

THE EFFECT OF CHLORIDE ON THE RATE OF THE THALLIUM(I) -THALLIUM (H) EXCHANGE REACTION IN 2. 194 SULFURIC ACID

> Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY Kenneth Ora Groves 1957

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THE EPFECT OF CHLORIDE ON THE BATE OF THE THALLIUM (1)-THALLIUM (111) EXCHANGE REACTION IN 2.19£ SULFURIC ACID

By

Kenneth Ora Groves

AN ABSTRACT

Submitted to the College of Arts and Science Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

Year 1957

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Approved _____ H. F. mul bon)

ABSTRACT

The rate of the exchange reaction between thallium (I) and thallium (III) in 2.19f sulfuric acid was determined as a function of chloride concentration.

The exchange rate was found to be considerably decreased for formal ratios of chloride to thallium (III) between 0:1 and 2.5:1 and strongly accelerated above the formal ratio of 2.5:1. The study was limited to ratios below 10:1 since precipitation occurred in the reaction mixtures of higher ratios.

The overall variation of reaction rate is on the order of 10^3 , with a minimum occurring at a chloride to thallium (III) ratio of about 2.5:1, followed by a rate increase with a chloride dependence slightly greater than second order.

The data were interpreted by a procedure developed by E. Penna-Franca and R. Dodson (1) in their interpretation of the very similar effect of cyanide on this exchange reaction in perchloric acid. Through this procedure an expression was derived which predicted the rate constants for $[C1^-]:[T1(III)]$ ratios less than 2:1 with a precision of $\stackrel{+}{=}$ 8.27.

The variation in exchange rate was concluded to be due to the formation of thallium (III) chloride complexes.

The relative magnitude of the association constants of the first two of these postulated thallium (III) chloride complexes, $TlCl^{++}$ and $TlCl_2^+$, was determined as 0.0130 for solutions of ionic strength 3.68f.

LITERATURE CITED

(1) E. Penna-Franca and R. W. Dodson, J. Am. Chem. Soc., 77, 2651 (1955).

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Assistant Professor C. H. Brubaker for his guidance and assistance throughout the course of this work.



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INTRODUCTION

Oxidation and reduction reactions are of great importance to the chemist. Arising from these types of reactions is an increasing interest in the mode of electron transfer which occurs. Electron exchange reactions, which involve the simultaneous exidation and reduction of atoms of the same element without affecting the everall concentrations of the two exidation states, are of great interest because they represent the simplest exidation and reduction reactions and may even involve the direct transfer of electrons from one species to the other. The rate of electron-transfer reactions is the tool, obtained from such investigations, with which the chemist hopes to expose the actual path used by an electron in transferring from one species to emother. Various factors may govern this rate of transfer. (1) The number of electrons involved should be considered; that is, the transfer of two electrons may be much more difficult than the transfor of one. (2) Electrostatic charges of involved species with like sign may hinder close approach and decrease the probability of electren transfer. (3) The structure and composition of the reacting species is important. For example, groups surrounding the central atom (e.g. H20, NH3, Cl", CN") may hinder electron transfer by interferring with the extension into space of the orbitals involved in electron transfer, or they may aid transfer by increasing the sizes of the reacting species and decreasing the forces of coulombic repulsion between them. Another possibly important factor is the similarity in the structures of the reacting species. According to the Franck-Condon principle, electronic transitions are very rapid compared

to the motion of nuclei; and, therefore, the most probable electronic transitions are those that do not require the relative position of the nuclei to change. (4) The environment of the reactants is also a factor; metallic conductors in solution may offer an easy path for electron transfer and thus catalyze the reaction.

All of the above factors may affect the rate of electron transfer, but too little information is available to evaluate their relative importances.

In this experimental work the third factor is thought to be the most influential. The sensitiveness of reaction rates due to the addition of various anions such as chloride, cyanide and mitrate, which are capable of forming complexes with one or both of the reactants, has been observed by several workers.

The purpose of this work was to study the effect of chloride on the exchange rate of the thallium (I)-thallium (III) reaction in sulfuric acid of constant ionic strength of 3.68f.

HISTORICAL

The thallium (I)-thallium (III) exchange reaction was first investigated by two groups of workers, G. Harbottle and R. Dodson (2) and R. Prestwood and A. Wahl (3). Both groups have extended their work and have investigated the kinetics of the reaction. Under all the conditions that have been studied, the reaction rate has been found to be dependent on the first power of the thallium (I) concentration and the first power of the thallium (III) concentration.

Prestwood and Wahl (3) have observed the effect on the rate constant of the thallium (I)-thallium (III) reaction in perchloric acid at a constant ionic strength of 3.68f, with variations in the concentrations of the reactants, the hydrogen ion concentration and the nitrate concentration. Their results indicate a decrease in reaction rate with increasing hydrogen ion concentration. The dependence of the reaction rate with decreasing hydrogen ion concentration is interpreted as being due to the increase of an active exchange species formed by hydrolysis of the thallium (III). From kinetic data they interpret their results in terms of two reaction mechanisms:

(1) $T1^+ + *T1^{*++} \longrightarrow T1^{*++} + *T1^{*}$

(2) $T1^+$ + $T10H^{++} \rightarrow T10H^{++}$ + $T1^{+++}$.

A third mechanism of electron transfer is proposed for mixtures containing mitrate ions:

(3) $T1^+ + *T1NO_3^{++} \longrightarrow T1NO_3^{++} + *T1^+$.

They have also determined the variation of the exchange rate of the reaction mixture in the presence of platinum black and silica gel. The half time of exchange for the reaction in the presence of platinum black was decreased by a factor of 40. The presence of pulverized silica gel resulted in no measurable change in rate.

