

PRODUCT IDENTIFICATION STUDY IN THE URANIUM (IV) - THALLIUM (III) - TARTARIC ACID SYSTEM

Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY Jo Mc Adams Grimley 1966





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ABSTRACT

PRODUCT IDENTIFICATION STUDY IN THE URANIUM(IV)-THALLIUM(III)-TARTARIC ACID SYSTEM

by Jo McAdams Grimley

In the investigation of the oxidation of uranium(IV) by thallium(III) in the presence of tartaric acid in aqueous perchloric acid solution, it was found that some of the thallium(III) oxidized the tartaric acid instead of the uranium(IV). The purpose of this investigation was to determine the oxidation products of the tartaric acid and the stoichiometry of the reaction. The oxidation products of the tartaric acid were found to be glyoxal (OHC-CHO) and carbon dioxide. For each mole of glyoxal that was formed in the reaction, two moles of carbon dioxide were evolved, 1.40 moles of thallium(III) were reduced to thallium(I), and 0.37 mole of uranium(IV) was oxidized to uranium(VI).

PRODUCT IDENTIFICATION STUDY IN THE URANIUM(IV)-THALLIUM(III)- TARTARIC ACID SYSTEM

Ву

Jo McAdams Grimley

A THESIS

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DEDICATION

This thesis is dedicated to my mother and father, Mr. and Mrs. J. Mark McAdams, to show, in one small way, my appreciation for the educational opportunities that they afforded me.

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I. INTRODUCTION

Within recent years, much work in inorganic chemistry has been concerned with determination of reaction mechanisms. Within this field lies the determination of the mechanisms of oxidation-reduction and electron exchange reactions.

Taube and his co-workers have done much work on the oxidation-reduction system with chromium(II) as the reducing agent and a mono acido pentammine cobalt(III) complex as the oxidizing agent (1, 2, 3, 4). In these reactions, various conjugated and non-conjugated mono- and di-carboxylic acids have been used as the organic ligands. It has been found that all or part of the organic ligand is transferred to the reducing agent, the chromium(II), from the oxidizing agent. Based on these results, Taube has formulated a mechanism for electron transfer in which the ligand forms a bridge through which electrons can flow from the reducing agent to the oxidizing agent.

Libby (5, 6) has applied the Franck-Condon principle to oxidation and reduction reactions among the transition elements, paying particular attention to the kinetic data of Taube and co-workers. Recognizing that electrons can be transferred much faster than solvent molecules can be re-oriented to a new environment, it can be seen that

electrons must make transitions against an energy barrier which is comparable in magnitude to the energy necessary for re-orientation of solvent molecules. Libby's theory is that the role of the bridge is to reduce the dissimilarities of the environments of the oxidizing and reducing agents, thus lowering the energy barrier against electron exchange.

In some systems, there seems to be definite evidence of the formation of a bridge between the reducing and oxidizing agents by anions present in the reaction. Brubaker and Mickel (7) have proposed the formation of a sulfate bridge in the electron exchange between thallium(I) and thallium(III) in sulfuric acid. A double chloride ion bridge between thallium(I) and thallium(III) has been proposed in the mechanism for the electron exchange reaction in aqueous hydrochloric acid (8, 9).

In the cases of electron exchange between similar ions such as ferri- and ferrocyanide (10) and permanganatemanganate (11) there seems to be a tunneling mechanism in effect. The substitution inert coordination spheres rule out the possibility of a bridge forming between the two species.

The third mechanism for oxidation-reduction reactions that has been proposed is atom or group transfer. One example of a reaction in which this mechanism is probably operative is in the exchange between iron(II) and iron(III)

in water (12, 13), in which hydrogen atom transfer effects exchange. Another such exchange is between phosphorus trichloride and phosphorus pentachloride in anhydrous carbon tetrachloride (14), in which a chlorine molecule is involved in the exchange.

II. HISTORICAL BACKGROUND

A. <u>Previous Work on the Uranium(IV)</u>-<u>Thallium(III) Reaction</u>

The basic kinetic study of the uranium(IV)-thallium(III) system was made by Harkness and Halpern (15), who followed the change in the uranium(IV) concentration at the 650 m_{μ} absorption peak of uranium(IV). They used the following conditions;

 $[U(IV)]_{0} = 3.5 \times 10^{-3} \underline{M}$ $[T1(III)]_{0} = 9.0 \times 10^{-3} \underline{M}$ $[H^{+}] = 1.76 \underline{M}$ $\mu = 2.9 \underline{M}$

Temperature = 25° C.

