oxidations.

Sweep Time hrs.	Organic m Moles	CO ₂ m Moles	Recovery %
2.00	4.00	3.86	96.5
1.75	2.40	2.45	102.3
2.00	2.40	2.37	99.3

D. Beta-Phenyl Lactic Acid

Beta-phenyl lactic acid ($\text{C}_6\text{H}_5\text{CH}_2\text{CHOHCO}_2\text{H}$) was prepared by treating an acetic acid solution of phenylalanine with sodium nitrite. The reaction mixture was extracted with benzene and the solvent removed by distillation. The infra-red spectrum of the resultant yellow syrupy liquid is consistent with beta-phenyl lactic acid (9). The purity of the material was determined by titration with standard base to be 97.4%.

Based on a two electron oxidation to the aldehyde, the acid is only about half oxidized by the cerium reagent using the direct method. In the indirect method 85% of the acid is oxidized after 5 minutes and 93% oxidized after 1 1/2 hours. Even though beta-phenyl lactic acid is more reactive than either glycolic or lactic acids it is not at all comparable to mandelic acid and so must be grouped with those two aliphatic acids as not being amenable to determination with the cerium reagent.

II. Alpha-Hydroxy Carboxylic Acids without an Alpha-Hydrogen.

A. Phenylcyclopentylglycolic Acid

Thus far it appears that the alpha-hydroxy acids which have an alpha hydrogen produce an aldehyde as the product for the electron



oxidation. The aldehyde subsequently interferes with the attempt to utilize the direct method of titration. Phenylcyclopentylglycolic acid ($\text{C}_6\text{H}_5\text{C}(\text{C}_5\text{H}_9)\text{OHC}\text{O}_2\text{H}$) should produce a ketone as the product of a two electron oxidation and therefore provide accurate results in a direct titration. The phenylcyclopentylglycolic acid was used as received and dried in a vacuum desiccator. The reaction can be represented as:

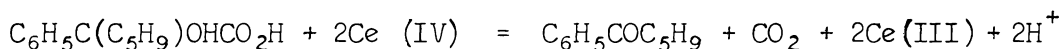


Table X. Phenylcyclopentylglycolic acid stoichiometry.

Organic mg.	Organic m Moles	Meq. Ce (IV) Reagent Used	Meq. Ce Reagent/ m Moles Organic
227.1	1.032	2.043 direct	1.98
227.1	1.032	2.043 direct	1.98
227.1	1.032	2.043 direct	1.98
51.0	0.232	0.470 indirect	2.02
52.2	0.238	0.475 indirect	2.00
38.4	0.175	0.347 indirect	2.01
34.4	0.156	0.314 indirect	1.99
56.2	0.256	0.510 indirect	2.00
69.2	0.315	0.631 indirect	2.01

The titration residues were combined and extracted with carbon disulfide and the 2,4-dinitrophenylhydrazone prepared. The melting point was 137°C . The derivative was recrystallized from ethanol and the melting point obtained was now $141-142^\circ\text{C}$.; depending upon the source cited (8,15,28), the melting point of this derivative of phenylcyclopentyl ketone is anywhere between 141 and 145°C .



Table XI. Carbon dioxide recoveries from phenylcyclopentylglycolic acid oxidations.

Sweep Time hrs.	Organic m Moles	CO ₂ m Moles	Recovery %
2	0.971	0.965	99.4
2	0.971	0.951	98.0
2	0.971	0.953	98.2

The direct titration is quite precise and is accurate to within 1%. The indirect method, while not as precise, is accurate to within 0.5% if the average value for the series of determinations is considered.

III. Alpha-Hydroxy Polycarboxylic Acids

A. Tartaric Acid

Smith (36) reported excess methods for tartaric acid ($\text{CO}_2\text{HCHOHCHOHCO}_2\text{H}$) showing consumption of 7.20 and 6.0 equivalents of Ce (IV) depending on whether aqueous sulfuric or aqueous perchloric acid is present; Sharma and Mehrota (34) used an excess method with aqueous sulfuric acid and found that 10 equivalents of Ce (IV) were required. Direct titrations with Ce (IV) have also been reported. Berry (6) claimed that 3.51 equivalents were required, but did not mention the means by which the end point was detected. Ashworth reported a method, attributed to Michalski, to be a direct one, but a reading of the reference in Chemical Abstracts would indicate that it is actually a back titration of excess cerium (IV) with oxalate (26).

In making up solutions of known concentrations of tartaric acid, the values given on the bottle labels were used. In the absence of perchloric acid, tartaric gives a yellow precipitate with the cerium



reagent. It takes about a week for the precipitate to decompose, leaving a clear solution. The precipitate was isolated in the same manner as the glycolic acid precipitate and an infra-red spectrum was obtained. While the infra-red spectra of tartaric acid, sodium tartrate, and the cerium-tartrate precipitate were complicated (Figures 3a, 3b, 4a, 4b, 5a, 5b) it is possible to ascertain the presence of nitrate and coordination of cerium through a hydroxyl group in the precipitated material (5). Kirschner and Kiesling (22) in their studies on the structure of copper (II) tartrate trihydrate, concluded that a secondary hydroxyl group at 1097 cm^{-1} was split to 1080 cm^{-1} and 1063 cm^{-1} by coordination with copper. In the precipitate the hydroxyl band is apparently not split but, as in the case of glycolic acid, merely shifted from 1076 cm^{-1} to 1061 cm^{-1} .

In order to get decent biamperometric data it was necessary to clean the electrodes with concentrated nitric acid before each titration.

Table XII. Stoichiometry of tartaric acid oxidations by direct titration.

Organic m Moles	Ml. of 0.0459N Ce (IV) Reagent	Meq. Ce Reagent/ m Moles Organic
0.1327	13.19	4.56
0.1327	13.22	4.59
0.1335	12.95	4.45
0.1335	12.95	4.45
0.1335	12.95	4.45

In order to ascertain the overall stoichiometry an excess method was used.

Table XIII. Stoichiometry of tartaric acid oxidations by an excess method.

Organic m Moles	Reaction Time min.	Ce (IV) Meq.	Meq Ce Reagent/ m Moles Organic
0.1661	80	1.035	6.23
0.1661	90	1.079	6.50
0.1661	95	1.033	6.21

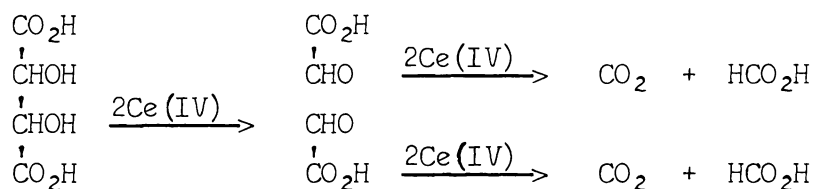
Carbon dioxide recoveries were run by adding 4.50 meq. of Ce (IV) per mmole of tartaric acid.

Table XIV. Carbon dioxide recoveries from tartaric acid oxidations

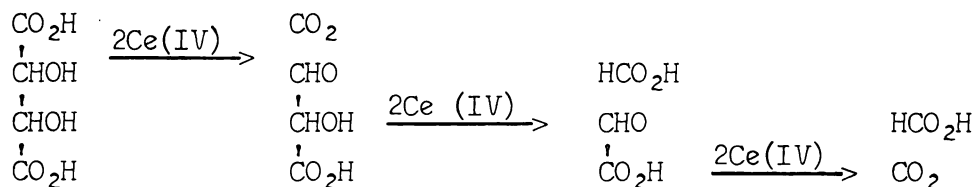
Sweep Time Hr.	Organic m Moles	CO ₂ m Moles	m Moles CO ₂ / m Moles Organic
1	0.204	0.429	2.10
1	0.204	0.431	2.11
1	0.204	0.425	2.08

Upon inspection of the molecular structure of tartaric acid, three possible routes for its oxidation by Ce (IV) are apparent:

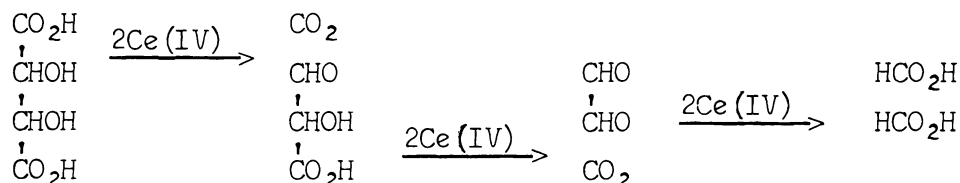
- 1) by glycol cleavage followed by decarboxylation,



- 2) by a decarboxylation followed by a glycol cleavage with a subsequent decarboxylation,



3) by two successive decarboxylations followed by a glycol cleavage,



Three possible intermediates in these routes are glyoxylic acid (CHOCO_2H), glyoxal (CHOCHO), and tartronaldehydic acid ($\text{CHOCHOHCO}_2\text{H}$). Glyoxylic acid was prepared and examined as the sodium salt (42). The end point in the direct titration procedure appears when 97.8% of the theoretical amount of the cerium reagent has been added to the sample; so it can be said that glyoxylic acid is rapidly oxidized by the cerium reagent. Carbon dioxide recoveries showed that 0.987 moles of carbon dioxide per mole of glyoxylic acid are produced. In the direct titration of glyoxal the end point appears when about 66% of the theoretical amount of the cerium reagent has been added to the sample. Carbon dioxide recoveries showed that 0.006 moles of CO_2 per mole of glyoxal are produced.

Tartaric acid produces 2.1 moles of carbon dioxide per mole of tartaric acid upon the addition of 4.5 equivalents of Ce (IV). Route #1 would require the consumption of 6 equivalents of Ce (IV) for the production of 2 moles of carbon dioxide per mole of tartaric acid. Hence this route can be readily eliminated. Route #2 can just as readily be eliminated since 4.5 equivalents of Ce (IV) would result in

the production of one and a fraction moles of carbon dioxide per mole of tartaric acid.

