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"ONE AND TWO ELECTRON TRANSFER REACTIONS"

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Submitted by

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I. Personnel

During the period from the inception of the research contract on 1 March 1970 through the period 28 February 1971, the following persons will have contributed to the program:

Research Assistants:

Robert Buchacek, 12 months, half-time

Eugene Grimley, 8 months, half-time

Martin Ondrus, 12 months, quarter-time

Robert J. Seyse, 12 months, quarter-time

Kenneth Bridges, 6 months, quarter-time

Robert Silverman, 6 months, quarter-time

Research Associates:

Dr. Hiroshi Tomiyasu, 4 months, full-time

Research Supervisor:

Gilbert Gordon, 12 months 1/5-time

II. Research Accomplished and in Progress

Since the last Progress Report, seven papers and two Ph.D. theses have either been published or accepted for publication late in 1970 or early in 1971. The titles and co-authors of the manuscripts and the appropriate journal citations are listed below:

- (1) "Ligand Substitution Reactions: Definitive Experiments and a Test of the Eigen Mechanism," Proc. 3rd Symp. Coord. Chem., M.T. Beck, Ed., Akademiai Kiado, Budapest, p 35-43 (1970), Gilbert Gordon and William Melvin.
- (2) "One vs. Two Electron Transfer Reactions," Proc. XIII Int. Conf. Coord. Chem., Zakopane, Poland (1970), p 11, Gilbert Gordon.
- (3) "The Effect of Halide Ions on the Rate of Aquation of trans-iodo-aquotetraamminechromium(III)," Inorg. Chem. 9, Dec.(1970), Robert Buchacek, Donald Hoppenjans and Gilbert Gordon.
- (4) "Aquation and Chromium(II)-Catalyzed Aquation Reactions of the Iodoaquo- and Chloriodotetraamminechromium(III) Complexes," Inorg. Chem., 10, Feb. (1971), Donald Hoppenjans and Gilbert Gordon.

- (5) "Oxygen Diffusion in Single Crystals of Titanium Dioxide," J. Inorg. & Nucl. Chem., April (1971), Theodore B. Gruenwald and Gilbert Gordon.
- (6) "The Reaction of Tris(1,10-phenanthroline)iron(II) Ion with Chlorine(I) Species," Inorg. Chem., 10, Jan. (1971), Martin Ondrus and Gilbert Gordon.
- (7) "Mechanistic Implications of the Role of Phenol in the Uranium(IV)-Chlorine(III)-Phenol Reaction," Inorg. Chem., 10, Jan. (1971), Eugene Grimley, Robert Buchacek and Gilbert Gordon.

The titles of the two Ph.D. thesis which were submitted to the Graduate School at the University of Iowa are given below:

- (a) "A Kinetic and Product Study of the Reaction of Phenol with Chlorine Oxidants and of Uranium(IV) with Chlorine(III) in the Presence of Phenol" by Eugene Burhans Grimley III.
- (b) "Inorganic Reaction Mechanisms. Part I: A Kinetic Study of the Reduction of Chlorate Ion by Oxovanadium(IV) in Acidic Media. Part II: The Kinetics of Substitution Reactions of Poly(Ethylene-diamine)Nickel(II) Complexes" by William Stephen Melvin.

The abstracts of these theses are appended to this Progress Report.

The titles of these papers and manuscripts gives a general summary of the types of research presently underway and coming to fruition under this research contract. The past year has been particularly successful in terms of completed manuscripts, but the next 18 to 20 months should be at least as productive or most likely, even more productive. The combination of kinetic measurements, stoichiometric analysis and stable isotope tracer studies seems to be the most effective method of studying the factors which effect electron transfer reactions.

One of the types of systems most frequently studied in coordination chemistry is the reaction in which the net result is the transfer of one or more electrons between different states of the oxidizing and the reducing agent. The question often arises as to whether these processes actually take place directly by one or two electron transfer or by the transfer of atoms or ions. Complete interpretation of kinetic results in many of these

systems is frequently hampered by the lack of availability of detailed stoichiometric and tracer results.

