THE OXIDATION OF BENZOIN AND RELATED MOLECULES IN GLACIAL ACETIC ACID

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ABSTRACT

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by Robert E. Aufuldish Jr.

In an effort to propose a mechanism for the oxidation of oxygenated organic molecules in glacial acetic acid, a method of isolation of products first was accomplished. This was achieved by obtaining data for the acetic acid-carbon disulfide-water system. By using the results obtained, a procedure for carbon disulfide extraction was established.

Direct titrations, using ammonium hexanitratocerate in glacial acetic acid as the oxidizing agent, were possible on benzilic acid and benzohydroxamic acid and the isolation of oxidation products was achieved.

The possible reason that the direct titrations were successful is that due to the formation of a gas as an oxidation product of these two molecules the oxidation was forced to completion.

In the case of all other molecules studied, the detection of the end point was not observed by direct titration.

Two excess methods were outlined and the oxidation of benzoin and a-benzoin oxime with the identification of oxidation products was accomplished.

A possible mechanism was outlined and it was proposed that a 7 membered cyclic intermediate occurs as the oxidation step.

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By

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INTRODUCTION

The practical applications of cerium as a powerful analytical oxidizing agent were reviewed by Smith (28). Of particular interest in his work was the revelation of the broad range of reduction potentials of cerium, depending on the mineral acid and concentration used. It was found that the redox potential of cerium 1N with respect to perchloric acid was 1.70 volts and 1.87 volts in an 8N perchloric acid solution.

As a result of this phenomenon it was suggested that by using glacial acetic acid as solvent and varying the concentration of perchloric acid the reduction potential of cerium could be made high enough for the quantitative oxidation of oxygenated organic molecules.

Procedures for the use of cerium in glacial acetic acid and the quantitative oxidation of some oxygenated organic molecules were described by Hinsvark (13). An extension of this work to nitrogen compounds was done by Harris (11) who studied the oxidation of sodium azide and hydroquinone in this medium. In a study of the decomposition of ammonium hexanitratocerate in glacial acetic acid, Bowman (3) introduced the kinetics of this decomposition and postulated that an excess method of oxidation was not feasible.

The object of the present work was to study the oxidation of various oxygenated aromatic organic molecules using as the reagent ammonium hexanitratocerate in glacial acetic acid. Also of concern was the isolation and identification of the products of these oxidations with the end result being the postulation of a mechanism which would allow future predictions of oxidation products.

EXPERIMENTAL

I. Reagents

The reagents used were of analytical grade unless otherwise stated.

Baker and DuPont glacial acetic acid.

Baker and Mallinckrodt 70% perchloric acid.

Baker dimethylglyoxime and potassium hydrogen phthalate.

Eastman benzaldehyde, benzoic acid, hydroxylamine hydrochloride and p-methoxybenzoic acid.

Fischer Scientific Company barium hydroxide and sodium hydroxide.

G. Fredrick Smith Chemical Company ammonium hexanitratocerate.

Mallinckrodt sodium oxalate.

Matheson, Coleman and Bell ligroin (90-120).

Merck carbon disulfide.

The following Eastman chemicals were recrystallized from ethanol: benzil, m.p. 93-94°C. (literature m.p. 95°C.) (15); benzoin, m.p. 133-134°C. (literature m.p. 133-137°C) (16); benzoin oxime, m.p. 154°C. (literature m.p. 151-152°C.) (16). Benzilic acid, m.p. 148.5°C. (literature m.p. 150°C.) (15) was recrystallized from water.

For calibration of the thermometer the m.p. of benzoic acid was 121°C. (literature m.p. 122°C.) (16).

Elanco's anisoin was recrystallized from ethanol m.p. 108-110°C. (literature m.p. 113°C) (9).

Benzohydroxamic acid was prepared according to the method of Adams (1) m.p. 128.5-129°C. (literature m.p. 131-132°C.) (16).

Diphenylfuroxan was prepared according to the method of Boyer (4) m.p. 115.0-115.5°C. (literature m.p. 117-118°C.) (4).

γ-Diphenylglyoxime was prepared according to the method of Boyer (5) and recrystallized from acetone m.p. 163°C. (literature m.p. 164-165°C.) (16).

II. Apparatus

A Sargent "Model III" manual polarograph equipped with platinum-platinum electrodes was used to detect the end points. A magnetic stirrer and amber buret were used for all titrations.

Reaction products were identified by using The Perkin Elmer Infrared Spectrophotometer, Model 21, with sodium chloride optics and a slit setting of 980. Since carbon disulfide absorbs from 6.1-7.5 μ and carbon tetrachloride from 11.3-14.0 μ, it was necessary to use both as solvents to obtain a complete infrared spectrum of the molecule.

For the determination of carbon dioxide, nitrogen gas was passed into a 250 ml., 3 necked round bottom flask, which contained the sample dissolved in 50 ml. glacial acetic acid and 8 ml. perchloric acid. The flask was equipped with a glass stopper and an outlet tube which was connected to a trap in a dry ice-acetone bath for the purpose of removing organic vapors from the carrier gas. Finally the gas was passed into a 300 ml. washing tower to which was added 15.00 ml. barium hydroxide standard solution and 100 ml. water after the nitrogen was passed through the system for 15 minutes to remove all carbon dioxide from the system. Then an excess of the reagent was added and after various lengths of time the excess barium hydroxide was titrated with a standard hydrochloric acid solution using phenolphthalein indicator. A blank run under similar conditions showed no absorption of carbon dioxide from the system by the barium hydroxide.

In an attempt to identify the number of products obtained after extraction of the reaction mixture with carbon disulfide, a Beckman GC-2 Gas Chromatograph was used. The instrument was equipped with a six foot Beckman 12449 gas-liquid partition chromatography column made of quarter inch stainless steel tubing filled with firebrick coated with Dow-Corning silicon Fluid.

For the identification of the nitrous oxide, approximately one gram of sample and 8 grams of solid reagent were added to a 125 ml. Erlenmeyer flask. The flask was equipped with a rubber stopper and an outlet tube which was connected to a drying tube containing wet potassium hydroxide for the purpose of removing acetic acid vapors from the gas. The other end of the drying tube was connected to a cell for infrared measurement of gases. To the flask was added 40 ml. glacial acetic acid and 8 ml. perchloric acid. After allowing the mixture to stir for 5 minutes, the gas was passed into the absorption cell by partially evacuating the cell. An infrared spectrum was then taken on the gas.

It is possible to identify nitrous oxide from the other oxides of nitrogen by observing the absorption peaks obtained from an infrared spectrum. Figure 1, page 31, shows where the various peaks occur in relation to each other (7, 19, 22).

III. Solutions

The reagent was prepared by adding to a two necked, two liter round bottom flask approximately 120 grams of ammonium hexanitratocerate, 1950 ml. of glacial acetic acid and 36 ml. of water. The solution was heated to 60°C. and that temperature was maintained for four hours with stirring at all times. The solution was then allowed to cool slowly to room temperature with stirring continued overnight. The reagent was then carefully poured into a dark two and a half liter bottle. No filtration was necessary.

The flask was protected at all times from the light by enclosing any exposed portion with dark weighing paper, black side towards the flask. For best results a wrap around heating mantle also may be used. The hood light was turned off during the preparation and at no time during the preparation or storage of the reagent was direct sunlight allowed to fall on the container.

Immediately after preparation of the reagent, 120 grams of ammonium hexanitratocerate was placed in a 150 ml. beaker inside a desiccator to be used for the next preparation of the reagent.

Using this technique the reagent would always be 0.06-0.07N initially.

The reagent was standardized against a solution of sodium oxalate approximately 0.07-0.08N in glacial acetic acid made 1N with respect to perchloric acid.

Carbonate-free sodium hydroxide was prepared using a 50% solution of sodium hydroxide and filtering off the insoluble sodium carbonate and diluting to the approximate volume required. The solution was protected by means of an absorption tube filled with soda lime.

By adding 17 grams of barium hydroxide and one gram of barium nitrate to two liters of water, carbonate-free barium hydroxide was prepared. The solution was protected from carbon dioxide by means of an absorption tube filled with ascarite.

Approximately 0.15N hydrochloric acid solution was prepared by adding 27 ml. of concentrated hydrochloric acid to two liters of water.

Seaman's(20)method was used to prepare Karl Fischer reagents.

IV. Procedures

1. Standardization of sodium oxalate solution.

The reagent first was standardized against weighed samples of sodium oxalate using the procedure of Hinsvark (13). Then the sodium oxalate solution was compared against the known reagent. Over a period of three months the 0.1N solution changed in normality by -0.0009.

2. Standardization of sodium hydroxide and barium hydroxide.

Weighed samples of potassium hydrogen phthalate and phenolphthalein as indicator were used to standardize both the sodium hydroxide and barium hydroxide solutions.

3. Standardization of hydrochloric acid solution.

The hydrochloric acid solution was standardized by the comparison of it against the standard sodium hydroxide using methyl red as indicator.

4. Standardization of Karl Fischer reagent.

Weighed samples of pure water were used to standardize the Karl Fischer reagent.

5. Analysis of the acetic acid-carbon disulfide-water system.

The following saturated solutions were prepared by mixing the stated volumes of carbon disulfide and glacial acetic acid and adding water to saturation keeping the samples stoppered and in a water bath at 25°C. ± 1°C.

Sample No.	1	2	3	4	5	6	7	8	9
Ml. CS_2	10	20	30	40	50	60	70	80	90
Ml. HOAc	90	80	70	60	50	40	30	20	10

The solutions were analyzed by taking one portion for titration with standard sodium hydroxide and another portion for titration with Karl Fischer reagent.

The following mixtures were placed in a water bath at 25°C. ± 1°C. and allowed to separate into layers. Both the upper and lower layers were analyzed for water and acetic acid for the purpose of obtaining tie lines.

Sample No.	12	13	14	15	16
Ml. H_2O	15	30	45	60	75
Ml. HOAc	45	35	25	20	10
Ml. CS_2	40	35	30	20	15

6. Carbon disulfide extraction of oxidation residues.

From the experimental data obtained, the following procedure for carbon disulfide extraction was established.

To a 300 ml. separatory funnel containing the resulting solution after titration, a volume of water was added equal to twice the total volume of the oxidation residue.

The diluted solution was extracted with three 25 ml. portions of carbon disulfide.

The carbon disulfide extracts were combined in a 300 ml. separatory funnel and a volume of water equal to twice that of the volume of carbon disulfide was added. The mixture was shaken vigorously and the carbon disulfide layer collected in a 150 ml. beaker was allowed to stand. Only 0.003 milliequivalent of acetic acid remains in the carbon disulfide layer after this washing step.

Care should be taken during the extraction to frequently release the pressure built up inside the separatory funnel.

In working with carbon disulfide it must be remembered that its low closed cup flash point of -30°C. dictates that it should be handled with care. Also the effects in half an hour of the presence of 1100 p.p.m. of carbon disulfide are those of a severe chronic general nerve poison. It is also warned that in high concentrations carbon disulfide may be a narcotic (6).

