Role of coordination complexes in oxidation reactions involving ions

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ROLE OF COORDINATION COMPLEXES IN OXIDATION REACTIONS INVOLVING IONS

by

Robert F. Bremer

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

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INTRODUCTION

An oxidation-reduction reaction is generally considered as a transfer of an electron from one body to another. The electron transfer may occur by two general mechanisms: direct transfer by collision, or by intermediate coordination complex formation. The former mechanism would require that the reacting bodies have sufficient kinetic energy to dislodge an electron from a comparatively stable environment within a high potential barrier. It is conceivable that this mechanism could be important in gas reactions at high temperatures. For reactions carried out in solution at room temperatures, the possibility of two bodies having the high kinetic energies required is hardly to be expected. The latter mechanism appears as the more probable path for the oxidation reaction. The formation of an intermediate coordination complex in which atomic and/or molecular orbitals might interact could facilitate the reaction in one of two ways or in a combination of both: the closer contact of two bodies entering into a coordination complex could either lower the potential barrier to an extent that the electrons might easily pass over this barrier, or it might decrease the width of the barrier making possible the transfer by tunneling.
Coordination complexes may hasten the rate of oxidation or may be responsible for the retardation and, in some cases, the actual cessation of the reaction. The observed retardation is generally due to complex formation of the oxidant or reductant with ions or molecules in solution which are stable to oxidation or reduction.

Complex formation has been observed in the case of very nearly all ions in solution and it is generally accepted that dissolved substances coordinate molecules of the solvent. If the oxidant is fully coordinated by the solvent, then, upon addition of reductant, a number of these coordinated solvent molecules must be displaced by reductant ions or molecules entering into a complex with the oxidant.

The solvent molecules may also be displaced by other inert ions or molecules in solution. This fact is demonstrated by the coordination complexes used in colorimetric analysis. The highly colored copper ammines, titanium-chloride, and cobalt ammines are only a few such complexes encountered. That mixed coordination complexes are not uncommon is evidenced by the nitrato-ammine-cobalt complexes which have been prepared (10). If these ions or molecules which displace the solvent molecules are held more strongly to the oxidant than the solvent molecules, it is reasonable to expect that the reductant would not be able to enter into complex formation as easily and hence
the overall rate of oxidation would decrease.

The theory that coordination complexes are a determining factor in oxidation reactions was proposed by Manchot and Haunschild (51), Manchot and Pflaum (52), and more recently by Duke (17). Although this theory has received support in a number of kinetic studies, it has not been generally accepted that these complexes are involved in all oxidation reactions. In this thesis the presence of coordination complexes will be supported by experimental evidence and reactions which have been studied mechanismically will be surveyed to offer evidence that the theory is correct.
A number of oxidation reactions have been studied for the purpose of proposing a mechanism. A few of these reactions were examined in great detail by a number of authors and a variety of mechanisms suggested. This review will treat each reaction separately, where practicable, and present them in an historical sequence. Editorial remarks are made where the reaction mechanisms proposed are believed to be in error or misleading. The mechanism of cerate oxidation of organic compounds is given in the introduction to the experimental part of the thesis.

Trivalent Manganese-Oxalate Reaction

A mechanism for the reaction of trivalent manganese and oxalate was first proposed by Skrabal (69) when he studied the oxidation of oxalic acid by permanganate ion in acid solution. His mechanism for the reaction required that a small amount of permanganate react with divalent manganese or oxalic acid to form manganic ion. The manganic ion so formed would then react very rapidly in two ways: direct reaction with oxalic acid resulting in reduction of trivalent manganese to manganous ion, or formation of a coordination complex containing one oxalic acid and one trivalent manganese. The manganous ion formed
in the first reaction reacted with permanganate ion to produce more trivalent manganese. He proposed that the measurable step was the dissociation of the manganic-oxalic acid complex and that the actual reduction of trivalent to divalent manganese was a very rapid trimolecular reaction involving one oxalic acid molecule and two manganic ions.

Launer (46) and later Launer and Yost (47) again studied the permanganate-oxalate reaction. They concluded that the reaction involved oxalate ion and not undissociated oxalic acid. It was also noted that the rate of reaction was inversely proportional to the concentration of oxalic acid. From this observation, they concluded that the manganic-oxalate complexes formed were merely reservoirs for manganic ion, effectively reducing active trivalent manganese concentration. The mechanism proposed was very similar to that of Skrabal, the slow step was considered the dissociation of the manganic-oxalate complexes. It differed from Skrabal's in that the rapid step was bimolecular; one trivalent manganese and one oxalate ion reacting to form manganous ion, carbon dioxide, and a negatively charged carbon dioxide ion.

Fessenden and Redmon (26) studied the permanganate-oxalate reaction and recognized the possibility of more than one complex being formed. The mechanism they proposed was very similar to the previous mechanisms but involved in
addition to the mono- and dioxalate complexes a trioxalate complex. Again, the decrease in rate of reaction was attributed to the coordination of active manganic ion in the form of complexes. In support of this mechanism in which manganic-oxalate complexes did not disproportionate directly, they added salts of aluminum, zinc, and cadmium which were known to complex oxalate ion. These cations were found to produce a marked increase in rate and the authors attributed this action to the reversal of the equilibrium for the formation of manganic-oxalate complexes. That the higher complexes proposed by Fessenden and Redmon are possible was demonstrated by Cartledge and Ericks (12) who prepared dioxalate-diaquo, trioxalate, and difluo-dioxalate manganate salts. In no case was the monooxalate complex isolated.

Bradley and Van Pragh (8) again studied the permanganate oxalate reaction and proposed intermediate complexes \( \text{Mn(C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^- \) and \( \text{Mn(C}_2\text{O}_4)_3^- \). They noted that upon increasing oxalate ion concentration, the solutions changed from yellow to pink; the yellow solutions reacted more rapidly than the pink solutions and the reaction was unimolecular. The rate of reaction was found to be proportional to hydrogen ion concentration. They proposed a reaction between hydrogen ion and the dioxalate-diaquo manganate complex to form free manganic ion. Addition of
potassium fluoride resulted in the rate being directly proportional to oxalate ion concentration. This, they concluded, was caused by formation of stable mangan fluoride complexes which prevent the formation of the oxalate complexes. Their mechanism was very similar to that of Launer.

The various authors who supported the mechanism in which the complex was only a reservoir for manganic and oxalate ions were undoubtedly hampered in two ways; the data used for the proposal of a mechanism was a part of that obtained from a very complicated reaction, the permanganate oxidation of oxalate ion, which is not completely understood even today, and the firm belief that the complex was a dead end merely causing a decrease in overall reaction rate. Bradley and Van Pragh might have realized the real significance of intermediate complexes for they had conclusive proof that two different complexes existed and that these two complexes disproportionated at different rates. Undoubtedly, the work of earlier investigators greatly influenced them in their interpretation of data.