In an attempt to understand the factors which influence these types of reactions, we have undertaken a systematic study of electron transfer reactions which utilize oxygen-containing oxidizing agents such as bi-chromate ion, chlorate ion, chlorine dioxide, chlorous acid and hypochlorous acid. The specific reducing agents we have chosen include vanadium(II), vanadium(III), uranium(IV), and trisphenanthrolineiron(II).

Chlorine reacts with trisphenanthrolineiron(II) via an outer sphere mechanism which produces trisphenanthrolineiron(III) as the sole product. In the pH region between 7 and 9, hypochlorous acid reacts by both this mechanism and by a second mechanism which necessitates the preliminary dissociation reaction

The subsequent redox reaction proceeds with a second order rate constant of about 3×10^5 liter/mole-second and results in the production of an iron(III)-phenanthroline dimer. This dimer appears to be formed by the reaction of an iron(IV) species with trisphenanthrolineiron(II). The iron(IV) is presumed to have formed in a two electron reaction similar to that proposed for the corresponding acid reaction.¹

Hypochlorous acid reacts with Fe(phen)_3^{++} by two paths, one which is dependent upon dissociation of the iron complex and one which is independent of dissociation. The reaction was studied at 15°, 25°, and 40° under pseudo first order conditions with the oxidant being in excess. At 25° and constant pH, plots of the pseudo-first order rate constant as a function of $[\text{Cl(I)}]$ are linear with equal non-zero intercepts and slopes that increase with increasing $[\text{H}^+]$. The following rate law is obeyed.

$$k_{\text{obs}} = k_0 + \left[\frac{k_1 [\text{H}^+]/K + k_2}{[\text{H}^+]/K + 1} \right] [\text{Cl(I)}]$$

At 25°C $k_0 = 7.5 \pm 0.2 \times 10^{-5} \text{ sec}^{-1}$, $k_1 = 2.2 \pm 0.14 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$, and $k_2 = 2.0 \pm 0.16 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$. The rate constants were calculated using a value of 2.90×10^{-8} for the acid dissociation constant of hypochlorous acid at 25°C.

Activation parameters for k_0 , k_1 , and k_2 were calculated simultaneously using a subroutine of our non-linear least-squares program. The values are listed in Table I where the uncertainties represent the computer calculated standard deviations. The activation parameters for k_0 agree within less than one standard deviation with ΔH^* and ΔS^* measured for k_d .

Table I
Activation Parameter Data for the Fe(phen)_3^{++} - Cl(I) Reaction

rate constant	H^* kcal/mole	S^* e.u.
k_d	30.2 ± 0.3	23.7 ± 1.1
k_0	30.5 ± 0.6	24.8 ± 1.9
k_1	16 ± 2	-12 ± 6
k_2	25.3 ± 2.8	14.1 ± 9.5

The rate constants k_1 and k_2 belong to a dissociation independent oxidation of Fe(phen)_3^{++} by hypochlorous acid and hypochlorite ion, respectively. The mechanism probably involves a one-electron oxidation similar to the oxidation of Fe(phen)_3^{++} by chlorine or chlorine dioxide. Such a mechanism is expected to yield Fe(phen)_3^{+++} as a product. However, Fe(phen)_3^{+++} is unstable in solutions containing low hydrogen ion concentration and decomposes readily to the yellow dimer. The magnitudes of the enthalpies of activation assigned to these rate constants are not unreasonable. They reflect the two-electron oxidant chlorine(I) reacting by a less favorable one-electron pathway. An outer-sphere or non-bridging two-electron transfer reaction seems less likely since the Frank-Condon barrier for such a mechanism would be exceptionally high.

Vanadium(II) reactions are particularly interesting in that oxygen tracer techniques can once again be used to follow the transfer of oxygen from the oxidizing agent to the oxovanadium(IV) product. Tracer experiments in our laboratories have indicated that the lifetime of the ^{17}O oxygen on the oxovanadium(IV) is directly measurable by standard oxygen-17 or oxygen-18 tracer techniques. One of the advantages of the vanadium system is that the rate of formation of the oxovanadium(IV) product can be compared directly with the rates of the vanadium(II) and the vanadium(III) reactions and with the measured rates of water exchange.² The two-electron transfer reaction appears to require substitution of the oxygen-containing oxidizing agent into the first coordination sphere of the metal ion and coordination through the oxygen. Normally, this can only occur if the rate of the electron transfer process is slower than the corresponding rate of water exchange for the reducing agent. We would like to suggest that the two electron transfer reaction and the transfer of oxygen can be faster than the rate of water exchange if an intermediate of increased coordination number is formed. The possibility of forming a seven coordinated intermediate in which the oxygen-containing oxidizing agent can be coordinated to the vanadium(II) via the trigonal face of the first coordination sphere appears to be very feasible.