G. Harbottle and R. Dodson (2), working with mixtures of sodium perchlorate and perchloric acid in which the ionic strength was maintained at 6.0f, studied the variation of exchange rate with decreasing acid concentrations. They also found that the rate of exchange decreases with increasing hydrogen ion concentration. They suggest that hydrolysis of thallium (III) ion occurs and that the hydrolyzed species exchanges more rapidly. They interpret their data as indicating that both thallium (III) and hydroxo-thallium (III) are present in significant concentrations, but only the hydroxo-thallium (III) exchanges with the thallium (I). These results are in agreement with the previous work of Prestwood and Wahl (3), but the variation of exchange rate does not follow the Prestwood and Wahl rate law.

More recently C. H. Brubaker and J. P. Mickel (8) have investigated this exchange reaction in 2.19f sulfuric acid solutions of the same constant ionic strength, 3.68f, and hydrogen ion concentration that Prestwood and Wahl (3) had used for their investigations of the reaction in perchloric acid. They found that the rates of reaction are about 200 times those reported by the latter investigators.

They have correlated their data with the following equation

$$\frac{R}{ab} = \frac{0.0345 + 0.7(H^{+})^{2}(SO_{4}^{2}) + 12(H^{+})^{2}(SO_{4}^{2})^{3}}{\left[(H^{+})^{2} + K_{1}(H^{+}) + K_{1}K_{2} + K_{3}(SO_{4}^{2})\right] \left[1 + K_{4}(SO_{4}^{-})\right]}$$

$$K_{1} = \frac{(T10H^{++})(H^{+})}{(T1^{+})}, \quad K_{2} = \frac{(T10^{+})(H^{+})}{(T10H^{++})}$$

$$K_{3} = \frac{(T1SO_{4}^{+})}{(T1^{+})(SO_{4}^{-})}, \quad K_{4} = \frac{(T1SO_{4}^{-})}{(T1^{+})(SO_{4}^{-})}.$$

where

•



They have suggested that a combination of exchange processes such as

$$*T1^{+3}$$
 $*$ $T1SO_{4}^{-}$ \longrightarrow $T1^{+3}$ $*$ $*T1SO_{4}^{-}$

and

*T1S04 + T1(S04)2
$$\longrightarrow$$
 T1S04 + *T1(S04)2

may be the reason for the increased rate of exchange.

All workers have used the assumption that the activity coefficients of the reactants are constant at constant ionic strength. The decrease in rate with increasing acid concentration could be entirely due to changing activity coefficients of the reactants and transition states involved in the transfer mechanisms (7).

Dodson and Marbottle (2) have also investigated electron transfer rates for mixtures containing mixed hydrochloric and perchloric acids at constant ionic strength 6.0f. They found the rate to be considerably depressed by low concentrations of chloride, while it is strongly accelerated at higher chloride concentrations. The minimum rate occurs at a [C1"]: [T1(III)] ratio of 1.5 and subsequently rises. The increase is little less than second order in chloride. These data, supplemented with transference measurements, were interpreted as resulting from the formation of thallium (III) chloride complexes. The initial depression is believed due to the formation of less reactive TICl++ and TlCl2⁺ species while the acceleration upon increased chloride comcentration is believed due to the formation of a more reactive TlCl4° species and possibly a weakly associated thallium (I) complex such as the TICI3 or TICI4 proposed by Fromhers and Lik (6). The postulated existence of stable thallium (III) chloride complexes is compatible with the observations of Benoit (5), who has estimated dissociation

constants of $10^{-8.1}$, $10^{-5.5}$, $10^{-2.2}$ and $10^{-2.2}$ for the successive complaxes from TlCl⁺⁺ to TlCl₄⁻.

E. Penna-Franca and R. Dodson (4), working with reaction mixtures of cyanide and perchloric acid solutions of constant ionic strength of 0.5f, have observed that cyanide has a drastic effect on the rate of electron exchange. A total variation of about 10,000 fold in the rate is observed. Small amounts diminish the rate, a minimum at less than 1% of the initial value is observed at a [CN"]:[T1(III)] ratio of 3.5, followed by an increase in rate about as the third power of (CN⁻). They believe the rate variation is best explained by the formation of thallium (III) cyanide complexes. The initial effect is attributed to the formation of $TICM^{++}$ and $TICM_2^{++}$ complexes which are inert to the exchange reaction. The increase in rate is ascribed to the formation of higher thallium (III) cyanide complexes. They infer that $Tl(CR)_3$ or $Tl(CR)_4$ reacting with Tl^4 are responsible for the increase near the minimum. Evidence for the lower complexes TICN++ and TLCN2⁺ is further substantiated by kinetic data which enabled them to calculate the relative magnitudes of the equilibrium constants of these two species.

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MATERIALS

Thallium (I) nitrate was obtained from E. H. Sargent and Company, sodium dichromate from Merck and Company, sodium cyanide from the Mallinckrodt Chemical Works and all acids and annonium hydroxide from E. I. du Pont de Namours and Company.

Rediosctive thallium $(T1^{204})$ was obtained as the nitrate from the U. S. Atomic Energy Commission, Oak Ridge, Tennessee.

The thallium (I) sulfate and radioactive thallium (III) sulfate solutions used were prepared by C. Knop according to the procedure outlined by J. P. Mickel (12).

The thallium (III) sulfate solution was prepared from a saturated solution of recrystallised thallium (I) sulfate. The sulfate was exidized to thallium (III) exide with potassium hexacyanoferrate (III) in 0.1f sodium hydroxide. The exide was washed free of hexacyanoferrate (II) and (III) by decanting the supernate and washing with distilled water. Thallium (III) sulfate was then prepared by dissolving the exide in 20 ml of 10.6f sulfuric acid. The volume of solution was increased to 200 ml. The resulting thallium (III) sulfate solution was analyzed for total thallium content by reduction and precipitation as thallium (I) chromete. The thallium (III) content of the sulfate solution was determined with another sample by precipitation as the exide. The procedure used in both precipitations is described by Lundell and Hillebrand (1). The analyzes agreed within 1.0% indicating that the thallium content of the sulfate solution is essentially completely thallium (III).

