# FURTHER ADVANCES IN THE STUDY OF MECHANISMS OF REDOX REACTIONS

A. G. Sykes

Department of Chemistry, The University, Leeds, England

## I. Introduction

Since the first review in this series by Taube (*377*), and in part no doubt as a direct result of it, there has been considerable interest in the field of oxidation-reduction reactions. Some attempt is made here to present an up-to-date account of the subject with particular reference to work reported during the last eight years. Other reviews concerned with various aspects of the field are by Stranks (*346*), Halpern (*181*), Sutin (*359*, *361*), Marcus (*253*), and Strehlow (*350*).

The present review is concerned with reactions of metal ions in which the oxidation state of the metal ion changes as a result of the reaction. Such reactions are believed to occur by an electron-transfer process, although in some cases at least atom transfer may be a possibility. Some of the questions which arise are, first of all, if the reaction is other than a straightforward single-stage process, what are the elementary steps which together account for the overall reaction? At the time of electron transfer, how close together are the two reactants, and is the reaction of the inner- or outer-sphere type? If a reaction is of the inner-sphere type (the metal ions have a ligand in common in the activated complex), what effect do different bridging groups have, and is the same reactivity pattern observed with other metal ion reactants? What effect do non-bridging ligands have? Is there any evidence for the interpenetration of coordination spheres in outer-sphere reactions? Do the rate constants observed agree with calculated values, and is the simultaneous or near-simultaneous transfer of two electrons possible?

A wide range of experimental techniques has been used to study redox reactions. For exchange reactions isotopic labeling techniques are used whenever possible, and in a few special cases it has been possible to follow the exchange by measuring the change in optical rotation. The faster exchange reactions can in some cases be studied by NMR and ESR methods. For the slower reactions in which there is a net chemical change conventional spectrophotometric techniques are generally preferred, but volumetric and electrometric methods have also been used. The faster reactions may be studied by polarographic, stopped-flow, and relaxation techniques. The latter finds less use for redox reactions, since (if spectrophotometric techniques are to be used) an essential requirement is that the reaction should have a measurable equilibrium position, and in only relatively few instances is this possible. Further details of these various methods can be found elsewhere (*346, 366*). For a comprehensive survey of the methods used for fast reactions, the reader is referred the recent text on "Fast Reactions in Solution" by Caldin (*72*).

Abbreviations which are used are of the standard type. Thus for the ferric ion the formula $Fe^{III}$ is generally used to refer to the total ferric present, i.e., $Fe^{3+} + FeOH^{2+}$, etc., it being understood that $Fe^{3+}$ is in fact the hexaquo ion $Fe(H_2O)_6^{3+}$ and that $FeOH^{2+}$ is $Fe(H_2O)_5OH^{2+}$, etc.

## II. One-Equivalent Exchange Reactions

One-equivalent electron-exchange reactions constitute a relatively simple class of chemical reaction in that the reactants and products are identical, there is no free energy change, and in the case of outer-sphere reactions no chemical bonds are made or broken. As in other reactions, however, activation free energy requirements must be met for the reaction to proceed, and these requirements vary appreciably from one reaction to another.

The exchange is generally studied by isotopic labeling of one of the reactants, e.g.,

$$Fe^{2+} + {}^{*}Fe^{3+} \rightleftharpoons Fe^{3+} + {}^{*}Fe^{2+}$$

the approach of an equilibrium, $K = 1$, being measured. Rate constants are evaluated, using the McKay equation,

$$\log_{10}(1 - F) = -\frac{kt}{2.303}(a + b) \tag{1}$$

where $a$ and $b$ are the reactant concentrations, and $F$ is the fraction of exchange at a time $t$.

## A. Transition Metal Ions

Exchange reactions between the II and III oxidation states of iron, chromium, and cobalt have been extensively studied, and provide much of the material for this section. Other reactions which have been studied include the exchange of vanadium(II) with vanadium(III), vanadium(III) with vanadium(IV), manganese(VI) with manganese(VII), and silver(I) with silver(II). The systematic study of other reactions which are referred to has, for a variety of reasons, proved more difficult.

Although the reaction of iron(II) with iron(III) was one of the first isotopic exchange reactions to be studied, details of the mechanism, whether inner- or outer-sphere, remain for the most part uncertain. This is largely because the inner-coordination spheres of both $Fe^{II}$ and $Fe^{III}$ aquo ions are labile, so that the exact composition of these immediately before and after the exchange is difficult to determine.

When the exchange is studied in aqueous perchloric acid solutions in the absence of catalytic anions,[1] the rate may be expressed as

$$\text{Rate} = k_{obs}[\text{Fe}^{II}][\text{Fe}^{III}] \tag{2}$$

where $k_{obs}$ shows an inverse dependence on the hydrogen-ion concentration (*341*):

$$k_{obs} = a + b[\text{H}^+]^{-1} \tag{3}$$

This expression suggests that there are two paths for exchange:

$$\text{Fe}^{2+} + \text{Fe}^{3+} \rightarrow \tag{4}$$

$$\text{Fe}^{2+} + \text{FeOH}^{2+} \rightarrow \tag{5}$$

If reaction (5) is of the inner-sphere type (with symmetrical $OH^-$ bridging), then it can be assumed that the $Fe^{2+}$–$FeOH^{2+}$ path is relevant

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[1] The perchlorate ion is a poor donor group and is the least complexing of common anions. With transition metal ions at least interactions with $ClO_4^-$ are probably of the outer-sphere type, as in the case of $Fe^{3+}$ (*373*), and it is unlikely that these play an important part in redox reactions. In more concentrated perchlorate solutions (> 3 *M* say), inner-sphere complexes may well be formed and may be important. In 5–10 *M* perchloric acid, for example, there is evidence for the formation of a perchloratochromium(III) complex (*224*).

rather than the $FeOH^+$–$Fe^{3+}$ path since the acid dissociation constant for $Fe^{3+}$ ($K_d \sim 10^{-3}$) is much greater than that for $Fe^{2+}$ ($K_d \sim 10^{-6}$). The product of the concentration terms $[Fe^{2+}][FeOH^{2+}]$ is therefore much larger than the product $[FeOH^+][Fe^{3+}]$, and as long as the rate constants for the two paths are not widely different the $Fe^{2+}$–$FeOH^{2+}$ path will predominate. If anything, the rate constant for the $FeOH^+$–$Fe^{3+}$ path is probably smaller since the $FeOH^+$ ion has first to substitute into the coordination sphere of the $Fe^{3+}$ ion, and $\Delta G^\ddagger$ is probably $> 10$ kcal mole$^{-1}$ for such a reaction. If, on the other hand, the reaction is of the outer-sphere type, then using the principle of balanced states (*324*, p. 32) it is possible that the rates $k[Fe^{2+}][FeOH^{2+}]$ and $k'[FeOH^+][Fe^{3+}]$ will be equal (i.e., $k' \gg k$). In short, although the $Fe^{2+}$–$FeOH^{2+}$ path is generally assumed relevant, the possibility that under certain conditions the $FeOH^+$–$Fe^{3+}$ path may make a significant contribution should not be overlooked. Similar reasoning applies to other reactions and to reactions studied in the presence of anions $X^-$. In Eq. (3) the rate constant $k_{obs}$ may be expressed as

$$k_{obs} = k_1 + k_2 K_d[H^+]^{-1} \tag{6}$$

where $K_d$ is the acid dissociation constant for $Fe^{3+}$:

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \tag{7}$$

If $K_d$ is known, both the *true* rate constants $k_1$ and $k_2$ may be evaluated.

When the exchange is studied in the presence of anions other than $ClO_4^-$, there is almost invariably an increase in rate and further terms in $[X^-]$ are obtained in the rate equation. If other than small quantities of $X^-$ are used, terms in $[X^-]^2$ and higher powers of $[X^-]$ have to be considered, and under these conditions the $Fe^{II}$ may play some part in bringing anions into the activated complex. Reaction paths having a first-order dependence in $[X^-]$ can be interpreted in terms of $FeX^{2+}$ participation, where the reaction sequence is believed to be:

$$Fe^{3+} + X^- \rightleftharpoons FeX^{2+} \qquad (K_a) \tag{8}$$

$$Fe^{2+} + FeX^{2+} \xrightarrow{k_3} \text{products} \tag{9}$$

If the equilibrium in Eq. (8) is rapid, the expression for $k_{obs}$ is:

$$k_{obs} = \frac{k_1 + k_2 K_d[H^+]^{-1} + k_3 K_a[X^-]}{1 + K_a[X^-]} \tag{10}$$

In the fluoride-catalyzed reaction, Menashi *et al.* (*261*) have obtained evidence for a reaction sequence as in Eqs. (8) and (9). By using a large excess of ferrous it was possible to make the isotopic exchange rate comparable to the rate of formation of the inner-sphere complex $FeF^{2+}$.

Under these conditions the exchange rate was found to be dependent on the rate of formation of $FeF^{2+}$, as is to be expected if the reactants are $Fe^{2+}$ and $FeF^{2+}$, but not if the fluoride is brought into the activated complex by the ferrous, or in the form of an ion-pair complex $Fe(H_2O)_6^{3+} \cdot F^-$. This does not mean that the reaction is necessarily of the inner-sphere type, however, or that the fluoride is a bridging ligand.

TABLE I

KINETIC DATA FOR $Fe^{II}$–$Fe^{III}$ EXCHANGE REACTIONS

(AT 0° AND $\mu = 0.55\ M$)

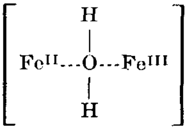
| Reaction | $k$ ($l \cdot mole^{-1}\ sec^{-1}$) | $\Delta H^\ddagger$ ($kcal\ mole^{-1}$) | $\Delta S^\ddagger$ (eu) | Reference |
|---|---|---|---|---|
| $Fe^{2+} + Fe^{3+}$ [a] | 0.87 | 9.3 | −25 | *(341)* |
| $Fe^{2+} + FeOH^{2+}$ [a] | $1.1 \times 10^3$ | 6.9 | −18 | *(341)* |
| $Fe^{2+} + FeF^{2+}$ | 9.7 | 8.6 | −21 | *(213)* |
| $Fe^{2+} + FeCl^{2+}$ [b] | 5.4 | 11.0 | −15 | *(362)* |
| $Fe^{2+} + FeBr^{2+}$ | 4.9 | 8.0 | −25 | *(204)* |
| $Fe^{2+} + FeNCS^{2+}$ [c] | 4.2 | 9.2 | −21 | *(205)* |
| $Fe^{2+} + FeN_3^{2+}$ | $1.9 \times 10^3$ | 13.3 | 7 | *(68)* |
| $Fe^{2+} + FeF_2^+$ | 2.5 | 9.0 | −22 | *(213)* |
| $Fe^{2+} + FeCl_2^+$ | 15 | 9.7 | −20 | *(341)* |

[a] Fukushima and Reynolds *(144)* have redetermined kinetic data for these reactions and there is essentially good agreement.