The most important conclusion that we have reached is that two-electron transfer does not occur unless the first coordination sphere of the reducing agent is penetrated by the oxidizing agent. It should also be noted that although this appears to be a necessary condition, it is not a sufficient condition in that many reactions which occur by an inner sphere pathway are not two-electron reactions. In the systems which we have investigated, two-electron transfer reactions also appear to be associated with oxygen bonding in the first coordination sphere. The lack of

two-electron transfer, or the preference for one-electron transfer in systems which occur by means of inner sphere or pseudo inner-sphere (seven coordinated intermediates) pathways, may be associated with direct halogen bonding--rather than oxygen bonding. One last point worth noting: we have not discovered any examples of direct two-electron transfer reactions which can be classified as truly outer sphere reactions.

The reactions of the oxygen-containing oxidizing agents are more easily classified in the case of uranium(IV) where meaningful tracer experiments can be carried out.³ For example, hypochlorous acid oxidizes uranium(IV) directly to form uranium(VI) by means of an oxygen-transfer reaction. In this reaction, less than 0.1% of the reaction occurs by the one-electron path and the concomitant formation of uranium(IV).

We have also reported evidence for the presence of a reactive chlorine intermediate in the reaction of uranium(IV) with chlorine(III) in acidic aqueous solution.⁴ When phenol is added to this system as an initial reactant, the resultant kinetics, stoichiometry and product identification indicate that an intermediate chlorine species has been scavenged by phenol. The results of the present study were aimed at the determination of the scavenged intermediate chlorine species in the above reaction.

The first step of the overall reaction is rate determining and produces chlorine(I) by a two electron transfer process which is effected by oxygen atom transfer⁵ from chlorine(III) to uranium(IV). Chlorine(I) refers to hypochlorous acid which would be the predominant species in the acid range of 0.18 M to 1.50 M perchloric acid. The reaction between hypochlorous acid and chlorine(III) has been reported by Emmenegger and Gordon to be rapid.⁶ Therefore, the chlorine(I) formed in reaction 1 could react rapidly in a second step with chlorine(III) to produce the observed stoichiometry and chlorate ion.

Feldman and Gordon⁴ report that the reactant stoichiometry is reduced to 1:1 when phenol is initially added to the uranium(IV)-chlorine(III) reaction in the range of 0.18 M to 1.5 M HClO₄ at 25°C. Robert Buchacek has determined the apparent rate law for the uranium(IV)-chlorine-(III)-phenol reaction in 0.11 M to 1.5 M perchloric acid at 25°C to be

$$-\frac{d[U(IV)]}{dt} = k_{\text{obs}} \frac{[U(IV)][Cl(III)]}{[H^+]}$$

In 2 M ionic strength and 0.1 M phenol, the values of k_{obs} is $13.1 \pm 0.2 \text{ sec}^{-1}$ at 25°C.

The apparent role of phenol is to scavenge an intermediate chlorine species. What is the chlorine-containing species? In order to answer this question, a rate comparison must be made to determine which of the known chlorine species are able to react with phenol rapidly enough to account for the observed scavenger reaction.

Table II summarizes the results found for the reaction of known chlorine oxidants with phenol. The reaction comparison is made under conditions of 1.00 M perchloric acid, unit ionic strength and 25°C.