The residual sulfuric acid concentration was calculated by determining the amount of sulfuric acid which had reacted with

thallium (III) oxide according to the reaction

$$T1_{2}0_{3} + 3H_{2}S0_{4} \rightarrow T1_{2}(S0_{4})_{3} + 3H_{2}0_{4}$$

The amount determined was then subtracted from the initial formality of the acid, indicating the formality of the residual sulfuric acid in the sulfate solution.

A standard sodium hydroxide solution was prepared free of carbonate and standardized with potassium acid phthalate. Standard acids were then prepared and analyzed by comparison with this sodium hydroxide solution.

All of the reactions were run in 2.19f sulfuric acid solutions. From equilibrium concentrations of sulfate, bisulfate and hydrogen ion data obtained by H. M. Smith (9) and by a method described by T. F. Young and L. A. Blatz (10), J. P. Mickel (12) has calculated the ionic strength of a 2.19f sulfuric acid solution as 3.68f. Since the concentration of added chloride ranged between 0.0091f and 0.06f, its effect on the ionic strength of any solution was considered negligible; and a constant ionic strength of 3.68f is assumed for all reactions.

The concentrations of all solutions in thallium (I) and thallium (III) were variable. They ranged between 0.0105f to 0.0064f in thallium (III) and 0.010f to 0.005f in thallium (I), depending upon the formal concentration of the chloride. All reactions were carried out in 100 ml volumetric flasks.

FROCEDURES

Reaction mixtures were prepared by the addition of an appropriate amount of each stock solution to 100 ml volumetric flasks. The sulfuric acid was first added to each flask, followed by the addition of the thallium (I), thallium (III) and hydrochleric acid solutions. Enough distilled water was then added to each flack to bring the final volume to approximately one ml less than 100 ml. The flacks were then immersed in a water bath kept at 24.94[±] 0.01°C. These flacks remained in the bath for at least three hours in order for the solutions to reach thermal equilibrium before the active thallium (III) sulfate was added.

The active theilium (III) sulfate was then added (1.2 ml). The flask was then shaken and brought upright twelve times. The zero time was taken as the time of first shaking. Separation of the exidation states was accomplished by precipitation of the thallium (I) as the chromate. The first precipitation was usually done within three minutes.

Before each precipitation a Whatman #540, 2.7 cm filter paper was dried for at least one hour and weighed.

Preshly prepared precipitant was used for each precipitation. The composition of the precipitant was sodium dichromate 0.2f, sodium cyanide 2.0f, annonium hydroxide 9.0f and 10% by volume ethyl alcohol. The precipitant was saturated with thallium (I) sulfate, filtered, and stored in an ice bath prior to use.

From data obtained by J. P. Mickel (12), half times for the isotope exchange were calculated and ten precipitations were timed to vary between sere and ten times the calculated half time.

A 5 ml aliquot of the reaction mixture was pipetted into a 150 ml Erlenmeyer flask containing twice its volume in freshly prepared precipitant, except for runs in which the total thallium content was approximately 0.01f. in which case 10 ml aliquots were used. The solution was swirled in an ice bath during the addition of the sample to counteract the heat of neutralization. For more efficient separation the solution was allowed to age for at least five minutes before the thallium (I) chromate was collected on a filter. The filtration was carried out in a steel funnel with a removable chimney. The filter paper was placed on the flat support and the chimney on top. At the point of contact with the filter paper the chimney was 19 mm in diameter. The filtration was sided by an aspirator. Included in the aspiration system was an arrangement for bleeding in air in order to completely control the rate of filtration. Too rapid a filtration greatly reduces the efficiency of the separation. The time of contact between the precipitate and supernate from precipitation to separation was kept to within thirty minutes in all cases. Prestwood and Wahl (3) have shown that the heterogeneous exchange between the complexed thallium (III) species and the thallium (I) chromate is very slow and would be negligible under these conditions. After filtration the precipitate was washed with four 0.5 ml portions of the precipitant followed by four 0.5 ml portions of distilled water. The chimney was removed, and the precipitate was transferred to a metal plate. A metal cylinder was placed on top of it to prevent the filter paper from curling upon drying. They were dried for at least one hour at 110° C, weighed and mounted on $3\frac{1}{2} \times 2\frac{1}{2}$ inch cardbeard cards which were marked for centering. Cellulose tape was placed directly

over the sample. Each sample was mounted directly in front of and 4 cm from the one inch and window of a G-N tube. An R.G.L. Mark 13, Nodel 1, Serial A-189 scalar was connected to the G-N tube. The tube had a flat plateau of over 200 volts. Samples were counted using a voltage 100 volts above the "knos". Sample weights varied from 7 mg to 12 mg. The samples usually weighed between 10 mg and 12 mg. However, because the rate of filtration of the precipitates involving the 10 ml aliquots was increased to keep the contact time between precipitate and supernate within the thirty-minute limit, there was some lose of precipitate and 7 - 10 mg samples resulted.

The samples were counted over an interval of time sufficiently long to obtain 10,000 counts. An average of three such counting intervals for each sample was used as the correct value. The dead time for the G-M tube used in these measurements was 4×10^{-4} sec. Coincidence and background corrections were made for each reading. Equilibrium specific activity was taken as the activity of that sample precipitated after a time interval of ten half lives. Since the half life of $T1^{204}$ is 4.0 years, it was unnecessary to correct for radioactive decay.