Route #3 which requires that 4 equivalents of Ce (IV) produce 2 moles of carbon dioxide per mole of tartaric acid appears to be the actual route. Additional supporting information is that the addition of p-nitrophenylhydrazine to the reaction mixture after only 2 equivalents of Ce (IV) per mole of tartaric acid produces a precipitate which upon recrystallization from nitrobenzene melted at 307-308°C. (a second sample melted at 311-312°C.); according to the literature (10) the p-nitrophenylhydrazone of tartronaldehydic acid has a melting point of 310°C. Synthetic reaction mixtures containing glyoxylic acid give no precipitate. Furthermore it should be possible to detect glyoxal after 4 equivalents of Ce (IV) per mole of tartaric acid have been added. Spot tests using dianisidine (8) give clear positive tests for the presence of glyoxal. However, whereas synthetic mixtures with glyoxal give a precipitate with 2,4-dinitrophenylhydrazine the actual reaction mixtures do not.

Attempts to analyze for the residual formic acid did not provide quantitative results. In one instance 6 equivalents of Ce (IV) per mole of tartaric acid was added and after the reaction was complete (7 days later), a solution of mercuric chloride was added (2). There was no precipitate of mercurous chloride. The next reaction mixture was made 0.2M in perchloric acid and the reaction was complete within the day. The addition of mercuric chloride did produce a precipitate of mercurous chloride, but the best results were no better than 24% of the theoretical yield.

It appears that the value of 4.5 equivalents of Ce (IV) per mole of tartaric acid obtained upon direct titration is an artifact, and does not correspond to any definite stage in the oxidation. The cerium reagent reacts preferentially with the hydroxy-acid functional group, but not to the exclusion of some diol cleavage. Naturally neither the direct nor the indirect methods could be considered as approaches to the determination of tartaric acid.

B. Citric Acid

Excess methods reported by Smith (36) show that citric acid ($\text{CO}_2\text{HCH}_2)_2\text{CHOHCO}_2\text{H}$) consumes 15.85 equivalents of Ce (IV) in aqueous sulfuric acid solutions and 14.0 equivalents of Ce (IV) in aqueous perchloric acid solutions. Ashworth's reference to Michalski's work on citric acid is as incongruent as that on tartaric acid (26).

The value given on the label of the bottle for the percent purity of citric acid was used in preparing solutions of known concentration.

Citric acid also gives a yellow precipitate with the cerium reagent in the absence of perchloric acid, but is so unstable as not to be isolatable.

The electrodes again required cleaning with nitric acid in order to obtain consistent end points.

Table XV. Direct titration of citric acid.

Organic m Moles	ml of 0.0459N Ce (IV) Reagent	Meq. Ce Reagent/ m Moles Organic
0.0250	21.56	3.95
0.0250	21.64	3.97
0.0250	21.83	4.00

In order to ascertain the overall stoichiometry the excess method was used.

Table XVI. Indirect titration of citric acid.

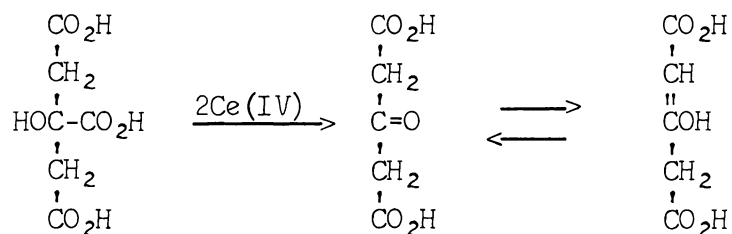
Organic m Moles	Reaction Time min.	Ce (IV) meq.	Meq. Ce Reagent/ m Moles Organic
0.115	25	1.506	13.1
0.0645	85	0.890	12.6
0.0645	85	0.878	12.5
0.0645	85	0.820	11.6

The carbon dioxide recoveries were run with the addition of 4 equivalents of Ce (IV) per mole of citric acid.

Table XVII. Carbon dioxide recoveries from citric acid oxidations.

Sweep Time hrs.	Organic m Moles	CO ₂ m Moles	m Moles CO ₂ / m Moles Organic
1	0.2293	0.309	1.36
1	0.2293	0.323	1.41
1	0.2293	0.313	1.37

If it is assumed that the first two equivalents of Ce (IV) are involved in the decarboxylation of citric acid, the first intermediate should be either acetone dicarboxylic acid or its enol form.



Accordingly, acetone dicarboxylic acid was synthesized (20). The preparation was found to be 98.6% pure by titration with standard base.

Table XVIII. Direct titration of acetone dicarboxylic acid.

Organic mg	Organic m Moles	Ce(IV) Reagent meq.	Meq. Ce Reagent/ m Mole Organic
63.2	0.432	1.372	3.32
49.1	0.336	0.9448	3.15
53.3	0.365	1.242	3.41
65.5	0.448	1.446	3.23

Carbon dioxide recoveries were run after the addition of 3.3 equivalents of Ce (IV) per mole of acetone dicarboxylic acid, and also run with the addition of only two equivalents of Ce (IV) per mole of acetone dicarboxylic acid.

Table XIX. Carbon dioxide recoveries from acetone dicarboxylic acid oxidations.

Organic m Moles	Meq. Ce (IV)/ m Moles Organic	CO ₂ m Moles	m Moles CO ₂ / m Moles Organic
0.373	3.3	0.342	0.917
0.428	3.3	0.399	0.933
0.392	3.3	0.373	0.954
1.048	2.0	0.446	0.434
1.048	2.0	0.479	0.457
1.048	2.0	0.522	0.497
1.048	2.0	0.514	0.490
0.761	2.0	0.335	0.440

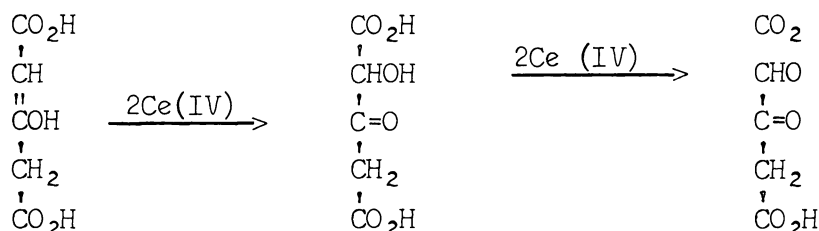
The average value for the direct titration of acetone dicarboxylic acid is 3.3 equivalents of Ce (IV) per mole rather than the expected 2.0.

Two possible explanations are: one, that acetone dicarboxylic acid is

not an intermediate or two, that the value of 4.0 equivalents of Ce (IV) per mole for citric acid and 3.3 equivalents of Ce (IV) per mole for acetone dicarboxylic acid are artifacts. The results from the direct titration of tartaric acid lend support to the latter explanation.

There is hardly any correspondence between the amount of carbon dioxide produced and the number of equivalents of Ce (IV) added. Four equivalents of Ce (IV) per mole of citric acid produce more than one mole of carbon dioxide, and 2 equivalents of Ce (IV) per mole of acetone dicarboxylic acid produce a significant amount of carbon dioxide.

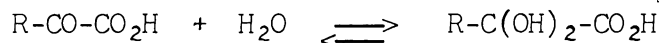
The oxidation of the enol form of acetone dicarboxylic acid could produce carbon dioxide by the following sequence:



The products of the oxidation of both citric and acetone dicarboxylic acids appear to be quite reactive and compete for the cerium reagent making any interpretation regarding the sequence of oxidations difficult.

IV. Alpha-Keto Carboxylic Acids

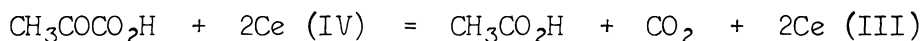
The alpha-keto acids studied were pyruvic acid, benzoylformic acid, and mesitoylformic acid. Considering the following equilibrium:



it is likely that the alpha-keto acids would react with the cerium reagent as the alpha-hydroxy acids do.

A. Pyruvic Acid ($\text{CH}_3\text{COCO}_2\text{H}$)

An excess method utilizing Ce (IV) in aqueous sulfuric acid medium has been reported by Fromageot and Desnuelle (13); two equivalents of Ce (IV) were consumed and the products were acetic acid and carbon dioxide. Sengupta and Aditya (33) have reported the direct titration of pyruvic acid with Ce (IV) in aqueous perchloric acid solution, using elevated temperatures and ammonium molybdate as a catalyst. Its oxidation was represented by:



The percent purity of pyruvic acid was determined by adding standard sodium hydroxide and titrating the base with standard sulfuric acid. The stoichiometry was determined by using the excess method.

Table XX. Indirect titration of pyruvic acid.

Organic m Moles	Ce (IV) Reagent meq.	Meq. Ce Reagent/ m Mole Organic
0.644	1.294	2.01
0.644	1.280	1.99
0.644	1.288	2.00

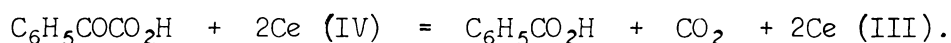
Table XXI. Direct titration of pyruvic acid.

Organic m Moles	ml. of 0.0461N Ce (IV) Reagent	% Organic Reacted
0.387	16.11	95.9
0.387	15.82	94.1
0.387	15.12	90.0
0.387	15.46	92.0
0.387	15.72	93.6
0.387	15.78	93.9

The lines drawn for the determination of the end point in the biamperometric titrations were quite linear. The lack of 100% reaction could be due to the possibility that some of the pyruvic acid is polymerized and under the conditions of the direct titration does not depolymerize as completely as under the conditions of the excess method. Nevertheless, pyruvic acid reacts more rapidly than its analog lactic acid and can be readily determined by the excess method.

B. Benzoylformic Acid ($\text{C}_6\text{H}_5\text{COCO}_2\text{H}$).

At this time no references to the use of cerium for the determination of benzoylformic acid were known to the author. It is presumed that the oxidation can be represented as:



The benzoylformic acid was dried in an Abderhalden pistol drier at the boiling point of chloroform. The stoichiometry was determined by using the excess method.