Table II

A comparison of estimated half-lives for reactions between phenol and chlorine oxidants with 0.100 M phenol

<u>Oxidant in Reaction with Phenol</u>	<u>Estimated Half-lives, seconds</u>	<u>Conditions and Remarks</u>
ClO ₄ ⁻	> 10 ⁶	N. R. in a month
ClO ₃ ⁻	> 10 ⁵	N. R. in weeks
ClO ₂	15	[ϕ OH] ₀ >> [ClO ₂]
ClO ₂ ⁻	> 10 ³	N.R. in hours
HClO ₂	> 180	slow
[Cl ₂ O ₂]	< 0.0001	indirect evidence
HOCl	14	Ag ⁺ present
Cl ₂	0.0003	[ϕ OH] >> [Cl ₂]

A comparison of calculated half-lives extrapolated from the work of Emmenegger and Gordon⁶ on the reactions of hypochlorous acid with chlorous acid and of chlorine with chlorous acid are shown in Tables 3 and 4. The extrapolated half-lives are calculated under the same conditions used for comparison of the potential scavenger reactions. The chlorine-chlorous acid reaction was assumed to be first order in both reactants.

Table 3

Calculation of second order rate constants
from the chlorine(0)-chlorine(III) interaction data
in 0.8 M perchloric acid at 23°C

Chlorine(III) Concentration $\underline{M} \times 10^3$	Chlorine Concentration $\underline{M} \times 10^3$	Reported Half-lives seconds	Calculated Rate Constants $\underline{M}^{-1} \text{ sec}^{-1} \times 10^4$
2.54	1.24	0.030 ± 0.002	1.06
1.27	0.64	0.060 ± 0.003	1.06
1.27	1.27	0.063 ± 0.002	1.25
Ave. 1.1 ± 0.1			

Table 4

Calculation of second order rate constants
from the chlorine(I)-chlorine(III) interaction data
in 0.2 M perchloric acid at 25°C

$[\text{HClO}_2]$ $\underline{M} \times 10^3$	$[\text{HOCl}]$ $\underline{M} \times 10^3$	Temp.	Reported Half-lives seconds	Calculated Rate Constants at 25°C $\underline{M}^{-1} \text{ sec}^{-1}$
0.29	0.29	23° C	3.5	985
18.0	0.15	23° C	0.84	46
0.90	9.0	11° C	0.08	≈ 1900
0.50	0.50	11° C	6.2	≈ 540
0.90	9.0	1° C	0.15	≈ 2000

It is evident from these results that at least 10% of the hypochlorous acid formed by the reduction of chlorine(III) by uranium(IV) would react

with chloride ion to form chlorine. The remainder of the hypochlorous acid would be involved in the formation of $[Cl_2O_2]$ owing to the hypochlorous acid-chlorine(III) reaction. Concomitantly, the chlorine and $[Cl_2O_2]$ formed would react with phenol to produce ortho- or parachlorophenol. Thus, the intermediate species scavenged by phenol must be chlorine and $[Cl_2O_2]$. It is to be emphasized, however, that the chloride ion concentration could not be so high such that chlorine could account for the entire amount of chlorine species scavenged by phenol. The fact that neither chlorine(V) nor chlorine dioxide are formed under these conditions implies that direct reaction of the $[Cl_2O_2]$ intermediate must occur with phenol. Furthermore, at a pH greater than or equal to 1, the scavenged species must be almost entirely the $[Cl_2O_2]$ intermediate.

Based on these arguments, the following mechanism is presented:

where $t_{1/2}^a \leq (0.1) t_{1/2}^b$.

Ardon⁷ has reported that chloride ion and bromide ion replace iodide ion in the iodopentaaquochromium(III) ion without intermediate formation of hexaaquochromium(III). His results were interpreted in terms of an S_N1 mechanism in which the solvent and ambient ions compete for a pentaaquochromium(III) intermediate. During a subsequent investigation,⁸ it was learned that if iodopentaaquochromium(III) is allowed to aquate in H_2O^{18} , the product hexaaquochromium(III) contains two labelled water molecules.

Since the rate of water exchange of the hexaaquochromium(III) species is slow, this information is inconsistent with the explanation offered by Ardon.

A new mechanism which involves a strong trans labilization by iodide ion was proposed.⁸ The incorporation of ambient anions into the first coordination sphere of the chromium(III) product can be explained in terms of this mechanism which is given in equations (1) and (2).