Gonzalez Barredo and Senent (28, 29) and Senent Perez (68) studies the reaction of manganic and oxalate ions and agreed that the higher complexes of trivalent manganese were present but that the fast step involved the complex \( \text{Mn(C}_2\text{O}_4\text{)}\text{(H}_2\text{O)}\text{(SO}_4\text{)}\text{)}^\text{2-} \). Their results indicated the reaction
to be unimolecular and dependent only on the concentration of the above complex.

Taube (79) studied the catalytic effect of chloride on the manganic-oxalate reaction. He concluded that the dissociation of the complex was not the rate determining step but that direct, irreversible disproportionation of the trivalent manganese-oxalate complexes to products was the measurable step. It was explained that at low oxalate concentrations, the reaction is slow because of increased dissociation of the manganic-oxalate complexes. At high oxalate concentrations, the rate is again slow due to the formation of the dioxalate complex which disproportionates at a slower rate than the mono-oxalate complex. Taube (81) repeated the work with bromide and found the mechanism was the same.

Duke (17) studied the non-catalyzed reaction of manganese (III) and oxalate ion and arrived at the same conclusion that it was the disproportionation of the complex that determined the reaction rate. He found the reaction to be unimolecular at concentrations of oxalate ten times larger than trivalent manganese concentration. The rate decreased with increasing oxalate concentration and increased with increasing hydrogen ion concentration. At the oxalate concentrations used, the manganese (III) was assumed to be mono- and dioxalate complex species.
Duke developed a rate expression which involved the equilibrium constant between the two complexes and took into account the fact that both complexes could disproportionate. The rate expression could be used to account for both increase in rate with increasing hydrogen ion concentration and the decrease with increasing oxalate concentration. This was in agreement with Taube's conclusion that the di-oxalate complex disproportionated at a slower rate than the monooxalate complex. Taube (80) coincidently worked on the non-catalyzed oxidation and confirmed Duke's results.

The work of Gonzalez Barredo and Senent, Senent Perez, Duke and Taube was carried out starting with solutions of Manganese (III). They were, therefore, not troubled by the complicated reaction for the reduction of Manganese (VII) to Manganese (III). Careful compilation and interpretation of data has allowed these authors to determine both the equilibrium constant for the formation of the complexes and the rate at which each complex disproportionates.

Periodate Oxidation of Polyalcohols

The use of periodic acid for analysis of polyalcohols has been extensively used. Malprade (48, 49). Fleury and Lange (27), and Criegee, Kraft, and Rank (15) pointed out that for each polyalcohol of the type \([\text{CH(OH)}]_n(\text{CH}_2\text{CH})_2\)
there were reduced \((n + 1) \text{HIO}_4\) to \(\text{HIO}_3\) with the formation of \(2 \text{HCHO}\) and \(n \text{HCO}_2\text{H}\).

Evidence that periodate would form complexes was first presented by Malprade (50). He pointed out that periodate complexes Co, Ni, Cu, Mn, Bi, Pb, Fe, Ti, and others. More specifically he found that periodate would form two complexes with cobalt, tetracobaltiperiodate and monocobaltiperiodate.

Criegee (14) and Criegee, Kraft, and Rank (15) studied the reaction of periodate and ethylene glycol. They concluded the periodate ion coordinated one or more water molecules and a molecule of glycol displaced two water molecules to form a cyclic diester. The cyclic diester decomposed very rapidly to iodic acid, water, and a very active free radical which instantaneously rearranged to yield two carbonyl groups. No conclusions were reached as to which of the two reactions, the esterification or disproportionation of the ester, was the rate controlling step.

Price and Knell (61) investigated the ethylene glycol-periodate reaction and found the reaction to proceed by the mechanism suggested by Criegee (14). It was concluded the slow step was the ester formation. They investigated the difference on rate of oxidation of cis- and trans-cyclohexene glycols by periodate and found the cis isomer reacted more readily. This was accounted for by assuming that no
intermediate inversion was necessary for the cis isomer to form the cyclic diester.

Heidt, Gladding and Purves (32) studied the reaction between periodate and ethylene glycol. Based on these experimental results and data available in the literature, they concluded that any oxidant able to cleave glycols must have the following four physical properties: (1) The central atom of the oxidant must have a diameter of 2.5 to $3.0 \times 10^{-8}$ cm., which is large enough to bridge the space between the hydroxyl groups in a 1,2 glycol. (2) The central atom of the oxidant must be able to coordinate at least two hydroxyl groups in addition to groups already attached to it. (3) The valence of the central atom must exceed by two units, rather than by one or three, the valence of the next lowest stable state. (4) The oxidant should have a standard $E_0$ oxidation potential in the neighborhood of -1.7 volts with respect to the next lowest stable valence state. These conclusions are not correct for an oxidant need have none of the above requirements. An excellent example of an oxidant which possesses none of the stated requirements is tetravalent cerium; the diameter of the ceric ion is $2.02 \times 10^{-8}$ cm. (59), the glycol is found to displace groups coordinated to the cerium (21), the valence of the cerium changes by only one when it is reduced and the standard $E_0$ is -1.45 volts (73). They
agree with Criegee (14) that a cyclic diester is the intermediate complex.

Duke (18) repeated the work of Price and Knell (61) and found the rate determining step to be the disproportionation of the ester. He concluded that at the pH Price and Knell had worked, the periodate was coordinating hydroxyl ions rather than water molecules and the hydroxyl ions are more difficult to displace than the water molecules.

Hughes and Nevell (39) studied the oxidation of glucose by periodate and found the stoichiometry of the reaction to agree with that proposed by earlier workers (15, 27, 48, 49). One glucose unit reacted with five periodate ions to form five molecules of formic acid, one molecule of formaldehyde and five iodate ions. They concluded the cyclic diester applied in this case and that of the α glycol group of the glucose was the first oxidized. The first step was considered the disproportionation of an intermediate into a pentose and formic acid. Successive stages consist of formation of similar intermediate complexes from a pentose, tetrose, triose, and biose which disproportionate into formic acid and a tetrose, triose, biose and formaldehyde respectively.
Chromic Acid Oxidation

Spitalsky and Koboseff (78) studied the kinetics of hydrogen peroxide decomposition by chromic acid. They concluded that the reaction was not simple and proposed the first step to be the formation of three complex intermediates. They admit their data are insufficient to determine the stoichiometric composition of the other intermediates. Kobozev and Gal'braikh (44) continued the work of Spitalsky and Koboseff. They proposed that the intermediates were bichromate and acid bichromate ions. Bobtelsky, Glasner, and Bobtelsky-Chaikin (5) repeated this work in a variety of solvents. Their results indicate that there are two intermediate complexes, a blue and a violet, and the blue species was the only complex which contributed to hydrogen peroxide decomposition. Their results also indicated the two complexes were in equilibrium with each other. They did not have enough data to determine the chemical composition of the complexes. Abel (1) studied this same reaction and postulated an intermediate complex which he believed to be Cr(HO$_2$)$_3$. The results obtained for the hydrogen peroxide decomposition by chromic acid cannot be critically examined. Decomposition involving hydrogen peroxide are very often found to be complicated by both side and chain reactions. The work on this reaction was not sufficient to resolve completely the mechanism and could
indicate that complexes were involved.