They found that the reaction was first order in uranium(IV) and first order in thallium(III) at constant hydrogen ion concentration and ionic strength.

Wear (16) has reported a study of the oxidation of uranium(IV) by thallium(III) over an extended concentration range. Jones and Amis (17) reported on the reaction between uranium(IV) and thallium(III) in water-ethanol media.

Quinn (18) studied the uranium(IV)-thallium(III) reaction in the presence of various dibasic organic acids such as maleic, fumaric, malic, tartaric, oxalic, succinic, and malonic. He used conditions that were similar to those of Harkness and Halpern (15). He found that malonic acid had no effect on the reaction, oxalic and succinic acids inhibited the reaction, and maleic, fumaric, malic, and tartaric acids increased the rate of the reaction,

B. <u>Previous Work on the Uranium(IV)-</u> <u>Thallium(III) Reaction in the</u> <u>Presence of Tartaric Acid</u>

In Love's (19) study of the kinetics of the oxidation of uranium(IV) by thallium(III) in the presence of tartaric acid, he found that the reaction orders with respect to uranium(IV), thallium(III), tartaric acid, and hydrogen ion were 0.93, 0.05, 0.37 and -0.91, respectively. The reaction was studied by following the changes in uranium(IV) concentration by use of the 650 mu absorption peak.

In all runs, the ionic strength was maintained at 2.9 \underline{M} by the addition of sodium perchlorate. A typical kinetic run had the following conditions:

 $\begin{bmatrix} U(IV) \end{bmatrix}_{0} = 3.5 \times 10^{-3} \underline{M} \\ \begin{bmatrix} TI(III) \end{bmatrix}_{0} = 9.0 \times 10^{-3} \underline{M} \\ \begin{bmatrix} Tartaric Acid \end{bmatrix}_{0} = 6.0 \times 10^{-3} \underline{M} \\ \begin{bmatrix} H^{+} \end{bmatrix} = 1.76 \underline{M} \\ \mu = 2.9 \underline{M} \\ \end{bmatrix}$ Temperature = 25° C.

The above concentrations were used for uranium(IV), thallium(III), tartaric acid, and hydrogen ion except when

effects of concentration variations of the different species were being studied.

Love found that all reactions in the presence of more than just a small amount of tartaric acid proceeded for a length of time and then stopped, leaving some unoxidized uranium(IV). This was explained as being due to the disappearance of thallium(III). Because there was almost a three-fold excess of thallium(III) over uranium(IV) at the beginning of the reaction, it seemed that some of the thallium(III) was being consumed in oxidation of tartaria acid. In a polarographic study of thallium(III)- tartaric acid solutions, Love found that they are stable for relatively long periods of time. Other results obtained indicated that tartaric acid catalyzed air oxidation of uranium(IV), but the reaction was slow compared to the uranium(IV)-thallium(III)-tartaric acid reaction. The presence of uranium(VI) or thallium(I) and the exclusion of oxygen were shown to have no effect on the reaction kinetics.

Love also tested a spent kinetic solution with 2,4-dinitrophenylhydrazine. A precipitate was obtained, which indicated the presence of aldehydes and/or ketones. He found that thallium(III) gives a 2,4-dinitrophenylhydrazine derivative, but thallium(III) had been reduced to thallium(I) and therefore, should not have interfered with the test.

C. Oxidation Products of Tartaric Acid

Since a precipitate had been obtained when 2,4dinitrophenylhydrazine was added to a spent kinetic solution, it seemed that paper chromatography would be the best method for determining the oxidation products. Using paper chromatography, the R_f value of the unknown 2,4-dinitrophenylhydrazone that was obtained from the spent solution could be determined. This R_f value could then be compared with those of 2,4-dinitrophenylhydrazine derivatives of other known products of tartaric acid oxidations.

When tartaric acid is carefully oxidized, the likely products are dihydroxymaleic acid, tetrahydroxysuccinic acid, and hydroxymalonic acid (tartronic acid); stronger oxidizing agents decompose it to formic acid and carbon dioxide (20).