[b] More than one activated complex is involved *(73)*.

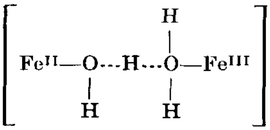
[c] Previous data of Laurence *(247)* may be less precise *(209)*.

Rate constants and activation parameters for a number of $Fe^{II}$–$Fe^{III}$ reactions are shown in Table I. Because there is so little variation in rate constants for $X^- = F^-$, $Cl^-$, $Br^-$, and $NCS^-$, compared to reactions of $Cr^{2+}$ with $CrX^{2+}$, which are known to be inner-sphere with $X^-$ the bridging ligand, it has been argued that some or all of the $Fe^{II}$–$Fe^{III}$ reactions must proceed by an alternative mechanism. One possibility is that water molecules bridge the two reactants as in either (I) or (II), and that $X^-$ plays a relatively minor role as a nonbridging ligand. The



$$\left[\mathrm{Fe^{II}\cdots\overset{H}{\underset{H}{O}}\cdots Fe^{III}}\right]$$

(I)



$$\left[\mathrm{Fe^{II}-\underset{H}{O}\cdots H\cdots\overset{H}{\underset{H}{O}}-Fe^{III}}\right]$$

(II)

first of these, at least, now seems unlikely, since in recent work (*56*, *300*) it has been shown that nonbridging anions can have a marked effect on rate constants. The suggestion that in (II) there is H-atom transfer between the $Fe^{2+}$ and $Fe^{3+}$ coordination spheres, with the formation of $FeOH^{2+}$ and $FeH_3O^{3+}$, is unlikely on energetic grounds (higher activation energies of $\sim 20$ kcal mole$^{-1}$ would be expected) (*181*), but that there is H-atom bridging as in (II) is not unreasonable (*213*).

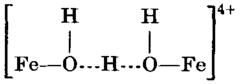
That the rate constants for the $Fe^{2+}$–$Fe^{3+}$ and $Fe^{2+}$–$FeOH^{2+}$ reactions are lowered by a factor of about 2 in $D_2O$ (*212*) was thought to be evidence supporting a hydrogen-atom bridging mechanism. A similar effect has been observed for the $Fe^{2+}$–$FeCl^{2+}$ reaction (*362*). Doubts were expressed about this approach when a $k_{H_2O}/k_{D_2O}$ ratio of 1.3 was found for the $Cr^{2+}$–$Co(NH_3)_5Cl^{2+}$ reaction (*414*), which is known to proceed by an inner-sphere mechanism with chloride bridging. Since, moreover, the $D_2O$ isotope effect on the equilibrium

$$Fe^{3+} + Cl^- \rightleftharpoons FeCl^{2+} \tag{11}$$

is of the same order of magnitude (*362*), clearly this type of evidence is not conclusive. The acid dissociation constant for the reaction

$$Fe^{3+} + D_2O \rightleftharpoons FeOD^{2+} + D^+ \tag{12}$$

also differs from that in $H_2O$, and activation parameters for the reaction between $Fe^{2+}$ and $FeOD^{2+}$ have been shown to be $\Delta H^\ddagger = 11.5 \pm 0.5$ kcal mole$^{-1}$ and $\Delta S^\ddagger = -4.0 \pm 1.8$ eu (*144*). Since these values differ significantly from those for the reaction between $Fe^{2+}$ and $FeOH^{2+}$, it might in this one instance be argued that they provide evidence for a H-atom bridging mechanism with an activated complex:



$$\left[\begin{array}{c} \phantom{Fe—}\overset{\displaystyle H}{\overset{|}{O}}\cdots H\cdots\overset{\displaystyle H}{\overset{|}{O}}\phantom{—Fe} \\[-1.2em] Fe—\phantom{O}\cdots\phantom{H}\cdots\phantom{O}—Fe \end{array}\right]^{4+}$$

Until more is known of $D_2O$ and $H_2O$ solvent effects the importance of these results is difficult to assess. Other redox reactions which have been studied in $D_2O$ are listed in Halpern's review (*181*).

The use which Sutin and co-workers in particular have made of the stopped-flow method to demonstrate inner-sphere mechanisms is illustrated by their work on the $Fe^{2+}$–$Fe^{3+}$–$Cl^-$ system (*73*). In the first series of experiments the ferrous-catalyzed dissociation (i.e., aquation) of $FeCl^{2+}$ was studied. The rate equation is

$$k_d = k_1 + k_2[H^+]^{-1} + k_3[Fe^{2+}] \tag{13}$$

where $k_1$ and $k_2$ correspond to substitution processes, and $k_3$ to an electron-transfer process which results in the dissociation of the chloride.

At 25° and ionic strength $\mu = 3.0\ M$, $k_1 = 1.1\ \text{sec}^{-1}$, $k_2 = 3.4\ \text{sec}^{-1}$, and $k_3 = 12.1\ \text{l·mole}^{-1}\ \text{sec}^{-1}$. For $k_3$ the activated complex $[\text{FeClFe}]^{4+}$ cannot be effective, since it would almost certainly result in the transfer of the chloride to the newly formed ferric and there would be no dissociation. In the second series of experiments the isotopic exchange reaction was studied under identical conditions and in the presence of chloride, and $k_4$ for the chloride-dependent exchange was found to be 57.6 $\text{l·mole}^{-1}\ \text{sec}^{-1}$. From the difference between $k_4$ and $k_3$ it can be concluded that ~ 65% of the exchange is by the inner-sphere mechanism with an activated complex $[\text{FeClFe}]^{4+}$. The other 35% of the reaction (which corresponds to the $\text{Fe}^{2+}$-catalyzed dissociation of $\text{FeCl}^{2+}$) may be accounted for by either inner- or outer-sphere paths. Other inner-sphere activated complexes which are probably relevant are $[\text{FeH}_2\text{OFeCl}]^{4+}$ and $[\text{FeOHFeCl}]^{3+}$ (*423*). A similar study has been made of the $\text{Fe}^{2+}$-catalyzed dissociation of $\text{FeNCS}^{2+}$ (*418*).

TABLE II

A COMPARISON OF DATA FOR THE $\text{Fe}^{\text{II}}$–$\text{Fe}^{\text{III}}$ EXCHANGE CATALYZED BY SULPHATE AT 25°

| $\mu M$ | $k_1$ ($\text{l·mole}^{-1}\ \text{sec}^{-1}$) | $k_2$ ($\text{l·mole}^{-1}\ \text{sec}^{-1}$) | Reference |
|---|---|---|---|
| 0.25 | 693 | 19,400 | (*322*) |
| 0.50 | 346 | — | (*403*) |
| 0.75 | 586 | 20,700 | (*322*) |
| 1.00 | 295 | 17,500 | (*33*) |
| 1.00 | 360 | — | (*403*) |
| 1.00 | 515[a] (*760*) | — | (*337*) |
| 1.00 | 540[b] | — | (*322*) |

[a] Recalculated by Reynolds and Lumry (*324*) using improved values of $K_1$ and $K_a$.

[b] Extrapolated by Reynolds and Lumry (*324*) from data obtained by Reynolds and Fukushima (*322*) at various $\mu$ values.

In 1963 four independent studies of the sulfate-catalyzed exchange between $\text{Fe}^{\text{II}}$ and $\text{Fe}^{\text{III}}$ were reported (*33*, *322*, *337*, *403*). Terms in $[\text{SO}_4^{2-}]$ and $[\text{SO}_4^{2-}]^2$ were identified and these are believed to correspond to the reaction paths:

$$\text{Fe}^{2+} + \text{FeSO}_4{}^{+} \xrightarrow{k_1} \tag{14}$$

$$\text{Fe}^{2+} + \text{Fe[SO}_4]_2{}^{-} \xrightarrow{k_2} \tag{15}$$

That $k_1$ values show considerable variation (Table II) would seem to be in some part due to the different values of the association constants for the reactions

$$Fe^{3+} + SO_4^{2-} \rightleftharpoons FeSO_4^+ \qquad (K_1) \tag{16}$$

$$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^- \qquad (K_a) \tag{17}$$

which were used, and those used by Sheppard and Brown (*337*) would seem to be particularly suspect. Because Willix (*403*) neglects contributions to the exchange from the $[SO_4^{2-}]^2$ path, his activation parameters for $k_1$ ($\Delta H^\ddagger = 9.0$ kcal mole$^{-1}$ and $\Delta S^\ddagger = -19$ eu) are probably less reliable than these of Bächmann and Leiser (*33*) ($\Delta H^\ddagger = 13.8$ kcal mole$^{-1}$ and $\Delta S^\ddagger = -1.2$ eu). Reynolds and Fukushima (*322*) have identified a further term in the rate equation which is dependent on $[SO_4^{2-}]$ and the inverse hydrogen-ion concentration. They suggest that the reaction is between $FeSO_4$ and $FeOH^{2+}$, but the reaction of $Fe^{2+}$ with $Fe(OH)SO_4$ is also a possibility.

The exchange in the presence of azide is of particular interest, and at present quite unique in that the Arrhenius plot is curved at temperatures greater than 13° (*68*). Below 13° the rate-determining step may be the substitution process leading to the formation of an inner-sphere complex $[Fe{-}N{=}N{=}N{-}Fe]^{4+}$ from $Fe^{2+}$ and $FeN_3^{2+}$, while above this temperature the rate of decomposition of the complex and electron exchange may be comparable. Halpern and Orgel (*188*) and Wilkins and Eigen (*401*) have considered the possibility that in some reactions the formation of a bridged intermediate (rather than electron transfer within the intermediate) may be rate-determining.

Oxalate ions have a strong catalytic effect, the rate constant for the $Fe^{2+}$–$FeC_2O_4^+$ exchange being of the order of $2 \times 10^3$ l·mole$^{-1}$ sec$^{-1}$ at 20°, but again there is a lack of agreement between two sets of activation parameters (*206*, *337*). With tartrate ions the reaction between $Fe^{2+}$ and $Fe(HTar)_2^+$, and not $Fe^{2+}$ and $Fe(HTar)^{2+}$, has been shown to predominate (*258*). Phosphate (*337*), acetate, succinate, and phenolate ions and silver foil also catalyze the exchange (*206*), but benzoic and *o*-phthalic acids have little effect probably because they are only weakly ionized (*206*). Fumaric acid has no catalytic effect when present in concentrations equivalent to those of the $Fe^{II}$ and $Fe^{III}$ (*258*).

The exchange between $FeEDTA^{2-}$ and $FeEDTA^-$ is fast (*6*), and an outer-sphere mechanism seems likely, although partial dissociation of the complexes cannot be excluded since both ions are spin-free. In the exchange of $Fe^{2+}$ with $FeEDTA^-$ a carboxyl group of the EDTA may act as a bridging group, although it is not transferred to the newly formed ferric ion:

$$Fe^{II} + FeEDTA^- \rightarrow Fe^{III} + FeEDTA^{2-} \tag{18}$$

The slow rate $k \leqslant 4.0 \times 10^{-4}\ \mathrm{l \cdot mole^{-1}\ sec^{-1}}$ reflects the unfavorable free energy change of 15 kcal $\mathrm{mole^{-1}}$ for this reaction (*323*).