7. Direct titration technique.

Direct titrations were carried out by dissolving the sample in glacial acetic acid, adding perchloric acid to 1N, and titrating with the reagent. The end point was detected biamperometrically. During the titration it is suggested to set the sensitivity at 1/1000 until approximately 1-2 ml. from the end point, then increase the sensitivity as needed.

8. Indirect Titration, 5-90 minutes.

To 50 ml. of glacial acetic acid in a 250 ml. iodine flask was added sufficient cerium reagent calculated to be an excess for the sample. The flask was stoppered and placed in the dark for 5 minutes. The solution then was poured into another 250 ml. iodine flask containing the sample dissolved in a minimum amount of glacial acetic acid. The flask was stoppered and placed in the dark for various lengths of time from 15-75 minutes. The resulting mixture was poured into a 150 ml. beaker, the solution was made 1N with respect to perchloric acid, and the excess reagent was titrated with the standard sodium oxalate solution. The end point was detected biamperometrically (13) at 1/20 sensitivity. The current fell off very rapidly, then either remained constant or started to rise again at the end point.

It also was possible to detect the end point visually. As the solution faded from light orange to colorless, the final change was quite easily seen.

9. Indirect Titration, 1-3 minutes.

To 40 ml. of glacial acetic acid in a 150 ml. beaker was added sufficient cerium reagent calculated to be an excess for the sample. The solution then was allowed to stand for one minute with no precautions taken about light falling on the solution. The solution was poured into a 150 ml. beaker containing the sample dissolved in a minimum amount of glacial acetic acid. The solution was stirred for various lengths of time from 1-3 minutes. The resulting mixture then was made 1N with respect to perchloric acid, and the excess reagent was titrated with the standard sodium oxalate solution. The end point can be detected as explained in Indirect Titrations, 5-90 minutes.

Blanks were run in a like manner to calculate the normality of the reagent.

10. Electrode and Instrument Care.

The instrument and the electrodes should be grounded. Before daily use the electrodes should stand in concentrated nitric acid for 5-10 minutes.

After each titration the electrodes should be cleaned with a stream of acetone. This washes the ammonium perchlorate precipitate from the electrodes and allows the electrodes to be dry for the next titration.

11. Gas Chromatography.

The conditions under which the instrument was operated were: helium gas 30 lbs./in.^{2} current 270 milliamps, power +, attenuator 2, displacement M, range 2.5, temperature range 40-190°C., time one hour.

DISCUSSION AND RESULTS

Previous investigations (11, 13) on the oxidation of oxygenated organic molecules, using ammonium hexanitratocerate in glacial acetic acid, failed to identify all of the products of oxidation. It was the purpose of this study to isolate oxidation products and to propose a mechanism for these reactions.

In order to identify the products, a method of isolation had to be first worked out. The method chosen by this author was a carbon disulfide extraction, which proved to be quite acceptable.

After isolation of the products, routine steps of identification were carried out. The use of the infrared was very useful as the preliminary identification step. Then the melting point, milliequivalent weight and preparation of a derivative were used to complete the identification.

It first was observed that benzil[1] did not consume reagent upon direct titration, despite its having been made 8N with respect to perchloric acid.

It then was decided to try γ-diphenylglyoxime, a molecule which was postulated to give benzil as a product, along with nitrogen or an oxide of nitrogen upon oxidation.

However, direct titration of γ-diphenylglyoxime was not successful and an indirect method of titration was needed.

Hinsvark (13) and Bowman (3) theorized that an excess method in which perchloric acid was present was not possible; however, Harris (11) used such a method. This author then decided an excess method containing no perchloric acid might be the solution. It will be shown that this method was found to be quite successful.

Upon indirect titration of γ-diphenylglyoxime, it was found that 4 plus equivalents of reagent were consumed. Since no gas was observed it was decided to try simpler molecules whose structures were related to γ-diphenylglyoxime.

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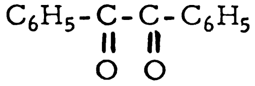
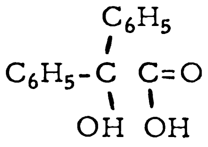
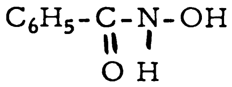
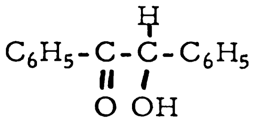
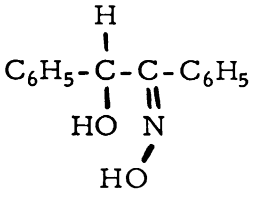
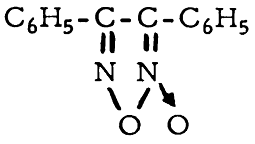
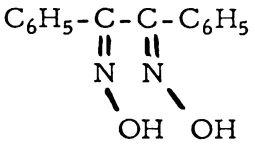
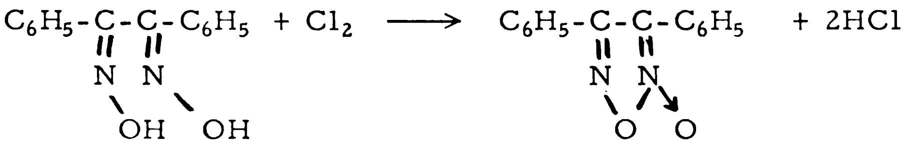
[1] See Table 1 for structures of all molecules used.

Table 1. Structures of Molecules Used in Oxidation Study

A. Benzil	 $C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-C_6H_5$
B. Benzilic acid	 $C_6H_5-\underset{OH}{\overset{C_6H_5}{C}}\ \ \underset{OH}{C}=O$
C. Benzohydroxamic acid	 $C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{H}{N}-OH$
D. Benzoin	 $C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{OH}{\overset{H}{C}}-C_6H_5$
E. a-Benzoin oxime	 $C_6H_5-\underset{HO}{\overset{H}{C}}-\underset{\underset{HO}{N}}{\underset{\|}{C}}-C_6H_5$
F. Diphenylfuroxan	 $C_6H_5-\underset{N}{\underset{\|}{C}}-\underset{N \rightarrow O}{\underset{\|}{C}}-C_6H_5$, N–O–N
G. γ-Diphenylglyoxime	 $C_6H_5-\underset{\underset{OH}{N}}{\underset{\|}{C}}-\underset{\underset{OH}{N}}{\underset{\|}{C}}-C_6H_5$

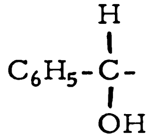
Among those chosen was diphenylfuroxan on the basis of a literature report of the dehydrogenation of diphenylglyoxime (5).



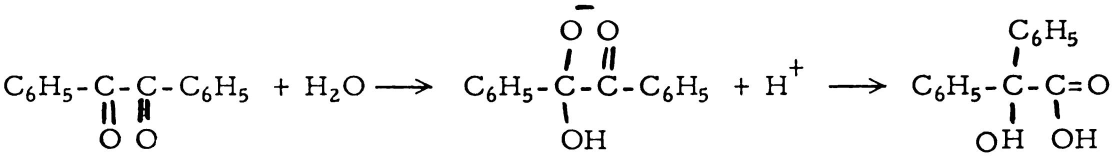
$$C_6H_5-\underset{\substack{\| \\ N \\ \diagdown \\ OH}}{C}-\underset{\substack{\| \\ N \\ \diagdown \\ OH}}{C}-C_6H_5 + Cl_2 \longrightarrow C_6H_5-\underset{\substack{\| \\ N \\ \diagdown \\ O}}{C}-\underset{\substack{\| \\ N \\ \diagup \searrow \\ O}}{C}-C_6H_5 + 2HCl$$

In an attempt to learn what happens to the -C=N- group, α-benzoin oxime was chosen.

Benzohydroxamic acid was chosen since it was decided it was an intermediate in the benzoin oxime oxidation.

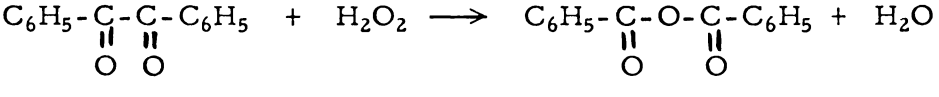
Benzoin was chosen in an attempt to learn what happens to the  $C_6H_5-\overset{\substack{H \\ |}}{\underset{\substack{| \\ OH}}{C}}-$ group.

The literature reports that benzil undergoes the following rearrangement when treated with 32% alcoholic KOH at 100°C. to give benzilic acid (30). Since this rearrangement is well-known, benzilic acid was included in this study.



$$C_6H_5-\underset{\substack{\| \\ O}}{C}-\underset{\substack{\| \\ O}}{C}-C_6H_5 + H_2O \longrightarrow C_6H_5-\overset{\substack{O^{-} \\ |}}{\underset{\substack{| \\ OH}}{C}}-\overset{\substack{O \\ \|}}{C}-C_6H_5 + H^{+} \longrightarrow C_6H_5-\overset{\substack{C_6H_5 \\ |}}{\underset{\substack{| \\ OH}}{C}}-\underset{\substack{| \\ OH}}{C}=O$$

Benzil was chosen since it is the simplest of 1, 2 aromatic oxygenated organic molecules and the literature reports that when refluxed with 25 ml. glacial acetic acid, 1 ml. perchloric acid and 1 ml. of hydrogen peroxide, the following oxidation results (17).



$$C_6H_5-\underset{\substack{\| \\ O}}{C}-\underset{\substack{\| \\ O}}{C}-C_6H_5 + H_2O_2 \longrightarrow C_6H_5-\underset{\substack{\| \\ O}}{C}-O-\underset{\substack{\| \\ O}}{C}-C_6H_5 + H_2O$$

I. Acetic Acid-Carbon Disulfide-Water System

A method was required for the isolation of oxidation products from the oxidation mixture. Solubility data suggested the use of carbon disulfide.

To obtain a procedure for a carbon disulfide extraction, it was necessary to obtain more complete data on the acetic acid-carbon disulfide-water system. A summary of the data obtained is found in Table 2, while the complete data are presented in Appendix 1. The phase diagram of this system can be seen in Figure 2 (page 32).

Table 2. Summary of Data for the Acetic Acid-Carbon Disulfide-Water System

a. Saturated One Layer System

Average Found		By Difference
% Water	% Acetic Acid	% Carbon Disulfide
0.29	15.70	84.01
0.44	26.36	73.20
0.47	30.22	69.31
0.63	37.58	61.79
0.67	40.41	58.92
1.24	52.28	46.48
1.50	61.63	36.87
2.38	74.24	23.38
4.78	81.20	14.02
11.41	83.05	5.54
48.67	50.60	0.73

b. Two Layer System

Upper			Lower		
Average Found		By Difference	Average Found		By Difference
% Water	% HOAc	% CS_2	% Water	% HOAc	% CS_2
23.55	73.00	3.45	0.38	3.71	95.91
45.35	54.00	0.65	0.40	1.45	97.15
62.36	36.86	0.78	0.17	0.72	99.11
74.00	25.90	0.10	0.16	0.42	99.42
86.60	13.62	-	0.17	0.13	99.70

Using the extraction procedure outlined previously, it was found that 91% benzoic acid was removed from water and 34% recovered from glacial acetic acid made 1N with respect to perchloric acid.