It has been reported that manganese dioxide oxidation of tartaric acid yields acetaldehyde and carbon dioxide (21), and oxidation with manganese(III) pyrophosphate gives formic acid and carbon dioxide (22). Formic acid and carbon dioxide are also the products of cerium(IV) sulfate oxidation (23, 24) and sodium metaperiodate oxidation (25). Glyoxylic acid is the intermediate in the latter reaction. Oxidation by selenous acid in the presence of a small quantity of potassium permanganate yields dihydroxymaleic acid (26). It was reported that in

the oxidation by dichromate in the presence of sulfuric acid, there is a fast reaction to give hydroxymalonic acid and then a slow reaction to produce mesoxalic acid (27, 28). Investigations of the kinetics of the reaction between potassium persulfate and tartaric acid showed that the products of the reaction are carbon dioxide and water, and the suggested intermediate is hydroxymalonic acid (29). The products of oxidation of sodium tartrate by manganese(III) alum are glyoxalcarbonic acid and a small amount of glyoxal (30), Glyoxal is also one of the products obtained when tartaric acid is photochemically oxidized in the presence of uranium(IV). Other products obtained in the reaction are oxalic acid, carbon dioxide, carbon monoxide, and water (31, 32). When tartaric acid is treated with an ammoniacal solution of a silver salt, oxalic acid is the product (33), When tartaric acid is oxidized by hydrogen peroxide in the presence of iron(II) salts, the product is dihydroxymaleic acid (34). The same author reports that the semialdehyde of mesoxalic acid is obtained from oxidation by chlorine in the presence of iron.

III. EXPERIMENTAL

A. <u>Preparation and Standardization</u> of Reagents

1. Perchloric Acid

The perchloric acid stock solution was prepared by diluting "Baker Analyzed" reagent perchloric acid (70-72%) with demineralized, distilled water. The concentration of this solution was determined by titration with standard sodium hydroxide solution to the methyl red end point.

2. Tartaric Acid

To prepare a solution of approximately 0.1 <u>M</u> tartaric acid, 3.7678 gms. of d-tartaric acid, "Baker Analyzed" reagent grade (99.6%), was dissolved in boiled (19) demineralized water in a sterilized flask, and diluted to 250 ml. The concentration of the solution was determined by titrating with standard sodium hydroxide to the phenolphthalein end point.

3. Nitrogen Purification

In order to obtain oxygen-free nitrogen for use with the uranium(IV) perchlorate solution, a nitrogen purification train was adapted from the works of Quinn (35), Love (36), and Gordon (37).

Prepurified nitrogen was passed over copper gauze heated to 465° C in a tube furnace, and then through a heated column of active copper deposited on kieselguhr. The temperature in the center of the kieselguhr column was 205° C. The temperatures of the tube furnace and of the kieselguhr column were controlled with variable autotransformers. After passing through the kieselguhr column, the nitrogen gas passed through four gas washing towers equipped with fritted disks. The first tower acted as a trap in order to avoid a back-up into the kieselguhr column. The second tower contained a solution of chromium(II) sulfate over zinc amalgam. The chromium(II) sulfate and zinc amalgam were prepared according to the method of Stone and Beeson (38) as found in Dodd and Robinson (39). The third tower contained demineralized water for washing the nitrogen. The fourth tower contained a perchloric acid solution whose concentration was equal to the sum of the total uranium and free perchloric acid molarities in the uranium(IV) stock solution. The purpose of the fourth tower was to minimize volume changes in the uranium(IV) stock solution.

4. Uranium(IV) Perchlorate

The uranium(IV) perchlorate stock solution was prepared by electrolytic reduction of a uranium(VI) stock solution. The apparatus for preparing and storing

the uranium(IV) perchlorate stock solution was used by Love (36).

The uranium(VI) stock solution that had been prepared by Love (36) was diluted with perchloric acid and demineralized water to a volume of 860 ml., so that the uranium(IV) concentration was 0.13 \underline{M} and the hydrogen ion concentration was 1.2 \underline{M} .

The electrolysis flask had an L-shaped side arm fitted with a fritted disk, which was the anode compartment. The cathode compartment consisted of a small piece of glass tubing leading from the bottom of the flask to which was connected a piece of tygon tubing.

The anode compartment contained 1.20 \underline{M} perchloric acid. The level of the acid was the same as the level of the uranium(VI) solution in the flask. A platinum electrode dipped into the perchloric acid. The anode reaction is:

 $H_20 \rightarrow 2H^+ + 1/2 0_2 + 2e^-$

The cathode consisted of a pool of reagent grade mercury in the bottom of the flask with a piece of platinum wire dipping into the mercury in the side arm. The mercury was cleaned according to the procedure given in the "Handbook of Chemistry and Physics" (40). The main cathode reaction is:

 $UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$

The electrolysis was conducted at 11 v. and 0.7 amp using a "Heathkit" Battery Eliminator Model BE-4 direct current power supply,

The complete system was swept with nitrogen for 24 hours before beginning the electrolysis. An ice-salt bath was used to cool the electrolysis flask and its contents before and during the electrolysis.