The demonstration of direct anation reactions in aqueous solution and of the existence of pentacoordinated intermediates sufficiently long-lived to discriminate between various entering ligands is not so common as to make further investigation in this direction unwarranted.⁹ Results of our study of the reactions of trans-Cr(NH₃)₄(Cl)(I)⁺ suggested that the reactions of cis- and trans-Cr(NH₃)₄(H₂O)I²⁺ could be similar to that reported for Cr(H₂O)₅I²⁺. Thus, in the present investigation we wish to report the effect of added halide ions on the rate of decomposition of trans-Cr(NH₃)₄(H₂O)I²⁺ and the nature of the reaction products.

The pseudo-first-order rate constants for the reaction of trans-Cr(NH₃)₄(H₂O)I²⁺ ion were measured in the presence of varying chloride ion concentrations. The observed rate constant can be expressed by the following equation: $k_{\text{obs}} = k_1 + k_2(\text{Cl}^-)$. Values for k_1 of $6.6 \times 10^{-4} \text{ sec}^{-1}$ and $1.45 \times 10^{-3} \text{ sec}^{-1}$ at hydrogen ion concentrations of 1.0 M and 0.1 M respectively, compare favorably with values reported elsewhere. The values of k_2 are $3.1_3 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ and $3.6_3 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$ at hydrogen ion concentrations of 1.0 and 0.1 M, respectively.

The observed rate constants for various anionic media are presented in Table II. Chloride and bromide ions substantially accelerate the rate of aquation in comparison to the rate in perchloric acid. The rate of aquation in HI is essentially the same as in perchloric acid.

TABLE II

Pseudo First-Order Rate Constants for Reactions of $\text{trans-Cr(NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$
As a Function of the Ambient Anion at Unit Ionic Strength and 40°

<u>1.0 M Acid</u>	<u>$10^4 k_{\text{obs}}, \text{sec}^{-1}$</u>
HClO ₄	6.6 ± 0.03
HCl	9.7 ± 0.07
HBr	7.5 ± 0.03
HI	6.5 ± 0.12

The products of the spontaneous aquation of $\text{trans-Cr(NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$, in the presence of chloride and bromide ions, were separated by ion-exchange chromatography. In addition to $\text{trans-Cr(NH}_3)_4(\text{H}_2\text{O})_2^{3+}$, a considerable amount of $\text{trans-Cr(NH}_3)_4(\text{H}_2\text{O})\text{X}^{2+}$ ($\text{X} = \text{Cl}^-$ or Br^-) was detected. More halo-complex was found than can be accounted for by the corresponding anation reactions of $\text{trans-Cr(NH}_3)_4(\text{H}_2\text{O})_2^{3+}$. A comparison of these results is shown in Table III.

TABLE III

The Effect of Halide Ions on the Products of the Aquation
And Anation Reactions at 40°

<u>Complex</u>	<u>Added Anion(X)</u>	<u>$\%[\text{Cr(NH}_3)_4(\text{H}_2\text{O})\text{X}^{2+}]$</u>	<u>$\%[\text{Cr(NH}_3)_4(\text{H}_2\text{O})_2^{3+}]$</u>
$\text{trans-Cr(NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$	1M HCl	22	78
$\text{trans-Cr(NH}_3)_4(\text{H}_2\text{O})_2^{3+}$	1M HCl	3	97
$\text{trans-Cr(NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$	1M HBr	13	87
$\text{trans-Cr(NH}_3)_4(\text{H}_2\text{O})_2^{3+}$	1M HBr	2	98
$\text{cis-Cr(NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$	1M HCl	7	93
$\text{cis-Cr(NH}_3)_4(\text{H}_2\text{O})_2^{3+}$	1M HCl	3	97

The increased rate in HCl and HBr and the fact that a considerable amount of the halo-complex is produced suggests that the halide ion is incorporated into the first coordination sphere of chromium prior to the loss of iodide. These results also suggest a strong trans labilization of the coordinated water molecule by coordinated iodide. This conclusion is reinforced by the fact that only a small amount of cis-Cr(NH₃)₄(H₂O)Cl²⁺ ion is produced when cis-Cr(NH₃)₄(H₂O)I²⁺ aquates in 1.0 M hydrochloric acid.

The spontaneous aquation reactions of the cis- and trans-[Cr(NH₃)₄(H₂O)I][ClO₄]₂ in oxygen-18 enriched water are in progress to determine the extent of labilization of coordinated water molecules.