The hexacyano, tris(1,10-phenanthroline), and tris(bipyridyl) complexes of iron(II) and iron(III) are all spin-paired, and as a result are inert to substitution. Since electron transfer between such reactants is generally rapid, and the coordination spheres remain intact, it can be concluded that reactions are of the outer-sphere type. That the reactions are rapid is probably related to the fairly extensive delocalization of electrons from the central metal atom. The kinetics of the isotopic-exchange reaction between ferrocyanide and ferricyanide ions have been studied in potassium hydroxide and tetraphenylarsonium hydroxide ($\phi_4$AsOH) solutions (*234*). In the latter the reaction is first order in $\mathrm{Fe(CN)_6^{3-}}$, but the dependence of the rate on the concentration of $\mathrm{Fe(CN)_6^{4-}}$ is affected by the nature and concentrations of cations present. In the presence of $2.5 \times 10^{-4}$ *M* EDTA (to complex cationic impurities) and with 0.01 *M* $\phi_4$AsOH, the expression

$$\mathrm{Rate} = k[\mathrm{Fe(CN)_6^{4-}}][\mathrm{Fe(CN)_6^{3-}}] \tag{19}$$

is obeyed and $k = 28\ \mathrm{l \cdot mole^{-1}\ sec^{-1}}$ at 0.1°. The rate has been shown to increase with the first power of $[\phi_4\mathrm{As^+}]$,

$$\mathrm{Rate} = k'[\mathrm{Fe(CN)_6^{4-}}][\mathrm{Fe(CN)_6^{3-}}][\phi_4\mathrm{As^+}] \tag{20}$$

$k'$ having a value of 2800 $\mathrm{l^2 \cdot mole^{-2}\ sec^{-1}}$ at 0.1°. In 0.01 *M* KOH rates are much faster than in 0.01 *M* $\phi_4$AsOH, and, at 0.1°, $k$ as defined in Eq. 19 is $356\ \mathrm{l \cdot mole^{-1}\ sec^{-1}}$. On varying the concentration of potassium ions, the rate equation has been shown to be of the form:

$$\mathrm{Rate} = [\mathrm{Fe(CN)_6^{3-}}][\mathrm{Fe(CN)_6^{4-}}]\frac{k_1K_1[\mathrm{K^+}] + k_2K_1K_2[\mathrm{K^+}]^2}{1 + K_1[\mathrm{K^+}] + K_1K_2[\mathrm{K^+}]^2} \tag{21}$$

The terms in $[\mathrm{K^+}]$ and $[\mathrm{K^+}]^2$ correspond to reactions of $\mathrm{KFe(CN)_6^{3-}}$ and, in all probability, $K_2\mathrm{Fe(CN)_6^{2-}}$. Further details of these various studies have now been published (*417*). The rate of exchange has also been determined by measuring the nitrogen-14 NMR line width (*339*). With the addition of cations the rate increases in going from $\mathrm{H^+}$ to $\mathrm{Cs^+}$ and from $\mathrm{Mg^{2+}}$ to $\mathrm{Sr^{2+}}$ (*339*).

Isotopic exchange and NMR line-broadening techniques have also been used to determine the lower limit of the rate constant for the exchange between $\mathrm{Fe(phen)_3^{2+}}$ and $\mathrm{Fe(phen)_3^{3+}}$ ($k > 1 \times 10^5\ \mathrm{l \cdot mole^{-1}\ sec^{-1}}$ at 0°) (*105*), and a similar high value is expected for the reaction between $\mathrm{Fe(bipy)_3^{2+}}$ and $\mathrm{Fe(bipy)_3^{3+}}$. With four complexes having methyl substituted 1,10-phenanthroline ligands the rate constants are all $> 10^5$

$l \cdot mole^{-1} sec^{-1}$ at 25° (*246*), and there is no suggestion of steric hindrance by the methyl groups.

The $Fe^{II}$–$Fe^{III}$ exchange has been studied in a number of nonaqueous solvents. In nitromethane (*250*) and anhydrous alcohols (*207*, *358*) exchange is extremely slow, which suggests that water may play a specific role in the reaction. Horne (*207*) has also studied the exchange in mixed water-acetone, water-methanol, and water-ethanol media, and finds the activation energy for exchange to be the same as in aqueous solutions. The decrease in rate with the decrease in concentration of water is consistent with the H-atom bridging mechanism. In dioxane and allyl alcohol the iron(II) component is rapidly oxidized by the solvent (*207*).

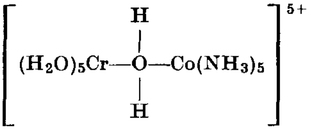
In dimethyl sulfoxide (DMSO), Menashi *et al.* (*262*) report a fairly rapid rate of exchange. In the absence of added water the reaction is independent of the hydrogen-ion concentration, and only when the mole fraction of water is greater than 0.05 is there a decrease in rate constants with the addition of increasing amounts of acid. This suggests that, in the absence of water, exchange is between iron(II) and iron(III) species containing only DMSO in their coordination spheres. Hydrogen-atom bridging is hardly a possibility, since it would involve hydrogen atoms of the methyl groups, and the mechanism is probably outer-sphere or inner-sphere with a sulfur-oxygen bridge between the two metal ions (*262*). It is surprising (and possibly a coincidence) that the activation parameters for the reaction in DMSO are approximately equal to those in water. Chloride ions catalyze the exchange (*391*) and, since there is evidence for inner-sphere complexing of the chloride to the ferric, the most likely paths for exchange are of $Fe(DMSO)_6^{2+}$ with $Fe(DMSO)_5Cl^{2+}$ and $Fe(DMSO)_4Cl_2^{+}$, respectively. In the first of these the rate is the same as in water (suggesting a similar mechanism), but with $Fe(DMSO)_4Cl_2^{+}$ the rate is approximately 3.5 times faster in DMSO.

An exchange which proceeds rapidly in nonaqueous solvent is that between $Fe(C_5H_5)_2$ and $Fe(C_5H_5)_2^{+}$. In acetone the rate constant is $> 1 \times 10^5$ $l \cdot mole^{-1} sec^{-1}$ at 26° (*105*), while in methyl alcohol $k$ is $> 7 \times 10^6$ at 25° and $9 \times 10^5$ at −75° (*347*).

Recent work on the $Fe^{II}$–$Fe^{III}$ exchange in a solid ice matrix (*205*, *208*) is more difficult to explain in terms of compact inner- or outer-sphere mechanisms, since the $Fe^{2+}$ and $Fe^{3+}$ ions are rigidly held in the lattice. Exchange occurs even when the reactants are on an average 100 Å apart, and H-atom transfer by a Grotthus mechanism would seem to be a possible explanation. Because the Arrhenius plot is a continuation of that observed in the liquid phase, it can be argued that a similar mechanism must be effective in the liquid phase. The same behavior is observed in 7.5 $N$ perchloric acid over the temperature range 0° to −84° (*47*) and, since the latter is a perchloric acid/water eutectic mixture, a phase separation seems unlikely. Chloride ions have no effect on the rate of exchange in ice (*208*). In a further study (*424*) some difficulty was experienced in obtaining reproducible results.

Information regarding the closeness of approach of the reactants in the exchange between chromium(II) and chromium(III) species is generally easier to obtain, because the chromium(III), but not the chromium(II), is inert to substitution. For the exchange in aqueous perchloric acid solutions there is an inverse hydrogen-ion dependence (*22*), which is consistent with a reaction of $Cr^{2+}$ with $CrOH^{2+}$. The hydrogen ion-independent path makes little or no contribution ($k \leqslant 2 \times 10^{-5}$ l·mole$^{-1}$ sec$^{-1}$ at 25°). Although it has yet to be demonstrated that the hydroxide ion is transferred to the newly formed chromium(III), there seems little doubt that this is so, as in the reaction of $Cr^{2+}$ with $Co(NH_3)_5OH^{2+}$ (*244*).

It is not easy to explain why the reaction of the two hexaquo ions should not be more effective, as it is in the exchange of iron(II) with iron(III) (*341*), cobalt(II) with cobalt(III) (*171*), and vanadium(II) with vanadium(III) (*242*). Reactions between two hexaquo ions are often assumed to be of the outer-sphere type, in which case it may simply be a reluctance of the $Cr^{2+}$ and $Cr^{3+}$ to react by an outer-sphere mechanism. In the reaction of $Cr^{2+}$ with $Co(NH_3)_5H_2O^{3+}$, the water molecule is known to bridge the two metal ions in the intermediate (*244*),



$$\left[ (H_2O)_5Cr\text{—}\overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{O}}}\text{—}Co(NH_3)_5 \right]^{5+}$$

and there seems at first no obvious reason for excluding the inner-sphere path in the case of the $Cr^{2+}$–$Cr^{3+}$ reaction. Once an intermediate of the above type has formed, it might be expected to lose a proton fairly rapidly, to give a hydroxo-bridged intermediate which is more stable. If this is the case a possible explanation for the absence of a significant $Cr^{2+}$–$Cr^{3+}$ path is that the binuclear intermediate (with a water molecule as a bridging group) might tend (a) to revert to mononuclear ions or (b) to lose a proton before electron transfer can occur. The former would seem to be a particularly strong possibility with $Cr^{2+}$ since this ion is so very labile (*103*, *263*). In the reaction of $Cr^{2+}$ with $Co(NH_3)_5H_2O^{3+}$, electron transfer may be more rapid once a binuclear intermediate has formed (with $H_2O$ or $OH^-$ as a bridging group) due to the more favorable overall free energy change.

In the exchange between $Cr^{2+}$ and $CrX^{2+}$ species (Table III), transfer of the $X^-$ to the newly formed chromium(III) has been demonstrated:

$$^{*}Cr^{2+} + CrX^{2+} \rightarrow (^{*}CrXCr)^{4+} \rightarrow {}^{*}CrX^{2+} + Cr^{2+} \qquad (22)$$

Since the net effect of exchange is the transfer of an X atom, these reactions are sometimes referred to as atom-transfer reactions. This term is perhaps best avoided, however, because the function of the bridging group is uncertain. Possibilities which have been considered by Halpern and Orgel (*188*) are that the bridging group (a) helps to bring the metal ions closer together so that a direct exchange between overlapping metal orbitals can occur (*direct exchange*), (b) provides vacant orbitals which serve to delocalize electrons on the metal ions and hence help in their migration (*superexchange*), (c) assists in electron transfer by accepting an electron from the reductant and at the same time losing an electron to the oxidant (*double exchange*), and (d) assists electron transfer by being temporarily oxidized or reduced (*chemical mechanism for exchange*). Transfer of the bridging group need not necessarily accompany electron transfer, however, and in one case at least it has been reported that the bridging group remains attached to the same metal ion throughout. The case in point is in the reaction of $Cr^{2+}$ with $IrCl_6^{2-}$ (*272*). An intermediate $IrCl_6^{2-}$ is believed to be formed but $Cr^{3+}$ and $IrCl_6^{3-}$ are the final products.