Exchange half times were then determined from graphs of log (1-F) versus time, where F is defined as the ratio of the specific activities (counting rate per mg of sample) of time t to time t_{∞} (ten times t_{0}). Each graph was prepared using from six to nine experimental points.

Rate constants were calculated from half times and concentrations of thallium (I) and (III). Graphs of exchange reactions with

short half times usually gave excellent straight lines. However, graphs of these exchange reactions involving long half times were semetimes scattered. Maximum deviations of the calculated half times of these reactions were within $\frac{1}{2}$ 10%. This maximum deviation is in agreement with that assigned to this reaction by Brubaker and Mickel (8). The variation in rate of the thallium (I)-thallium (III) exchange reaction in 2.19f sulfaric acid of constant ionic strength was determined as a function of chloride concentration.

The rate data were interpreted in terms of the McKay (11) formula, applicable to exchange reactions which are first order in the overall concentration of each oxidation state and occur at equilibrium

$$\ln (1 - x/x_{m}) = - R/ab (a + b)t.$$

The x and x_{∞} are the specific activities at time t and at infinite time (ten times the presentively. Specific activity is defined as the ratio of the activity in counts per second per milligram of precipitated thallium (I) chromate. The a and b are the overall formal concentrations of thallium (I) and thallium (III), respectively; and R is the rate of exchange of the electron transfer reaction in units of formality⁻¹time⁻¹.

The rate of exchange of the thallium (I)-thallium (III) reaction in 2.19f sulfuric acid was shown, by C. H. Brubaker and J. P. Mickel (3), to be dependent on the first powers of the thallium (I)-thallium (III) concentrations. They assumed

$R = k [T1(I)]^{\alpha} [T1(III)]^{\beta}$

and found that alpha equals 0.98 ± 0.06 and beta equals 1.09 ± 0.01 .

The half time of reaction, the time when x/x_{∞} equals $\frac{1}{2}$, can be evaluated from a plot of ln $(1 - x/x_{\infty})$ versus time. Typical exchange rate data interpreted by the above formula are indicated in Figure I.



Fig. I - Typical rate data. Curve A, [Cl⁻]:[Tl(III)] 0:1, curve B, [Cl⁻]:[Tl(III)] 0.87:1; curve C, [Cl⁻]:[Tl(III)] 1.06:1.

It can be seen in Figure I that at time zero there is between 5% and 10% exchange indicated. This apparent zero-time exchange is due to an accelerated exchange rate occurring either during the short time between mixing and separation or during the separation. However, by keeping the amount separated and the rate of precipitation as constant as possible for all precipitations of any given run, the error due to this apparent zero-time exchange will be a constant factor and not affect the slope of the exchange plot, from which the half time of reaction is determined. This 5% to 10% apparent zero-time exchange is in agreement with previous work (2, 8) on this exchange reaction where separation was effected by precipitation of thallium (I) ekremate.

Substitution into the above equation, $x/x_{\infty} = \frac{1}{2}$ when $t = t_{2}^{2}$, gives the equation

$$2/ab = 0.63915/(a + b)t_2.$$

Thus, R/ab may be calculated from the known concentrations of a and b and the measured half time of reaction.

The effect of increasing chloride concentration on the rate of exchange is shown in Table I.

It can be seen that the rate of exchange is extremely sensitive to variation in chloride concentration. The initial effect is a gradual decrease in rate followed by a drastic reduction in rate starting at an approximate $[C1^-]$: [T1(III)] ratio of 0.5:1 and reaching a minimum at a $[C1^-]$: [T1(III)] ratio of approximately 2.5:1. At this point the overall effect is a rate decrease on the order of 10^{-3} . At higher $[C1^-]$: [T1(III)] the rate again increases with a chloride dependence slightly greater than second order. The study was limited to

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a maximum [C1"] : [T1(III)] ratio of 10:1. Preparation of reaction mixtures above a ratio of 10:1 was accompanied by the formation of a precipitate. The precipitate has an empirical formula, Tl_2Cl_3 .

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| DEPENDENCE OF EXCHANGE RATE ON CHLORIDE CONCENTRATION AT 25°C., | | | | | |
|---|-------------------|----------|-------------|-----------------|----------|
| Cl ⁻ (f) | T1(III)(f) | T1(1)(f) | c1-/T1(III) | R/ab f-lmin1 | th(nin.) |
| 9.000 | 0.0105 | 0.010 | 0.00:1 | 0.796 | 40.5 |
| 0.0091 | 0.0105 | 0.010 | 0.866:1 | 0.167 | 203 |
| 0.012 | 0.0115 | 0.010 | 1.06:1 | 0.0895 | 360 |
| 0.014 | 0.0115 | 0.010 | 1.23:1 | 0.0485 | 665 |
| 9.017 | 0.0115 | 0.010 | 1.49:1 | 0.0137 | 2,345 |
| 0.023 | 0.0115 | 0.010 | 2.00:1 | 0.0026 | 13,248 |
| 0.025 | 0.0115 | 0.010 | 2.17:1 | 0.0021 | 15,408 |
| 0.027 | 0.0115 | 0.010 | 2.35:1 | 0.0019 | 16,416 |
| 0.035 | 0.0114 | 0.010 | 3.07:1 | 0.0025 | 12,960 |
| 0.025 | 0.0065 | 0.005 | 3.85:1 | 0.00408 | 14,758 |
| 0.030 | 0.0065 | 0.005 | 4.61:1 | 0.00641 | 9,400 |
| 0.035 | 0.0064 | 0.005 | 5.47:1 | 0.00928 | 6,560 |
| 0.061 | 0.0065 | 0.005 | 9.53:1 | 0.0344 | 1,800 |

The effect on the rate of reaction with increasing chloride can be explained on the same basis that R. W. Bodson and co-workers (2, 4) have used in their interpretation of the effect of chloride and cyanide on reaction rates in perchloric acid of constant ionic strength (6.0f).