Other molecules qualitatively extracted were benzaldehyde, benzil, benzoin and benzophenone.

II. Direct Titrations

A. Benzilic Acid

The direct titration of benzilic acid was achieved with the oxidation requiring 2 equivalents of reagent per mole of benzilic acid.

Samples for benzilic acid were obtained by diluting 0.2975 grams to 50.00 ml. with glacial acetic acid and 5.00 ml. aliquots taken with the results of oxidation in Table 3.

Table 3. Benzilic Acid Stoichiometry

G. Taken	Mmoles	Meq. Reagent Used	Meq. Reagent/Mmole
0.0298	0.130	0.258	1.98
0.0298	0.130	0.257	1.98
0.0298	0.130	0.257	1.98
0.0298	0.130	0.257	1.98

1. Identification of benzophenone.

After oxidation, a carbon disulfide extraction was carried out on the mixture. The extract was scanned in the infrared region and the remaining carbon disulfide was allowed to evaporate to dryness. The spectrum obtained was identical to that of benzophenone.

A 2,4-dinitrophenylhydrazone derivative was prepared by applying the procedure of Shriner (24) to the residue after carbon disulfide evaporation. The m.p. of the derivative obtained was 240.0 - 240.5°C. (literature m.p. of benzophenone-2, 4-dinitrophenylhydrazone 239°C.) (26). A mixed m.p. with prepared benzophenone-2, 4-dinitrophenylhydrazone and the derivative obtained was 239.0 - 240.5°C.

2. Determination of carbon dioxide.

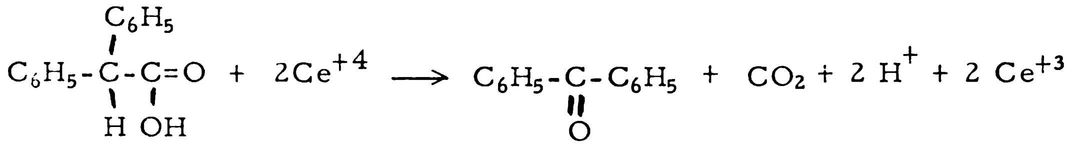
From the identification of benzophenone and the 2 equivalents of cerium consumed per mole of benzilic acid, it was suggested that carbon dioxide was a product of oxidation.

The procedure as previously outlined was used and the results in Table 4 were obtained.

Table 4. Carbon Dioxide Evolution

G. Taken	Mmoles	Time	Mmoles CO_2	Mmoles CO_2/Mmole
0.1221	0.535	2.5 hrs.	0.572	1.07
0.1334	0.584	1.0 hr.	0.540	0.926

The equation for the reaction may be written:



$$C_6H_5\text{-}\underset{H}{\overset{C_6H_5}{C}}\text{-}\underset{OH}{C}\text{=}O + 2Ce^{+4} \longrightarrow C_6H_5\text{-}\underset{\overset{\|}{O}}{C}\text{-}C_6H_5 + CO_2 + 2\,H^{+} + 2\,Ce^{+3}$$

B. Benzohydroxamic Acid

Benzohydroxamic acid was titrated directly with the oxidation requiring 2 equivalents of reagent per mole of benzohydroxamic acid. The oxidation results are given in Table 5.

Table 5. Benzohydroxamic Acid Stoichiometry

G. Taken	Mmoles	Meq. Reagent Used	Meq. Reagent/Mmole
0.0121	0.0882	0.174	1.98
0.0119	0.0867	0.174	2.01
0.0151	0.110	0.221	2.00
0.0631	0.460	0.922	2.01
0.0521	0.380	0.760	2.00

1. Identification of benzoic acid.

A carbon disulfide extract was carried out on the mixture after oxidation. A spectrum was obtained from the extract which was identical to that of benzoic acid. The remaining carbon disulfide was allowed to evaporate to dryness.

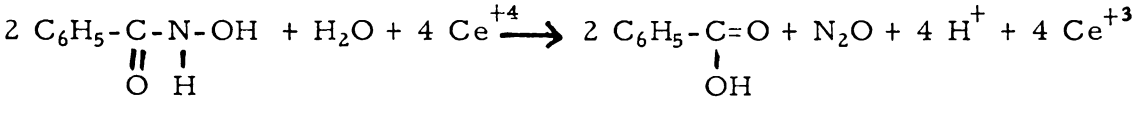
After evaporation a white solid remained in the residue. Several residues were combined and the solid was recrystallized twice from water. The m.p. of the product obtained was 120-121°C. (literature m.p. benzoic acid 122°C.) (16).

2. Identification of nitrous oxide.

It was suggested that an oxide of nitrogen was a product of oxidation from the identification of benzoic acid and the consumption of 2 equivalents of cerium per mole of benzohydroxamic acid.

The gas was collected and scanned in the infra-red region as previously described. The principle split peak of nitrous oxide at 4.5 μ was observed plus the two secondary peaks at 7.7 and 7.8 μ (19). A blank was run using only acetic acid and all other peaks obtained were cancelled out.

The equation for the reaction may be written:



$$2\,C_6H_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}\underset{\underset{H}{|}}{N}\text{-}OH + H_2O + 4\,Ce^{+4} \longrightarrow 2\,C_6H_5\text{-}\underset{\underset{OH}{|}}{C}{=}O + N_2O + 4\,H^{+} + 4\,Ce^{+3}$$

Direct titrations were attempted on the following molecules and although they consumed reagent, no end point was detectable: anisoin, benzoin, a-benzoin oxime, dimethylglyoxime, diphenylfuroxan, γ-diphenylglyoxime and hydroxylamine hydrochloride.

III. Excess Methods

It was necessary to establish an excess method for those molecules whose end points could not be detected by direct titration.

A time study, 5-90 minutes was run on the reagent with the results obtained in Table 6.

Table 6. Excess Method 5-90 Minutes

Initial N	Ml. Reagent	Time	Meq. Sodium Oxalate	N Reagent Calculated
0.0338	15.70	5 min.	0.488	0.0311
0.0338	14.90	10 min.	0.456	0.0306
0.0338	15.20	15 min.	0.481	0.0316
0.0338	15.50	30 min.	0.483	0.0312
0.0338	14.40	45 min.	0.448	0.0311
0.0338	14.80	60 min.	0.460	0.0311
0.0338	14.90	75 min.	0.454	0.0305
0.0338	15.00	90 min	0.432	0.0288

Another time study, 1-3 minutes, was run on the reagent with the results obtained in Table 7.

After the initial normality drop, it was observed that no significant change in normality appeared during the time study. It then was apparent that from the above data, two excess methods based on extended oxidation times were possible. The procedures worked out were applied to the following molecules.

Table 7. Excess Method 1-3 Minutes

Initial N	Ml. Reagent	Time	Meq. Sodium Oxalate	N Reagent Cal.
0.0555	10.00	60 sec.	0.534	0.0534
0.0555	10.40	90 sec.	0.553	0.0532
0.0555	9.60	120 sec.	0.515	0.0533
0.0484	10.00	60 sec.	0.468	0.0468
0.0484	11.00	120 sec.	0.513	0.0466
0.0484	11.95	180 sec.	0.558	0.0467

As the results show, the 1-3 minute method works as well as the 5-90 minute method. In the 5-90 minute excess section, only oxidation data is presented. Identification of products is presented in the 1-3 minute excess section.

IV. Excess Method 5-90 Minutes

A. Benzil

Samples were obtained by diluting 0.6267 grams to 100.0 ml. with glacial acetic acid and 10.00 ml. aliquots were taken. The results of oxidation are given in Table 8.

Table 8. Benzil Stoichiometry

G. Taken	Mmoles	Time	Meq. Reagent	Meq. Reagent Mmole
0.0627	0.298	30 min.	0.197	0.661
0.0627	0.298	40 min.	0.169	0.578
0.0627	0.298	50 min.	0.130	0.436
0.0627	0.298	60 min.	0.126	0.427

B. Benzoin

By diluting 0.3257 grams to 50.00 ml. with glacial acetic acid and taking 10.00 ml. aliquots, samples of benzoin were obtained. The results of oxidation are listed in Table 9.

Table 9. Benzoin Stoichiometry

G. Taken	MMoles	Time	Meq. Reagent	Meq. Reagent/ Mmole
0.0651	0.306	10 min.	0.819	2.67
0.0651	0.306	15 min.	0.721	2.35
0.0651	0.306	35 min.	0.701	2.29
0.0651	0.306	40 min.	0.718	2.34
0.0651	0.306	45 min.	0.695	2.27

C. Dimethylglyoxime

In an attempt to determine the per cent purity of dimethylglyoxime, the method of Banks (2) was used with very erratic results obtained. The oxidation data were of no meaning because the per cent purity could not be determined. If 100% purity is assumed, approximately 3 equivalents of reagent per mole of dimethylglyoxime were consumed as shown in Table 10.

Table 10. Dimethylglyoxime Stoichiometry

G. Taken	MMoles	Time	Meq. Reagent	Meq. Reagent/ Mmole
0.0228	0.248	45 min.	0.748	3.02

D. Diphenylfuroxan

Samples were obtained by diluting 0.3124 grams to 50.00 ml. with glacial acetic acid and 5.00 ml. aliquots were taken. The results of oxidation are cited in Table 11.

Table 11. Diphenylfuroxan Stoichiometry

G. Taken	Mmoles	Time	Meq. Reagent	Meq. Reagent/ Mmole
0.0312	0.131	50 min.	0.135	1.03
0.0312	0.131	55 min.	0.130	0.995
0.0312	0.131	60 min.	0.133	1.01

E. γ-Diphenylglyoxime

It was observed that a γ-diphenylglyoxime solution in glacial acetic acid upon standing turned yellow. An infrared spectrum was obtained on the carbon disulfide extract of the product but it was not identified (Figure 3, page 33).

Samples for analysis were weighed individually. Oxidation results are in Table 12.

Table 12. γ-Diphenylglyoxime Stoichiometry

G. Taken	Mmoles	Time	Meq. Reagent	Meq. Reagent/ Mmole
0.0390	0.162	60 min.	0.747	4.63
0.0436	0.181	60 min.	0.823	4.53
0.0309	0.129	60 min.	0.582	4.52
0.0362	0.151	20 min.	0.678	4.50
0.0303	0.126	45 min.	0.550	4.36
0.0327	0.136	45 min.	0.626	4.65

V. Excess Method 1-3 Minutes

The results obtained by this method were very similar to those achieved by the 5-90 minute procedure. It is recommended that all future work be based upon this speedier procedure.