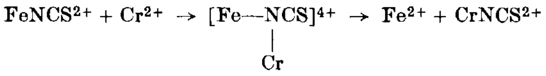
TABLE III

KINETIC DATA FOR $Cr^{II}$–$Cr^{III}$ EXCHANGE REACTIONS

| Reaction | Temp. (°C) | $k$ ($l \cdot mole^{-1} sec^{-1}$) | $\Delta H^{\ddagger}$ (kcal $mole^{-1}$) | $\Delta S^{\ddagger}$ (eu) | Ref. |
|---|---|---|---|---|---|
| $Cr^{2+} + Cr^{3+}$ | 25 | $\leqslant 2 \times 10^{-5}$ | — | — | (*22*) |
| $Cr^{2+} + CrOH^{2+}$ | 25 | 0.7 | 12.8 | −16.4 | (*22*) |
| $Cr^{2+} + CrF^{2+}$ | 0 | $2.4 \times 10^{-3}$ | 13.7 | −20 | (*40*) |
| $Cr^{2+} +$ *cis*-$CrF_2^+$ | 0 | $1.2 \times 10^{-3}$ | 13.0 | −24 | (*86*) |
| $Cr^{2+} + CrCl^{2+}$ | 0 | 9 | — | — | (*40, 343*) |
| $Cr^{2+} +$ *trans*-$CrCl_2^+$ | 2 | $\sim 1.7 \times 10^2$ | — | — | (*233*) |
| $Cr^{2+} + CrBr^{2+}$ | 0 | $> 60$ | — | — | (*40*) |
| $Cr^{2+} + CrNCS^{2+}$ | 25 | $1.4 \times 10^{-4}$ | — | — | (*40*) |
| $Cr^{2+} + CrN_3^{2+}$ | 0 | 1.23 | 9.6 | −22.8 | (*343*) |
| $Cr^{2+} + CrSCN^{2+}$ | 25 | 42 | — | — | (*176*) |
| $Cr^{2+} +$ *cis*-$(CrN_3)_2^+$ | 0 | 60 | — | — | (*342*) |

Details of the chromium(II) attack on complexes $CrNCS^{2+}$, $CrSCN^{2+}$, and $CrN_3^{2+}$, whether adjacent or remote from the chromium(III) atom, are of considerable interest. In a very thorough study of the $Cr^{2+}$–$Fe^{3+}$–$SCN^-$ system, using stopped-flow techniques, Haim and Sutin (*176*) have obtained information regarding the nature of these reactions. On mixing a solution of $Fe^{III}$ and $SCN^-$ with one containing excess $Cr^{2+}$, three distinct changes in absorbance are observed. These suggest that the $Cr^{2+}$ attacks both the remote and adjacent positions of the thiocyanate, which is assumed to be nitrogen-bonded to the ferric. The first stage, which is believed to be due to the reaction of $Cr^{2+}$ with $FeNCS^{2+}$, is too rapid to be followed ($k \geqslant 2 \times 10^7$ l·mole$^{-1}$ sec$^{-1}$). The second, of which only the tail is observed, is associated with the $Cr^{2+}$–$Fe^{3+}$, $Cr^{2+}$–$FeOH^{2+}$, and $Fe^{3+}$–$Cr^{2+}$–$SCN^-$ reactions, and the third corresponds to the chromium(II)-catalyzed isomerization of the complex $CrSCN^{2+}$ which is formed in the first stage. The rates of the $Cr^{2+}$–$Fe^{3+}$ and $Cr^{2+}$–$FeOH^{2+}$ reactions are known, and that for the $Fe^{3+}$–$Cr^{2+}$–$SCN^-$ reaction, which does not involve $FeNCS^{2+}$ as a reactant, can be obtained by mixing a solution containing $Cr^{2+}$ and $SCN^-$ with a solution of $Fe^{3+}$. These studies show that approximately 35% of the product from the $Cr^{2+}$–$FeNCS^{2+}$ reaction is in the form $CrSCN^{2+}$, and that there is both remote and adjacent attack by the $Cr^{2+}$:

$$FeNCS^{2+} + Cr^{2+} \rightarrow [Fe{-}NCS{-}Cr]^{4+} \rightarrow Fe^{2+} + CrSCN^{2+} \qquad (23)$$


(24)

$$FeNCS^{2+} + Cr^{2+} \rightarrow [Fe{-}\underset{\substack{|\\Cr}}{NCS}]^{4+} \rightarrow Fe^{2+} + CrNCS^{2+} \qquad (24)$$

From the third stage of this study it was possible to determine the rate constant for the reaction of $Cr^{2+}$ with $CrSCN^{2+}$ ($k = 42$ l·mole$^{-1}$ sec$^{-1}$). If it is assumed that the exchange of chromium between $Cr^{2+}$ and $CrNCS^{2+}$ is slow ($k = 1.4 \times 10^{-4}$ l·mole$^{-1}$ sec$^{-1}$), because the less stable sulfur-bonded isomer is first formed, then the equilibrium constant for the reaction

$$CrSCN^{2+} \rightleftharpoons CrNCS^{2+} \qquad (25)$$

is simply the ratio of the rate constants for the $Cr^{2+}$–$CrNCS^{2+}$ and $Cr^{2+}$–$CrSCN^{2+}$ reactions (i.e., $3 \times 10^5$ at 25° and $\mu = 1.0$ *M*). Using this approach the nitrogen-bonded isomer is about 7.5 kcal mole$^{-1}$ more stable than the sulfur-bonded isomer. It is not surprising therefore that the reaction of $Cr^{2+}$ with $CrSCN^{2+}$ is faster than the reaction of $CrN_3^{2+}$ (there is a favorable free energy change in the former), or that the reaction of $Cr^{2+}$ with $CrNCS^{2+}$ is slower (the free energy change is unfavorable). What is perhaps surprising is that there should be both remote and adjacent attack in the $Cr^{2+}$–$FeNCS^{2+}$ reaction, but only remote attack in the $Cr^{2+}$–$CrNCS^{2+}$ reaction. This point has been considered by Haim and Sutin (*177*). It can also be argued that remote attack of chromium(II) on $CrN_3^{2+}$ is about $10^3$ times more favorable than adjacent attack.

Reactions between chromium(II) and (*cis*)-$CrX_2^+$ complexes can proceed by two mechanisms, one of which leads to exchange via a double-bridged activated complex:

$$^*Cr^{2+} + cis\text{-}CrX_2^+ \longrightarrow \left[\mathrm{Cr}\begin{matrix}\diagup X \diagdown\\ \\ \diagdown X \diagup\end{matrix}\mathrm{Cr}\right]^{3+} \rightarrow cis\text{-}{}^*CrX_2^+ + Cr^{2+} \qquad (26)$$

The other leads to a dissociation of one of the $X^-$ ligands via a single-bridged activated complex:

$$^*Cr^{2+} + cis\text{-}CrX_2^+ \rightarrow [^*CrXCrX]^{3+} \rightarrow {}^*CrX^{2+} + Cr^{2+} + X^- \qquad (27)$$

The double-bridged activated complex is formed in the reaction of $Cr^{2+}$ with *cis*-$Cr(N_3)_2^+$ (*342*), the rate being about 45 times faster than in the corresponding reaction with $CrN_3^{2+}$. In contrast, *cis*-$CrF_2^+$ reacts by the single-bridged activated complex (*86*), and *cis*-$CrF_2^+$ and $CrF^{2+}$ react at about the same rate. More recently Haim (*174*) has shown that the reactions of $Cr^{2+}$ with *cis*-$Co(NH_3)_4(N_3)_2^+$ and *cis*-$Co(en)_2(N_3)_2^+$ proceed concurrently by both single- and double-bridged paths (the ratios of single- to double-bridged paths are 1.6 : 1 and 5 : 1, respectively), and that there is a small contribution from a single-bridged path in the reaction of *cis*-$Cr(N_3)_2^+$ with $Cr^{2+}$. Johnson and Reynolds (*223*) report that $Cr^{2+}$ reacts with *cis*-$CrCl_2^+$ at about the same rate as *trans*-$CrCl_2^+$, and this has now been confirmed (*420*). The single-bridged activated complex appears to be formed in both instances.

The rate equation for the reaction of $Cr^{2+}$ with $CrCl^{2+}$, which results in a net dissociation of the chloride from the chromium(III), is of the form:

$$\text{Rate} = k[CrCl^{2+}][Cr^{2+}][H^+]^{-1} \qquad (28)$$

The latter is consistent with the formation of an activated complex $[CrOHCrCl]^{3+}$ (*11*). The reaction is most likely between $Cr^{2+}$ and $Cr(Cl)OH^+$, in which case the true rate constant is $20 \pm 2.5\ l \cdot mole^{-1}\ sec^{-1}$ at 20°. The ratio of the rate constants for the reaction of $Cr^{2+}$ with *trans*-$CrCl_2^+$ and $Cr(Cl)OH^+$ is about the same as for the reactions of $Cr^{2+}$ with $CrCl^{2+}$ and $CrOH^{2+}$. For the series of reactions with different $CrX^{2+}$ complexes, where $X^-$ is a halide ion, the relative efficiency of $X^-$ as a nonbridging ligand is $I^- > Br^- > Cl^- > F^-$ (*12*, *300*). This order is the reverse of the order of thermodynamic stability of the $CrX^{2+}$ complexes, $CrF^{2+}$ being more stable than $Cr^{3+}$. Orgel (*292*) and Taube (*376*, *377*) have considered the effect which nonbridging ligands can have on the rates of redox reactions. Electron transfer to the vacant $d_{z^2}$ orbital on the chromium(III) will take place more readily the lower the energy of the $d_{z^2}$ orbital. For the *trans*-$Cr(X)OH^+$ complexes the energy of the $d_{z^2}$ orbital is lowered (a) by $X^-$ having a weak ligand field (*292*), and (b) by movement of the ligands in the $d_{z^2}$ direction away from the metal atom (*376, 377*). The order of decreasing ligand-field strength is

TABLE IV

DATA FOR THE CHROMIUM(II)-INDUCED DISSOCIATION OF $Cr(NH_3)_5X^{2+}$ COMPLEXES (AT 25° AND $\mu = 1.0\ M$) (*291*)

| Reaction | $k$ (l·mole$^{-1}$ sec$^{-1}$) | $\Delta H^\ddagger$ (kcal mole) | $\Delta S^\ddagger$ (eu) |
|---|---|---|---|
| $Cr^{2+} + Cr(NH_3)_5F^{2+}$ | $2.7 \times 10^{-4}$ | 13.4 | −30 |
| $Cr^{2+} + Cr(NH_3)_5Cl^{2+}$ | $5.1 \times 10^{-2}$ | 11.1 | −23 |
| $Cr^{2+} + Cr(NH_3)_5Br^{2+}$ | 0.32 | 8.5 | −33 |
| $Cr^{2+} + Cr(NH_3)_5I^{2+}$ | 5.5 | — | — |

$F^- > Cl^- > Br^- > I^-$, so that on this basis the order of reactivity should be $I^- > Br^- > Cl^- > F^-$, which is as observed. The ease with which the Cr—X bond is stretched is probably related to the ease with which the $X^-$ ligand in $CrX^{2+}$ complexes is replaced by a water molecule (*56*), in which case the order of effectiveness should again be $I^- > Br^- > Cl^- > F^-$. The halide ions are probably much less effective in the *cis*-$Cr(X)OH^+$ complexes, although a significant contribution from this path cannot be excluded. The relative effectiveness of the nonbridging halide ions in these reactions ($I^-$ is $\sim 10^4$ times more effective than $F^-$) is of the same order of magnitude as is observed for similar series of reactions in which the halide ion is the bridging ligand (see Tables III and IV).