Upon completion of electrolysis, the uranium(IV) stock solution was passed from the electrolysis flask to the storage flask, in which it was kept under a nitrogen atmosphere. Uranium(IV) samples were then removed from this flask when needed.

To determine the uranium(IV) concentration in the uranium(IV) stock solution, a one ml. aliquot of the stock solution was placed in 40 ml. of $1:4::H_2SO_4:H_2O$ and then approximately 55 ml. of demineralized water was added. To this, 2 ml. of FeCl₃ (0.50 milliequivalents/ml.) and two drops of ferroin indicator were added. The solution was titrated with standard cerium(IV) sulfate solution to the appearance of a faint blue tint.

To determine the total uranium concentration in the uranium(IV) stock solution, aliquots of the stock solution were passed through a Jones reductor and then titrated with standard cerium(IV) sulfate. The Jones reductor was prepared according to directions given by Kolthoff and Belcher (41). Since some uranium(III) is formed in the

reduction process, air was bubbled through the reduced solution for five minutes to oxidize uranium(III) to uranium(IV) (42).

The uranium(IV) concentration was then calculated as the difference between the total uranium concentration and the uranium(IV) concentration.

The hydrogen ion concentration was determined by replacing the uranium(IV) and uranyl ions with hydrogen ions from a cation exchange resin and titrating the resulting solution with standard sodium hydroxide using phenolphthalein indicator. The cation exchange column was prepared in a 20 ml. buret using a 10 cm column of 100-200 mesh DOWEX 50W-X12 which is a strongly acidic, hydrogen ion form of cation exchange resin. The free hydrogen ion concentration was given by the titrated hydrogen ion molarity minus four times the uranium(IV) molarity and minus twice the uranium(VI) molarity.

5. Thallium(III) Perchlorate

The thallium(III) perchlorate solution that was used was prepared by Love (36). The thallium(III) perchlorate stock solution was prepared by anodic oxidation of a perchloric acid solution of thallium(I) perchlorate. The thallium(I) perchlorate was prepared by dissolving thallium(I) nitrate in an excess of hot concentrated perchloric acid, fuming to volatilize nitric acid, and then recrystallizing the precipitated thallium(I) perchlorate

three times from perchloric acid. The concentration of thallium(I) was determined in the same manner as was thallium(I) in the spent kinetic solutions.

The thallium(III) concentration was taken as the difference in the total thallium concentration and the thallium(I) concentration. The total thallium concentration was determined after aliquots of the thallium stock solution were reduced by bubbling sulfur dioxide through the solution for 20 minutes. The solution was then boiled for one hour to remove any excess dissolved sulfur dioxide, and titrated potentiometrically with standard potassium bromate solution.

The hydrogen ion concentration was determined by titration with standard sodium hydroxide solution to the methyl red end point. About a hundred-fold excess of browld ion was added to the solution prior to the titration in order to complex the thallium(III) ion.

6. Sodium Perchlorate

The sodium perchlorate stock solution that was used in this work was prepared by Love (36). The stock solution was prepared by dissolving twice recrystallized sodium perchlorate in demineralized water.

7. Cerium(IV) Sulphate

The cerium(IV) sulfate solution that was used to standardize the uranium(IV) stock solution was prepared by dissolving 130 gms. of $(NH_{4})_{4}Ce(SO_{4})_{4}\cdot 2H_{2}O$ in a solution

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of 100 ml. of concentrated sulfuric acid and 1000 ml. of demineralized water. The residue that remained in the solution was partially dissolved by digesting the mixture for about one hour at 80° C. The solution was allowed to stand undisturbed for one week and was then filtered through a medium fritted funnel. The solution was then diluted to two liters.

The solution was standardized against arsenic trioxide according to the procedure given by Kolthoff and Belcher (43).

8. Sodium Hydroxide

Standard sodium hydroxide solution was prepared according to the method given by Kolthoff and Sandell (44) using reagent grade sodium hydroxide pellets.

The solution was standardized against primary standard, potassium acid phthalate, using phenolphthalein as indicator.

9. Potassium Bromate

Reagent grade potassium bromate was dried at 160° C for 12 hours. To prepare a 0.1 \underline{N} solution, 2.7835 gms. was weighed, dissolved in demineralized water, and the solution was diluted to one liter.

10. Potassium Iodate

To prepare a 0.1 \underline{N} standard solution of potassium iodate, 3.567 gms. of "Baker Analyzed" reagent grade potassium iodate was weighed, dissolved in demineralized water, and diluted to one liter.