A. Benzil

Samples for benzil were obtained by diluting 0.6267 grams to 100.0 ml. with glacial acetic acid and taking 10.00 ml. aliquots. Results of oxidation are given in Table 13.

Table 13. Benzil Stoichiometry

G Taken	Mmoles	Time	Meq. Reagent	Meq. Reagent/ Mmole
0.0627	0.298	60 sec.	0.0997	0.334
0.0627	0.298	60 sec.	0.0981	0.329
0.0627	0.298	90 sec.	0.0997	0.334

A carbon disulfide extraction was carried out on the mixture after oxidation. The infrared absorption spectrum obtained from the extract resembled that of benzil, except for the presence of an aliphatic C-H peak (Figure 4-see arrow, page 34). Based upon available information, it is not clear what oxidation is occurring.

B. Benzoin

By diluting 0.4849 grams to 100.0 ml. with glacial acetic acid and taking 10.00 ml. aliquots on the same day, samples for benzoin were obtained. The results of oxidation are listed in Table 14.

Table 14. Benzoin Stoichiometry

G Taken	Mmoles	Time	Meq. Reagent	Meq. Reagent/ Mmole
0.0485	0.228	60 sec.	0.566	2.48
0.0485	0.228	60 sec.	0.567	2.48
0.0485	0.228	60 sec.	0.564	2.47

1. Identification of benzaldehyde.

The spectrum obtained on the carbon disulfide extract was identical to that of benzaldehyde. The remaining carbon disulfide was allowed to evaporate to dryness.

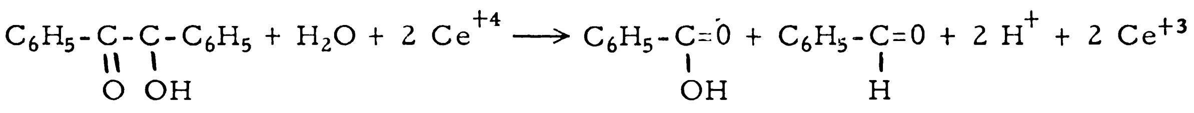
The procedure of Shriner (23) for the preparation of a phenylhydrazone derivative was applied to the carbon disulfide residue.

The m.p. of the derivative obtained was 155.0-155.5°C. (literature m.p. of benzaldehydephenylhydrazone 158°C.) (25). Benzaldehyde-phenylhydrazone was prepared (23) and the m.p. obtained was 156.5-157.0°C. A mixed m.p. of the obtained derivative and the prepared benzaldehydephenylhydrazone was 157°C.

2. Identification of benzoic acid.

Several carbon disulfide residues were combined and the resulting products recrystallized two times from water. A white solid remained m.p. 119.5-120.5°C. (literature m.p. benzoic acid 122°C.) (16). The spectrum of the solid dissolved in carbon disulfide was identical to that of benzoic acid. A 0.1035 gram portion of the solid was titrated with 23.21 ml. of 0.03645N sodium hydroxide and the meq. weight obtained was 0.1223. (calcd. meq. weight of benzoic acid 0.1221).

The equation for the reaction thus may be written:



$$C_6H_5-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle OH}{|}}{C}-C_6H_5 + H_2O + 2\,Ce^{+4} \longrightarrow C_6H_5-\underset{\underset{\displaystyle OH}{|}}{C}=0 + C_6H_5-\underset{\underset{\displaystyle H}{|}}{C}=0 + 2\,H^{+} + 2\,Ce^{+3}$$

Samples of benzaldehyde were weighed out and run by this procedure. They showed a consumption of about 0.2 meq. reagent/mmole, explaining why the value obtained for benzoin was greater than two.

C. α-Benzoin Oxime

Samples were obtained by diluting 0.2414 grams to 100.0 ml. with glacial acetic acid and taking 10.00 ml. aliquots. Results of oxidation are found in Table 15.

Table 15. α-Benzoin Oxime Stoichiometry

G Taken	Mmoles	Time	Meq. Reagent	Meq. Reagent/ Mmole
0.0241	0.106	30 sec.	0.386	4.58
0.0241	0.106	60 sec.	0.466	4.39
0.0241	0.106	60 sec.	0.448	4.22
0.0241	0.106	90 sec.	0.451	4.25
0.0241	0.106	120 sec.	0.438	4.13
0.0241	0.106	150 sec.	0.431	4.05

1. Identification of benzaldehyde.

The infrared results obtained from the carbon disulfide extract showed benzaldehyde as a product. The remaining carbon disulfide was allowed to evaporate to dryness.

A phenylhydrazone derivative was prepared as previously described (23). The m.p. of the derivative recrystallized once from ethanol was 156-157°C. A mixed m.p. of the derivative and the prepared benzaldehydephenylhydrazone was 156.5-157.5°C. (literature m.p. benzaldehydephenylhydrazone 158°C.) (25).

2. Identification of benzoic acid.

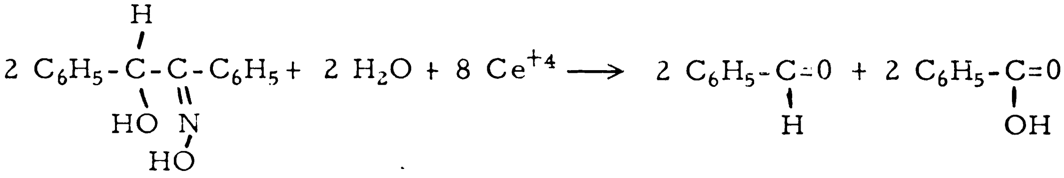
Several carbon disulfide residues were combined and the resulting products recrystallized two times from water. A white solid remained m.p. 119-120.5°C. (literature m.p. benzoic acid 122°C.) (16).

The spectrum obtained by dissolving the product in carbon disulfide showed the solid to be benzoic acid. A 0.1046 gram sample of the solid was titrated with 23.50 ml. of 0.03645N sodium hydroxide and the meq. weight obtained was 0.1221. (calcd. meq. weight benzoic acid 0.1221).

3. Identification of nitrous oxide.

The gas was collected as previously described and the infra-red spectrum obtained was identical to that obtained from the gas evolved by benzohydroxamic acid.

The equation for the reaction may be written:



$$2\ C_6H_5\text{-}\overset{\displaystyle H}{\underset{\displaystyle HO}{C}}\text{-}\underset{\displaystyle \overset{\|}{N}\text{-}HO}{C}\text{-}C_6H_5 + 2\ H_2O + 8\ Ce^{+4} \longrightarrow 2\ C_6H_5\text{-}\underset{\displaystyle H}{C}{=}0 + 2\ C_6H_5\text{-}\underset{\displaystyle OH}{C}{=}0$$

$$+\ N_2O + 8\ H^+ + 8\ Ce^{+3}$$

It is postulated by this author that benzohydroxamic acid is an intermediate in this oxidation.

The fractional meq. reagent per mmole obtained is due to partial oxidation of benzaldehyde as previously noted.

D. Diphenylfuroxan

By diluting 0.4427 gram to 50.00 ml. and taking 5.00 ml. aliquots and diluting 0.3124 gram to 50.00 ml. with glacial acetic acid and taking 5.00 ml. aliquots, samples for diphenylfuroxan were obtained. Results of oxidation are listed in Table 16.

Table 16. Diphenylfuroxan Stoichiometry

G Taken	Mmoles	Time	Meq. Reagent	Meq. Reagent/ Mmole
0.0312	0.131	60 sec.	0.131	1.00
0.0312	0.131	60 sec.	0.127	0.973
0.0443	0.186	60 sec.	0.206	1.11
0.0443	0.186	120 sec.	0.202	1.08
0.0443	0.186	150 sec.	0.200	1.07
0.0443	0.186	180 sec.	0.201	1.08

The spectrum obtained from the carbon disulfide extract was not identified, although it resembled that of diphenylfuroxan (Figure 5, page 35).

Resulting mixtures obtained after oxidation were combined and the acetic acid allowed to volatilize. A light yellow solid was obtained, m.p. 106-109°C. The reaction showed no evidence of gas evolution and the absorption spectrum of the solid dissolved in carbon tetrachloride showed the presence of the -C=N-bond at 6.3 μ (Figure 6, page 36).

E. γ-Diphenylglyoxime

Samples for analysis were weighed individually. Results of oxidation are found in Table 17.

Table 17. γ-Diphenylglyoxime Stoichiometry

G Taken	Mmoles	Time	Meq. Reagent	Meq. Reagent/ Mmole
0.0466	0.194	30 sec.	0.766	3.95
0.0193	0.0803	60 sec.	0.314	3.91
0.0440	0.183	60 sec.	0.742	4.05
0.0182	0.0758	90 sec.	0.307	4.05

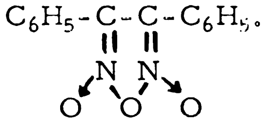
A carbon disulfide extraction was carried out on the mixture after oxidation and the spectrum obtained was the same as that acquired from the diphenylfuroxan residue (see Figure 5).

A light yellow solid was obtained from the carbon disulfide residues and after recrystallization from ligroin it melted at 105-108°C.

A mixed m.p. with this product and the one obtained from the diphenylfuroxan oxidation was 106-109°C., showing both products to be the same.

An analysis of the light yellow solid gave 68.8% C, 4.3% H, 11.1% N, and 15.8% O by difference.

A possible oxidation product would be



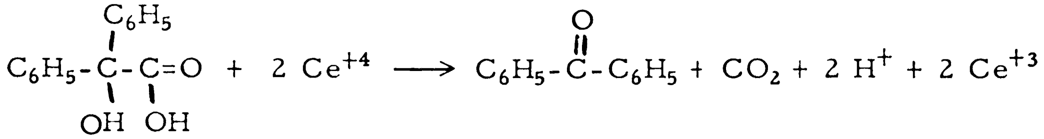
$C_6H_5-\underset{\underset{O\leftarrow N\,-\,O\,-\,N\rightarrow O}{\|\quad\quad\|}}{C-C}-C_6H_5.$

This would require 66.2% C, 3.9% H, 11.0% N, and 18.9% O. It also would account for the consumption of 4 equivalents of reagent per mole and the fact that apparently no bonds were broken. However, since the analytical data is not compatible, further study of this system is necessary.

VI. Discussion of Results

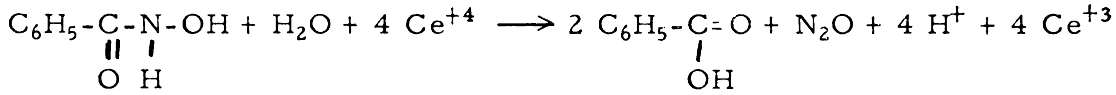
Direct titrations were achieved with benzilic acid and benzohydroxamic acid with the sample solutions being 1N with respect to perchloric acid and consuming 2 equivalents of reagent per mole. The equations for these reactions are as follows:

1.



$$C_6H_5-\overset{C_6H_5}{\underset{OH}{C}}-\underset{OH}{C}{=}O + 2\ Ce^{+4} \longrightarrow C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5 + CO_2 + 2\ H^+ + 2\ Ce^{+3}$$

2.



$$2\ C_6H_5-\underset{O}{\underset{\|}{C}}-\underset{H}{N}-OH + H_2O + 4\ Ce^{+4} \longrightarrow 2\ C_6H_5-\underset{OH}{C}{=}O + N_2O + 4\ H^+ + 4\ Ce^{+3}$$

The other molecules studied consumed reagent but no end point could be detected. There seemed to be some question as to whether an excess method could be successfully used in the presence of perchloric acid. Two methods have been worked out that do not require the presence of perchloric acid until the excess reagent is to be titrated.