We also report the synthesis of the cis- and trans-Cr(NH₃)₄(H₂O)I²⁺ ions and the details of both the spontaneous and the Cr(II)-catalyzed aquation reactions. The trans-Cr(NH₃)₄ICl⁺ ion has also been prepared and the kinetics of aquation investigated. Although the bis-ethylenediamine complexes of chromium(III) have been studied extensively, there have been few reports concerning the tetraammine analogs. Among the halogen derivatives, the iodo complexes should exhibit the extreme behavior: the iodo ligand should be the least strongly bound, and the possibilities of generating an intermediate of reduced coordination number and of observing isomerization should be maximized.

It has been suggested that a pentacoordinated intermediate is involved in the aquation of the Cr(H₂O)₅I²⁺ ion, although the peculiarities observed for this reaction have been attributed also to the activating influences of the trans iodide ion.^{7,8} This particular example is clouded by the inability to distinguish among the five aquo ligands and by the fact that there is no possibility for isomerization to accompany the aquation. The iodoaquotetraammines, however, have only one aquo ligand at a specified

geometry, and the aquation products can exist in both cis and trans forms.

Salts of cis- and trans- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$ and trans- $\text{Cr}(\text{NH}_3)_4\text{ICl}^+$ have been prepared and the stoichiometry and kinetics of their aquation reactions have been investigated. For these three ions as well as the cis- and trans- $\text{Cr}(\text{NH}_3)_4(\text{OH})\text{I}^+$ ions, replacement of coordinated iodide by water is first-order in complex concentration and occurs with retention of configuration. Rate constants and activation parameters for the hydrolysis of trans- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$ are: $k_0 = (1.75 \pm 0.12) \times 10^{-4} \text{ sec}^{-1}$, $\Delta H^\ddagger = 21.4 \pm 0.4 \text{ kcal/mole}$, $\Delta S^\ddagger = -5 \pm 1 \text{ eu}$ at $30.0 \pm 0.1^\circ\text{C}$; and for cis- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$, $k_0 = (1.12 \pm 0.03) \times 10^{-3} \text{ sec}^{-1}$, $\Delta H^\ddagger = 19.7 \pm 0.3 \text{ kcal/mole}$, $\Delta S^\ddagger = -6 \pm 1 \text{ eu}$ at $25.0 \pm 0.1^\circ\text{C}$. The observed first-order rate constants and activation parameters for the loss of coordinated iodide from trans- $\text{Cr}(\text{NH}_3)_4(\text{OH})\text{I}^+$ are: $k_{\text{OH}} = 0.367 \pm 0.003 \text{ sec}^{-1}$, $\Delta H^\ddagger = 18.7 \pm 0.3 \text{ kcal/mole}$, $\Delta S^\ddagger = 5.5 \pm 1 \text{ eu}$ at $10.0 \pm 0.1^\circ\text{C}$; for cis- $\text{Cr}(\text{NH}_3)_4(\text{OH})\text{I}^+$, $k_{\text{OH}} = 1.25 \pm 0.05 \text{ sec}^{-1}$, $\Delta H^\ddagger = 17.0 \pm 0.6 \text{ kcal/mole}$, $\Delta S^\ddagger = 2 \pm 2 \text{ eu}$ at $10.0 \pm 0.1^\circ\text{C}$; and for trans- $\text{Cr}(\text{NH}_3)_4\text{ICl}^+$, $k_0 = (3.28 \pm 0.05) \times 10^{-3} \text{ sec}^{-1}$, $\Delta H^\ddagger = 18.0 \pm 0.1 \text{ kcal/mole}$, $\Delta S^\ddagger = -9 \pm 0.5 \text{ eu}$ at $25.0 \pm 0.1^\circ\text{C}$. All rate measurements were made at unit ionic strength. The aquation of trans- $\text{Cr}(\text{NH}_3)_4\text{ICl}^+$ is not dependent on hydrogen ion in the concentration range 0.1 to 1.0 M.