Table XXII. Indirect titration of benzoylformic acid.

Organic m Moles	Ce (IV) Reagent meq.	Meq. Ce Reagent/ m Moles Organic
0.2828	0.580	2.04
0.2121	0.432	2.04
0.2121	0.427	2.01
0.2121	0.430	2.03

Table XXIII. Direct titration of benzoylformic acid.

Organic m Moles	ml. of 0.0459N Ce (IV) Reagent	% Organic Reacted
0.267	12.44	107.0
0.267	11.75	98.8
0.267	11.53	99.2
0.267	11.57	99.5
0.200	9.60	110.0

Table XXIV. Carbon dioxide recoveries from benzoylformic acid oxidations.

Organic m Moles	CO ₂ m Moles	m Moles CO ₂ / m Moles Organic
0.4242	0.516	1.21
0.4242	0.501	1.18
0.4242	0.477	1.13
0.4242	0.472	1.11

The experimental values, especially the carbon dioxide recoveries, are higher than expected. Since benzoic acid is very stable to the cerium reagent it is doubtful that the reaction is going further than the equation on page 29 indicates.

It was decided to convert the free acid into the sodium salt in order to see if the anomalous results persisted. By adding aqueous sodium hydroxide to a dioxane solution of benzoylformic acid, the sodium salt of benzoylformic acid was precipitated. It was recovered by filtration, washed with dioxane and ethanol and dried in a vacuum desiccator.

Table XXV. Indirect titration of sodium benzoylformate.

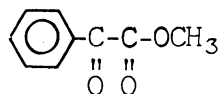
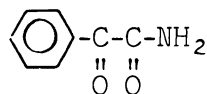
Organic m Moles	Ce (IV) Reagent meq.	Meq. Ce Reagent/ m Moles Organic
0.487	0.969	1.99
0.477	0.949	1.99
0.464	0.924	1.98

Table XXVI. Carbon dioxide recoveries from sodium benzoylformate oxidations.

Organic m Moles	CO ₂ m Moles	m Moles CO ₂ / m Moles Organic
0.9825	0.998	1.016
0.9825	1.008	1.025
0.9825	0.996	1.015

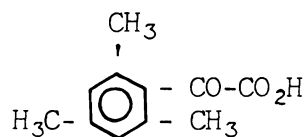
The values for the sodium salt, especially the carbon dioxide recoveries, are in line with the results expected and it is most likely that the benzoyl formic acid contained a carbon dioxide producing impurity. The carbon disulfide extraction of the titration residues provided a white crystalline material which sublimed at a moderate temperature (60°) and melted sharply at 122°C., the melting point of benzoic acid is 122-123°C. (16).

Two derivatives of benzoylformic acid were available; the amide and the methyl ester. After 22 hours 0.494 m moles of the amide showed



an apparent consumption of 0.077 meq. of the cerium reagent, and 0.551 m moles of the ester showed an apparent consumption of 0.038 meq. of the cerium reagent.

C. Mesitylformic Acid.

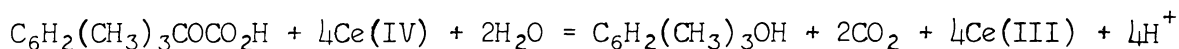


The sample was dried in a vacuum desiccator before use. The excess method gave the following results.

Table XXVII. Indirect titration of mesitylformic acid .

Organic m Moles	Ce (IV) Reagent meq.	Meq. Ce Reagent/ m Moles Organic
0.300	1.153	3.88
0.301	1.155	3.88
0.335	1.260	3.77

The stoichiometry suggests the following:



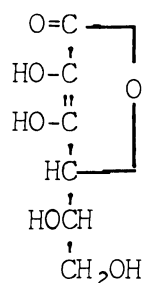
The carbon disulfide extract of the titration residues were examined for the presence of mesitol by trying to prepare a dibromo derivative according to the method described in Shriner and Fuson (35). A light brown powder was obtained which melted, but not too sharply, between 156° and 159°C., (lit. value for the dibromo derivative of mesitol is 158°C.) (35). A series (nine) of carbon dioxide recoveries gave results which ranged from 0.714 to 1.77 moles of carbon dioxide per mole of mesitylformic acid. It could well be that mesitylformic acid behaves like mesitoic acid in acid medium and decarboxylates (27). Nevertheless the best value does approach two moles of carbon dioxide. The reaction is possibly a two step oxidation, that is, mesitylformic

to mesitoic acid to mesitol. However, mesitoic acid consumes cerium reagent slowly and decarboxylates slowly. After about two days in an acetic acid solution which is 1M in perchloric acid 21% of the mesitoic acid has decarboxylated. It is therefore unlikely that mesitoic acid is an intermediate; and the reaction is more complex than merely two successive decarboxylations.

V. Miscellaneous Oxygenated Molecules.

Various other organic molecules were examined, such as ascorbic acid, propanediol, ethyl mandelate, acetylacetone, malonic acid, benzoyl-acetic acid, and flavanol.

A. Ascorbic Acid.



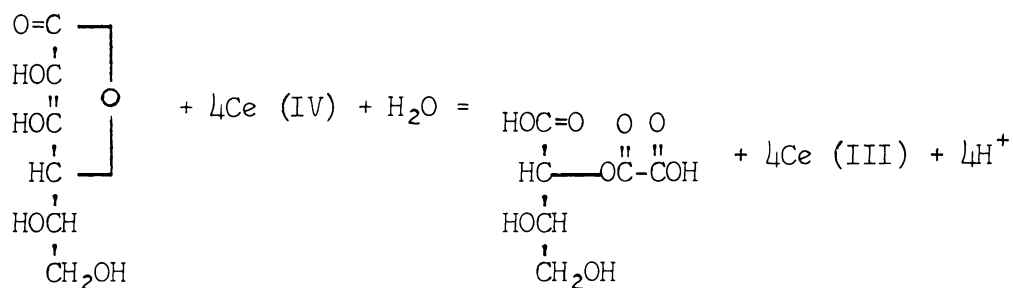
The direct titration of ascorbic acid with cerium has been reported by many investigators (3); Rao (30) reported that 4 equivalents of Ce (IV) per mole of ascorbic acid were consumed in acetonitrile.

Ascorbic acid is not readily determined by direct titration with the cerium reagent in acetic acid; the titration proceeds rapidly past the four equivalent stage but slows down quickly before the six equivalent stage is reached. In order to get some idea of the overall stoichiometry the excess method was used.

Table XXVIII. Indirect titration of ascorbic acid.

Organic m Moles	Reaction Time min.	Ce (IV) Reagent meq.	Meq. Ce Reagent/ m Moles Organic
0.0757	8	0.466	6.10
0.0722	22	0.458	6.35
0.0722	44	0.469	6.50
0.0921	82	0.635	6.90

Previous work (18) on the products of ascorbic acid oxidations would indicate that an oxalyl ester of threonic acid would be a likely product to attempt to recover after 4 equivalents of Ce (IV) had been added.



Calcium acetate was added to the reaction mixture, and a fine white precipitate settled out overnight. It gave a positive spot test for cerium, and reduced permanganate. A titration was performed with standard permanganate but the end point was not distinct.

Since ascorbic acid has a terminal diol function, the reactivity of propanediol was examined. It is slowly oxidized by the cerium reagent, and this would account for the changing stoichiometry for ascorbic acid.

B. Ethyl Mandelate.

Ethyl mandelate ($\text{C}_6\text{H}_5\text{CHOHCO}_2\text{C}_2\text{H}_5$) was washed with water to remove

any free mandelic acid or ethanol.

Table XXIX. Indirect titration of ethyl mandelate.

Organic m Moles	Reaction Time	Ce (IV) Reagent meq.
0.58	very short	0.0235
0.58	15 minutes	0.0469
0.58	very short*	0.1120

*The third titration was modified by adding the perchloric acid before the reagent, so that the increase in consumption of reagent could be due to the release of mandelic acid from the ester by the action of perchloric acid. At best it could be said that the ester is slowly oxidized by the cerium reagent.

C. Acetylacetone

Acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$) was distilled just before use and the percent purity was determined by the method described in Stone (38). According to Smith (36) the excess method in the presence of aqueous perchloric acid requires six equivalents of Ce (IV). The addition of the cerium reagent to acetylacetone produces a very dark brown color which soon disappears.

Table XXX. Indirect titration of acetylacetone.

Organic m Moles	Reaction Time	Ce (IV) Reagent meq.	Meq. Ce Reagent/ m Moles Organic
0.149	10 min.	0.636	4.27
0.149	20 hr.	0.630	4.24
0.149	20 hr.	0.639	4.29

D. Malonic Acid.

Malonic acid ($\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$), according to Smith (36) consumes six equivalents of Ce (IV) in the presence of aqueous perchloric acid.



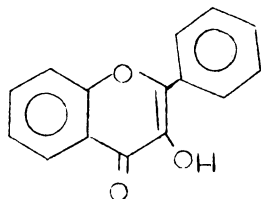
Table XXXI. Indirect titration of malonic acid.

Organic m Moles	Reaction Time min.	Ce (IV) Reagent meq.	Meq. Ce Reagent/ m Moles Organic
0.1690	15	0.790	4.68
0.1690	15	0.781	4.62
0.1690	15	0.789	4.68
0.1690	15	0.791	4.68
0.1690	117	0.751	4.45
0.1690	365	0.773	4.61

E. Benzoyl Acetic Acid.

Benzoyl acetic acid ($\text{C}_6\text{H}_5\text{COCH}_2\text{CO}_2\text{H}$), a beta-keto acid, is rather slowly oxidized by the cerium reagent; one mmole of the organic compound consumes about 0.6 meq. of Ce (IV) in about 16 hours.