11. Sodium Thiosulfate

Sodium thiosulfate standard solution was prepared according to Kolthoff and Belcher (45) using "Baker Analyzed" reagent grade sodium thiosulfate pentahydrate crystals.

The solution was standardized against the 0.1 \underline{N} potassium iodate solution using starch indicator.

12. Barium Hydroxide

A solution of approximately 0.1 \underline{N} Ba(OH)₂ was prepared by dissolving "Baker Analyzed" reagent grade barium hydroxide crystals in demineralized water. The water had been boiled and cooled under the tap to remove as much carbon dioxide as possible. The solution was stored in a large jug, barium carbonate was allowed to settle to the bottom, and the solution was siphoned when needed.

For the standardization procedure, see the section on determination of carbon dioxide.

13. Hydrochloric Acid

The hydrochloric acid solution was prepared by diluting approximately 84 ml. of concentrated reagent grade hydrochloric acid to two liters.

The solution was standardized by titrating against standard sodium hydroxide to the phenolphthalein end point.

14. 2,4-Dinitrophenylhydrazine

A 2,4-dinitrophenylhydrazine solution was prepared according to the method of Siggia (46). The solution, approximately 2 gms. of 2,4-dinitrophenylhydrazine dissolved in 500 ml. of 2 <u>M</u> hydrochloric acid, was kept refrigerated.

B. The Uranium(IV) Thallium(III) Reaction

In setting up runs, conditions were chosen that were similar to those of Love (19), from whose kinetic work this problem arose.

Two solutions were prepared, one containing uranium(IV) and the other containing thallium(III), but identical in all other respects. The tartaric acid concentration was 6.00×10^{-3} M, and both solutions were prepared with that tartaric acid concentration. In all runs, the uranium(IV) concentration was 3.50×10^{-3} M. In the original uranium(IV) solution the concentration was twice that value and the uranium(IV) was diluted two-fold upon mixing equal parts of the uranium(IV) and thallium(III) solutions. The thallium(III) concentration in all runs was 8.40×10^{-3} M. Again, the thallium(III) solution was prepared with twice that concentration. Both solutions were made 1.76 M in hydrogen ion by adding perchloric acid stock solution and recognizing that the uranium(IV) and thallium(III) aliquots contributed some hydrogen ion concentration. Sodium

perchlorate stock solution was added to give an ionic strength of 2.9 M. The ionic strength, μ , of the thallium and uranium solutions was calculated from the following relationships:

$$\mu = \frac{1}{2} \left\{ [H^+] + [Na^+] + 9[T1(III)] + [T1(I)] + [C10_{4}^{-}] \right\}$$

where

$$[Clo_{\mu}^{-}] = [H^{+}] + [Na^{+}] + 3[Tl(III)] + [Tl(I)]$$

and

$$\mu = \frac{1}{2} \left\{ [H^+] + [Na^+] + 16[U(IV)] + 4[U(VI)] + [C10^-_4] \right\}$$

where

$$[Clo_{4}^{-}] = [H^{+}] + [Na^{+}] + 4[U(IV)] + 2[U(VI)].$$

The two solutions for each run were prepared in 25 ml. volumetric flasks, with reagents added in the order of perchloric acid, sodium perchlorate, thallium(III) or uranium(IV), and tartaric acid. After addition of all reagents, the solutions were diluted to the mark with demineralized water, thoroughly mixed, and placed in a 25° C constant temperature bath for approximately 90 minutes.

To start the reaction, a 20 ml. aliquot of the thallium(III) solution was delivered into a 50 ml. volumetric flask followed by a 20 ml. aliquot of the uranium(IV) solution. The solution was thoroughly mixed, and then nitrogen was bubbled through the solution for at least two hours. The nitrogen was first bubbled through a solution with the hydrogen ion concentration equal to 1.76 M in order to minimize dilution effects. At the end of the bubbling period, the flask was stoppered and placed in the constant temperature bath.

At the end of five days, one portion of the spent solution was used to determine the remaining uranium(IV) concentration, samples were taken to determine the glyoxal concentration, and the remainder of the solution was air oxidized so the thallium(I) concentration could be determined. The glyoxal determinations were made immediately following the determination of the uranium(IV) concentration.

C. Chromatographic Procedures

Paper chromatography (47, 48, 49) was used to determine the identity of the 2,4-dinitrophenylhydrazine derivative that was obtained from spent kinetic solutions of the uranium(IV)-thallium(III)-tartaric acid reaction. Known 2,4-dinitrophenylhydrazones were run along with the unknown in order to determine the oxidation product of tartaric acid in the reaction.