In the reaction of $Cr^{2+}$ with $Cr(H_2O)_5NH_3^{3+}$ (*130*),

$$Cr^{2+} + CrNH_3^{3+} \rightarrow Cr^{3+} + Cr^{2+} + NH_3 \qquad (29)$$

there is no evidence for bridging by the ammonia ligand, and the dominant path is again the inverse hydrogen ion-dependent path.

The apparent lability of $Cr(NH_3)_5X^{2+}$ complexes in the presence of $Cr^{2+}$ (*291*) can be accounted for by the reaction

$$Cr^{2+} + Cr(NH_3)_5X^{2+} \rightarrow CrX^{2+} + Cr(NH_3)_5H_2O^{2+} \qquad (30)$$

in which an electron and the $X^-$ ligand are transferred to the newly formed chromium(III). This is followed by the rapid aquation of the labile chromium(II) complex:

$$Cr(NH_3)_5H_2O^{2+} + 5H^+ \xrightarrow{\text{fast}} Cr^{2+} + 5NH_4^+ \qquad (31)$$

Rate constants increase, $F^- < Cl^- < Br^- < I^-$ (Table IV), as the ligand field of the bridging group decreases, and as the polarizability of the bridging group increases.

A similar $Cr^{2+}$-induced solution of anhydrous $CrCl_3$ has been observed (*272*). The solid is insoluble in aqueous solution but quickly dissolves (within a few minutes) when $Cr^{2+}$ is added. Electron transfer between $CrCl_3$ and the $Cr^{2+}$ results in the formation of $CrCl^{2+}$ in solution.

Exchange between $Cr^{II}$ and $Cr^{III}$ can also be accelerated by the addition of anions which are not initially complexed to the chromium(III) (*215*). The order of effectiveness is EDTA > pyrophosphate > citrate $\sim PO_4^{3-} > F^- >$ tartrate $> SCN^- > SO_4^{2-}$, and since the chromium(III) ion is inert, the most likely mechanism is

$$Cr^{2+} + X^{n-} \rightleftharpoons CrX^{2-n} \tag{32}$$

$$CrX^{2-n} + CrOH^{2+} \rightarrow [XCrOHCr]^{4-n} \xrightarrow{H^+} Cr^{III}X^{3-n} + Cr^{2+} \tag{33}$$

the chromium(II) bringing the anion into the activated complex. The inverse hydrogen-ion dependence assumed for Eq. (33) has yet to be confirmed, and some of the reactions (with EDTA, for example) may be of the outer-sphere type, when Eq. (33) will not be applicable.

Exchange reactions between high-spin cobalt(II) and low-spin cobalt(III) are expected to be slow because of spin restrictions. The exchange may be represented by the equation,

$$^*Co^{II}(t_{2g}^5 e_g^2) + Co^{III}(t_{2g}^6) \rightarrow {}^*Co^{III}(t_{2g}^6) + Co^{II}(t_{2g}^5 e_g^2) \tag{34}$$

from which it can be seen that changes in electronic configuration of the two ions must take place in addition to electron transfer between the two ions. While many of the reactions are in fact slow (Table V), there are a number of exceptions. In particular, the rate constant for the $Co^{2+}$–$Co^{3+}$ exchange (*171*) is only half that for the $Fe^{2+} + Fe^{3+}$ exchange at 25°. The most likely explanation is that a small fraction of the $Co^{3+}$ is present in the high-spin state:

$$Co^{III}(t_{2g}^6) \rightleftharpoons Co^{III}(t_{2g}^4 e_g^2) \tag{35}$$

This is not unreasonable since $H_2O$ does not have a particularly strong ligand field, and $CoF_6^{3-}$ is known to be a high-spin complex. Magnetic susceptibility measurements do not exclude this possibility, but accurate measurements are difficult since $Co^{3+}$ slowly oxidizes water, and solutions are never completely free from $Co^{2+}$. Providing the interconversion is rapid and non-rate-determining, the above explanation is in no way contrary to the second-order kinetics which are observed.

TABLE V

KINETIC DATA FOR $Co^{II}$–$Co^{III}$ EXCHANGE REACTIONS

| Reaction | Temp. (°C) | $k$ ($l \cdot mole^{-1}\ sec^{-1}$) | $\Delta H^{\ddagger}$ (kcal $mole^{-1}$) | $\Delta S^{\ddagger}$ (eu) | Ref. |
|---|---|---|---|---|---|
| $Co^{2+} + Co^{3+}$ ($\mu = 0.5\ M$) | 18.4 | 1.2 | 10.4 | −22 | (*171*) |
| $Co^{2+} + CoOH^{2+}$ ($\mu = 0.5\ M$) | 18.4 | $6.6 \times 10^{3\ a}$ | — | — | (*171*) |
| $Co(phen)_3^{2+} + Co(phen)_3^{3+}$ | 0 | 1.1 | 16.5 | +4 | (*35*) |
| $Co(NH_3)_n^{2+} + Co(NH_3)_6^{3+}$ | 64.5 | $< 10^{-9}$ | — | — | (*347*) |
| $Co(NH_3)_n^{2+} + Co(NH_3)_6^{3+}$, $OH^-$ | 64.5 | $56.7 \times 10^{-4}$ | 12.6 | −35 | (*59*) |
| $Co(NH_3)_n^{2+} + Co(NH_3)_6^{3+}$, $Cl^-$ | 64.5 | $7.3 \times 10^{-4}$ | — | — | (*59*) |
| $Co(en)_n^{2+} + Co(en)_3^{3+}$ | 50 | $1.4 \times 10^{-4}$ | 13.2 | −31 | (*348*) |
| $Co(EDTA)^{2-} + Co(EDTA)^-$ | 100 | $1.4 \times 10^{-4}$ | 20 | −21 | (*6, 219*) |
| $Co(H{-}EDTA)^- + Co(EDTA)^-$ | 100 | $8.0 \times 10^{-4}$ | 24.0 | −9 | (*6, 219*) |
| $Co(PDTA)^{2-} + Co(PDTA)^-$ | 100 | $2 \times 10^{-4}$ | — | — | (*118*) |
| $Co(H{-}PDTA)^- + Co(PDTA)^-$ | 100 | $7 \times 10^{-4}$ | — | — | (*118*) |

[a] Other $k$ values can be obtained using more recent values for the acid dissociation constant for $Co^{3+}$ ($K_d$). These are $k = 35\ l \cdot mole^{-1}\ sec^{-1}$, using $K_d = 1.8 \times 10^{-2}$ mole $liter^{-1}$ (*357*), and $k = 2.9\ l \cdot mole^{-1}\ sec^{-1}$, using $K_d = 0.22$ mole $liter^{-1}$ (*95*).

The kinetics of the formation and dissociation of monochlorocobalt(III)

$$Co(H_2O)_6^{3+} + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (H_2O)_5CoCl^{2+} + H_2O \tag{36}$$

have been studied ($k_1 < 2\ l \cdot mole^{-1}\ sec^{-1}$ and $k_{-1} < 0.05\ sec^{-1}$ at 25° and $\mu = 3.0\ M$) (*95*). From these values it can be concluded that $Co(H_2O)_6^{3+}$ undergoes water exchange only relatively slowly, and that the stable state of $Co(H_2O)_6^{3+}$ is therefore the low-spin form. It has also been shown (*95*) that the rate constant for the cobalt(II)-catalyzed dissociation of $CoCl^{2+}$

$$Co^{2+} + CoCl^{2+} \rightarrow Co^{2+} + Co^{3+} + Cl^- \tag{37}$$

is $1.0\ l \cdot mole^{-1}\ sec^{-1}$ at 25° and $\mu = 2.0\ M$. In this reaction the chloride is a nonbridging ligand. Habib and Hunt (*171*) have found that, for the $Co^{II}$–$Co^{III}$ exchange in perchlorate solutions ($\mu = 0.5\ M$),

$$k_{obs} = k_1 + k_2 K_d [H^+]^{-1} \tag{38}$$

and, at 25°, $k_1 = 1.97\ l \cdot mole^{-1}\ sec^{-1}$ and $k_2 K_d = 1.517\ sec^{-1}$. A variety of $K_d$ values have been obtained for the acid dissociation:

$$Co^{3+} + H_2O \rightleftharpoons CoOH^{2+} + H^+ \tag{39}$$

The most recent is 0.22 mole liter$^{-1}$ (*95*), but other values ranging from $1.8 \times 10^{-2}$ to $1.0 \times 10^{-4}$ (*357*) have been reported. The latter has been used by Habib and Hunt (*171*) to evaluate $k_2$ (Eq. 38). Fluoride and sulfate ions produce a marked catalysis of the $Co^{II}$–$Co^{III}$ exchange (*171*).

The relatively high values of the rate constant for the $Co(phen)_3^{2+}$–$Co(phen)_3^{3+}$ exchange can be accounted for if a small fraction of the $Co(phen)_3^{2+}$ is present in the $(t_{2g}^6 e_g^1)$ spin-paired form (*35*):

$$Co^{2+}(t_{2g}^5 e_g^2) \underset{}{\overset{\text{fast}}{\rightleftharpoons}} Co^{2+}(t_{2g}^6 e_g^1) \tag{40}$$

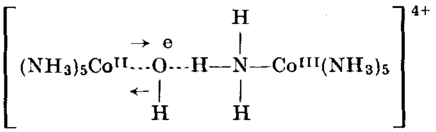
$$Co^{2+}(t_{2g}^6 e_g^1) + Co^{3+}(t_{2g}^6) \longrightarrow Co^{3+}(t_{2g}^6) + Co^{2+}(t_{2g}^6 e_g^1) \tag{41}$$

The large difference in the observed rate constant for this and the $Fe(phen)_3^{2+}$–$Fe(phen)_3^{3+}$ exchange (*105*) ($k > 1 \times 10^5$ l·mole$^{-1}$ sec$^{-1}$ at 25°) suggests that the equilibrium concentration of $Co^{2+}(t_{2g}^6 e_g^1)$ is small. The rate law and rate constants depend upon the anions present, and results have been discussed in terms of ion associations (*35*).