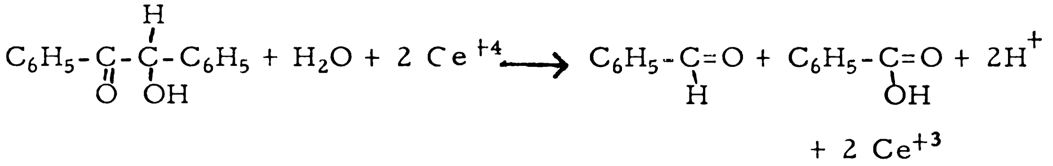
It has been shown that an aqueous solution of ammonium hexanitratocerate made 1N with respect to nitric acid is unstable (27).

Bowman (3) studied the decomposition of ammonium hexanitratocerate in glacial acetic acid and postulated the kinetics of that decomposition as second order with respect to perchloric acid. His suggestion of the equation

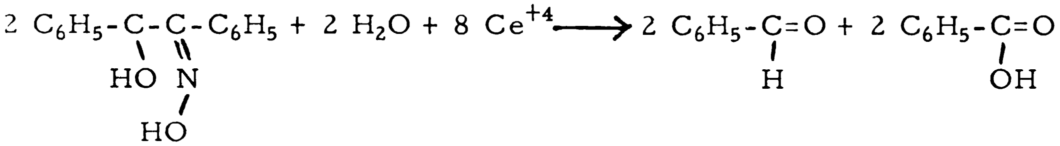
$$(NH_4)_2Ce(NO_3)_6 + CH_3COOH \xrightleftharpoons{H_2O} (NH_4)_2Ce(NO_3)_5(OAc)_x(OH)_y + HNO_3$$

where x + y = 1, leads this author to postulate that the reason for the initial drop in normality observed in the excess methods is due to the generation of the nitric acid.

Using the excess technique, the following oxidations were achieved.

1.


$$C_6H_5\text{-}\underset{O}{\overset{}{\underset{\|}{C}}}\text{-}\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}}\text{-}C_6H_5 + H_2O + 2\ Ce^{+4} \longrightarrow C_6H_5\text{-}\underset{H}{\underset{|}{C}}{=}O + C_6H_5\text{-}\underset{OH}{\underset{|}{C}}{=}O + 2H^+ + 2\ Ce^{+3}$$

2.


$$2\ C_6H_5\text{-}\underset{HO}{\underset{\backslash}{C}}\text{-}\underset{\underset{HO}{\underset{/}{N}}}{\underset{\|}{C}}\text{-}C_6H_5 + 2\ H_2O + 8\ Ce^{+4} \longrightarrow 2\ C_6H_5\text{-}\underset{H}{\underset{|}{C}}{=}O + 2\ C_6H_5\text{-}\underset{OH}{\underset{|}{C}}{=}O$$

$$+ N_2O + 8\ H^+ + 8\ Ce^{+3}$$

The problem now arises as to the role of the perchloric acid in the excess method.

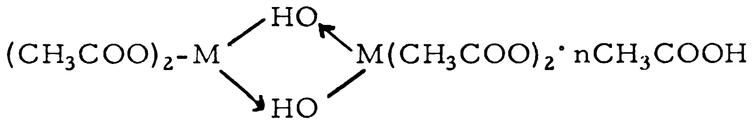
If the perchloric acid serves merely to raise the potential of the Ce^{IV}-Ce^{III} couple enough to allow the oxalate to reduce the excess Ce^{IV}, then the interpolation by Smith (29) would hold.

There is, however, evidence that upon addition of perchloric acid, the following proposed reaction takes place (3).

$$2(NH_4)_2Ce(NO_3)_5(OAc)_x(OH)_y + 2HNO_3 + 4HClO_4 \longrightarrow (NO_3)_3Ce\text{-}O\text{-}Ce(NO_3)_3 + 4NH_4ClO_4 + 6NHO_3.$$

In recent years, the theory of the formation of a dimeric species, Ce-O-Ce^{+6}, has gained support with conclusive evidence (8, 10, 12, 14, 21).

Seaton and co-workers (21), during their attempt to prepare anhydrous rare earth acetates from rare earth oxides in anhydrous acetic acid, isolated binuclear crystalline hydroxo- and oxo-acetate complexes,



and

$(CH_3COO)_2\text{-}M\text{-}O\text{-}M\text{-}(CH_3COO)_2 \cdot nCH_3COOH$

where M is La, Nd or Sm.

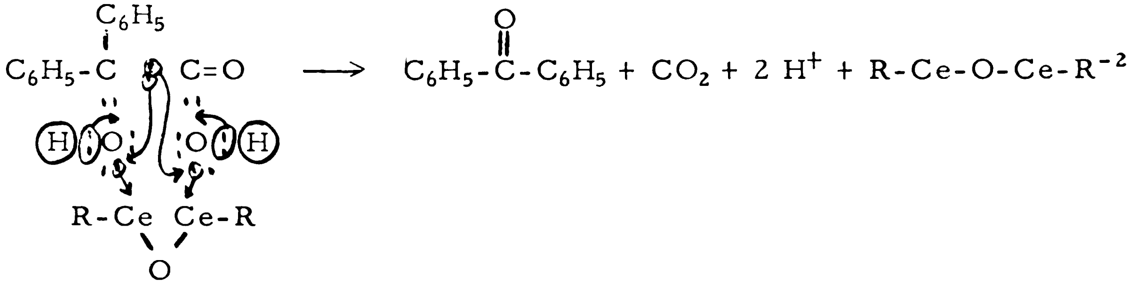
Although cerium was not used in this work, there is no reason to doubt that it would give the dimer.

It seems that the perchloric acid generates the dimer which then participates in the oxidation of the molecule by the removal of an electron pair from a bond. This would account for the even number of equivalents of reagent consumed in the reactions of the oxygenated organic molecules studied.

There is still no explanation of the mechanism involved in the glyoxime oxidation. The strange thing is that no apparent bond cleavage occurs.

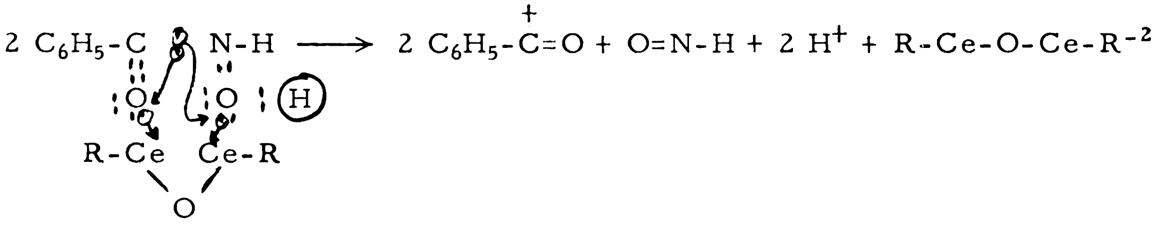
The following is then submitted as a possible mechanism involved in the oxidation of oxygenated organic molecules using ammonium hexanitratocerate in glacial acetic acid with the normality of the medium at least 1 with respect to perchloric acid, where R = $(NO_3)_3$

1.

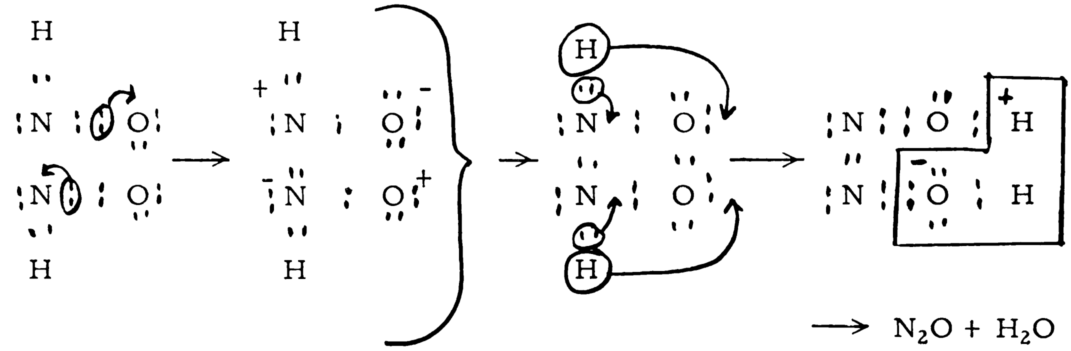


$$\longrightarrow C_6H_5\text{-}\overset{\overset{O}{\|}}{C}\text{-}C_6H_5 + CO_2 + 2\,H^+ + R\text{-}Ce\text{-}O\text{-}Ce\text{-}R^{-2}$$

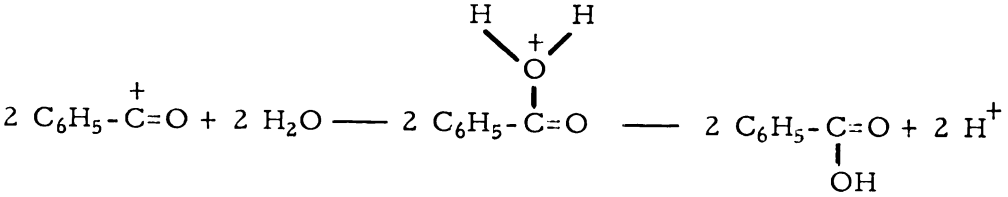
2.



$$\longrightarrow 2\,C_6H_5\text{-}\overset{+}{C}{=}O + O{=}N\text{-}H + 2\,H^+ + R\text{-}Ce\text{-}O\text{-}Ce\text{-}R^{-2}$$