For spotting on the chromatograms, all 2,4-dinitrophenylhydrazones were dissolved in ethyl acetate with the concentration being 2-3 mgm/ml.

The following solvent systems were used:

dibutyl ether: N,N-dimethylformamide: tetrahydrofuran 85:15:4

n-butanol: ethanol (95%): water 70:10:20 ethanol (95%): petroleum ether 80:20.

Descending technique was used on all paper chromatograms. The tank dimensions were 30 cm x 30 cm x 60 cm. The paper was suspended from a trough containing the solvent with a glass rod (U-shaped) laying on the paper to hold it firmly in place.

Whatman No. 1 paper was used. The following were the dimensions:



The paper was spotted using 10 λ micropipets. A 5cc syringe was used to manipulate the micropipets. The spotting was done with the paper placed in the trough, the trough resting on the edge of the laboratory bench, with the paper hanging freely over the edge.

Several hours before placing the paper in the tank, 100 ml. of the solvent to be used was placed in a crystallizing dish which was then put in the bottom of the tank. This allowed the chamber atmosphere to become saturated so that the solvent would not evaporate from the paper. To start the procedure, 50 ml. of the solvent was added to the trough through a funnel by moving the glass plate, which covered the tank, a few cm. Most chromatograms were allowed to develop between six and seven hours. A thermometer was suspended in the tank and temperature readings were taken periodically throughout each run.

At the end of the development period, the remaining solvent was pipetted from the trough, the rack holding the trough was placed in the hood, the solvent front was marked, and the paper was allowed to dry.

The resulting chromatograms were viewed under ultraviolet light. 2,4-Dinitrophenylhydrazones absorb in the ultraviolet region and show as dark spots on the chromatogram.

D. Determination of Uranium(IV) Concentration in Spent Solutions

The uranium(IV) concentration was determined spectrophotometrically with a Beckman Model DU Quartz Spectrophotometer at the 650 mµ absorption maximum. Silica absorption cells of 1.00 cm thickness were used with demineralized water in the reference cell.

To correlate uranium(IV) concentration and absorption, several solutions of varying uranium(IV) concentration were prepared, the absorbance of these solutions determined, and a Beer's Law graph was drawn.

E. Determination of Glyoxal Concentration in Spent Solutions

Glyoxal was determined quantitatively by a procedure given by Salzer (50) and Smith (51).

A known excess of semicarbazide hydrochloride (approximately 0.06 gms) was dissolved in demineralized water and the solution was made slightly basic by addition of 0.5 <u>N</u> NaOH. An aliquot of spent kinetic solution was added to the semicarbazide solution, and the precipitate that was formed was filtered and washed thoroughly. The filtrate was then analyzed for remaining semicarbazide.

Approximately 20 ml. of 5 $\underline{N} H_2 SO_4$ was added to the filtrate followed by a known volume of standard potassium iodate (0.1 \underline{N}). The reaction is given by:

 $5NH_2NH_0CNH_2 + 4HIO_3 = 5NH_3 + 5CO_2 + 7H_2O + 4I + 5N_2$. The solution was kept stoppered for three minutes and then approximately 3 gms. of potassium iodide was added, and the total free iodine was titrated immediately with standard sodium thiosulfate (approximately 0.1 <u>N</u>). The following relationship was used to calculate the amount of semicarbazide that was titrated:

 $\frac{N}{S_2O_3^{2-}} \times \frac{V_{S_2O_3^{2-}}}{S_2O_3^{2-}} = (\frac{N}{KIO_3} \times \frac{V_{KIO_3}}{S_3}) - \frac{4(\text{no. mmoles}}{\text{semicarbazide}})$ From that, the amount of semicarbazide that reacted with the glyoxal was calculated and the amount of glyoxal present was determined.

F. Determination of Thallium(I) Concentration in Spent Solutions

The thallium(I) concentration was determined by potentiometric titration with standard potassium bromate, using a method adapted from Kolthoff (52) and from Zintl and Rienäcker (53).

A portion of spent kinetic solution was first air oxidized so that all uranium(IV) was oxidized to uranyl ion. An aliquot of the solution was then added to a 5-8% hydrochloric acid solution which had been heated to 70° C. The end point was determined by using a Beckman Laboratory Model G pH meter with Beckman saturated calomel and platinum electrodes. Hydrochloric acid was used because it catalyzes the reaction. The elevated temperature also has a catalytic effect on the reaction and it prevents precipitation of thallium(I) chloride.