Reactions between $Co^{II}$ and $Co^{III}$ complexes in which the ligands are of intermediate ligand-field strength (i.e., between those of 1,10-phenanthroline and water) are invariably slow (Table V). The direct exchange between $Co(NH_3)_n^{2+}$ and $Co(NH_3)_6^{3+}$, for example, where $n$ has values ranging from 3 to 6, is extremely slow (*59*). The difference in the Co—N bond lengths in the cobalt(II) and cobalt(III) hexammines has been shown to be 0.15 Å (*45*), and not ~ 0.6 Å as was formerly supposed. Since the difference is no greater than the Fe—O bond distances in the hexaquo $Fe^{2+}$ and $Fe^{3+}$ ions, this factor can no longer be of first importance in explaining the slow rate of exchange between $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$. The most favorable path for exchange appears to be one involving ion-pair complexes, for example $Co(NH_3)_6^{3+},OH^-$ (*59*). Since $K$ for the formation of such ion-pairs

$$Co(NH_3)_6^{3+} + OH^- \rightleftharpoons Co(NH_3)_6{}^{-},OH^- \tag{42}$$

is known (*84*), rate constants for the exchange between $Co(NH_3)_n^{2+}$ and $Co(NH_3)_6^{3+},OH^-$ can be obtained. The activated complex is believed to be of the type



$$\left[(NH_3)_5Co^{II}\cdots\underset{H}{O}\cdots H\text{—}\overset{H}{\underset{H}{N}}\text{—}Co^{III}(NH_3)_5\right]^{4+}$$

an electron and the hydroxide ion being transferred as indicated. Evidence for such a path is as follows. First, the initial distribution of labile cobalt(II) complexes $Co(NH_3)_6^{2+}$, $Co(NH_3)_5H_2O^{2+}$, $Co(NH_3)_4$

$(H_2O)_2^{2+}$, etc. (*60*), is different from that of the cobalt(III) ammines produced. The difference suggests that conversion of $Co^{II}$ to $Co^{III}$ is accompanied by substitution into the inner sphere of the newly formed cobalt(III) complex. Second, the exchange shows an inverse hydrogen-ion dependence, which is in accordance with hydroxide ion participation. In the presence of chloride ions (concentration up to 0.75 *M*), ion pairs $Co(NH_3)_6^{3+} \cdot Cl^-$ are similarly effective. A consistent interpretation is possible if it is assumed that $Co(NH_3)_n^{2+}$ complexes from $n = 3$–$6$ react at the same rate (*59*).

## TABLE VI

### A Comparison of Data for $M^{II}$–$M^{III}$ Exchange Reactions at 25°

| Reaction | $k_1$ (l·mole$^{-1}$ sec$^{-1}$) | $k_2$ (l·mole$^{-1}$ sec$^{-1}$) | Reference |
|---|---|---|---|
| $Fe^{II} + Fe^{III}$ | 4.0 | $3 \times 10^3$ | (*144*) |
| $Cr^{II} + Cr^{III}$ | $\leqslant 2 \times 10^{-5}$ | 0.7 | (*22*) |
| $Co^{II} + Co^{III}$ | 1.97[a] | $6.3 \times 10^3$ [a,b] | (*171*) |
| $V^{II} + V^{III}$ | 0.01 | ~ 1.8 | (*242*) |

[a] Temperature 18.4°.

[b] Other possible values are 35 and 2.9 l·mole$^{-1}$ sec$^{-1}$ (see footnote to Table V).

Exchange between the tetrahedral 12-tungstocobaltate(II), $Co^{II}O_4W_{12}O_{36}^{6-}$, and 12-tungstocobaltate(III), $Co^{III}O_4W_{12}O_{36}^{5-}$ ions, has been studied in aqueous solutions (*320*). At 0° and $\mu = 0.6$ *M* the rate constant is 0.63 l·mole$^{-1}$ sec$^{-1}$. The mechanism is almost certainly of the outer-sphere type.

Exchange between the vanadium(II) and vanadium(III) aquo ions is first order in both reactants (*242*), the hydrogen-ion dependence being of the form:

$$k_{obs} = k_1 + k_2 K_d [H^+]^{-1} \tag{43}$$

Rate constants $k_1$ and $k_2$ have been determined and are shown in Table VI alongside data for other $M^{II}$–$M^{III}$ reactions. The wide range of rate constants observed for these reactions, all of which have zero free energy change, is surprising. For reactions which proceed by an inner-sphere mechanism there are three possible rate-controlling factors:

(a) The rate of formation of the activated complex.
(b) The rate of electron transfer within the activated complex.
(c) The rate of breakdown of the activated complex.

The slowness of the $V^{2+}$–$V^{3+}$ exchange *may* be due to the slow rate of formation of the activated complex, since it is known that substitution of water molecules in the $V^{2+}$ and $V^{3+}$ coordination spheres is relatively slow (Table VII). Because of this an outer-sphere mechanism may in this case be the more favorable path. For both inner-sphere and outer-sphere reactions, the ease of electron transfer is determined by the electronic configuration of the reactants (i.e., whether $t_{2g}$ or $e_g$ electrons are involved) and the energy required to reorganize solvation spheres. For

## TABLE VII

CHARACTERISTIC RATE CONSTANTS FOR THE REPLACEMENT OF A WATER MOLECULE IN THE INNER-COORDINATION SPHERE OF METAL IONS[a]

| Metal ions[b] | $k$ (sec$^{-1}$) | Electronic configuration | References |
|---|---|---|---|
| $Ti^{3+}$ [c] | $\sim 10^4$ | $d^1$ | (*103*) |
| $VO^{2+}$ [d,e] | $5 \times 10^2$ | $d^1$ | (*408*) |
| $V^{3+}$ [c] | $10^2$–$10^3$ | $d^2$ | (*52, 103, 243*) |
| $V^{2+}$ [c] | $10^1$–$10^2$ | $d^3$ | (*103, 243*) |
| $Cr^{3+}$ | $3 \times 10^{-6}$ | $d^3$ | (*216*) |
| $Cr^{2+}$ [d,f] | $10^8$–$10^9$ | $d^4$ | (*103, 263*) |
| $Mn^{3+}$ [g] | $> 10^4$ | $d^4$ | (*103*) |
| $Mn^{2+}$ [d] | $3 \times 10^7$ | $d^5$ | (*364*) |
| $Fe^{3+}$ [d] | $3 \times 10^3$ | $d^5$ | (*91*) |
| $Fe^{2+}$ [d] | $3 \times 10^6$ | $d^6$ | (*364*) |
| $Co^{3+}$ | $\leqslant 10^3$ | $d^6$ | (*90, 95*) |
| $Co^{2+}$ [d] | $10^6$ | $d^7$ | (*364*) |

[a] For inner-sphere reactions the rate of formation of the activated complex (a substitution process) may be rate-determining. Alternatively, an electron-transfer process may be too rapid for an inner-sphere mechanism to be possible.

[b] In the case of $Cu^{2+}$, $Hg^{2+}$, and $Tl^{3+}$, rate constants are probably $\sim 10^9$ sec$^{-1}$ [see, for example, Sutin (*361*) and references therein].

[c] The incoming ligand is $SCN^-$. The rate constant refers to the formation of an inner-sphere complex from an outer-sphere complex. The rate constant should be about the same (to within a power of ten) as for water exchange.

[d] Determined by the NMR method. The rate constant refers to the replacement of a particular water molecule, i.e., $1/k$ is equal to the lifetime of a given water molecule in the inner-coordination sphere of the metal ion.

[e] Assuming that four water molecules take part in the exchange (*409*).

[f] With bipyridine as the incoming ligand (*103*).

[g] With fluoride (either $F^-$ or HF) as the incoming ligand.

outer-sphere reactions, it can be reasoned that the lowest energy path is the one in which solvation spheres adjust their size to an intermediate value, before electron transfer occurs (*181*).

The rate equation for the exchange between vanadium(III) and vanadium(IV) (*145*) has one term only:

$$\text{Rate} = [V^{3+}][VO^{2+}][H^+]^{-1} \tag{44}$$

This is consistent with reaction of $VOH^{2+}$ with $VO^{2+}$ ($k = 1.0$ l·mole$^{-1}$ sec$^{-1}$ at 25°, $\Delta H^\ddagger = 10.7$ kcal mole$^{-1}$ and $\Delta S^\ddagger = -24$ eu), since $V^{3+}$ ($K_d = 2 \times 10^{-3}$ mole liter$^{-1}$) is more extensively hydrolyzed than $VO^{2+}$ ($K_d = 4.4 \times 10^{-6}$ mole liter$^{-1}$). Prior hydrolysis of the $V^{3+}$ will obviously favor its conversion to $VO^{2+}$. The corresponding exchange of titanium(III) with titanium(IV) has not yet been studied.

Exchange between vanadium(IV) and vanadium(V) is too fast to be followed by conventional techniques. Nuclear magnetic resonance line-broadening techniques have indicated a rate equation of the form

$$\text{Rate} = k[V^{IV}][V^{V}]^2 \tag{45}$$

and exchange of vanadium(IV) with a dimeric form of vanadium(V) seems likely (*170*).

Reactions of manganese(III) are difficult to study because the disproportionation reaction

$$2\,Mn^{III} \rightleftharpoons Mn^{II} + Mn^{IV} \tag{46}$$

readily occurs with the precipitation of manganese dioxide. This tendency can be countered by having a high hydrogen-ion concentration ($[H^+] \sim 3.0\ N$) and a high concentration of manganese(II) (*326*). In the most recent attempt to study the exchange of manganese(II) with manganese(III), the rapid exchange was probably induced by the separation procedure (*104*). Application of the Marcus theory to the reaction of manganese(III) with iron(II) and various substituted iron(II)-phenanthroline complexes, and to the reaction of cobalt(III) with manganese(II), leads to an estimate of $\sim 10^{-4}$ l·mole$^{-1}$ sec$^{-1}$ for the rate constant for the manganese(II)–manganese(III) exchange at 25° (*104*). Disproportionation of manganese(III) with the intermediate formation of manganese(II) and manganese(IV) may provide an alternative path for exchange which is energetically more favorable than the direct exchange (*2*).