The initial reduction in the exchange rate can be explained on the basis of the formation of thallium (III) complexes. These complexes apparently are of such a nature as to disfavor a rapid electron exchange mechanism. This will result in a decrease in the concentration of the

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thallium (III) exchange species normally present in the absence of chloride and a subsequent decrease in the overall reaction rate. The most probable formsef the complex thallium (III) ions are TlCl++ and TICL,*. The assumption that the thallium (III) and not the thallium (I) is involved in complex formation is based on the work of Bonoit (5), who has investigated the T1C1++ and T1C12+ ions and found them to be strong complexes with association constants on the order of 10⁸ and 10³, respectively. Further support for this assumption is gained from the recent work of Mair and Mancollas (13). They have measured the association constant for the TICL species and obtained the value 2.8 at 40°C. Comparison of this value with those values obtained by Sensit (5) for the thellium (III) complexes indicates that the latter would be the predeminant species. The subsequent increase in rate of reaction is thought to be due to the formation of TiCl3 and TiCl4", which apparently have a greater ability to exchange than the TiCl++ and TiCl2⁺. The association constants for these latter complexes were also determined by Beneit (5) and were estimated to be about 10².

If the increased rate is completely due to the formation of TICl₃ and TICl₄[•], the rate of exchange should approach a constant value when all of the thellium (III) has combined to form the TICl₄[•] complex. This should occur near a [Cl⁻]:[Tl(III)] ratio of 4:1. From an examination of Table I it can be seen that this is not the case. The constant rate increase from a [Cl⁻]:[Tl(III)] ratio of 4:1 to 10:1 must be due to the formation of weak thallium (I) chloride complexes which exchange rapidly with TICl₄. The formation of such thallium (I) complexes as TICl₃⁼ and TICl₄⁼ has been postulated by Fromherz and Lih (6). The exchange rate data were analyzed by a method used by **E.** Penna-Franca and R. H. Dodson (4) in their analysis of the thallium (I)-thallium (III) reaction in the presence of cyanide in perchloric acid of constant ionic strength (6.0f).

Included in the analysis are data on exchange rates for the reaction between a $[C1^-]:[T1(III)]$ ratio of 0.185:1 and 0.740:1, obtained by J. P. Mickel (12).

The following terms are defined:

$$\begin{bmatrix} T1^{+3} \end{bmatrix} : A \qquad \text{total uncomplexed thallium (III)} \\ \begin{bmatrix} T1(III) \end{bmatrix} : A_0 \qquad \text{total thallium (III)} \\ \begin{bmatrix} C1^{-} \end{bmatrix} : X_0 \\ \begin{bmatrix} T1C1^{++} \end{bmatrix} : AX \\ \begin{bmatrix} T1C1_2^{++} \end{bmatrix} : AX_2 \\ K_5 : \begin{bmatrix} T1C1^{++} \end{bmatrix} / \begin{bmatrix} T1^{+3} \end{bmatrix} \begin{bmatrix} C1^{-} \end{bmatrix} \\ K_6 : \begin{bmatrix} T1C1_2^{++} \end{bmatrix} / \begin{bmatrix} T1C1^{++} \end{bmatrix} \begin{bmatrix} C1^{-} \end{bmatrix} : AX_2 / AX(X) \\ \begin{bmatrix} 1 \end{bmatrix} \quad \underbrace{K_5} : \frac{AX^2}{AX_2(A)} \qquad \text{or} \qquad A : \underbrace{K_6 \quad AX^2}{K_5 \quad AX_2} \end{bmatrix}$$

The concentrations of chloride and thallium (III) can be expressed as

(2) $X_0 = AX + 2 AX_2$ assuming all Cl[®] is complexed

(3) A • A₀ - AX - AX₂

upon substitution of equation (2) into (3)

(4) $AX = 2 A_0 - X_0 - 2 A$

and (4) into (2)

and

(5) $AX_2 = A - A_0 + X_0$

The following relations are defined

$$A/A_0 = y_0$$
; $AX/A_0 = y_1$; $AX_2/A_0 = y_2$; $X_0/A_0 = \alpha$

upon dividing equation

(4) by
$$A_0$$

 $AX/A_0 = 2 - X_0/A_0 - 2 A/A_0$

OT

$$y_1 = 2 - 2y_0 - \infty$$

equation

$$MX_2/A_0 = A/A_0 + X_0/A_0 = 1$$

or

and equation

$$A/A_0 = \frac{K_6 (AX)^2 (A_0)}{K_5 (AX_2) (A_0)^2}$$

or

$$y_0 = \frac{K_6 y_1^2}{K_5 y_2} = \frac{K_6 (2 - 2y_0 - \alpha)^2}{K_5 (\alpha - 1 + y_0)}$$

upon rearrangement

(6)
$$K_6/K_5 = \frac{y_0 (\alpha - 1 + y_0)}{(2 - 2y_0 - \alpha)^2}$$

If one assumes that neither AX nor AX_2 react, and that higher complexes may be neglected for alpha less than 2, then $k/k_0 \equiv y_0$, where k is the observed second-order rate constant; and k_0 is its value in the absence of the complexing agent X.