Bobtelsky and Rosowkaja-Rossienskaja (4) investigated the oxidation of hydrogen bromide and hydrogen iodide by chromic acid. They were able to explain their results only if they assumed complexes were formed between chromic acid and the hydrogen halide.

Wagner (84) proposed but did not identify the intermediates formed in the oxidation of oxalic, lactic, tartaric and thiocyanic acids by chromic acid. Vannoy (83) repeated the oxidation of tartaric acid by chromic acid in the presence of arsenite. To explain his results, he postulated chromic acid-tartaric acid and arsenite-tartaric acid complexes.

Slack and Waters (70) examined the oxidation of diphenylmethane by chromic acid and concluded that in nearly neutral or slightly acid solutions the reaction was greatly hindered by hydration of the chromic acid.

Slack and Waters (71) investigated the oxidation of glycol with chromic acid and proposed an intermediate cyclic diester similar to that formed during the periodate oxidation of glycols. In glacial acetic acid they found the oxidation was stopped because of formation of an inactive \( \text{Cr(HCrO}_4\text{)(OAc)}_2 \) complex.

Snethlage (74, 75, 76) studied the oxidation of formic, malonic, and oxalic acids by chromic acid in sulfuric acid
in sulfuric acid solutions and found the oxidation to be incomplete at low acid concentrations. He attributed the incomplete oxidation to formation of complexes of the organic acid and reduction products of chromic acid.

Westheimer and Novick (86) studied the oxidation of isopropyl alcohol by chromic acid and found the slow rate-determining step involved formation of a complex containing one molecule of alcohol, one acid chromate ion, and two hydrogen ions. They were unable to determine whether the complex disproportionated in a one or two electron change; the one electron change would form a very reactive ketyl radical and a pentavalent chromium compound, the two electron change would yield acetone and a tetravalent chromium compound. Holloway, Cohen, and Westheimer (37) added further support to the mechanism of Westheimer and Novick by preparing the isopropyl ester of chromic acid in benzene solution.

Iodine-azide Reaction

The reaction in solution of triiodide ion and azide ion does not occur without the presence of a catalyst. Compounds that contain sulfide sulfur are found to catalyze the iodine-azide reaction. Examples are: all inorganic sulfides (23), thiocyanate (23), carbon disulfide (25), tri-, tetra, and pentathionate ions (53), and many organic sulfur compounds
containing sulfidic sulfur.

Rashig (62,63) described the catalytic effect of sodium thiosulfate and sodium sulfide on the reaction. Rashig proposed a mechanism for the sodium thiosulfate catalysis in which the first step was a reaction between sodium thiosulfate and iodine to form an intermediate sodium iodo-thiosulfate, \( \text{NaI}_2\text{S}_3\text{O}_3 \). This was followed by a third order reaction involving one sodium iodo-thiosulfate molecule and two sodium azide molecules to form sodium iodide, three nitrogen molecules, and the original sodium thiosulfate, the sodium iodo thiosulfate could also react with sodium thiosulfate to generate sodium tetrathionate and sodium iodide. Rashig assumed that tetrathionate did not catalyze the reaction. Since it is now known that tetrathionate does catalyze the reaction, the mechanism proposed by Rashig must be held as unlikely.

Hofman-Bang (34) studied the catalytic effect of tetrathionate ion on the iodine-azide reaction and concluded that the rate determining step was the reaction of the azide ion with tetrathionate ion to form a trivalent intermediate, \( \text{N}_3\text{S}_4\text{O}_6^{-3} \). Evidence that this is the first step is given by the fact that the overall reaction is proportional to the concentration of azide and tetrathionate ions but independent of iodine concentration. The \( \text{N}_3\text{S}_4\text{O}_6^{-3} \) reacts almost
instantaneously with iodine to form a dimer \((N_3S_4O_6)_{2}^{--}\) which then decomposes to form molecular nitrogen and regenerate the tetrathionate ion.

Browne and Hoel (11) studied the catalytic effect of carbon disulfide on the iodine-azide reaction. They proposed a mechanism in which the first step was the reaction of azide and carbon disulfide to form an intermediate complex \(SCSN_3^-\). This reacted with iodine to give iodide ion and a dimer \((SCSN_3)_2\) which in turn reacted with more azide ion to produce the complex \(SCSN_3^-\) and nitrogen. Browne and Hoel emphasized that the azido-dithiocarbonate ions are the catalyst and that the formation of this ion is irreversible and no carbon disulfide is regenerated.

Feigl and Chargoff (25) later studied this reaction and proposed a mechanism very similar to that of Browne and Hoel except that they required the carbon disulfide to be regenerated. Höfman-Bang and Szybalinski (35) again examined this reaction and agreed with Feigl and Chargoff that the carbon disulfide is regenerated. That the azido-dithiocarbonate ion exists was conclusively demonstrated by Sommer (77) who prepared salts of this ion.

Hofman-Bang (36) investigated the catalytic effect of penta- and hexathionate ions on the iodine-azide reaction. He proposed a mechanism similar to those previously described. The hexathionate ion was found to give the same
rate constants as the pentathionate ion. Hofman-Bang attributed this to the decomposition of the hexathionate ion to the pentathionate ion. The proposed coordination intermediate in this reaction was azido-pentathiocarbonate ion, $N_3S_5O_6^{-3}$.

Decomposition of Thiosulfate Ion

Griffith and Irving (31) studied the decomposition of thiosulfate ion in solutions containing iodide ion, nitrite ion, and iodine. The products of this reaction are tetra-thionate, sulfate, and iodide ions. The nitrite remains unchanged. To explain the reaction, Griffith and Irving had to propose a complicated mechanism. The thiosulfate could react in three ways; with iodide to form the complex $S_2O_3I^{-3}$ or with nitrite to form a complex $S_2O_3NO_2^{-3}$. These complex intermediates then reacted bimolecularly with either thiosulfate ion or with iodine, the resulting products were tetrathionate, sulfate, and iodide ions. The bimolecular reactions were very rapid and no conclusions could be made regarding the possibility of complexing. Griffith and Irving studied a reaction much too complicated to support any definite mechanism. Their overall mechanism appears to be an assemblage of all possible reactions that could lead to the final product.
Avtry and Connick (2) investigated the reaction of iodine and thiosulfate. Their experiments confirmed the intermediate complex $S_2O_3I^-^3$ postulated by Griffith and Irving. They proposed a mechanism in which $S_2O_3I^-^3$ would react with water to form a bisulfate ion which in turn was oxidized to sulfate.