G. Determination of Carbon Dioxide

The amount of carbon dioxide evolved in the reaction between uranium(IV), thallium(III) and tartaric acid was determined by bubbling the gas through a barium hydroxide solution (54,55). The resulting change in normality of the barium hydroxide solution was determined and the amount of carbon dioxide evolved was calculated.

Nitrogen was used as the sweep gas in the determination. It was first bubbled through a tower equipped with a fritted disk which contained a barium hydroxide solution (approximately 0.1 N). This was done to remove carbon dioxide from the nitrogen. The nitrogen was then bubbled through a 250 ml. Erlenmeyer flask which contained a 1.76 M perchloric acid solution. From this flask, it was directed into the flask (250 ml.) which contained the reaction solutions. A vial, placed in this flask, held the thallium solution and the uranium solution was in the bottom of the flask. The nitrogen swept the carbon dioxide given off in the reaction into another tower containing a barium hydroxide solution. This tower was equipped with a fritted disk and a side arm with take-off for sampling the solution. An ascarite drying tube was attached to the gas exit of the tower.

To determine carbon dioxide, 8 ml. of each solution, uranium(IV) and thallium(III), was placed in the Erlenmeyer flask as described above and 125 ml. of barium hydroxide solution was pipetted into the tower. Nitrogen was allowed to sweep the system for approximately eight hours and then samples of the barium hydroxide solution were removed through the side-arm stopcock to determine the exact normality of the solution before the run. To sample the barium hydroxide, 20 ml. aliquots of standard hydrochloric acid were placed in 25 ml. volumetric flasks. Then barium hydroxide solution was added to the mark. These solutions were poured into 300 ml. Erlenmeyer flasks, the volumetric flasks were rinsed thoroughly with demineralized water, and the excess acid was

determined by titrating with standard sodium hydroxide to the phenolphthalein end point. After determining the concentration of the barium hydroxide solution, the reaction between uranium(IV), thallium(III), and tartaric acid was initiated by tipping the flask to turn over the vial and swirling the flask to insure complete mixing of the uranium(IV) and thallium(III) solutions. The reaction was allowed to run for five days, and at the end of this time, the normality of the barium hydroxide solution was again determined. From the change in normality of the barium hydroxide solution, the amount of carbon dioxide evolved was calculated.

IV. RESULTS

A. Results of Paper Chromatography and Spectra

Table 1 gives the R_f values that were obtained for the various 2,4-dinitrophenylhydrazones tested in this work. The R_f values were obtained by dividing the distance the compound traveled on the chromatogram by the distance the solvent front traveled.

The R_f value of glyoxal-2,4-dinitrophenylhydrazone with the dibutyl ether: N,N-dimethylformamide: THF solvent system was 0.27. Glyoxal-2,4-dinitrophenylhydrazone tailed from the original spot approximately 6 cm with the ethanol: petroleum ether solvent system and with the n-butanol: ethanol: water solvent system. When the 2,4-dinitrophenylhydrazine precipitate from a spent kinetic solution was spotted and chromatographed in the above named solvent systems, results identical with that for known glyoxal-2, 4-dinitrophenylhydrazone were obtained.

In order to further substantiate the fact that glyoxal is the oxidation product of tartaric acid in the reaction, infrared and visible spectra were taken of the 2,4-dinitrophenylhydrazine precipitate from a spent kinetic solution. These spectra were compared with those of known glyoxal-2, 4-dinitrophenylhydrazone. The infrared spectra that were obtained are shown in Figures 1 and 2.

2,4-Dinitrophenyl- hydrazine Derivative of	D1butyl ether: N,N-D1methylformam1de: 85:15:4	N-Butanol: Ethanol: Water 70:10:20	Ethanol: Petroleum Ether 80:20
lyoxal	0.27	streaked	streaked
cetaldehyde	0.72	0.92	0.87
hallium(III)	0.93	0.90	0.86
lyoxylic Acid			streaked
lycoladehyde	0.30	0.87	0.75
1hydroxymale1c Ac1d			streaked
esoxal1c Ac1d		0.93	streaked
etrahydroxysuccinic Acid			streaked
nknown from reaction	0.27	streaked	streaked

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FROM URANIUM (III)- THALLIUM (III)- TARTARIC ACID REACTION (KBr PELLET).

E. Results of Stoichiometry Determination

The stoichiometry of the oxidation-reduction reaction between thallium(III) and uranium(IV) in the presence of tartaric acid was determined for solutions with the following concentrations and conditions:

 $[U(IV)]_{0} = 3.50 \times 10^{-3} \text{ M}$ $[T1(III)]_{0} = 8.40 \times 10^{-3} \text{ M}$ $[Tartaric Acid]_{0} = 6.00 \times 10^{-3} \text{ M}$ $[H^{+}] = 1.76 \text{ M}$ $\mu = 2.9 \text{ M}$ Temperature = 200 C.