The results obtained upon substitution of appropriate alpha and k/k_0 values into equation (6) are indicated in Table II.

| EVALUATION OF EQUAT | 10W (6), kg = 0 | .796 f-1 min1 |
|---------------------|-----------------|--------------------|
| alpha | k/k | K _é /K5 |
| *0.740 | 0.2701 | 0.0233 |
| 0.866 | 0.2098 | 0.0194 |
| \$0.9 26 | 0.1508 | 0.0311 |
| 1.06 | 0.1112 | 0.0369 |
| 1.23 | 0.0609 | 0.0421 |
| . +1.39 | 0.0239 | 0.0313 |
| 1.49 | 0.0172 | <u>9,0386</u> |
| | | vs. 0.0318 |

TABLE II

"k values obtained from J. P. Mickel (12).

It appears that the value K_6/K_5 is essentially a constant, with an average value of 0.0318.

Rearrangement of equation (6) and substitution of 0.0318 for \underline{K}_6 gives an equation of the form \underline{K}_5 (7) $y_0^2 + y_0(\alpha - 0.854) = 0.0364 (2 - \alpha)^2 = 0.$

This expression was solved for y_0 and evaluated for values of alpha between 0,185 and 1.80.

The agreement between the actual values of the reaction rate and those obtained from the above equation (k predicted) is indicated in Table III.

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| THALLIUM | (I)-THALLIUM | (III) EXCHANGE IN AND IONIC STRENG | THE PRESENCE OF | CHLORIDE AT 25°C. |
|---------------|--------------|---------------------------------------|-----------------|-------------------|
| alpha | 7. | k(experimental) | k(predicted) | % Deviation |
| *0,185 | 0.8196 | 9.68 | 0.66 | 2.8 |
| #0,278 | 0.7251 | 0.62 | 0.58 | 6.4 |
| 40.463 | 0.5479 | 0.41 | 0.43 | 4.9 |
| +0.740 | 0,2420 | 0,22 | 0.20 | 9.1 |
| 0.866 | 0.1930 | 0.17 | 0.15 | 12.0 |
| *0,926 | 0.1444 | 0.12 | 0.12 | 0 |
| 1.060 | 0.1040 | 0.090 | 0.083 | 8.6 |
| 1.230 | 0.0502 | 0.049 | 0.040 | 18.4 |
| *1.390 | 0.0240 | 0.018 | 0.019 | 5.5 |
| 1.490 | 0.0145 | 9.014 | 0.012 | 14.3 |
| 1.60 | 0.0079 | | 0.0063 | |
| 1.70 | 0.0040 | | 0.0031 | |
| 1.80 | 0.0020 | | 0.0016 | |
| *1.8 5 | 9.0008 | 0.0023 | 9.00064 | |
| | | | Â | s. 8.20% |

TABLE III

.

"k values obtained from J. F. Mickel (12).



Fig. II - Exchange rate as a function of chloride concentration. Broken line represents the calculated reaction rate curve. Solid line represents the experimentally determined reaction rate curve. O, reaction rates determined by J. P. Mickel (12).

Figure II is a log-log plot of reaction rate versus $[Cl^{-}]:[Tl(III)]$. The broken line represents those values of k obtained from equation (7), and the solid line represents experimental values of the reaction rate for the higher $[Cl^{-}]:|Tl(III)]$ ratios at which the assumptions made in the derivation of equation (7) are no longer valid.

The close agreements between experimental and predicted values for the rate constants lend support to the assumptions made in the derivation of equation (7): (1) neither AX nor AX_2 react; and (2) higher complexes may be neglected for [C1]: [T1(III)] ratios less than two. Apparently the formation of TICL** and TICL2* hinders electron exchange. This hindrance could be due to two factors: (1) the coulombic repulsion of species of like sign; and (2) the dissimilarity in the structures of reacting species, assuming the thallium (I) is present essentially as the T1⁺ ion. At low [C1⁻]: [T1(III)] ratios the predominant species are probably TlCl⁺⁺ and Tl⁺. Since these postulated reaction species are small ions with a relatively concentrated electrostatic charge, the coulombic repulsion effect may be the most important factor. For [C1⁻]:[T1(III)] ratios from 1:1 to 2:1 the predominant species are most likely $TlCl_2^+$ and Tl^+ , and in this case the dissimilarity in structure may be the important factor contributing to the retardation of the electron transfer. The increased rate, evident after a [C1⁻]: [T1(III)] ratio of 2:1, is thought to be due to two phenomena: (1) the formation of higher thallium (III) complexes, TlCl3 and TlCl₄"; and (2) the formation of thallium (1) chloride complexes. Possible mechanisms, involving these complexes, which favor electron

transfer are

(1)
$$*T1Cl_3 + T1Cl_2^- \longrightarrow *T1Cl_2^- + T1Cl_3$$

and

(2)
$$*T1C1_4^{\circ} + T1C1_3^{\circ} \longrightarrow *T1C1_3^{\circ} + T1C1_4^{\circ}$$
.

Mechanism (1) is considered to be favorable to an increased electron transfer rate by virtue of the absence of a coulombic repulsion between reacting species and structural similarity of the reacting species. Mechanism (2), at first glance, seems to disfavor rapid electron exchange because of coulombic repulsion effects; however, if the sizes of the reacting species are considered and the fact that the existing charges are spread out over a large ionic surface area, the structural similarity effect may very well predominate.

Consideration of the chloride and the very similar cyanide effect on this exchange reaction seems to favor a mechanism for the electron transfer reaction in sulfuric acid (8) similar to the type shown above. It may be that the increased exchange rate, compared to that observed by Prestwood and Wahl (3) in perchloric acid of similar ionic strength, may be best explained by the combination of processes

$$T1(SO_{L})^{\bullet} + T1^{\bullet} \longrightarrow T1(SO_{L})^{\bullet} + T1^{\bullet}$$

and

 $T1(S0_4)_2$ + $T1(S0_4)^-$ + $T1(S0_4)^-$ + $T1(S0_4)_2^-$.