F. Flavonol



Flavonol, which contains an alpha-keto hydroxyl group, as does benzoin, as part of a ring system, is not rapidly oxidized by the reagent in the absence of perchloric acid; the dark brown color formed upon mixing their solutions persists for several days. In a solution which is 1M in perchloric acid flavonol is rapidly oxidized, but in order to get decent amperometric data the reagent has to be added dropwise throughout the entire titration. One mole of flavonol consumes 6.04 equivalents of Ce (IV). Carbon dioxide recoveries were run after 6 equivalents of Ce (IV) per mole of flavonol were added.

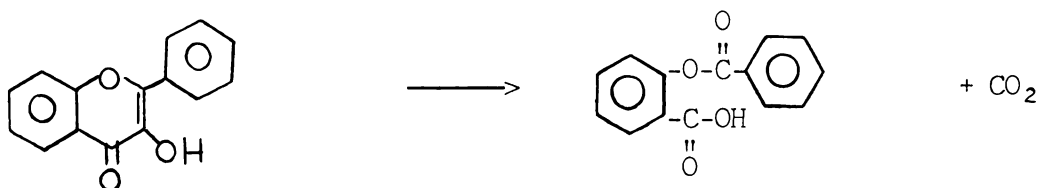


Table XXXII. Carbon dioxide recoveries from flavonol oxidations.

Organic m Moles	CO ₂ m Moles	m Moles CO ₂ / m Moles Organic
0.187	0.178	0.952
0.187	0.256	1.37
0.187	0.241	1.29
0.374	0.433	1.16
0.374	0.519	1.39

The carbon dioxide recovery would indicate that the oxidation does not proceed cleanly.

Assuming that the C-C bond between the keto and hydroxyl groups is split and that the hydroxyl carbon is oxidized to carbon dioxide, the primary product would be:



The infra-red spectrum of the residue of the evaporated carbon disulfide extract of the titration mixtures was examined (Figure 6a and 6b). The following structures appeared to be present: aromatic aldehyde (3.44 μ), ester carbonyl (5.84 μ), vinyl group (6.90 μ), benzoate (7.85-7.95, 8.95, 9.37 μ), phenyl-methylene ether (9.37 μ), mono-substituted benzene (13.55, 14.30 μ) (5). Spectra of phenyl benzoate, phenyl salicylate, and flavanol were available, but did not resemble the spectrum of the unknown. It is possible that the material is a mixture of:



VI. Cerium Species

In order to get more insight into the nature of the cerium reagent, an attempt was made to ascertain the role of the anions associated with the Ce (IV). There are not many Ce (IV) compounds which are stable and/or available. Ceric oxide, ceric sulfate, and ammonium tetrasulfatocerate (IV) are insoluble in acetic acid and ceric hydroxide is only slightly soluble. An attempt was made to prepare a basic ceric acetate as described in the literature (1). The material initially obtained was quite gelatinous, but subsequently dried to an amber colored powder. The analysis of the acetate to cerium ratio was about 2.3 to 1 rather than 3 to 1. An attempt was also made to prepare a basic ceric nitrate (40), but the syrup that was obtained was uncrystallizable. However, a saturated solution of ceric hydroxide in concentrated nitric acid appeared to be fairly stable in acetic acid. The same series of molecules studied by Aufuldish was re-examined with this reagent. Except for one of them, the stoichiometry was just about the same. The exception was diphenylfuroxan, which consumed one equivalent per mole when ammonium hexanitratocerate (IV) was the reagent and consumed two equivalents per mole when the ceric hydroxide-nitric acid combination was used. Solutions of nitric acid alone in acetic acid had no oxidizable effect. The carbon disulfide extract of both the titration residues gave material with the same melting point. Since the product of the oxidation was not identified, even with the aid of its infra-red spectra, not much can be inferred from this anomaly.

An ultra-violet spectral study of the nitrate ion in acetic acid was undertaken. Solutions of ammonium nitrate and nitric acid, suspected products of the solvolysis of the reagent, show different absorption maxima, apparently due to a cation association effect (21). Acetic acid, itself starts to absorb around 250 $m\mu$ so that only the less intense portion of the nitrate spectra is available. The limitation upon the whole scheme was that cerium also absorbs in this region, thus masking the spectra of nitrate ion in the solution of the reagent, (Figure 7).

The near infra-red was examined to ascertain the effect of water on solutions of the reagent. No useful data was forthcoming due to the hydroxyl group interaction of acetic acid with water.

CONCLUSION

It can be readily seen that organic molecules with the same functional groups are oxidized at radically different rates by the cerium reagent. Examination of the formal representation of the structure is not a reliable method for predicting the feasibility of utilizing either a direct titration method or an excess method. Nor can it be concluded, as Aufuldish did, that if a gas is a product the oxidation will be driven to conclusion at a reasonable rate with stiochiometry characterized by an integral number of equivalents. It is apparent that the limit of stability of the cerium reagent is often approached before the organic molecule is oxidized to a formally recognized stage.

The establishment of rules as concise and as thorough as those presented by Smith and Duke (37) were facilitated by the severity of the conditions they employed: $4M$ perchloric acid, excess reagent, extended reaction times and sometimes elevated temperatures, all of which insured that the molecule would be completely oxidized to formic acid and carbon dioxide. The methods under investigation here owe their primary value of rapidity and simplicity to the selectivity of the reagent. The lower concentration of mineral acid and the lower dielectric constant of the solvent system combining to magnify the rate differences of competing or consecutive oxidations. For example, mandelic acid is rapidly oxidized to benzaldehyde and carbon dioxide, the sharpness of the end point is due to the relative slowness of the oxidation of benzaldehyde by the cerium reagent under these conditions. Even in the excess method the stoichiometry indicates that the oxidation is simply

from the hydroxy acid to the aldehyde. In cases less favorable than mandelic acid, such as glycolic acid, variations in the concentration of perchloric acid might lead to a greater differentiation between the rates of oxidation of the hydroxy acid and the aldehyde.

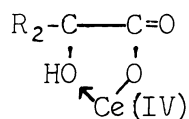
For molecules without alpha hydrogen such as phenylcyclopentylglycolic acid and pyruvic acid, for which the products are a ketone and an acid respectively, there is no problem in predicting the stoichiometry. However, where there are unusual structural features as in mesitoylformic acid, anomalous results may occur.

Because of the small number of compounds studied, only tentative generalizations as to the relative rates of oxidation of different functional groups can be advanced. That the diol function is not as reactive as the hydroxy-acid group in some molecules is clearly shown in the oxidation of tartaric acid. The sluggishness of lactic and glycolic acids compared to pyruvic and glyoxylic acids suggest a trend, particularly in the light of the rapid oxidation of both mandelic and benzoylformic acids. Derivatives such as the ester and amide of the more reactive molecules are unreactive, if not inert. Molecules such as acetylacetone and malonic acid which may react through their enol forms are reactive but give odd stiochiometry, quite unlike the values obtained by Smith and Duke using more severe conditions.

Previously (4, 7) the role of perchloric acid has been accounted for by advancing the idea that it promotes the formation of a dimeric Ce (IV) species which is the actual oxidizing agent. It has been this author's experience that the cerium reagent, in the absence of perchloric acid, can still effect oxidations at a reasonable rate in the case of

mandelic acid, pyruvic acid and benzoylformic acid. This would mean that some of the dimeric cerium species is present in the cerium reagent or that the oxidizing species is only monomeric cerium; of course, both alternatives can be true. Mehrotra has investigated the interactions of cerous chloride and palmitic acid in acetic acid and acetic anhydride (25) and has found no evidence for dimeric species similar to those reported by Audrieth (32) for some other rare earths. An attempt was made to prepare dimeric cerium compounds by refluxing acetic anhydride and solutions of ceric hydroxide in acetic acid. The result was the reduction of ceric to cerous and the production of large quantities of material whose infra-red spectrum appeared to be identical with that of cerous acetate, which was prepared by treating cerous carbonate with acetic acid.

Krishna and Tewari (23) in investigating the oxidation of mandelic acid by ceric sulfate in aqueous sulfuric acid, accounted for their kinetic data by postulating a fast complex formation between Ce (IV) and the organic molecule followed by its slow decomposition to Ce (III) and an organic radical. The infra-red spectra of the cerium-glycolate and cerium-tartrate precipitates indicate that complexes of the following can form:



This would allow one to postulate a five membered ring as an intermediate, rather than the seven membered ring based on the dimeric cerium species which had been previously proposed (4) as the intermediate in these oxidations.

Bowman found that his data on the cerium species in solution could be equally well interpreted by postulating a dimer cerium (IV) species or a "super acid" cerium (IV) species. It would seem that any further investigation into the nature of the cerium species should be based on the latter postulation.