The rapid exchange between manganate and permanganate ions has been studied by using radioactive tracers (*150*, *338*), and by NMR spin-echo (*63*) and NMR line-broadening (*273*) techniques. The results show good agreement. As in the reaction of $Fe(CN)_6^{4-}$ with $Fe(CN)_6^{3-}$, cationic effects, in this case $Cs^+ > K^+ > Na^+ \sim Li^+$, have been demonstrated (Table VIII). Since $MnO_4^{2-}$ and $MnO_4^-$ are substitution inert (there is only slow exchange of oxygen atoms in $H_2{}^{18}O$), formation of the inner-sphere activated complex $[O_3Mn—O—MnO_3]^-$ is not possible. The various cationic effects are consistent with the formation of outer-sphere bridged activated complexes, for example $[O_3MnOCsOMnO_3]^{2-}$. The activation parameters are $\Delta H^\ddagger = 10.5$ kcal mole$^{-1}$ and $\Delta S^\ddagger = -9$ eu in 0.16 *M* NaOH. Exchange between the ruthenate and perruthenate ions in basic solutions is too rapid ($k > 3.3 \times 10^4$ l·mole$^{-1}$ sec$^{-1}$) to be measured by conventional techniques (*249*). There is no suitable ESR signal which can be used to determine the rate.

TABLE VIII

RATE CONSTANTS FOR EXCHANGE OF $MnO_4^{2-}$ AND $MnO_4^-$ AT 0° (*150, 338*)

| Medium | $k$ (l·mole$^{-1}$ sec$^{-1}$) |
|---|---|
| 0.16 *M* LiOH | 700 |
| 0.16 *M* NaOH | 710 ± 30 |
| 0.16 *M* KOH | 800 |
| 0.16 *M* CsOH | 2470 |
| 0.08 *M* NaOH and 0.08 *M* CsOH | 1730 |
| 0.16 *M* NaOH and $10^{-3}$ *M* $Co(NH_3)_6 \cdot Cl_3$ | 1860 |

A rate law

$$\text{Rate} = k[\text{Ag}^{\text{II}}]^2 \tag{47}$$

has been obtained for the exchange between silver(I) and silver(II) (*151*). This is consistent with a disproportionation mechanism

$$2\,\text{Ag}^{\text{II}} \rightleftharpoons \text{Ag}^{\text{I}} + \text{Ag}^{\text{III}} \tag{48}$$

the rate of exchange being equal to the rate of disproportionation at equilibrium. The fast exchange between copper(I) and copper(II) in 12 *N* hydrochloric acid has been studied by NMR line-broadening techniques ($k = 0.5 \times 10^8$ l·mole$^{-1}$ sec$^{-1}$). Chloride bridging is no doubt effective in the activated complex (*259*).

Two other reactions which it is convenient to consider in this section are both multistage processes. The first is the exchange of chromium(III) with monomeric chromium(VI) (*13*), which in acidic aqueous solutions at 94.8° is governed by the rate law,

$$\text{Rate} = [\text{Cr}^{\text{III}}]^{4/3}[\text{Cr}^{\text{VI}}]^{2/3}(k[\text{H}^+]^{-2} + k')$$

On the basis of this rate law it can be concluded that the rate-determining step is the reaction of chromium(III) with chromium(V), the concentration of the latter being determined by the equilibrium

$$\mathrm{Cr^{III} + 2Cr^{VI} \rightleftharpoons 3Cr^{V}} \tag{49}$$

The reaction sequence leading to exchange is, in full,

$$\mathrm{{}^*Cr^{III} + Cr^{VI} \xrightleftharpoons{\text{fast}} {}^*Cr^{IV} + Cr^{V}} \tag{50}$$

$$\mathrm{{}^*Cr^{III} + Cr^{V} \xrightleftharpoons{} {}^*Cr^{IV} + Cr^{IV}} \tag{51}$$

$$\mathrm{{}^*Cr^{V} + Cr^{VI} \xrightleftharpoons{\text{fast}} {}^*Cr^{VI} + Cr^{V}} \tag{52}$$

there being kinetic evidence only for the existence of the $\mathrm{Cr^{IV}}$ and $\mathrm{Cr^{V}}$ states in solution. The slow step (Eq. 51) is believed to correspond to a change in coordination number. Thus the chromium(V) ion is probably tetrahedral and chromium(IV) octahedral.

Adamson (*2*) has reported a similar sort of dependence

$$\text{Rate} = k[\mathrm{Mn^{2+}}]^{3/2}[\mathrm{MnO_4^-}]^{1/2} \tag{53}$$

for the exchange of manganese(II) with manganese(VII). This is consistent with a rapid equilibrium step

$$\mathrm{3Mn^{II} + Mn^{VII} \rightleftharpoons 3Mn^{III} + Mn^{IV}} \tag{54}$$

followed by a rate-determining step involving $\mathrm{Mn^{III}}$ and $\mathrm{Mn^{IV}}$. Rosseinsky and Nicol (*328*) report a net chemical change for the reaction of manganese(II) with manganese(VII),

$$\mathrm{4Mn^{II} + Mn^{VII} \rightarrow 5Mn^{III}} \tag{55}$$

and a rate equation,

$$\text{Rate} = k[\mathrm{Mn^{II}}]^2[\mathrm{Mn^{VII}}] \tag{56}$$

The hydrogen-ion dependence of $k$ is of the form:

$$k = k_1[\mathrm{H^+}] + k_2 \tag{57}$$

Since the activated complex is tri-ionic in manganese,

$$\mathrm{2Mn^{II} + MnO_4^- \rightarrow [Mn_2 \cdot MnO_4]^{3+}} \tag{58}$$

they believe the $\mathrm{Mn^{2+} \cdot MnO_4^-}$ ion pair to be a possible precursor to the activated complex. The contradiction which appears to exist in these two studies is at present under investigation (*329*).

## B. LANTHANIDE IONS

The lanthanides form stable 3+ ions, but the II and IV oxidation states, if they exist, tend to be highly reactive. Thus europium(II) and ytterbium(II) are the most stable of the II states, while cerium(IV) is the most readily available of the ions in the IV oxidation state. Reactions of lanthanides are generally expected to be slow because the $f$ orbitals are members of an inner shell of electrons, and these are shielded by other electrons. An initial $f \rightarrow d$ electronic excitation, which might lead to faster reactions, is more difficult for the lanthanides than for the actinides. Coordination numbers in aqueous solutions are almost certainly greater than six, and in the case of cerium(IV) a coordination number of eight seems likely [see, for example, Wiberg (*399*, p. 246)].

Exchange between europium(II) and europium(III) in aqueous perchloric acid solutions is extremely slow (*260*). Using the Marcus theory (*253*), and rate constants for the $Eu^{2+}$–$V^{3+}$ and $V^{2+}$–$V^{3+}$ reactions, the rate constant for the $Eu^{2+}$–$Eu^{3+}$ exchange is $\sim 10^{-5}$ l·mole$^{-1}$ sec$^{-1}$ (*10*). The reaction is catalyzed by chloride (*260*), and at 22° the rate constant for the reaction of $Eu^{2+}$ with $EuCl^{2+}$ is $\sim 2.6 \times 10^{-4}$ l·mole$^{-1}$ sec$^{-1}$.

Ytterbium(II) (standard electrode potential −1.15 volts) is an even stronger reducing ion than europium(II). Adamson (*8*) has studied factors affecting the stability of ytterbium(II) with a view to studying the $Yb^{II}$–$Yb^{III}$ exchange, and concludes that ytterbium(II) is probably reacting with both perchlorate and hydrogen ions. Solutions in hydrochloric acid of pH > 2 were found to be reasonably stable (decay half-times of an hour or more), but a satisfactory study of the exchange was not possible.

The kinetics of cerium(IV) reactions are complicated by the extensive hydrolysis of $Ce^{4+}$, the first hydrolysis constant being ca. 0.5 at 0°. The $CeOH^{3+}$ ions are further hydrolyzed and also combine to form polynuclear ions. In the exchange between cerium(III) and cerium(IV) (*111*), the rate equation and relevant exchanging species are believed to be

$$\begin{aligned}\text{Rate} = {} & k_1[\text{Ce}^{3+}][\text{Ce(OH)}_2^{2+}] + k_2[\text{Ce}^{3+}][\text{Ce(OH)}_3{}^{+}] \\ & + k_3[\text{Ce}^{3+}][\text{CeOCeOH}^{5+}]\end{aligned} \tag{59}$$

with smaller contributions from less hydrolyzed forms. The reaction is strongly catalyzed by fluoride and sulfate ions (*340*), but the effect of chloride is only slight and over long periods the chloride is oxidized to chlorine. A feature of the exchange in the presence of sulfate ions (0.5 and 0.0025 *M* sulfuric acid) is the reaction path which is first order in $Ce^{3+}$ (*34*). This path is in addition to the sulfate-independent exchange, and the sulfate-dependent paths $CeSO_4^{2+}/Ce^{3+}$, $Ce(SO_4)_2/Ce^{3+}$, and $Ce(SO_4)_3^{2-}/Ce^{3+}$. The most likely explanation (*167*) is that excited $Ce^{III}$

ions are formed in the rate-determining step, possibly by collision with water molecules. The excited $Ce^{III}$ ions react rapidly with $Ce^{IV}$.

## C. Actinide Ions

An important factor to be taken into account in considering the reaction of actinide ions is the degree of hydrolysis of the reactants. In acid solutions, $pH < 1$, the uranium (IV), (V), and (VI) and neptunium and plutonium (III), (IV), (V), and (VI) oxidation states are present at least predominantly as $M^{3+}$, $M^{4+}$, $MO_2^+$, and $MO_2^{2+}$, respectively. The ions $UO_2^{2+}$ (*156*), $NpO_2^{2+}$ (*312*), and $PuO_2^{2+}$ (*256*) exchange their oxygen atoms with water only very slowly (rate constants $10^{-7}$–$10^{-9}$ $sec^{-1}$). The corresponding rate constants for $UO_2^+$ (*157*), $NpO_2^+$ (*312*), and $PuO_2^+$ (*318*) are somewhat faster and are of the order of magnitude $10^2$, 1, and $10^{-5}$ $sec^{-1}$, respectively. In other words, exchange rates vary with charge type, and the trends observed are such as to suggest that both $AmO_2^+$ and $AmO_2^{2+}$ should exchange their oxygen atoms with water at a slow rate (*312*).

Electron-exchange reactions between $M^{III}$ and $M^{IV}$ and between $M^V$ and $M^{VI}$ ions are generally much faster than reactions between $M^{IV}$ and $M^{VI}$ ions. This is as might be expected since in the one case the two reactants are simple aquo ions or are both oxycations of the type $MO_2^+$ and $MO_2^{2+}$, and in the other the reactants are one of each type. The extensive rearrangements required for the latter provide a barrier which tends to restrict reaction. Thus the exchange of $UO_2^+$ and $UO_2^{2+}$ is fast, and the rate constant is of the order of $10^2$–$10^3$ $l \cdot mole^{-1}$ $sec^{-1}$ (*257*), while direct exchange between $Np^{4+}$ and $NpO_2^+$ is slow (*354*). The various indirect paths possible in this system have been considered by Reynolds and Lumry (*324*). Exchange between $Pu^{4+}$ and $PuO_2^+$ is slow, but there is a fairly rapid redox reaction (*313*):

$$Pu^{IV} + Pu^{V} \rightarrow Pu^{III} + Pu^{VI} \qquad (60)$$

The second-order rate constant for the latter is 37.3 $l \cdot mole^{-1}$ $sec^{-1}$ at 25°.