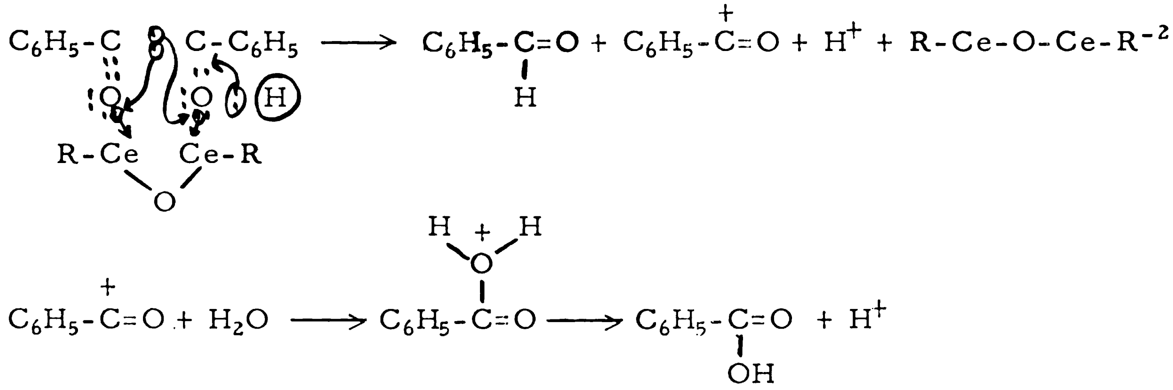


$$\longrightarrow N_2O + H_2O$$

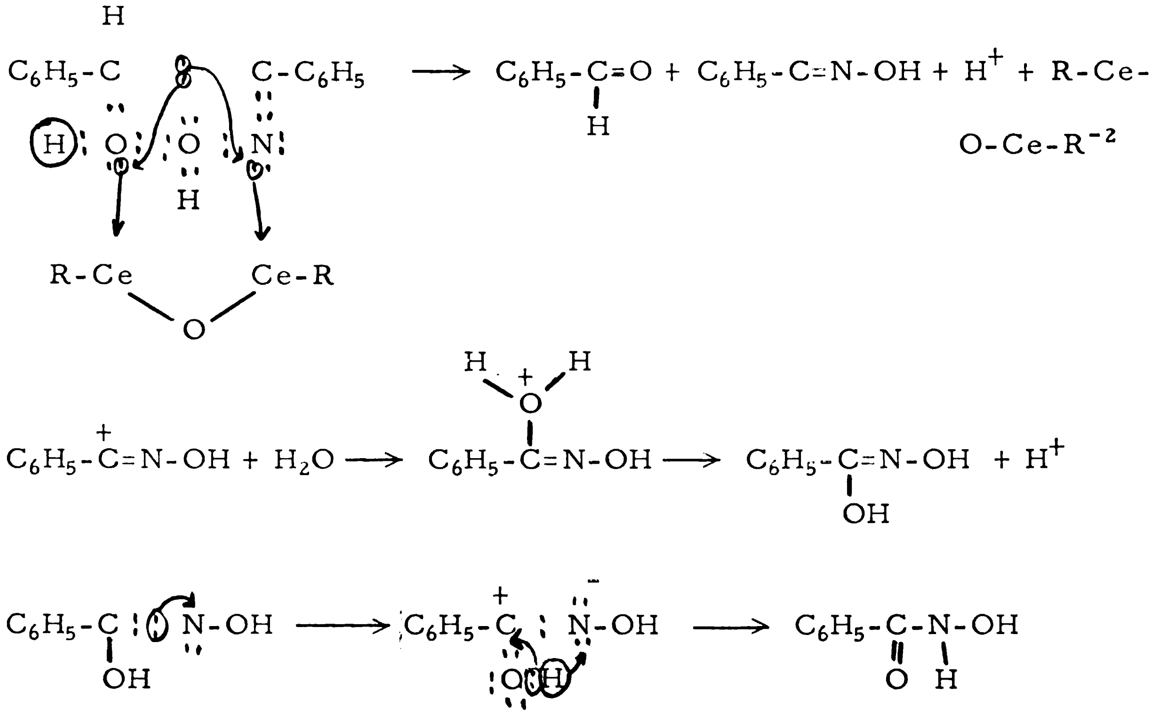


$$2\,C_6H_5\text{-}\overset{+}{C}{=}O + 2\,H_2O \longrightarrow 2\,C_6H_5\text{-}\overset{H_2\overset{+}{O}}{\overset{|}{C}}{=}O \longrightarrow 2\,C_6H_5\text{-}\underset{OH}{\underset{|}{C}}{=}O + 2\,H^+$$

3.



4.



The benzohydroxamic acid formed is now oxidized according to equation 2.

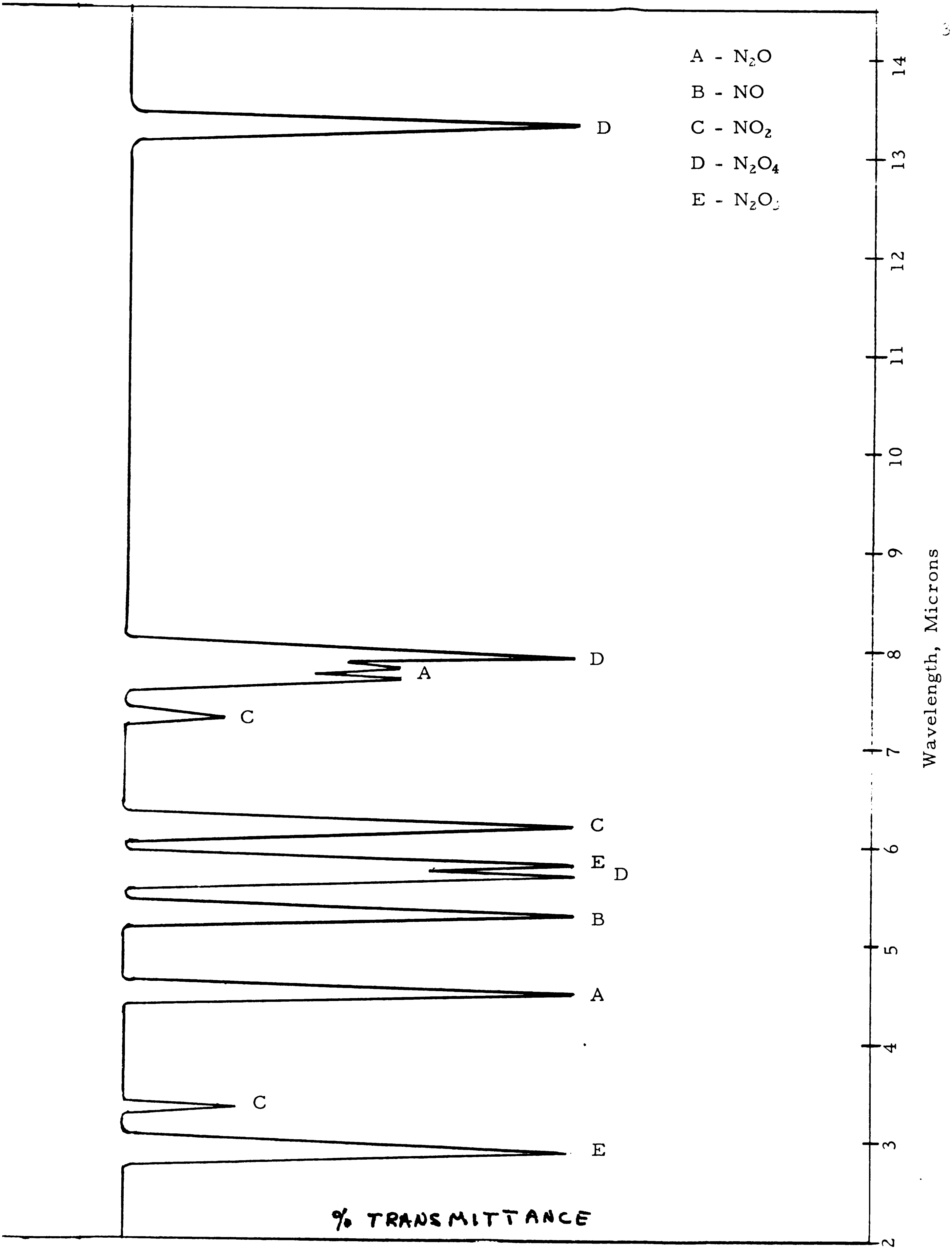
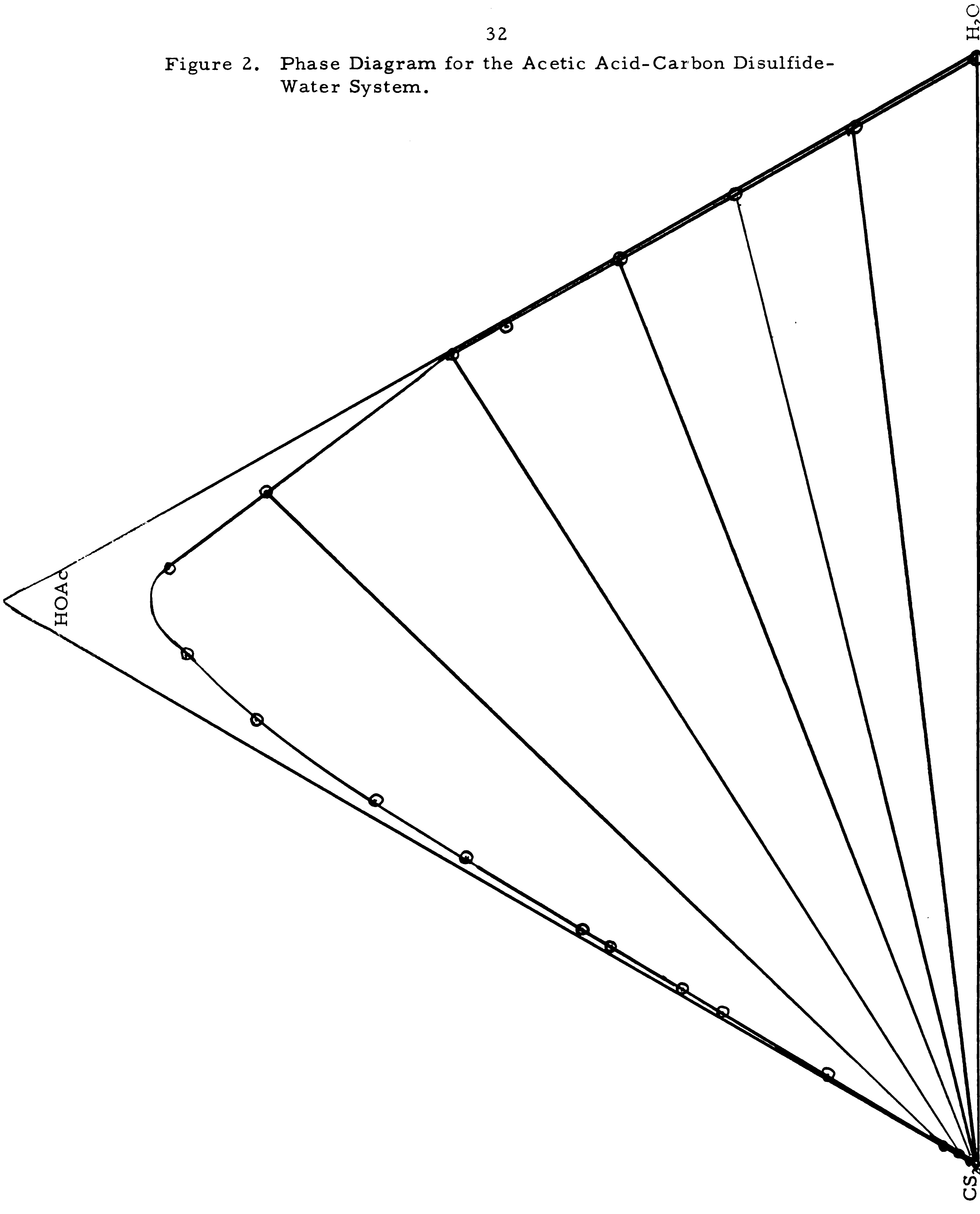


Figure 1. Infrared Spectrum of Oxides of Nitrogen.