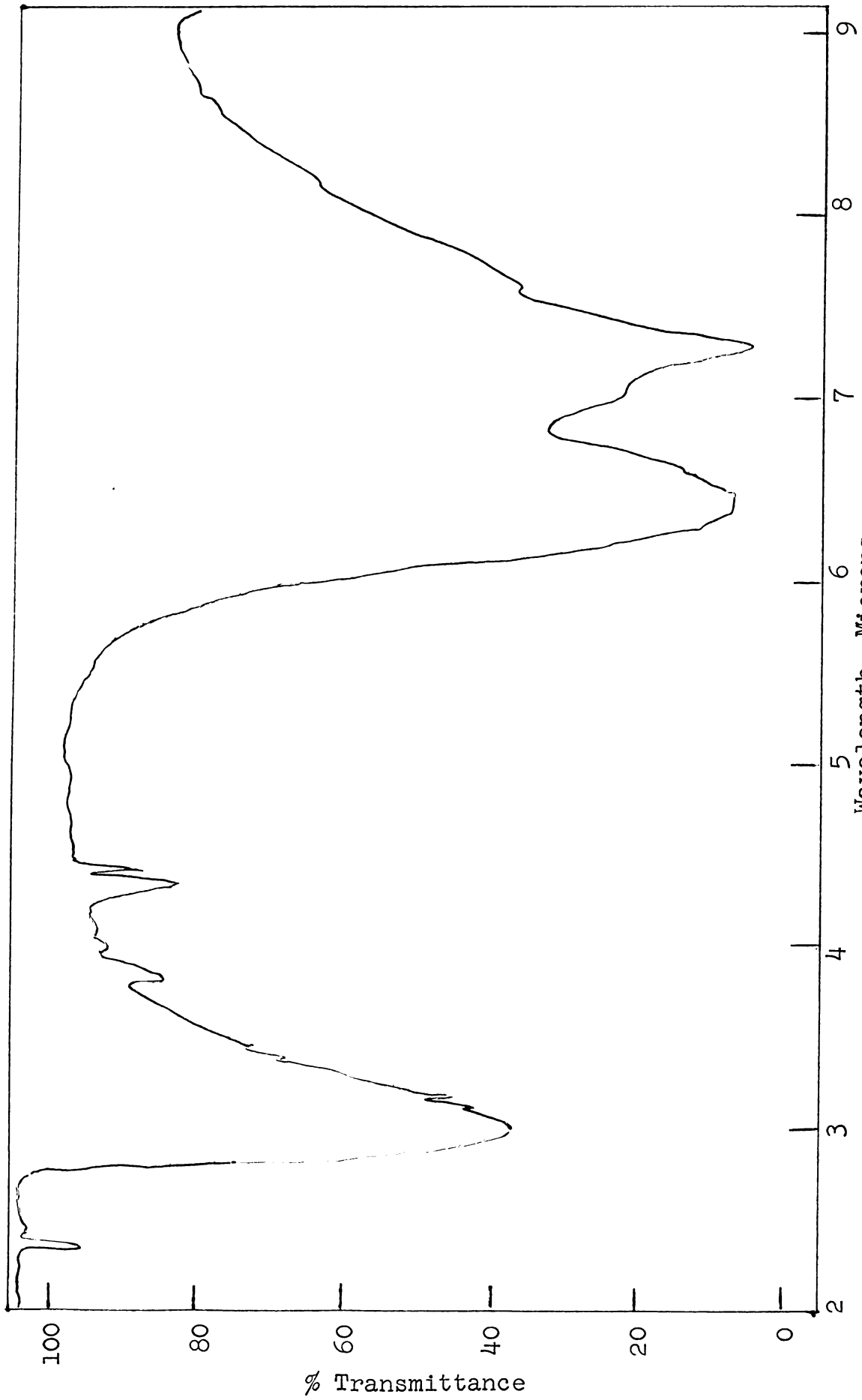
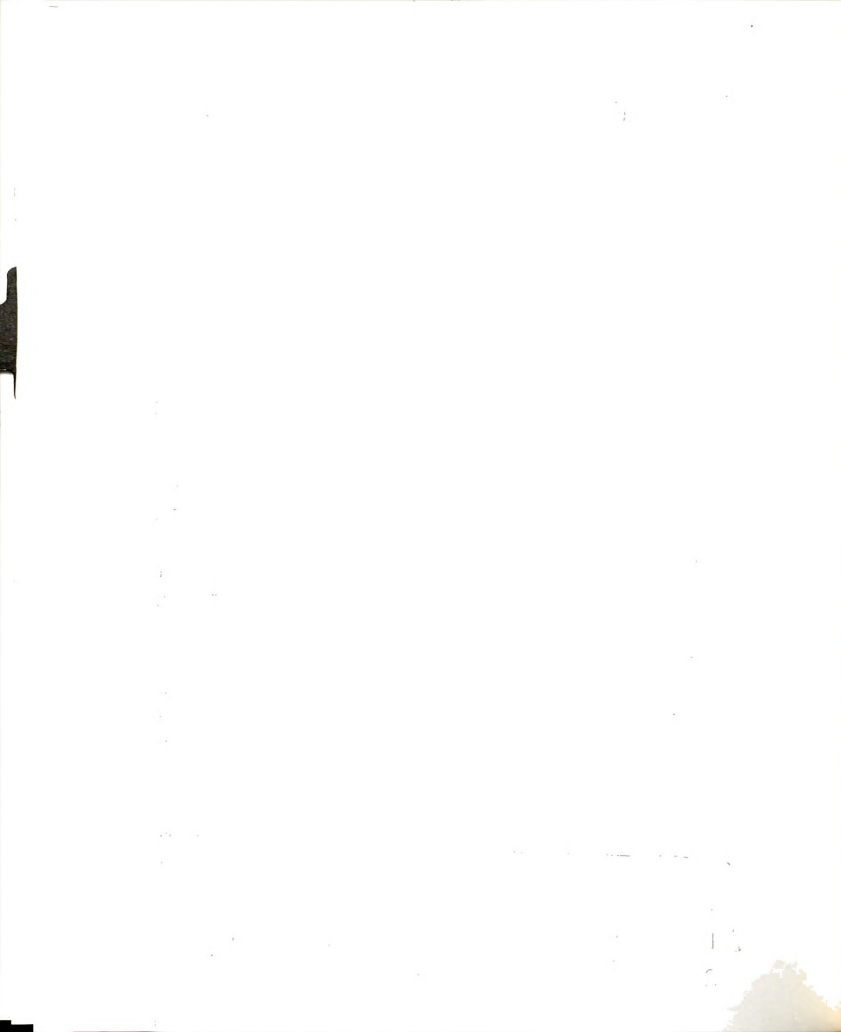


Figure 1a. Infrared Spectrum of Cerium-glycolate precipitate.



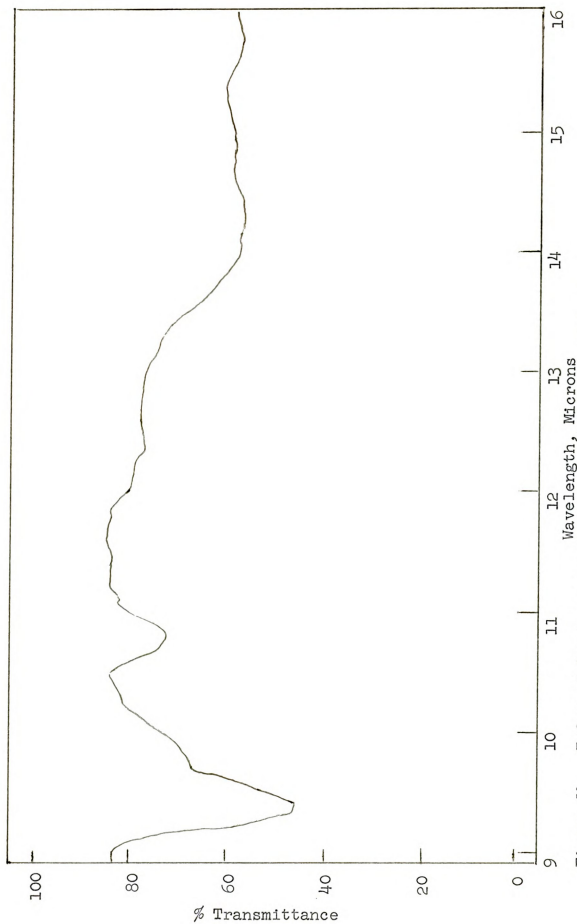


Figure 1b. Infrared Spectrum of Cerium-glycolate precipitate.

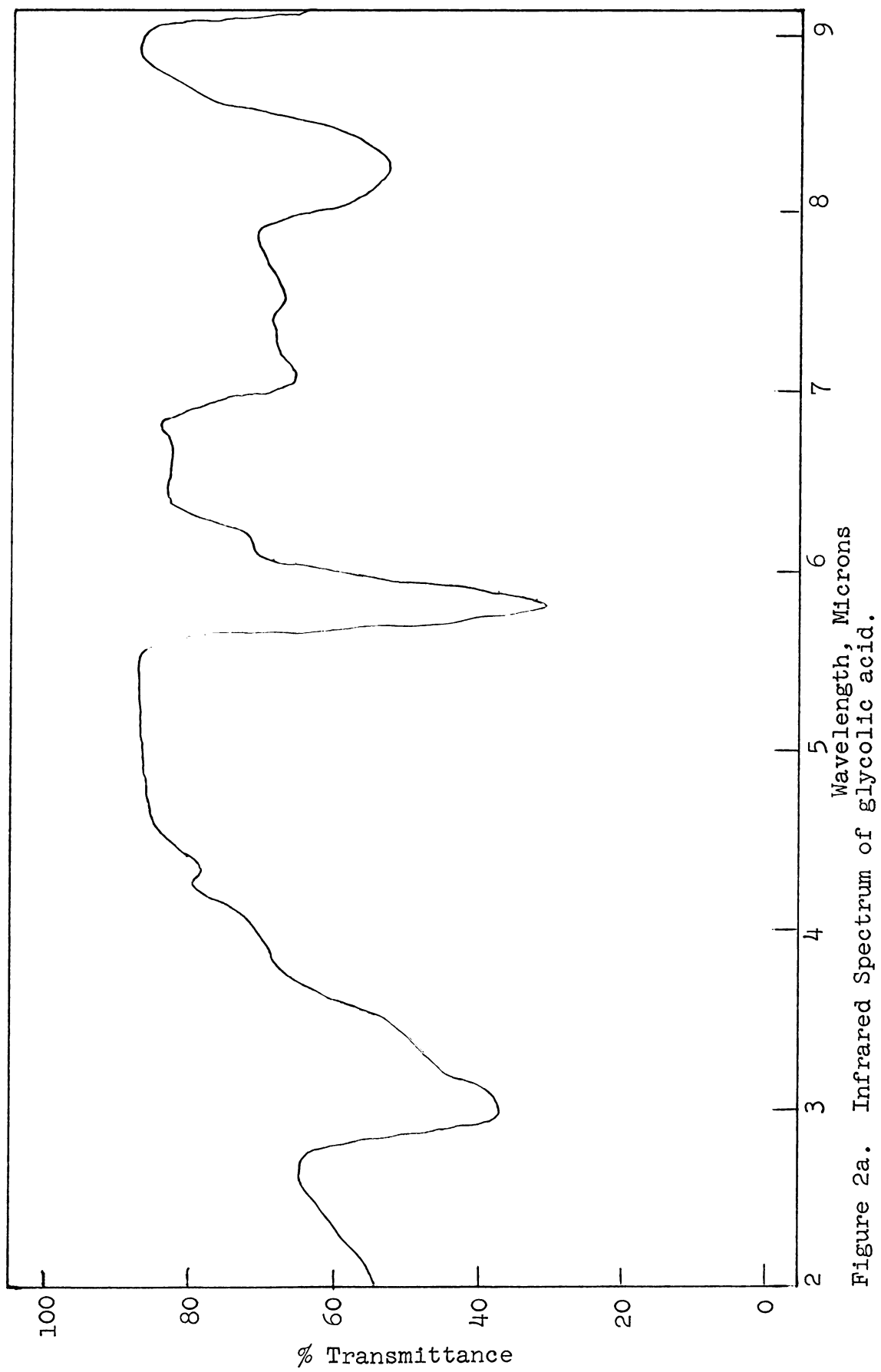


Figure 2a. Infrared Spectrum of glycolic acid.