The coulombic attraction effect afforded by the previously suggested processes (8) are overshadowed by the more favorable mechanism of electron transfer through a sulfate bridge indicated in the above processes. The value of 0.0318 for the ratio of the association constants of the TICl⁺⁺ and TICl₂⁺ complexes is not a true prediction of the relative magnitudes of these species. It was assumed in the derivation of the expression which leads to the evaluation of K_6/K_5 that A, the total uncomplexed thallium (III), was in the form of the T1⁺⁺⁺ ion. This was certainly not a valid assumption. Brubaker and Mickel (8) have shown that the thallium (III) species in 2.19f sulfuric acid is both hydrolyzed and complexed with sulfate. Therefore

A = [T1+3] = [T10+] + [T10H++] + [T1S04+] + [T10+3]

$$\begin{bmatrix} T10^{+} \end{bmatrix} = \underbrace{K_{2} \left[T10H^{+0} \right]}_{\left[H + 1\right]}; \begin{bmatrix} T10H^{+0} \right] = \underbrace{K_{1} \left[T1_{0}^{+3} \right]}_{\left[H + 1\right]}$$

$$\begin{bmatrix} T180_{4}^{+} \right] = K_{3} \left[T1_{0}^{+3} \right] \left[80_{4}^{2} \right]; \begin{bmatrix} T1_{0}^{+3} \right] = \text{ total uncomplexed } T1^{+3}$$

$$A = \begin{bmatrix} T1^{+3} \right] = \begin{bmatrix} T1_{0}^{+3} \right] \left[\underbrace{K_{2}K_{1}}_{\left[H^{+}\right]^{2}} + \underbrace{K_{1}}_{\left[H^{+}\right]} + K_{3} \left[S0_{4}^{2} \right] + 1 \right]$$

The values of the K's are

 $K_1 = 0.77$, $K_2 = 0.071$ (14), $K_3 = 2$ (15,8).

The values of H⁺ and SO₄⁼ for a 2.19f sulfuric acid solution are 2.90f and 0.70f, respectively (12).

Evaluation leads to the equation

A :
$$[T1^{+3}]$$
 : 2.44 $[T1_0^{+3}]$

Since it was assumed

$$\mathbf{x}_{6}/\mathbf{x}_{5} = [\underline{T}1^{+3}][\underline{T}1C1_{2}^{+}]$$

 $[\underline{T}1C1^{++}]^{2}$

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then the actual value of the ratio is

$$K_6/K_5 = 2.44 [T1_0^{+3}] [T1C1_2^+] [T1C1^{++}]^2 = 0.0318$$

 $K_6/K_5 = 0.0318/2.44 = 0.0130.$

Benoit (5) has determined the values of K_5 and K_6 at infinite dilution to be 1.28 x 10⁸ and 3.16 x 10⁵, respectively. These values were corrected for applicability with solutions of ionic strength, 3.68f. These corrected values give the ratio K_6/K_5 to be 0.0037. The deviation of this latter value from the value 0.013 is not surprising since the activity coefficients used in correcting Benoit's values were only approximate in nature. Activity coefficients were selected so that the ionic size and valence type were comparable to the species involved in each equilibria. Values for the activity coefficients of the actual species have not been determined.

SUBMARY

The variation in rate of the thallium (I)-thallium (III) electron exchange reaction in 2.19f sulfuric acid has been determined as a function of chloride concentration.

The overall rate of exchange was found to vary by a factor of 10^3 . The initial effect of adding chloride to the system was a rapid decrease in exchange.rate. This effect was attributed to the formation of the thallium (III) chloride complexes, $TlCl^{++}$ and $TlCl_2^{++}$, which are apparently inert to an electron exchange. A minimum rate was observed at a chloride to thallium (III) ratio of about 2.5:1, followed by a rapid increase in exchange rate. This increase in exchange rate was attributed to the formation of the thallium (III) chloride complexes $TlCl_3$ and $TICI_4^{-+}$. The increase has a chloride dependence slightly greater than second order. The failure of the reaction rate to approach a limiting value was believed due to the formation of thallium (I) chloride complexes favorable to a rapid exchange mechanism. Exchange mechanisms have been proposed. Those which appear favorable to an increased reaction rate involve electrop transfer through a chloride bridge.

By assuming (1) that higher complexes above $T1C1^{4+}$ and $T1C1_2^{+}$ may be neglected for $[C1^{-}]:[T1(III)]$ ratios below 2:1 and (2) that $T1C1^{4+}$ and $T1C1_2^{+}$ do not react, it was possible to derive an expression which predicted the rate constants for this reaction with a per cent precision of = 8.2 for $[C1^{-}]:[T1(III)]$ ratios less than 2:1,

Further mathematical development afforded an evaluation of the relative magnitudes of the association constants for the $TICl_2^+$

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and T1C1⁺⁺ complexes. Correction for hydrolysis and sulfate complex formation gave a value of 0.013 for the ratio K_6/K_5 in solutions of constant ionic strength, 3.68g; where

$$\frac{x_{5} = [1:c1^{++}]}{[1:c1^{+}][c1^{-}]} = [1:c1^{++}][c1^{-}].$$

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APPENDIX I

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INITIAL RESEARCH ASSIGNMENT

The initial research assignment was the preparation of compounds characterized by metallic ions of large ionic sizes, high charge, and which are not extensively hydrolyzed in solution. The preparation of platinum (IV) chelate compounds was considered to be the most promising approach to the solution of this problem.

Initial interest centered upon the preparation of a tris (2,2 dipyridyl) platinum (IV) compound.