Figure 2. Phase Diagram for the Acetic Acid-Carbon Disulfide-Water System.



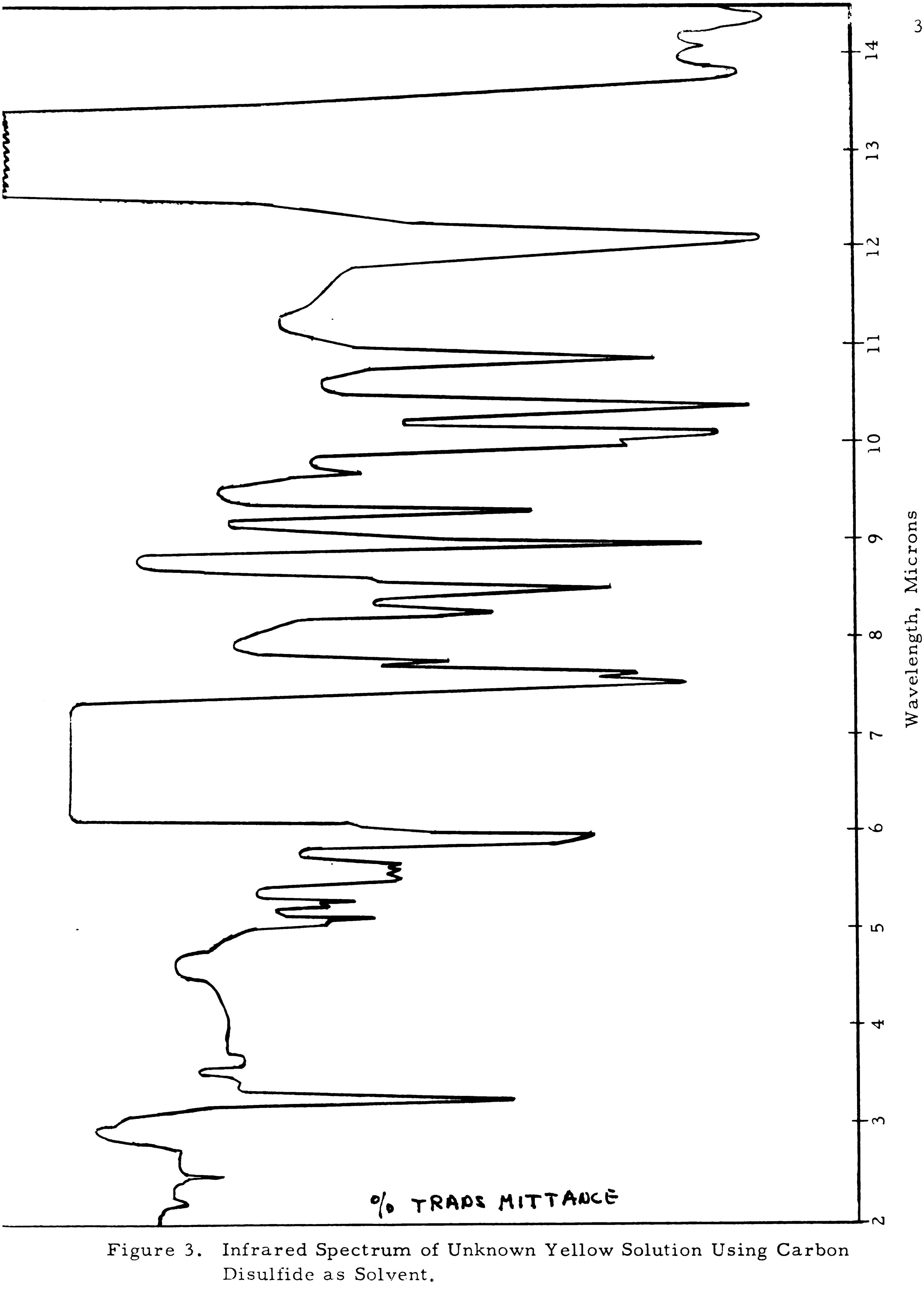


Figure 3. Infrared Spectrum of Unknown Yellow Solution Using Carbon Disulfide as Solvent.

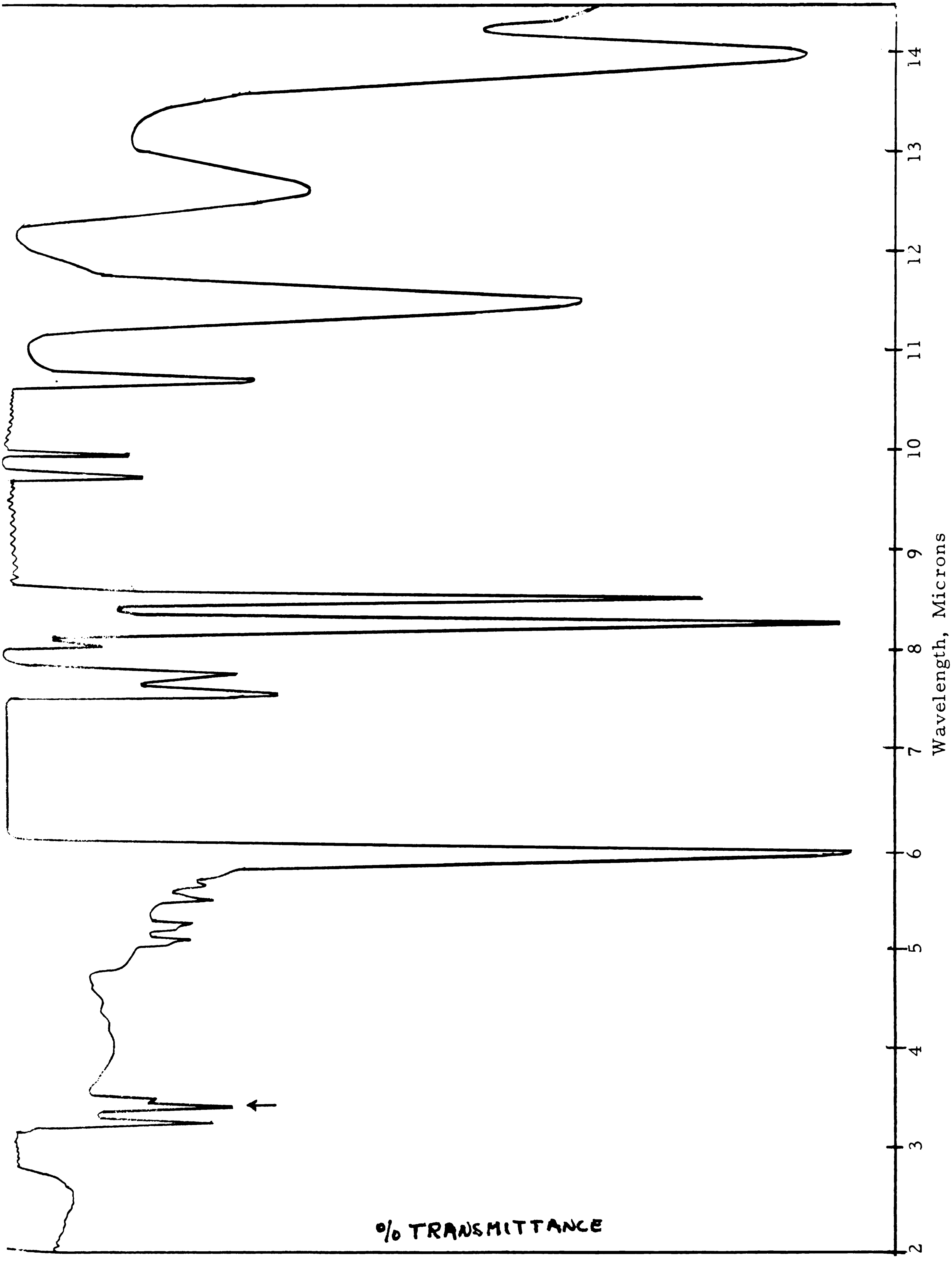


Figure 4. Infrared Spectrum of Benzil Oxidation Mixture Using Carbon Disulfide as Solvent.