Dinegar, Smellie, and La Mer (16) investigated the decomposition of thiosulfate ion in dilute solution. They added a further step to the mechanism by proposing that a bithiosulfate and a thiosulfate ion could react to form an intermediate complex $[HS_2O_3\cdot S_2O_3]^-^3$. This intermediate then decomposed in a unimolecular manner to form one sulfur and a sulfite ion. The work of Dinegar, Smellie and La Mer indicated that the previous investigators ignored a basic reaction in their mechanisms.

**Persulfate-iodide Reaction**

Brønsted (9) was the first to interpret this reaction mechanistically and concluded that the reaction proceeded in two steps. The first was the reaction of a persulfate and iodide ion to form a iodo-persulfate intermediate. The second step was the bimolecular reaction of the intermediate complex with another iodide ion to form two sulfate ions and molecular iodine.
Kiss and Zombory (42) studied the effect of the presence of iodine and concluded that the triiodide ion did not react with persulfate. The data of these workers are open to considerable criticism since, by their own admission, the persulfate used in their experiments contained an unknown impurity.

Jette and King (41) repeated the work of Kiss and Zombory and found the triiodide reacted with persulfate and at a different rate than did iodide. Their mechanism was the same as that of Bronsted, the only difference was formation of two complex ion intermediates, iodo-persulfate ion and triiodo-persulfate. The proposal of Bronsted and of Jette and King that a bimolecular reaction occurs after complex formation cannot be taken as evidence that intermediate complex formation is not necessary for reaction. It will be shown in the experimental section that a reaction which is actually unimolecular may appear to be bimolecular.

Howells (38) investigated the reaction in the presence of cadmium salts. He found the reaction was greatly retarded and concluded this was due to formation of a CdI$_4^{-2}$ complex which reduced the concentration of the active persulfate-iodide complex.
Reduction of Iron (III)

Sasaki (67) investigated the reaction of ferric and iodide ions in the presence of chloride ion. He concluded the forward reaction was not simple but must involve the ions FeCl$_2$$^{+2}$, FeICl$^+$, and FeI$_2^+$, all of which were in equilibrium with each other. Hershey and Bray (33) repeated the work in the absence of chloride ion. They also found the reaction to be complex. They interpreted their data to conclude the complexes FeI$_{+2}$, FeI$_2^+$, and FeI(OH)$_{+3}$ took part in the forward reaction and the complexes FeI$_2$ and FeI$_3^-$ were involved in the reverse reaction.

Gorin (30) studied the oxidation of stannous ion by ferric ion in perchlorate solutions assuming the perchlorate would not complex either the ferric or stannous ions. To interpret his results, he proposed the iron was present as Fe(H$_2$O)$_6^{+3}$, FeOH(H$_2$O)$_5^{+2}$, and Fe(OH)$_2$(H$_2$O)$_6^{+1}$. The hydroxylated ferric ions reacted with stannous ion. In this same paper he asserts from his thesis and the work of others (64, 82) that in chloride solution, the reaction involves both ferric and stannous chloride complexes. Weiss (85) and Krishna (45) believe the reaction is between ferric ion and a complex SnCl$_4^{-2}$ ion.

Robinowitch and Stockmeyer (65) determined the equilibrium constants of the ferric-chloride system. Duke and
Courtney (19) determined equilibrium constants of the stannous-chloride system. Duke and Pinkerton (22) used these equilibrium constants in addition to kinetic data to point out that the identification of the reacting ferric and stannous complexes was not possible and only the halide dependency could be determined.

A reaction involving iron (III), tin(II) and halide ion is another example of a reaction which is much too complicated to draw absolute conclusions. In all probability, the intermediates proposed by the various authors are involved but the limitations of species proposed by the investigators must not be considered as absolutely true.

Miscellaneous Reactions

Bogdanov (4, 6) investigated the decomposition of hydrogen peroxide by sodium and potassium tungstate in sulfuric acid solution. The kinetics of the reaction required two initial equilibria: reaction of hydrogen peroxide, hydroxyl ion, and tungstate ions to form a mono-hydrogen peroxide complex, for the reaction of this complex with hydrogen peroxide to form a di-hydrogen peroxide complex. Like other hydrogen peroxide decompositions, this is to be taken only as evidence that intermediate complexes occur.
Manchot and Haunschild (51) studied the reaction between ferrous salts and nitric oxide in sulfuric acid solutions. The mechanism arrived at required a complex containing nitric oxide, ferric ion and sulfate ion.

Miyamoto (54) examined the oxygen oxidation of stannous ion in sulfuric acid solution and proposed two stannous intermediates, \( H_2Sn_2(SO_4)_3 \) and \( H_2Sn(SO_4)_2 \). He believed the sulfate complex was necessary for oxidation to occur.

Baudisch (3) used ferricyanide to oxidize nitrogen containing compounds. Intensely colored unstable compounds were formed during the reaction which he believed to be nitroso-iron complexes.

Duke (19) investigated the oxidation of acetone by selenious acid. The stoichiometry of the reaction requires no hydrogen ion. He found the reaction to be first order in acetone, selenious acid, and hydrogen ion. This could well be interpreted as the necessary formation of an intermediate complex, \( (CH_3)_2CO\cdot HSeO_2 \), which disproportionated to regenerate the hydrogen ion.

Oliveri-Mondala (57) studied the oxidation of iodide ion with cupric ion in sulfuric acid solution. The mechanism proposed required the cupric ion and iodide ion to be in equilibrium with a cupric iodide complex. The cupric iodide then disproportionated to cuprous iodide and atomic iodine.
Nikolaev (55, 56) studied the decomposition of hydrogen peroxide with cupric copper. He found the cupric ammines were more effective than other copper salts and attributed this to the looser binding of ammonia. Pyrogallol added to the cupric ammines retarded the decomposition due to stable cupric-pyrogallol complexes. Excess ammonia in the solution also deactivated the cupric ammines. Cupric glycinate would also decompose hydrogen peroxide but excess glycine deactivated the copper. Nikolaev interpreted this to indicate that addition of excess of any simple ammine could result in deactivation of copper toward decomposition of hydrogen peroxide.

Yost and Zabaro (87) examined the oxidation of titanous ion with iodine. They concluded the first and slow step was the formation of an intermediate complex, $\text{TiOH I}_2^-$, which then disproportionated to quadrivalent titanium and $\text{I}_2^-$. 
CERATE-2,3 BUTANEDIOL REACTIONS
IN PERCHLORATE SOLUTIONS

Although the use of cerate ion as an oxidant of organic compounds has been extensively studied (72), the mechanism of the reaction has not been thoroughly investigated. Conant, Aston, and Tongberg (13) studied the rate of oxidation of formaldehyde by ceric salts in sulfuric acid solutions. They were unable to reach a definite mechanism but did determine that the process occurred by a fast reversible step followed by a slow irreversible rate controlling action.