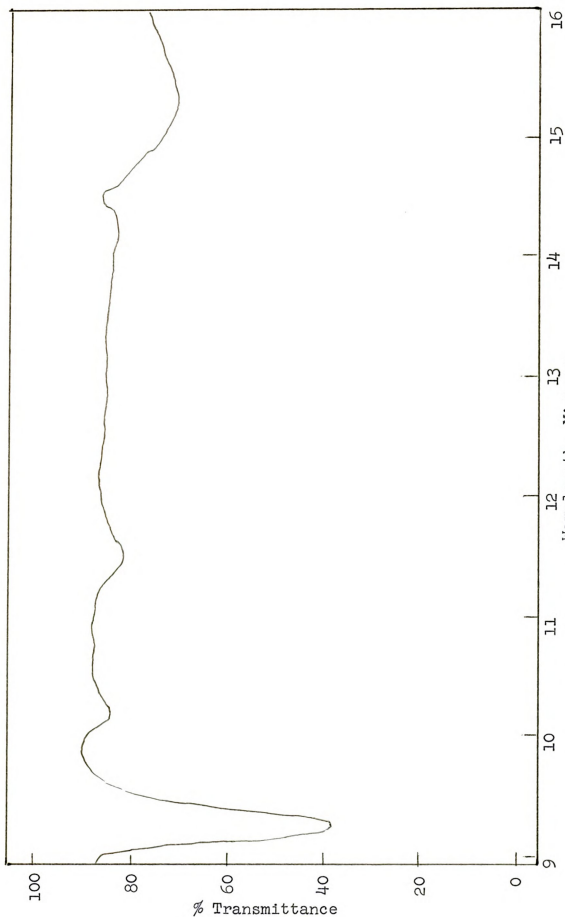


Figure 2b. Infrared Spectrum of glycolic acid.

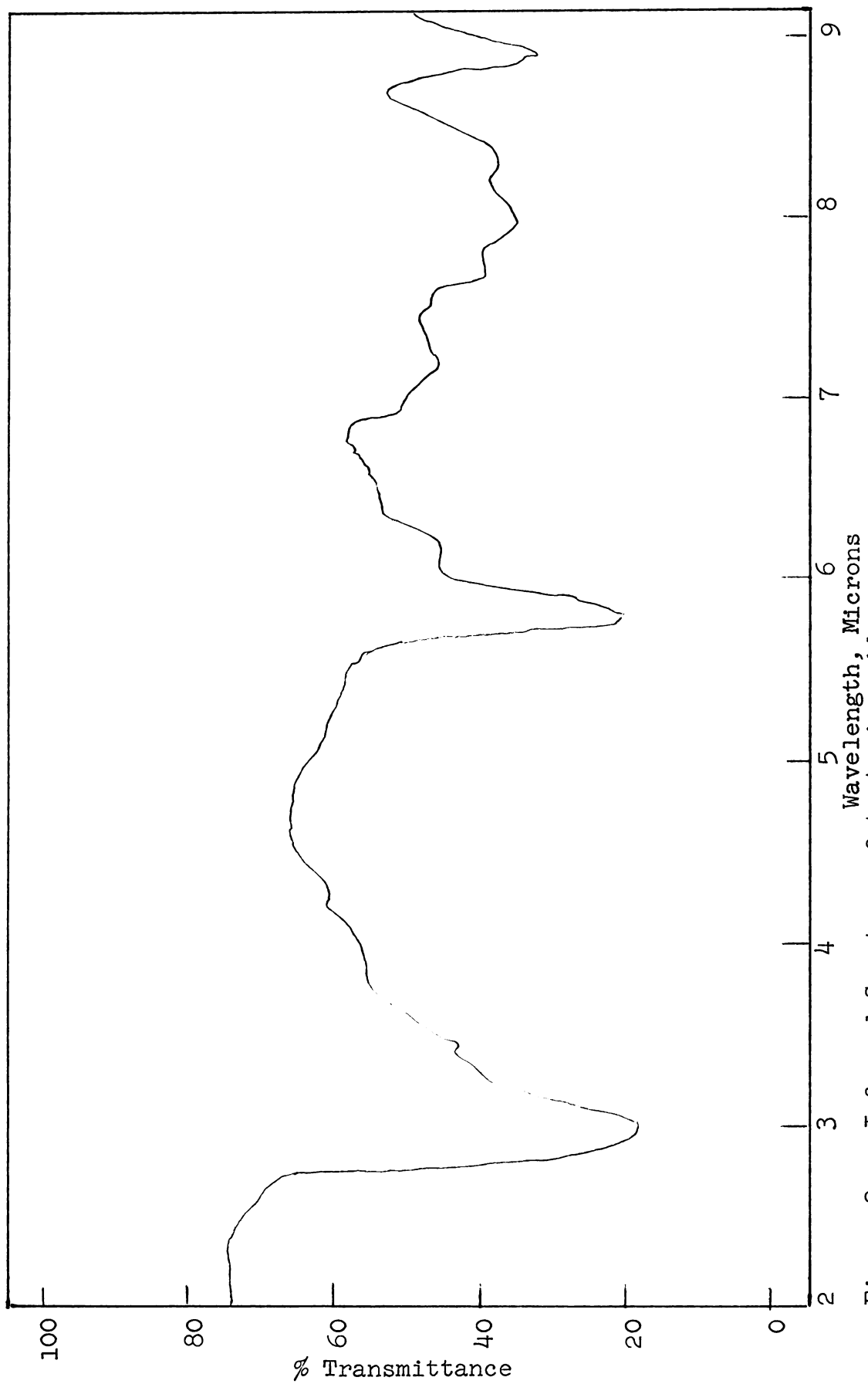


Figure 3a. Infrared Spectrum of tartaric acid.

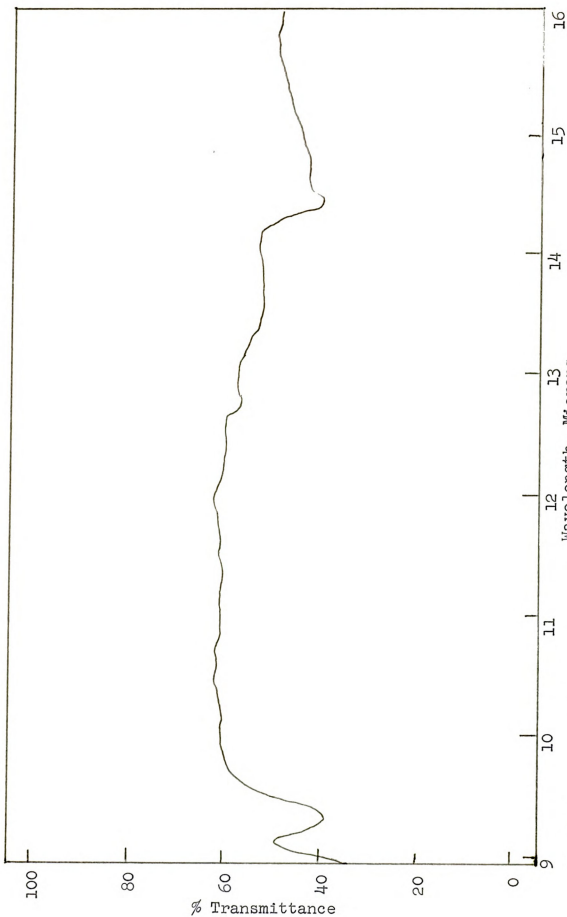


Figure 3b. Infrared Spectrum of Tartaric Acid.