An extensive preliminary search through the available literature revealed that the preparation of this compound had not been previously reported. However, preparations of similar compounds, e.g. $Bh(dipy)_3 Cl_3 \cdot 3H_2O$ (1), $Oe(dipy)_3 Cl_3 \cdot H_2O$ (2), and $Ru(dipy)_3 Cl_2$ (3) [where "dipy" is 2,2 dipyridyl] had been reported. The procedures for the preparation of the above complexes were noted with a view that similar procedures might prove useful in the synthesis of the tris (2,2 dipyridyl) platinum (IV) complex.

The first attempt at a synthesis involved the dissolution of H_2PtCl_6 in a saturated aqueous solution of dipyridyl. Upon heating and separation, the filtrate yielded a small amount of a red, waxy compound and the residue consisted of a yellow, fibrous, extremely insoluble compound.

Analysis of the residue indicated that this compound contained 39.3% platinum. It was believed to be Pt(dipy) Cl₄, which has a theoretical composition of 39.6% platinum.

On the basis of its greater ionic character, Pt(dipy)₃ Cl₄ should be the most soluble compound of the dipyridyl substituted

platinum (IV) chloride series, $[Pt(dipy) Cl_4]$, $[Pt(dipy)_2 Cl_2] Cl_2$, $[Pt(dipy)_3] Cl_4$. The red crystals obtained from the filtrate were considered to be $Pt(dipy)_3 Cl_4$. Efforts to increase the yields of this red compound led to experiments involving ethyl alcohol, acidic-equeous solutions, and water-alcohol mixtures as the solvent for the reaction. None of the above methods increased the yield appreciably, and in all cases the yellow insoluble complex was the predominant compound formed.

Further preparative attempts were based on a precedure used by F. M. Jaeger and J. A. van Dijk (1) in their synthesis of $Rh(dipy)_3$ $Cl_3 \cdot 3H_2O$. This procedure involved the addition of anhydrous $PtCl_4$ to boiling 2,2 dipyridyl. This mixture was then heated on a water bath, after the addition of some water and ethyl alcohol, for several hours. Separation of the reaction mixture yielded a small amount of a black residue and a dark red filtrate. Upon evaporation of this filtrate, the fibrous yellow compound began to form although the filtrate remained bright red in color.

Recrystallization was carried out several times until the yellow complex was no longer formed during crystallization. Several procedures were utilized for the crystallization process in an effort to prevent the formation of the yellow complex. These were slow evaporation at room temperature, vacuum distillation and evaporation at higher temperatures. None of the above procedures prevented the formation of the yellow complex during crystallization.

The final product obtained from repeated recrystallizations consisted of a dark red, hygroscopic compound.

This substance was dissolved in water and repeatedly extracted with ethyl ether until the ether extract, upon evaporation, showed no traces of dipyridyl.

Analysis of various preparations of this substance for platinum content did not give consistent results. The analysis ranged from 14% to 22% for platinum content. The theoretical composition of the Pt(dipy)₃ Cl₄ complex is 24.23% platinum. This inconsistency in analysis was thought to be due to dipyridyl hydrochloride impurities. Further liquid-solid extraction was done utilizing a soxhlet extractor and anhydrous ether as the extracting agent. Continuous extraction was carried out for eight to ten weeks. Evaporation of the extracting solvent indicated a substance similar to dipyridyl or dipyridyl hydrochloride was being extracted.

The final product was a hygroscopic, dark red, flat diamondshaped crystalline compound. It was easily soluble in alcohol and insoluble in benzene or other. The absorption spectrum of an aqueous solution of this substance shows a wide absorption band in the visible region with a maximum at 527 m/. The absorption spectrum for the ultra-violet region between 340 m μ and 240 m μ was more complex; however, absorption peaks were moted at 287 m μ , 297 m μ and a small side band at 320 m μ . The final yield of this substance was so small that analysis for platinum was not attempted.

A variation in the reaction procedure was tried in hopes that the red compound might be insoluble in molten dipyridyl in the absence of ethyl alcohol and water. If this were true, the

separation and crystallization steps could be eliminated from the above procedure. Experiment revealed that the yellow compound was formed almost immediately upon addition of $PtCl_4$ to molten dipyridyl but no trace of the red complex was detected even when the reaction was allowed to proceed for several days. However, upon the addition of ethyl alcohol and water the red substance appeared within a few hours.

Another variation employed was the use of ethyl alcohol alone as a solvent in the reaction procedure in order to reduce the time for evaporation.

Because of the low yields and the expense of the reagents these experiments were abandoned.

Interest next centered upon possible preparations of the similar compounds $Pt(py)_6$ Cl₄ and $Pt(phen)_3$ Cl₄ [where "py" is pyridine and "phen" is 1,10-phenanthroline]. The procedure for preparation of the pyridine complex consisted of dissolving anhydrous $PtCl_4$ in pyridine at a temperature slightly below boiling. Immediately upon mixing a yellow, fibrous compound was formed. This compound was found to be extremely insoluble in water. Evaporation of the filtrate gave no indication of the presence of another compound.

Preparation of Pt(phen); Cl4 was attempted by the same procedure used for the dipyridyl complex. This method resulted in an insoluble brown residue and an orange colored filtrate. Evaporation of the filtrate yielded a small amount of a waxy, orange compound. Repeated extraction with ethyl ether failed to remove enough of the impurities, believed to be excess phenanthroline, to give well defined crystals.

The results of these preparations cannot be considered conclusive; however, the following generalization might be made. Formation of tris(2,2-dipyridyl)platinum (IV) chloride and related compounds is apparently deterred by the initial production of the mono dipyridyl substituted compound. The extreme insolubility of this compound effectively removes it from solution and prevents further substitution from occurring.

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Groves, The effect of chloride on the rate of the thallium(I)-thallium(III) exchange reaction in 2.19f sulfuric acid.