The chromium(II)-catalyzed aquation reactions of the cis- and trans- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{2+}$ ions were observed to obey the rate law:

$$-d[\text{Complex}]/dt = k_2[\text{Cr(II)}][\text{Complex}]$$

and to result in the formation of the iodopentaaquochromium(III) ion. Second-order rate constants and activation parameters for the chromium(II)-assisted aquations are: $k_2 = 14.6 \pm 0.2 \text{ M}^{-1} \text{ sec}^{-1}$, $\Delta H^\ddagger = 8.7 \pm 0.1 \text{ kcal/mole}$,

$\Delta S^\ddagger = -24 \pm 1$ eu at $25.0 \pm 0.1^\circ\text{C}$ for cis- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{+2}$; and $k = 165 \pm 6 \text{ M}^{-1} \text{ sec}^{-1}$, $\Delta H^\ddagger = 7.1 \pm 0.1 \text{ kcal/mole}$, $\Delta S^\ddagger = -24 \pm 1$ eu at 25.0°C for trans- $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{I}^{+2}$, both at unit ionic strength with 1 M HClO_4 .

It is well known that the mobilities of lattice elements in a crystal are greatly affected by distortions and lattice imperfections in the solid. From the chemical point of view, there are two types of imperfections which should be considered; the impurity of foreign ions incorporated in the lattice and the non-stoichiometry of the compound. In both cases the ion defect concentration is altered and the rate of diffusion is enhanced. In titanium dioxide, known as a non-stoichiometric compound,¹⁰ both types of imperfections can be effective and one of the principal difficulties in the evaluation of the oxygen transport mechanism arises from the fact that under normal experimental conditions the two effects occur simultaneously and are inseparable for analysis.

The thermal reduction of titanium dioxide becomes important above 875°C ¹¹. Measurements of oxygen diffusion coefficients above this temperature¹² must involve reduction of the sample and it is impossible, under these conditions, to correlate the rates of diffusion either to the pure sample or to the doped, non-reduced sample.

In general, the activation energies for oxygen exchange processes are considerably less than that for oxygen diffusion. In the case of titanium dioxide, the activation energy for the oxygen exchange process is 23 kcal/mole and 61 kcal/mole in the temperature ranges of $950^\circ\text{-}1300^\circ\text{C}$ and $710^\circ\text{-}950^\circ\text{C}$ respectively. The corresponding activation energy for the diffusion process is 53 kcal/mole and 75 kcal/mole in the same respective temperature ranges. The surface exchange process and the diffusion process must be sequential reactions and the slower reaction must determine the overall changes in isotopic compositions in the gas phase. At relatively low

temperatures, the diffusion measurements can be complicated by the rate of exchange of the oxygen-18 tracer with the solid oxide. Thus, we have chosen 806°C which is high enough to minimize this problem, but low enough to eliminate problems due to sample reduction and the formation of a non-stoichiometric titanium dioxide.

This report is primarily concerned with demonstrating the effect of sample reduction on the diffusion coefficients of single crystals of titanium dioxide. This study also included an investigation of the possible influence of the grain size on the diffusion rate since it has been reported¹² that anion diffusion in the alkali halides depend on the grain size of the sample.

The self-diffusion coefficient of oxygen has been determined for non-reduced and reduced single crystals of rutile at 806°C. The rate of exchange between oxygen-18 enriched gas, solid single crystal plates and grains of the pure, non-doped, material has been measured. The influence of the particle size and the degree of reduction of the rutile samples on the diffusion rate has been determined. The diffusion coefficient for the stoichiometric, non-reduced samples was 1.7×10^{-15} cm²/sec in the direction perpendicular to the crystallographic c-axis and 3.2×10^{-16} cm²/sec parallel to it.

After short-term reduction at 1200°C, an increase in the diffusion rate was observed. This increase appeared to be independent of the duration of the heating (between 1-10 hours), but the amount of the increase was the same whether the reduction was performed in vacuum or in air. No influence of the particle size on the diffusion rates was observed but marked effects were noted for the surface exchange coefficients.

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III. Incident Reports

In compliance with the AEC regulation that reports be submitted on accidents, fires, and unusual operational incidents which occur in conjunction with work being performed under AEC contract, the following are reported:

1. Serious accidents	- none
2. Fires, explosions, etc.	- none
3. Other property damage	- none
4. Personal injuries	- none

Appendix (A) - Thesis Abstract

Eugene Burhans Grimley III

A Kinetic and Product Study of the Reaction of
Phenol with Chlorine Oxidants and of Uranium(IV)
with Chlorine(III) in the Presence of Phenol

This research was initiated with the purpose of determining the identity of the chlorine species scavenged by phenol in the reaction of uranium(IV) with chlorine(III) in purposes of comparison, it was necessary to determine the kinetic behavior of the reactions between phenol and the chlorine oxidants that are capable of existence in solution. The solution conditions were the same as those for the reaction of uranium(IV) with chlorine(III) in the presence of phenol.