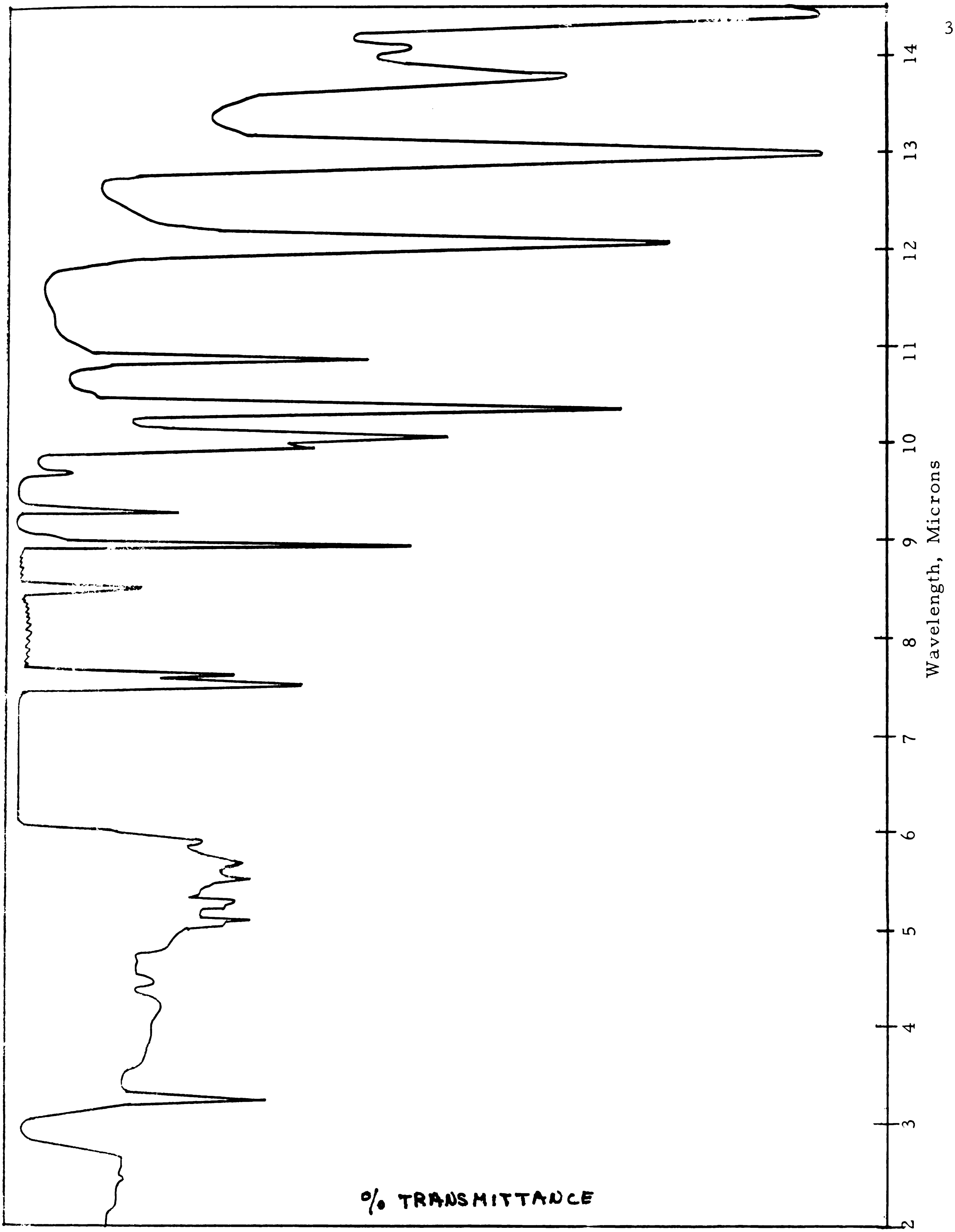


Figure 5. Infrared Spectrum of Diphenylfuroxan Oxidation Mixture Using Carbon Disulfide as Solvent.

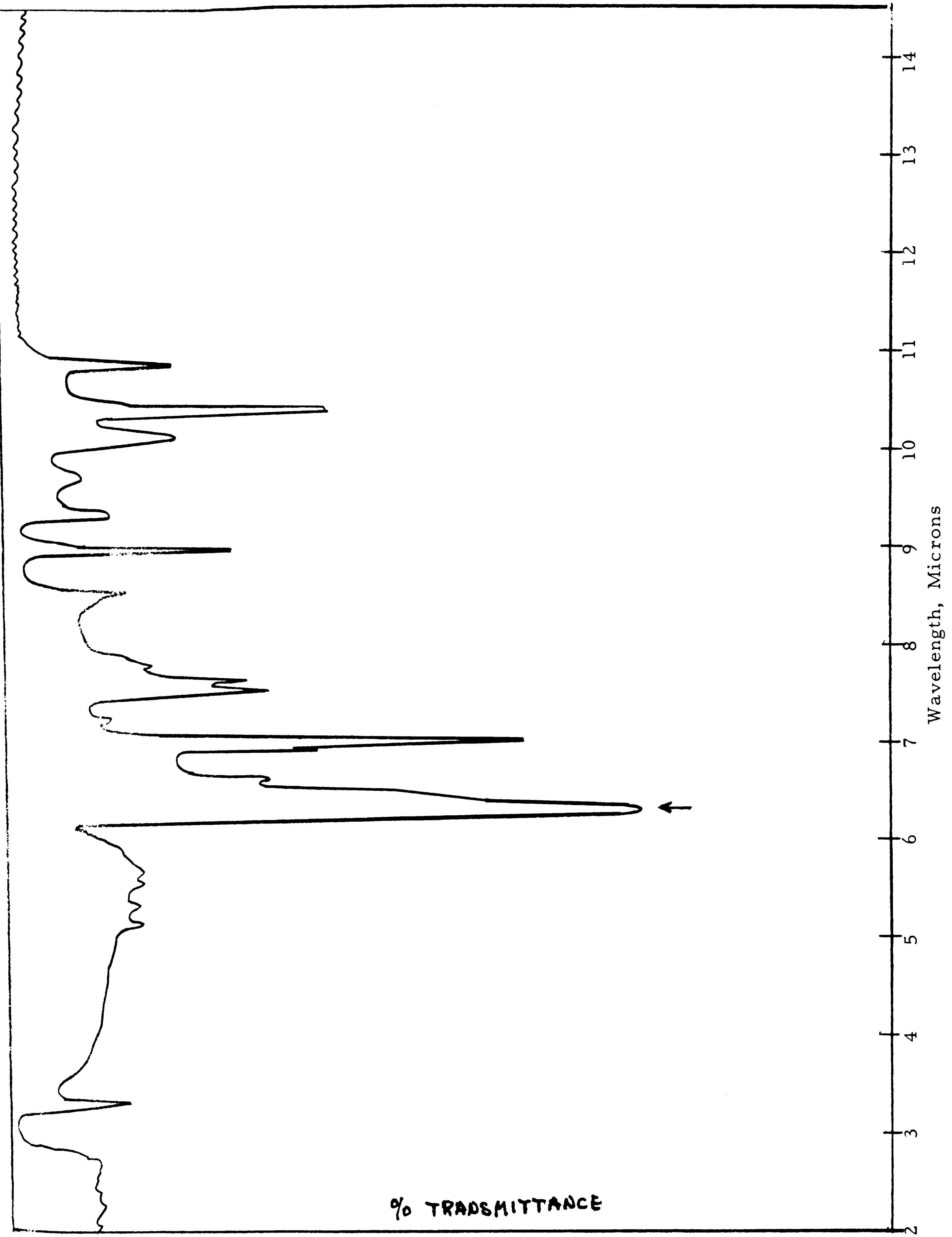


Figure 6. Infrared Spectrum of Unknown Yellow Solid Using Carbon Tetrachloride as Solvent.

SUMMARY

The following conclusions can be drawn from this work.

1. Ammonium hexanitratocerate is soluble in glacial acetic acid to the extent of approximately 0.06N.
2. The acetic acid-carbon disulfide-water system has been investigated and an extraction technique developed.
3. Direct titrations are possible for benzilic acid and benzohydroxamic acid. The products of oxidation were isolated and identified.
4. Two excess procedures have been outlined.
5. The excess method was used on benzoin and a-benzoin oxime. The products of oxidation were isolated and identified.
6. The excess method was used on benzil but the isolated product remained unidentified.
7. Diphenylfuroxan was oxidized by the excess method, however, the product isolated was not identified.
8. The excess method lead to oxidation of diphenylglyoxime, but the isolated light yellow solid was never identified.
9. A seven membered cyclic intermediate is proposed as the oxidation step.
10. If oxidation occurs on an hydroxyl oxygen, the hydrogen will leave as a proton, and the electron pair that formed the O-H bond will turn into the attached atom forming = O.

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APPENDIX I

DATA FOR ACETIC ACID-CARBON DISULFIDE-WATER SYSTEM

Standardization of Karl Fischer Reagent # 1

Grams water	ml. reagent	mg. water/ml.
0.0406	26.40	1.538
0.0391	25.20	1.552
	Ave.	1.545

Standardization of sodium hydroxide solution

Grams KHP	ml. NaOH	N NaOH
0.9088	30.50	0.1459
1.1014	37.04	0.1456
1.1165	37.45	0.1460
	Ave.	0.1458N

	Water			Acetic acid		
Sample #	Grams sample	ml. reagent	%H_2O	Grams sample	ml. NaOH	%HOAc
1	0.3107	22.80[1]	11.37	0.2237	21.25	83.17
	0.4215	31.15	11.45	0.2903	27.50	82.94
2	0.4340	13.35	4.77	0.2840	26.30	81.08
	0.4539	14.00	4.78	0.3364	31.27	81.38
3	1.0519	15.90	2.34	0.4042	34.25	74.18
	1.0214	16.00	2.43	0.3779	32.07	74.30
5	1.0917	10.80	1.53	0.6419	45.11	61.67
	1.1661	11.05	1.47	0.5275	37.10	61.58
6	1.0369	4.55	0.68	1.0647	49.20	40.46
	1.1034	4.60	0.65	1.0317	47.56	40.37
7	1.1035	4.50	0.63	0.6999	30.19	37.76
	1.0429	4.25	0.63	0.7214	30.81	37.39
8	1.1608	3.30	0.44	1.1239	33.81	26.34
	1.1397	3.20	0.44	1.0767	32.45	26.39
9	1.1793	2.20[1]	0.29	1.2239	17.32	15.60
	1.1775	2.25	0.30	1.1805	16.91	15.79

Numbers 7 and 5 A were repeated and in addition a 50 - 50 water acetic acid mixture was saturated with carbon disulfide. (5 X).

	Water			Acetic acid		
Sample #	Grams sample	ml. reagent	%H_2O	Grams sample	ml. NaOH	%HOAc
7	1.1633	3.65	0.49	0.7626	26.30	30.20
	1.1055	3.30	0.46	0.7051	24.35	30.24
5 A	1.0752	8.45	1.22	0.5310	31.73	52.32
	1.0609	8.40	1.26	0.6077	36.12	52.24
5 X	0.1478	23.55[2]	48.78	0.4182	24.20	50.67
	0.1756	27.85	48.56	0.5039	29.10	50.56

Standardization of new Fischer solution # 2

Grams water	ml. reagent	mg. water/ml.
0.1142	37.30	3.062
0.1093	35.60	3.070
		used 3.062

12 U	0.2706	20.70[2]	23.42	0.4601	38.45	73.17
	0.2961	22.90	23.68	0.4950	41.21	72.89
12 L	1.1341	2.90[1]	0.40	0.7618	3.23	3.71
	1.2095	2.90	0.37	1.1357	4.82	3.72
13 U	0.1127	16.70[2]	45.37	0.4515	27.82	53.95
	0.1145	16.95	45.32	0.5726	35.32	54.00
13 L	1.1873	3.20[1]	0.42	1.1502	1.90	1.45
	1.2545	3.10	0.38	1.1479	1.90	1.45
14 U	0.2104	42.80[2]	62.28	0.4949	20.80	36.80
	0.2172	44.30	62.45	0.4784	20.18	36.93
14 L	1.1040	0.60	0.17	1.2412	1.02	0.72
	1.1989	0.62	0.17	1.2154	1.02	0.74
15 U	0.1594	38.80[2]	74.53	0.5853	17.29	25.86
	0.1706	40.95	73.51	0.4686	13.90	25.97
15 L	1.2000	0.60	0.16	1.1015	0.58	0.46
	1.0967	0.60	0.20	1.1649	0.52	0.39

	Water			Acetic acid		
Sample #	Grams sample	ml. reagent	%H_2O	Grams sample	ml. NaOH	%HOAc
16 U	0.1188	33.60	86.60	1.0495	16.32	13.62
				0.8743	13.60	13.62
16 L	1.0872	0.60	0.17	1.1748	0.17	0.13
	1.1000	0.60	0.17	1.0644	0.16	0.13

In an article by Nüni (18) it is reported that the solubility of carbon disulfide in water is 0.29 ± 0.01 weight per cent and water in carbon disulfide is 0.005 weight per cent at 20°C.