Ross and Swain (66) investigated the oxidation of oxalic acid by ceric ion in sulfuric acid solutions. They assumed that when the concentrations of ceric and oxalate ions were very small, the complexes of these two ions would be negligible. Their data indicated that the reaction was bimolecular. The work of this thesis will illustrate that bimolecular data are possible for a reaction which is in reality a unimolecular disproportionation of a complex formed from two reactants.

Duke and Forist (21) studied the kinetics of the oxidation of 2,3 butanediol by cerate ion in nitrate solutions. Their data indicated the oxidation proceeded through the disproportionation of a mono-glycolated coordination...
intermediate. At higher glycol concentrations, poly-glycolated intermediates were formed. They also found that in nitric acid solutions, the tetravalent cerium was coordinated with nitrate ions, hydroxyl ions, and water molecules. The composition of these nitrate-hydroxyl-water-ceric complexes varied with nitric acid concentration.

The present investigation was carried out to determine if tetravalent cerium would coordinate perchlorate and what cerate-glycol complexes were involved in the reaction.

Theory

The stoichiometry of the oxidation of 2,3 butanediol by cerium (IV) requires that two cerate ions be consumed for each glycol oxidized. The reaction is found, however, to be first order in cerium (IV) and first order in glycol. To explain this order of reaction, it is proposed that two oxidation-reduction reactions occur consecutively. The first is the reaction of one cerate ion and one glycol to yield acetaldehyde, hydrogen ion, cerous ion, and a free radical. The second is the reaction of cerate ion with the free radical to yield acetaldehyde, hydrogen ion and cerous ion. It is generally accepted that free radicals react very rapidly in the presence of oxidizing agents. It is therefore concluded that the first step is the rate determining
stage of the reaction.

Tetravalent cerium has, as indicated by its complexes which have been isolated, a coordination number of six. If it is also assumed each glycol occupies two coordination positions, the following equilibria are possible:

\begin{align*}
\text{CeX}_6 + G &\rightleftharpoons \text{CeX}_6G + 2X & (1) \\
\text{CeX}_6G + G &\rightleftharpoons \text{CeX}_2G_2 + 2X & (2) \\
\text{CeX}_2G_2 + G &\rightleftharpoons \text{CeG}_3 + 2X & (3)
\end{align*}

G is 2,3 butanediol, Ce is tetravalent cerium, and X is any non-oxidizable body occupying a coordination position of cerium. Since Equations (1), (2) and (3) represent equilibrium reactions, the following equilibrium constant expressions are obtained:

\begin{align*}
K_1 &= \frac{[\text{CeX}_6G][X]^2}{[\text{CeX}_6][G]} & (4) \\
K_2 &= \frac{[\text{CeX}_2G_2][X]^2}{[\text{CeX}_6G][G]} & (5) \\
K_3 &= \frac{[\text{CeG}_3][X]^2}{[\text{CeX}_2G_2][G]} & (6)
\end{align*}

It is possible by a simple analytical method to determine the total amount of tetravalent cerium, T_{Ce}, in the solution and this quantity is represented by the expression:

\[ T_{Ce} = [\text{CeX}_6] + [\text{CeX}_6G] + [\text{CeX}_2G_2] + [\text{CeG}_3] \]  

(7)

The disappearance of cerium (IV) is dependent on the concentration and rates of disproportionation of CeX₆G,
CeX$_2$G$_2$, and CeG$_3$, and is independent of the concentration of CeX$_6$. The kinetics expressed as the rate of disappearance of total cerium (IV) in time $t$ is:

$$ - \frac{dT_{Ce}}{dt} = k_1 \text{CeX}_4G + k_2 \text{CeX}_2G_2 + k_3 \text{CeG}_3 \quad (8) $$

Solution of Equation (8) is not possible in the form given when total cerium is determined as a function of time. Equations (4), (5), (6) and (7) make possible the expression of the quantities CeX$_4$G, CeX$_2$G$_2$ and CeG$_3$ in terms of $T_{Ce}$. These expressions are:

$$ \text{CeX}_4G = \frac{K_1 \text{G} X^4 T_{Ce}}{X^6 + K_1 \text{G} X^4 + K_1K_2 \text{G} \text{X}^2 + K_1K_2K_3 \text{G}^3} \quad (9) $$

$$ \text{CeX}_2G_2 = \frac{K_1K_2 \text{G} \text{X}^2 T_{Ce}}{X^6 + K_1 \text{G} X^4 + K_1K_2 \text{G} \text{X}^2 + K_1K_2K_3 \text{G}^3} \quad (10) $$

$$ \text{CeG}_3 = \frac{K_1K_2K_3 \text{G} \text{X}^3 T_{Ce}}{X^6 + K_1 \text{G} X^4 + K_1K_2 \text{G} \text{X}^2 + K_1K_2K_3 \text{G}^3} \quad (11) $$

Substitution of Equations (9), (10) and (11) in Equation (8) gives a differential equation which can be solved if the glycol and quantity can be considered constant. Combining all terms over the common denominator gives the kinetics expression:

$$ - \frac{dT_{Ce}}{dt} = \frac{k_1K_1 \text{G} X^b + k_2K_1K_2 \text{G} \text{X}^b + k_3K_1K_2K_3 \text{G}^3}{X^b + K_1 \text{G} X^4 + K_1K_2 \text{G} \text{X}^2 + K_1K_2K_3 \text{G}^3} T_{Ce} \quad (12) $$
At high glycol concentrations \( \frac{G}{T_{Ce}} = 4 \), the term within the brackets of Equation (12) is a pseudo first order rate constant \( k' \) for the disappearance of cerium (IV). Substitution of this notation into Equation (12) and integration gives:

\[
- \ln T_{Ce} = k't + C
\]  

(13)

The evaluation of \( k' \) from Equation (13) is easily obtained from a plot of \( \ln T_{Ce} \) vs. \( t \); the negative of the slope is numerically equal to \( k' \).