Chlorine dioxide was found to react with phenol via parallel paths to give a multi-term law. There was a hydrogen ion dependent and a hydrogen ion independent term. A term was also found for the reaction of a $[\text{Cl}_2\text{O}_4]^-$ complex with phenol in the presence of large amounts of added chlorine(III). In 1 M ionic strength at 25°C, the observed second order rate constants were found to be 0.48 and 1.57 $\text{M}^{-1} \text{sec}^{-1}$. The kinetic evidence indicates that the first step of the reaction is a one electron transfer from chlorine dioxide to phenol.

Consecutive reactions were observed in the reactions of aqueous chlorine with phenol. The first reaction corresponds to the formation of a $[\text{Cl}_2 \cdot \text{OH}]$ complex with an observed second order rate constant equal to $(2.3 \pm 0.5) \times 10^4 \text{ M}^{-1} \text{sec}^{-1}$ at 5.0°C. The second reaction is a first order decomposition of the complex via three parallel paths: a hydrogen ion and chloride ion dependent path; a hydrogen ion dependent path; and a hydrogen ion and chloride ion independent path.

The major phenolic products found for all the systems studied, including the uranium(IV)-chlorine(III) reaction in the presence of phenol, were chlorophenols.

The comparison of kinetic results indicates that the intermediate species scavenged by phenol must be chlorine and $[\text{Cl}_2\text{O}_2]$. Chlorine accounts for at least 10% of the scavenged species in 1 M perchloric acid and would account for greater than 10% of the scavenged species with addition of chloride ion. Under the reaction conditions studied, it is not possible for chlorine to account for the entire scavenged species, therefore, $[\text{Cl}_2\text{O}_2]$ must be scavenged, also.

Appendix (B) - Thesis Abstract

William Stephen Melvin

Inorganic Reaction Mechanisms

Detailed studies on the reduction of oxychlorine oxidizing agents by transition metal ions which may undergo both one- and two-electron oxidations have been reported. In the hope of obtaining meaningful comparisons between one- and two-electron transfer reactions, these studies were extended to include a metal ion which is limited to a single electron oxidation. In the present study an attempt is made to determine if it is possible to restrict oxychlorine oxidizing agents to a single electron transfer with oxovanadium(IV).

The reduction of chlorate ion by oxovanadium(IV) was studied at 25°C. at an ionic strength of 2.0 M under a variety of hydrogen ion concentrations from 0.40 to 1.9 M and chloride ion concentrations from 10^{-4} to 1.50 M. Under the condition where the concentration of oxovanadium(IV) is in excess relative to the oxidizing agent, the overall stoichiometry of the reaction is described by the following equation:

The kinetics of the reduction of chlorate ion by oxovanadium(IV) are consistent with the following rate law

$$-\frac{d[\text{VO}^{+2}]}{dt} = \left[\frac{k_1 + k_2 K[\text{Cl}^-]}{1 + K[\text{Cl}^-]} + k_3[\text{H}^+] \right] [\text{VO}_2^+][\text{ClO}_3^-]$$

The parameters k_1 , k_2 , and K are independent of hydrogen ion concentration and correspond to the values $(3.74 \pm 0.06) \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$, $(2.24 \pm 0.18) \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$, and $1.60 \pm 0.52 \text{ M}^{-1}$, respectively. The hydrogen ion dependent term is calculated to be $(1.13 \pm 0.04) \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$.

Marked deviations from the second-order rate equation become apparent when the concentration of the ultimate reduction product, chloride ion,

becomes significant. The departure from the second-order rate equation is accounted for by a change in stoichiometry which occurs after the rate determining step when small amounts of chloride ion are present in that chloride ion moderately inhibits the rate of reaction. The results are discussed in terms of possible complex formation between vanadium(IV) and chloride ion.