In addition, two solutions were prepared with all concentrations and conditions as given above except for the hydrogen ion concentration. The hydrogen ion concentrations in these solutions were 2.78 <u>M</u> and 0.90 <u>M</u>.

The results that were obtained are given in Table 2

In all cases, the absorbance of the spent kinetic solutions was 0.075. This corresponds to a uranhum(IV) concentration of 1.26 x 10^{-3} M; therefore, 2.24 x 10^{-3} M uranium(IV) was oxidized to uranium(VI) by thallium(III). The average of the values obtained for the thallium(I) concentration was $9.8\% \times 10^{-3}$ M. The thallium(I) concentration at the beginning of the reaction was 1.44×10^{-3} M; therefore, 8.40×10^{-3} M thallium(III) was reduced to thallium(I) in the reaction. The average of the values obtained for the glyoxal concentration was 5.91×10^{-3} M. In the determination of the amount of carbon dioxide evolved from the oxidation of tartaric acid, the value obtained was $0.0121 \ \underline{M}$ (0.1937 mmole from 16 ml. of solution).

Solution	[v ⁴⁺] <u>M</u>	[T1 ⁺] <u>M</u>	[онс-сно] м
[H ⁺] = 1.76 <u>M</u>	1.26 x 10 ⁻³	9.80 x 10 ⁻³ 9.89 x 10 ⁻³ 9.80 x 10 ⁻³	5.43 x 10 ⁻³
[H ⁺] = 1.76 <u>M</u>	1.26×10^{-3}	9.89 x 10 ⁻³ 9.89 x 10 ⁻³	6.06 x 10 ⁻³ 7.62 x 10 ⁻³
[H ⁺] = 2.78 <u>M</u>	1.26 x 10 ⁻³	9.89 x 10^{-3} 9.75 x 10^{-3} 9.75 x 10^{-3} 9.87 x 10^{-3}	5.49 x 10 ⁻³
[H ⁺] = 0.90 <u>M</u>	1.26×10^{-3}	9.84 x 10^{-3} 9.87 x 10^{-3}	4.93 x 10 ⁻³

Table 2.-- Data obtained from quantitative determinations.

V. DISCUSSION OF RESULTS

The following mechanism for the uranium(IV)thallium(III)-tartaric acid reaction was proposed by Love (19):

$$\begin{array}{c} U(IV) + TI(III) & \xrightarrow{k'} & U(VI) + TI(I) \\ H_2 Tar & \xrightarrow{ka} & HTar^- + H^+ \\ U^{4+} + HTar^- & \xrightarrow{k_1} & (UHTar^{3+})_I \\ (UHTar^{3+})_I + TI^{3+} & \xrightarrow{k_2} & TI^+ + U^{4+} + X \\ (UHTar^{3+})_I & \xleftarrow{k_3} & (UHTar^{3+})_{II} \\ (UHTar^{3+})_I & \xleftarrow{k_3} & (UHTar^{3+})_{II} \\ (UHTar^{3+})_{II} + TI^{3+} + 2H_2O & \xrightarrow{k_4} & TI^+ + UO_2^{2+} + \\ \end{array} \right\} Path C \\ HTar^- + 4H^+.$$

In the mechanism, \underline{X} represents the oxidation product of tartaric acid. This was found to be glyoxal (OHC-CHO) and carbon dioxide.

The fact that all of the tartaric acid is oxidized in the reaction (when sufficient T1(III) is present) indicates that the second equation of path B is the predominate reaction taking place. The bitartrate ion that is given as a product in the second equation of path C would necessarily yield glyoxal by path B.

Since 1.40 moles of thallium(III) are reduced to thallium(I) and 0.37 mole of uranium(IV) are oxidized to

uranium(VI) for every one mole of glyoxal that is formed, it appears as if one mole of thallium(III) oxidizes one mole of tartaric acid to yield one mole of glyoxal. The 0.37 mole of uranium(VI) is formed by reaction of the remaining thallium(III) with uranium(IV).

The fact that a change in hydrogen ion concentration changes the rate of the reaction and not the stoichiometry indicates, once again, that path B is the predominate reaction taking place. A decrease in hydrogen ion concentration would make formation of the bitartrate complexes easier, thus increasing the rate of formation of glyoxal, but would not affect the amount of glyoxal formed. LITERATURE CITED

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