At very low concentrations of glycol and cerium (IV), the equilibria represented by Equations (2) and (3) are unimportant and only the formation of monoglycolated cerium is responsible for disappearance of cerium (IV). At low concentrations of cerate ion and glycol and if the value of \( K_1 \) is not large, a pseudo second order rate constant \( k_{II} \) can be experimentally determined for a reaction that is in reality unimolecular. The classical kinetic expression for a second order reaction is:

\[
\frac{dx}{dt} = k_{II} (a-x)(b-y)
\]  

(14)

To adapt Equation (14) to this problem, let \( a \) be the initial concentration of cerium (IV), \( b \) the initial concentration of glycol, \( x \) the amount of cerate ion reacted at time \( t \) and \( y \) the amount of glycol reacted at time \( t \). To simplify the equation, let \( a \) and \( b \) be present in equivalent
amounts, then $b = a/2$ and $y = x/2$. The classical record order equation becomes:

$$\frac{dx}{dt} = k_{II} /2 (a-x)^2 \tag{15}$$

Integration of Equation (15), imposing the limits on $x$ of 0 to $x$ and on $t$ of 0 to $t$, the equation becomes:

$$\frac{ak_{II}}{2} t = \frac{x}{a-x} \tag{16}$$

Solution of Equation (16) is obtained graphically; plot $\frac{x}{a-x}$ vs. $t$ and the slope is numerically equal to $\frac{ak_{II}}{2}$.

If $K_2$ and $K_3$ are small compared to $K_1$, a glycol concentration exists at which Equation (12) can be applied assuming insignificant concentrations of di- and triglycolated cerium. At this glycol concentration, Equation (12) reduces to:

$$- \frac{dT_{Ce}}{dt} = \frac{k_1 K_1 [G] [X]^k}{[X]^6 + K_1 [G] [X]^k} T_{Ce} \tag{17}$$

and

$$k' = \frac{k_1 K_1 [G] X^k}{[X]^6 + K_1 [G] [X]^k} \tag{18}$$

Combining Equation (14) and Equation (17) gives:

$$k_{II} = \frac{k_1 K_1 [X]^k}{[X]^6 + K_1 [G] [X]^k} \tag{19}$$

A further simplification of Equation (19) is justifiable if the value of $K_1$ is small and if $k_{II}$ is determined at very low glycol concentration. The numerical value of the
product $K_1 [G] [X]^k$ is negligible compared to $X^6$. Then:

$$k_{II} = \frac{k_1 k_4}{[X]^2} \quad (20)$$

Thus if the value of $[X]$ and $k_{II}$ are known, $k_1$ and $K_1$ can be evaluated. Substitution of this value into Equation (18) for a given $k'$ and $[G]$ gives an expression solvable for $K_1$ and hence $k_1$.

To solve for $k_2$ and $K_2$, numerical values of $k'$ are determined from Equation (18) using the known quantities $k_1$, $K_1$ and increasing values of $[G]$. A plot of $k'$ vs. $[G]$ for experimentally and calculated values of $k'$ will reveal the glycol concentration limit for which Equation (18) can be applied. The terms due to diglycolated cerium are then added to Equation (18) to give:

$$k' = \frac{k_1 K_1 [G] [X]^k + k_2 K_1 K_2 [G]^2 [X]^2}{[X]^6 + K_1 [G] [X]^k + K_1 K_2 [G]^2 [X]^2} \quad (21)$$

Selection of two values of $k'$ above the point where Equation (18) deviates from experimental values to obtain two equations in two unknowns, $k_2 K_1 K_2$ and $K_1 K_2$, and hence $k_2$ and $K_2$.

Repeating the same process and adding the triglycolated cerium terms to Equation (21) the values of $k_3$ and $K_3$ can be determined.
Experimental

Tetravalent cerium was prepared by electrolytic oxidation of pure cerous perchlorate. The cerous salts available from commercial sources were found to contain sulfate ion. To eliminate the sulfate ion, the cerous salts were dissolved in dilute perchlorate acid and the cerous ion precipitated with oxalate ion. The insoluble cerous oxalate was washed with dilute perchloric acid until no precipitate of barium sulfate was formed on addition of excess barium chloride to the washings. The cerous oxalate was then boiled in excess 72 percent perchloric acid to oxidize the oxalate ion to carbon dioxide. The resulting solution was evaporated to near dryness to expel the chloride formed in the oxidation of oxalate ion. Dilution of the residue gave a solution of suitable concentration free of sulfate and chloride ions.

Sodium perchlorate solution of desired concentration was prepared by neutralization and dilution of 72 percent c.p. perchloric acid with c.p. sodium hydroxide.

Meso-2,3 butanediol was purified by triple vacuum distillation of a mixture of D, L and Meso-2,3 butanediol. The fraction having refractive index between 1.4326 and 1.4334 at 35°C (43) was collected and used in these experiments.
Experimental temperature was maintained at 0°C in a melting ice bath. 50 ml. volumetric flasks with an additional 48 ml. mark were used as reaction vessels. Glycol, perchloric acid and sodium perchlorate were mixed in the flasks to give the desired concentration and diluted to 48 ml. This solution was placed in the ice bath for 45 minutes to attain a temperature of 0°C. Two ml. of .25 N Ce⁺⁺ at the bath temperature were added making [Ce⁺⁺]=.01N.

The reaction rate was followed by removing five ml. samples at as rapid intervals as possible. These samples were quenched in potassium iodide solution and the liberated iodine titrated with standard thiosulfate. The time of sampling was recorded uniformly to the nearest second.

The following mixtures were studied.

A. \([\text{Ce}^{++}] = 0.01N, \ [\text{H}^+] = 0.1N, \ [\text{ClO}_3^-] = 1.0N, \ [\text{G}] = 0.04 \text{ to } 0.40 \text{ M}

B. \([\text{Ce}^{++}] = 0.01N, \ [\text{H}^+] = 1.0N, \ [\text{ClO}_3^-] = 1.0N, \ [\text{G}] = 0.04 \text{ to } 0.40\text{M}

C. \([\text{Ce}^{++}] = 0.01N, \ [\text{H}^+] = 0.1 \text{ to } 1.0N, \ [\text{ClO}_3^-] = 1.0N, \ [\text{G}] = 0.10\text{M}

D. \([\text{Ce}^{++}] = 0.01N, \ [\text{H}^+] = 1.0N, \ [\text{ClO}_3^-] = 1.0 \text{ to } 5.0N, \ [\text{G}] = 0.05\text{M}

E. \([\text{Ce}^{++}] = 0.01N, \ [\text{H}^+] = 0.1, 0.5, 1.0N, [\text{ClO}_3^-] = 1.0N, \ [\text{G}] = 0.005\text{M}
Data

Pseudo first order rate constants, $k'$ were determined for experimental parts A, B, C, and D. The constants were determined graphically from the graph $\ln T_{Ce} \text{ vs. } t$, the negative of the slope is numerically equal to $k'$. Figure 1 is illustrative of the data obtained and makes clear the first order nature of the reaction at moderately high glycol concentrations. The values of $k'$ listed in Table 1 are averages of three or more trials. The maximum deviation from the average values was three percent.

Pseudo second order rate constants, $k_{II}$, were determined for experimental part E. The listed values in Table 1 were determined graphically from the graph $\frac{x}{a-x} \text{ vs. } t$, $a$ is the initial concentration of cerate ion and $x$ is the amount of cerate ion consumed at time $t$. The values are averages of three or more trials and have a maximum deviation from the average of less than four percent. Figure 2 is a graphical representation of the data obtained.