100

100

100

100

100

100

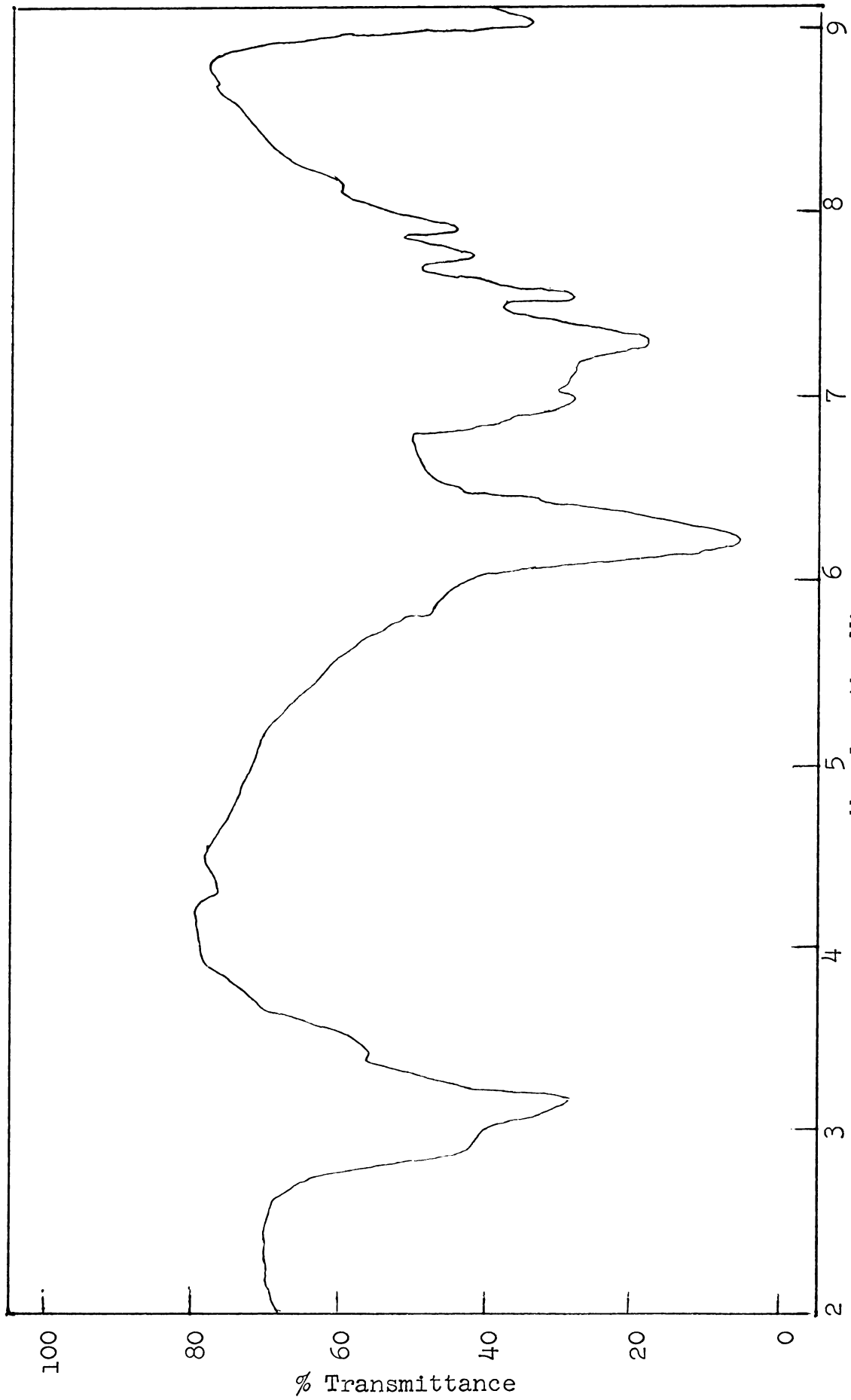


Figure 4a. Infrared Spectrum of Disodium Tartrate.



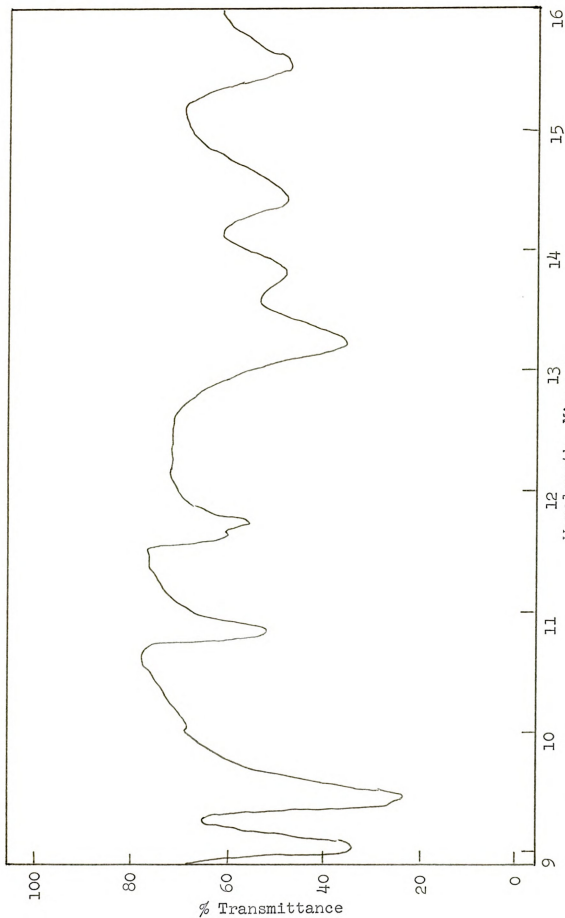


Figure 4b. Infrared Spectrum of Disodium Tartrate.



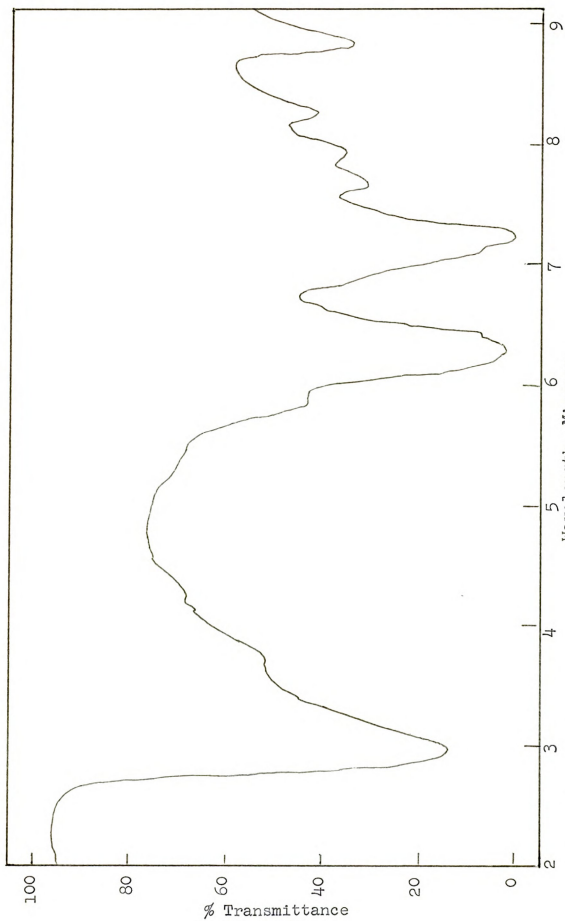


Figure 5a. Infrared Spectrum of Cerium-Tartaric Acid Precipitate.



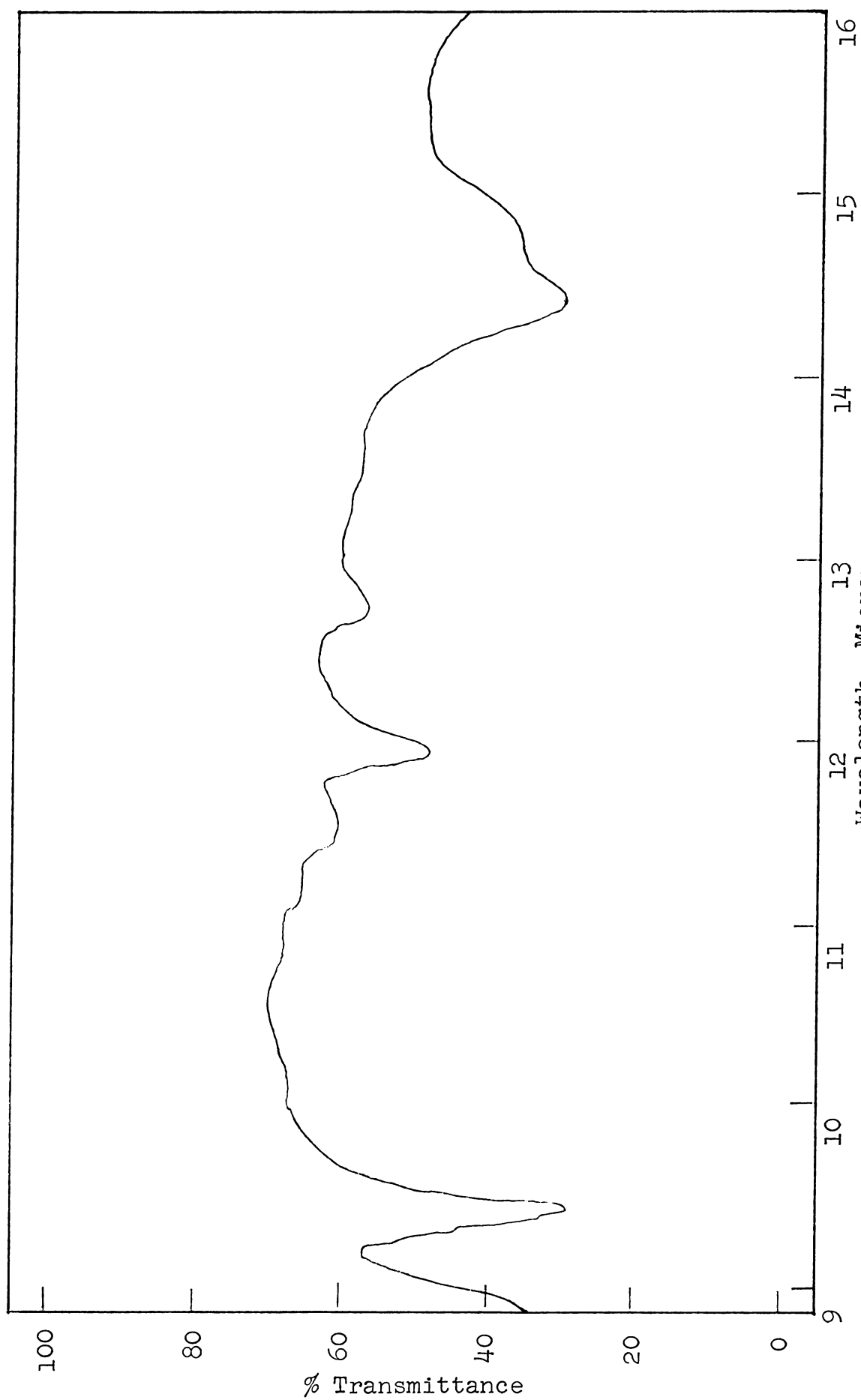


Figure 5b. Infrared Spectrum of Cerium-Tartaric Acid Precipitate.