Interpretation of Data

The results of experimental part D are interpreted as indicating that perchlorate ion is not coordinated by cerate ion. Figure 3 is a graphical representation of the data illustrating the marked increase in rate with increasing
Figure 1. First order graph $\ln \text{Ce}^{4+}$ vs. $t$; $[\text{H}^+] = 1.0 \text{ N}$, $[\text{Ce}^{4+}] = 0.01 \text{ N}$, $\alpha = 1$.
<table>
<thead>
<tr>
<th>Part A</th>
<th>Part B</th>
<th>Part C</th>
<th>Part D</th>
<th>Part E</th>
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Figure 2. Second order graph $\frac{x}{a-x}$ vs. $t$; $[\text{Ce}^{3+}] = 0.01N$, $[\text{H}] = 0.005N$, $a = 1 a-x$
Figure 3. Graph \( k' \) vs. \( \left[ \text{ClO}_4^- \right] \); \( [H^+] = 1.0 \text{N}, \left[ \text{Ce}^{4+} \right] = 0.01 \text{N}, [G] = 0.05 \text{M}, \mathcal{M} = 1 \)

Figure 4. Graph \( k' \) vs. \( [H^+] \); \( \left[ \text{Ce}^{4+} \right] = 0.01 \text{N}, [G] = 0.07 \text{M}, \mathcal{M} = 1 \)
The data of experimental part C, shown graphically in Figure 4, are sufficient to indicate the reaction is hydrogen ion dependent at low hydrogen ion concentrations. Examination of the graph further indicates that the reaction rate is a linear function of hydrogen ion concentration. These data are interpreted as indicating that hydrated cerium is involved in a hydrolysis equilibrium.

It has been shown that perchlorate ion does not form coordination complexes with tetravalent cerium and that the reaction at low hydrogen ion concentrations is dependent to the first power in hydrogen ion concentrations. The species of cerate involved in the reaction with glycol are
Ce(H₂O)₆ and Ce(OH)(H₂O)₅. Since inclusion of all the equilibrium and rate constants would unnecessarily complicate the kinetics expression for disappearance of cerium (IV), the equation is now developed for use at low glycol concentrations (<0.1M) where it is assumed that only monoglycolated complexes exist. The presence of two species of cerate ion necessitate the proposal of two additional cerium (IV)-glycol complexes, Ce(OH)(H₂O)₃G and Ce(OH) (H₂O)G₂, and an additional non-glycolated cerium (IV), Ce(OH)(H₂O)₅. These must be added to Equation (7) for total cerium (IV) concentration.

The following low glycol concentration equilibrium reactions may occur:

\[
\begin{align*}
\text{Ce}(H_2O)_6 & \rightleftharpoons \text{Ce}(OH)(H_2O)_5 + H^+ & (22) \\
\text{Ce}(H_2O)_6 + G & \rightleftharpoons \text{Ce}(H_2O)_6G + 2H_2O & (23) \\
\text{Ce}(OH)(H_2O)_5 + G & \rightleftharpoons \text{Ce}(OH)(H_2O)_3G + 2H_2O & (24)
\end{align*}
\]

Ce and G have the same meaning as in previous equations. The custom of omitting water concentrations in expressions for equilibrium in aqueous solutions is now adopted giving the following equilibrium constant expressions:

\[
\begin{align*}
K_a &= \frac{[\text{Ce}(OH)(H_2O)_5][H^+]}{[\text{Ce}(H_2O)_6]} & (25) \\
K_{12} &= \frac{[[\text{Ce}(H_2O)_6]G]}{[\text{Ce}(H_2O)_6][G]} & (26)
\end{align*}
\]
The double subscript used in Equations (26) and (27) are easily interpreted; the first number of the subscript refers to the number of glycols coordinated to the cerium in the numerator and the second number refers to the species of cerium, (1) hydroxylated or (2) hydrated. This same system of subscripts is used to identify the rate constants.

The kinetics equation for disappearance of cerate ion at low glycol concentrations assuming only monoglycolated complexes present is:

\[ \frac{dT_{Ce}}{dt} = k_{11} \text{Ce(OH)(H}_2\text{O)}_3G + k_{12} \text{Ce(H}_2\text{O)}_4G \quad (28) \]

The equation for total cerium (IV) concentration is:

\[ T_{Ce} = \text{Ce(H}_2\text{O)}_4^+ + \text{Ce(OH)(H}_2\text{O)}_5^+ + \text{Ce(H}_2\text{O)}_6^+ \quad (29) \]

Use of the same mathematical methods used in the theoretical section for the development of Equation (12), Equation (28) becomes:

\[ \frac{dT_{Ce}}{dt} = \frac{(k_{11}K_{11}K_a/ H^++ k_{12}K_{12}) G}{1 + K_a/ H^+ + K_{11} K_a/ H^+ + K_{12} G} \quad T_{Ce} \quad (30) \]

If it is assumed that at very low glycol concentrations (ca. 0.005M) the term \((k_{11} K_a/ H^+ + K_{12}) G\) is negligible compared to \(1 + K_a/ H^+\), then by analogy with Equation (19)

\[ k_{II} = \frac{k_{11}K_{11} K_a/ H^+ k_{12}K_{12}}{1 + K_a/ H^+} \quad (31) \]
Three values of $k_{I}$ are available from experimental part E which allow the solution of three equations with three unknowns. $K_a$ has the value of 0.09, $k_{12}$ $K_{12}$ the value 0.329, and $k_{11}K_{11}K_3$ very nearly zero (0.0001). Therefore either $k_{11}$ or $K_1$ is negligible. The observation that the rate is independent of hydrogen ion concentration at high glycol concentration indicates that $K_{11}$ is small and the Ce(OH) $(H_2O)_3G$ formed contributes very little toward the total cerium concentration. Since very little Ce(OH)$(H_2O)_3G$ is formed, it is assumed that the diglycolated species of hydroxylated cerium may be neglected.

Making use of the conclusions thus far formulated, Equation (12) becomes:

$$\frac{dT_{Ce}}{dt} = \frac{k_{12}K_{12} G + k_{22}K_{12}K_{22} G^2 + k_{32}K_{12}K_{22}K_{32} G^3}{1 + K/[H^+] + K_{12} G + K_{12}K_{22} G^2 + K_{12}K_{22}K_{32} G} T_{Ce} \tag{32}$$

The values of $k_{12}$ and $K_{12}$ were determined using the value of $k_{12}K_{12}$ obtained in the preceding paragraph in conjunction with a value of $k'$ determined at low glycol concentration, 0.05 M, and assuming the concentration of diglycolated cerium is negligible, $K_{12}$ has the value of 15 and $k_{12}$ is 0.0225 sec.$^{-1}$.