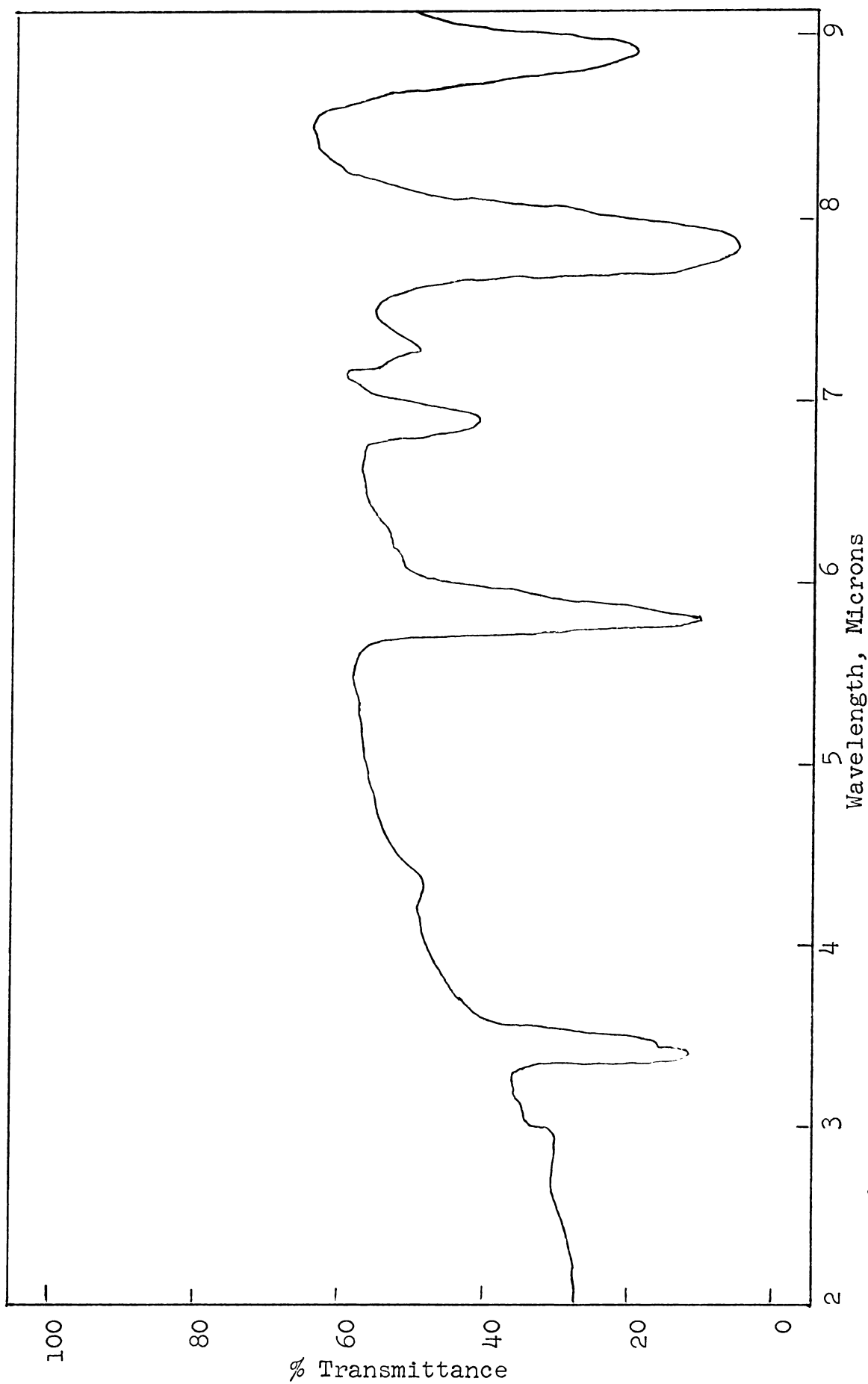


Figure 6a. Infrared Spectrum of Product of Flavanol Oxidations.

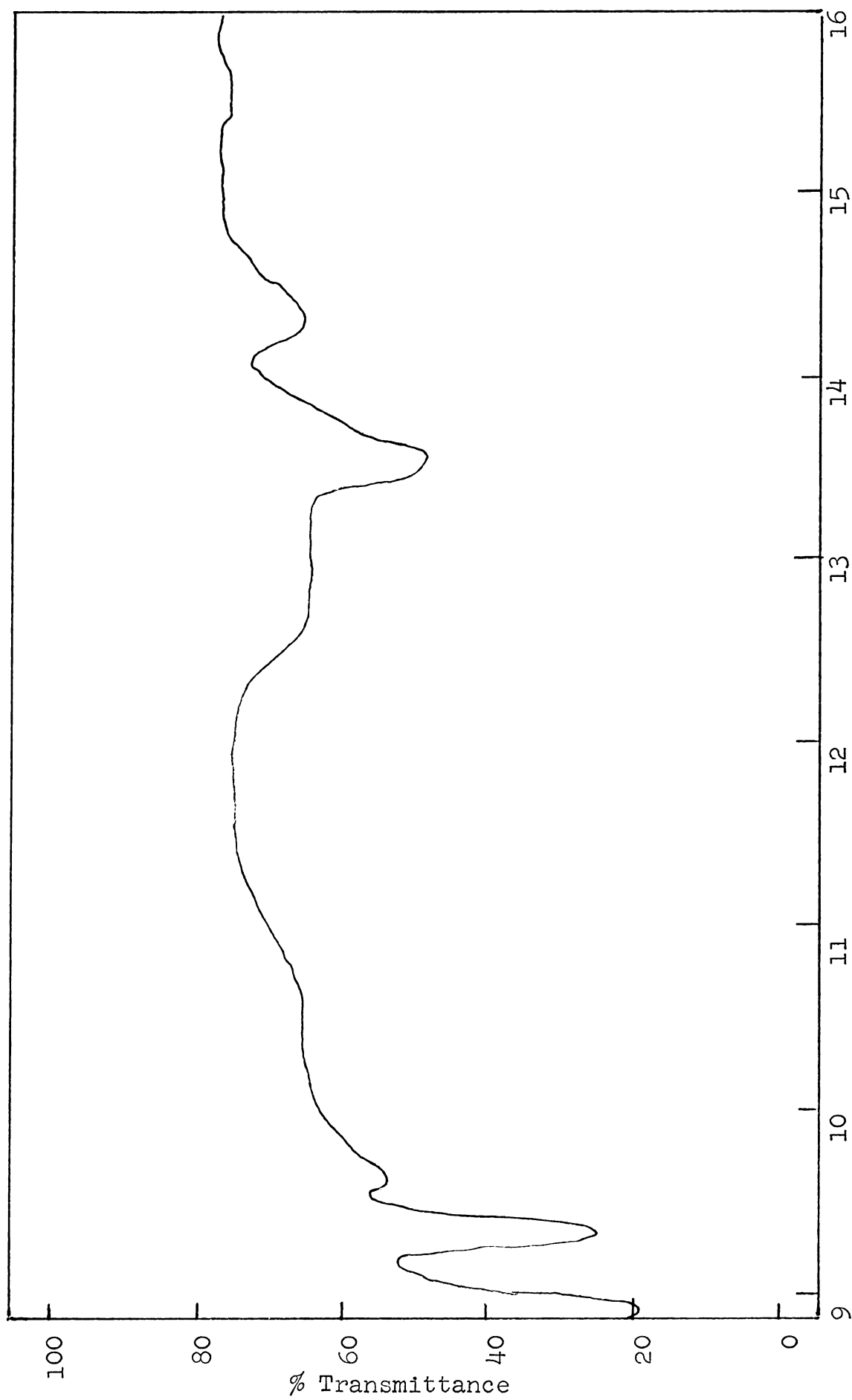


Figure 6b. Infrared Spectrum of Product of Flavanol Oxidation.

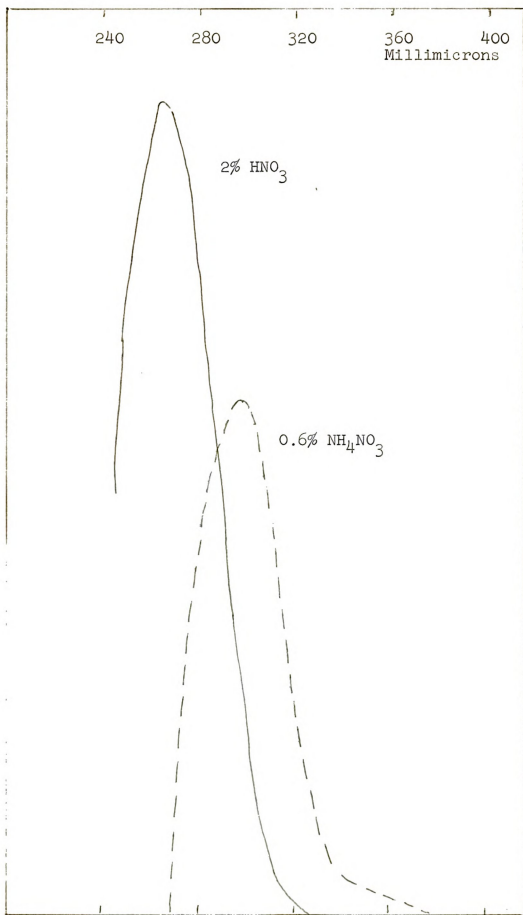


Figure 7. Ultraviolet Spectra of Nitrate Ion.

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