Neglecting polyglycolated cerium (IV) and using the determined values of $K_a$, $k_{12}$ and $k_{12}$, a series of values of $k'$ were calculated for increasing glycol concentration. The calculated values of $k'$ are found to fit experimental data
only at lower glycol concentrations (< 0.12M). Two experimental values of $k'$ for glycol concentrations above the point of deviation were selected and two equations for $k'$;

$$k' = \frac{k_{12}K_{12} [G] + k_{22}K_{12}K_{22} [G]^2}{1 + K_a/[H^+] + K_{12} [G] + K_{12}K_{22} [G]^2}$$  (33)

were solved for $k_{22}$ and $K_{22}$. It was found $k_{22}$ has a value 0.0117 sec.$^{-1}$ and $K_{22}$ a value of 2.3.

The procedure for calculating $k'$ values was repeated using Equation (33) and it was found that the postulation of triglycolated cerium complexes was not necessary to fit experimental data.

In view of the uncertainties encountered in the experimental determination of pseudo rate constants, the values of rate constants and equilibrium constants are assigned the limits of error in Table 2.

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
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<tbody>
<tr>
<td>$K_a = 0.09 \pm 0.02$</td>
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<tr>
<td>$K_{12} = 15 \pm 1$</td>
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<tr>
<td>$K_{22} = 2.3 \pm 0.4$</td>
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<td>$k_{12} = .0225 \pm .0010$ sec.$^{-1}$</td>
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<tr>
<td>$k_{22} = .0117 \pm .0020$ sec.$^{-1}$</td>
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Figure 5 is the graphical representation of the results from Parts A and B. The solid lines are those calculated from values tabulated in Table 2 with Equation (33). The circles represent experimental values.
Figure 5. Graph $k^*$ vs. $[G]$; $[Ce^{+k}] = 0.01, \mu = 1$
DISCUSSIONS AND CONCLUSIONS

The role of coordination complexes in oxidation reactions can be conveniently divided into two parts: complex formation of oxidant or reductant with inert ions or molecules in the solution may result in either an increase or a decrease in the overall reaction rate, and complex formation of oxidant with reductant preceding the reaction.

The retarding effect due to complex formation of oxidant or reductant with inert ions or molecules is supported by many authors. At low hydrogen ion concentration, the periodate oxidation of ethylene glycol proceeds very slowly. Duke (18) attributes this to the displacement of water from periodate by hydroxyl ion which is held more strongly to periodate than water. Slack and Waters (71) found that in glacial acetic acid, the chromate oxidation of glycol did not go to completion due to formation of a chromic-chromate-acetate complex. Howells (38) concluded that when cadmium ion was present during the oxidation of iodide by persulfate, the reaction was greatly retarded by formation of the complex CdI₄⁻².

In contrast, the complex formation with inert molecules or ions may increase the overall reaction rate and in some cases is necessary for the reaction to occur. Gorin (30)
found that hydrated ferric ion in aqueous solution reacted very slowly with tin (II) but if one or two of the water molecules were replaced by hydroxyl ion, the reaction proceeded more rapidly. An example of the necessity of complex formation of a non-oxidizable body is offered by the iodine-azide reaction. Iodine and azide ion present in solution without a sulfidic sulfur compound or ion do not react to any measurable extent. Addition of a sulfidic sulfur compound causes the reaction to proceed smoothly and rapidly. It is proposed that this is due to formation of a complex of azide ion and sulfidic sulfur compound followed by reaction with iodine.

Complex formation of oxidant with reductant has been shown to occur in a number of reactions. It is proposed that in homogeneous oxidation reactions, complex formation is a necessary condition for an oxidation to occur. That complex formation of oxidant with reductant is a necessary condition has not been completely accepted. A large number of publications concerning reaction mechanisms propose second order reactions of the type:

\[ A + B \rightarrow \text{products} \]

A mechanism could equally well be proposed in which rapid equilibrium be established between A, B and a complex (AB) followed by the disproportionation of (AB). The experimental section of this thesis includes an illustration of how this reaction can lead to a second order kinetics expression.
SUMMARY

Careful examination of the literature has revealed a number of reactions which have been studied for the purpose of proposing a mechanism. The reactions surveyed are: the trivalent manganese-oxalate reaction, the periodate oxidation of polyalcohols, chromic acid oxidation, the iodine-azide reaction, decomposition of thiosulfate ion, the persulfate-iodide reaction, the reduction of iron (III), cerate oxidation of organic compounds, sodium and potassium tungstate decomposition of hydrogen peroxide, oxidation of ferrous salts by nitric oxide, oxygen oxidation of tin (II), ferricyanide oxidation of nitrogen containing compounds, oxidation of acetone by selenious acid, copper (II) oxidation of oxide ion, copper (II) decomposition of hydrogen peroxide and oxidation of titanium (III) by iodine. Complex formation was proposed in all these reactions.

The cerate oxidation of meso-2,3 butanediol in perchlorate solutions was examined in detail. The experimental data were interpreted to indicate that cerate ion did not coordinate perchlorate ion but coordinated hydroxyl ion at low hydrogen ion concentration, and that di- and triglycolated cerate complexes were involved in the oxidation.

Evidence was presented that coordination of inert ions or molecules in solution may retard or hasten the overall
rate and that in some cases, coordination of an inert ion or molecule may be necessary for the reaction to occur.

The proposal was made that complex formation of oxidant with reductant is a necessary condition for the oxidation reaction to occur. It was shown in the interpretation of experimental data that a second order kinetics expression can be derived for a reaction which is actually a unimolecular disproportionation of an intermediate complex.
LITERATURE CITED

1. Abel, E., Monatsh., 81, 955 (1950)
3. Baudisch, O., Ber., 68B, 769 (1935)
15. Crieger, R., Kraft, L. and Rank, B., Ann., 507, 159 (1933)
27. Fleury, P. and Lange, J., *Compt. rend.*, 195, 1395 (1932)
50. Malprade, L., *Bull. soc. chim.*, 6, 223 (1939); *C.A.*, 33, 8518 (1939)
74. Snethlage, H. C. S., *Rec. trav. chim.*, 59, 111 (1940); 
   *C. A.*, 34, 3570 (1940)

75. Snethlage, H. C. S., *Rec. trav. chim.*, 60, 877 (1941); 
   *C. A.*, 37, 3424 (1943)

76. Snethlage, H. C. S., *Rec. trav. chim.*, 61, 213 (1942); 
   *C. A.*, 37, 4294 (1943)

77. Sommer, F., *Ber.*, 48, 1833 (1915)

78. Spitalsky, E. and Koboseff, N., *Z. physik Chem.*, 127, 
   (1927)


82. Timofeev, W. F., Muchen, G. E. and Gurewitch, W. G., 
   *Z. physik. Chem.*, 115, 161 (1925)


   506 (1943)

   1181 (1926)
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