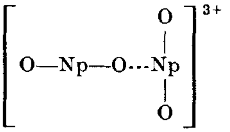
The reaction between $NpO_2^+$ and $NpO_2^{2+}$ has been extensively studied (*354*). The rate may be expressed as

$$\text{Rate} = k_1[NpO_2^+][NpO_2^{2+}] + k_2[NpO_2^+][NpO_2^{2+}][H^+] \qquad (61)$$

and at 4.5° $k_1 = 74$ $l \cdot mole^{-1}$ $sec^{-1}$ and $k_2 = 15$ $l^2 \cdot mole^{-2} sec^{-1}$. The second term is thought to correspond to the reaction of protonated $NpO_2^+$:

$$NpO_2H^{2+} + NpO_2^{2+} \rightarrow \qquad (62)$$

Since the solvent $D_2O$ effect $k_{H_2O}/k_{D_2O} = 1.4$ (*355*) is about the same as that observed for the reaction of $Cr^{2+}$ with $Co(NH_3)_5Cl^{2+}$, an inner-sphere activated complex of the type



$$\left[\begin{array}{r} \mathrm{O} \\ | \\ \mathrm{O{-}Np{-}O\cdots Np} \\ | \\ \mathrm{O} \end{array}\right]^{3+}$$

is not unreasonable. With chloride ions there are further terms in $[Cl^-]$ and $[Cl^-]^2$ (*87*). Recently Amis (*14*) has studied the rates, orders, and temperature coefficients of exchange reactions involving uranium and neptunium ions, and in particular the reaction of $NpO_2{}^+$ with $NpO_2^{2+}$ in pure and mixed solvents and in the presence of inert salts.

In view of the charges involved, the hydrogen-ion dependence of the reaction between $Pu^{III}$ and $Pu^{IV}$ is not as marked as might have been expected (*230*):

$$\text{Rate} = k_1[Pu^{3+}][Pu^{4+}] + k_2[Pu^{3+}][Pu^{4+}][H^+]^{-1} \tag{63}$$

In this equation, $k_1 = 20.0$ l·mole$^{-1}$ sec$^{-1}$ and $k_2 = 1.1 \times 10^3$ sec$^{-1}$ at 25°. That $k_1$ is some $10^2$ times larger than the rate observed for the $Fe^{2+}$–$Fe^{3+}$ reaction supports the belief that charge repulsions are not of first importance in electron-transfer reactions.

## III. Two-Equivalent Exchange Reactions

The main concern of this section is with exchange reactions between ions (and molecules) of subgroup B elements. These are generally two-equivalent overall reactions since, with the exception of mercury(I) and mercury(II), stable oxidation states differ by two electrons. The two-equivalent exchange between platinum(II) and platinum(IV) complexes is also considered.

The only reaction between aquo ions which it has been possible to study in a perchloric acid medium is that between thallium(I) and thallium(III). The rate equation is of the form

$$\text{Rate} = k_1[Tl^+][Tl^{3+}] + k_2[Tl^+][TlOH^{2+}] \tag{64}$$

and at 25° and $\mu = 3.0$ *M*, $k_1 = 7.03 \times 10^{-5}$ l·mole$^{-1}$ sec$^{-1}$ and $k_2 = 2.47 \times 10^{-5}$ l·mole$^{-1}$ sec$^{-1}$ (*325*). Although in 6 *M* perchlorate media $k_2$ is slightly bigger than $k_1$, hydroxide ions clearly do not have the strong catalytic effect which they have in many other reactions.

On the other hand, hydroxide ions do not have the even stronger inhibitory effect which chloride (*191*, *392*), bromide (*81*), and cyanide

(*299*) ions have on the exchange. For a series of runs with the addition of increasing amounts of chloride, the experimental second-order rate constants first decrease to a minimum and then increase (*148*). By using association constants for thallic chloride species, this variation can be accounted for by a rate equation

$$\begin{aligned}\text{Rate} = {} & k_0[\text{Tl}^+][\text{Tl}^{3+}] + k_3[\text{Tl}^+][\text{TlCl}^{2+}] + k_4[\text{Tl}^+][\text{TlCl}_4^-] \\ & + k_5[\text{TlCl}_2^-][\text{TlCl}_4^-] + k_6[\text{TlCl}_3][\text{TlCl}_4^-] \end{aligned} \tag{65}$$

where $k_0$ is the rate constant for the exchange in 1.0 $M$ perchloric acid in the absence of chloride (*392*). In Eq. (65) $k_0 = 6.6 \times 10^{-5}$, $k_3 = 0.28 \times 10^{-5}$, $k_4 = 4.58 \times 10^{-5}$, $k_5 = 1.32$, and $k_6 = 18.9$ $\text{l}\cdot\text{mole}^{-1}$ $\text{sec}^{-1}$ at 25°. Electron exchange occurs therefore only when the activated complex contains zero, one, four, six, and seven chloride ions. The reaction paths with one and four chlorides are actually slower than with zero chloride, while $\text{TlCl}_2^+$ is within experimental accuracy quite unreactive. Since at the higher chloride ion concentrations a $D_2O$ solvent effect becomes negligible (*148*), some of the chloride-dependent paths at least are probably of the inner-sphere type.

For a similar series of experiments in which bromide ions are added (*81*), the rate first decreases, increases to a maximum, falls to a second minimum, and then increases again. The rate equation is of the form

$$\begin{aligned}\text{Rate} = {} & k_0[\text{Tl}^+][\text{Tl}^{3+}] + k_3[\text{TlBr}_2^+] + k_4[\text{TlBr}_3] + k_5[\text{Tl}^+][\text{TlBr}_4^-] \\ & + k_6[\text{TlBr}_2^-][\text{TlBr}_4^-] \end{aligned} \tag{66}$$

a feature of the reaction being the first-order terms in $k_3$ and $k_4$. Such terms are consistent with thallium(III) oxidation of bromide:

$$\text{TlBr}_2^+ \rightarrow \text{Tl}^+ + \text{Br}_2 \tag{67}$$

$$\text{TlBr}_3 \rightarrow \text{Tl}^+ + \text{Br}_2 + \text{Br}^- \tag{68}$$

With the addition of cyanide there is a similar sort of decrease and then increase in rates (*299*). With sulfate (*67*, *400*) and nitrate (*304*), however, the catalysis is more straightforward and in the expected manner. It has been concluded from spectroscopic observation (*147*) that, whereas chloride and bromide form inner-sphere complexes with thallium(III), complexing with sulfate is of the outer-sphere type, $\text{Tl(H}_2\text{O)}_n^{3+}, \text{SO}_4^{2-}$. Unlike $\text{TlCl}^{2+}$ and $\text{TlBr}^{2+}$, the sulfate complex reacts faster with $\text{Tl}^+$ than does $\text{Tl}^{3+}$, which suggests that the activated complex may be of the outer-sphere type. A term in $[\text{SO}_4^{2-}]^3$ is also effective in the rate equation (*66*), but there is a no term in $[\text{SO}_4^{2-}]^2$. The symmetry of the activated complex may be important in determining which paths are effective (*65*), but it is difficult to see how symmetry could be important unless inner-sphere activated complexes are involved.

Whether or not there is a simultaneous or near-simultaneous transfer of two electrons between thallium(I) and thallium(III) has been the subject of much discussion (*359*). The kinetics give no information as to whether the reaction proceeds directly,

$$*Tl^{I} + Tl^{III} \rightarrow *Tl^{III} + Tl^{I} \tag{69}$$

or indirectly,

$$*Tl^{I} + Tl^{III} \longrightarrow *Tl^{II} + Tl^{II} \tag{70}$$

$$*Tl^{II} + Tl^{II} \xrightarrow{\text{fast}} *Tl^{III} + Tl^{I} \tag{71}$$

since both possibilities would be expected to give a rate equation which is first order in [$Tl^{I}$] and [$Tl^{III}$]. Thallium(II) is known to be formed as a highly reactive intermediate in a number of noncomplementary reactions, for example that of iron(II) with thallium(III) (*30*). Following their study of the thallium(I)–cerium(IV) reaction in 6.18 *N* nitric acid at 53.9°, Gryder and Dorfman (*168*) conclude that either the $Tl^{I}$–$Tl^{III}$ exchange or the $Tl^{I}$–$Ce^{IV}$ reaction, or both, must involve a two-electron transfer. Since a two-electron transfer is unlikely for the reaction of thallium(I) with cerium(IV), it is probable that the thallium(I)–thallium(III) exchange is a single-stage two-equivalent process. Similar conclusions were possible following a study of the vanadium(IV)–thallium(III) reaction at 80° (*367*):

$$2V^{IV} + Tl^{III} \rightarrow 2V^{V} + Tl^{I} \tag{72}$$

When vanadium(V) is added initially it produces a marked retardation, but the rate is unaffected by the addition of an excess of thallium(I) up to 0.13 *M*. This is consistent with the mechanism:

$$V^{IV} + Tl^{III} \rightleftharpoons V^{V} + Tl^{II} \tag{73}$$

$$V^{IV} + Tl^{II} \rightarrow V^{V} + Tl^{I} \tag{74}$$

A full kinetic treatment is difficult, however, as the thallium(III) slowly decomposes to thallium(I) and molecular oxygen (*197*). Since the thallium(I)–thallium(III) exchange is known to proceed at an appreciable rate under the conditions of these experiments, it is unlikely that $Tl^{II}$ is formed as an intermediate. If it were, then the progress of the reaction of vanadium(IV) with thallium(III) in Eqs. (73) and (74) would be affected by the addition of $Tl^{I}$.

Using pulse radiolysis techniques, Cercek *et al.* (*84a*) have been able to measure the rate of the $Tl^{II}$ disproportionation and, in view of the fast rate ($k = 2.3 \times 10^{9}$ l·mole$^{-1}$ sec$^{-1}$), the formation of $Tl^{II}$ as an intermediate in the thermal exchange, where the $Tl^{II}$ ions do not have time to escape from a solvent cage, cannot be excluded. Platinum black produces a marked catalysis of the exchange, but the activation energy is surprisingly large (11.7 kcal mole$^{-1}$) (*349*). In the photo-induced $Tl^{I}$–$Tl^{III}$ exchange, thallium(II) is formed as an intermediate but, since this system is extremely sensitive to the presence of added or accidental impurities, it again seems unlikely that thallium(II) is important in the thermal exchange (*349*).

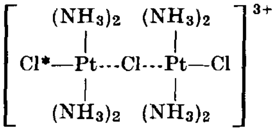
Complexing anions play an important and essential role in the exchange between platinum(II) and platinum(IV) (*46*). For the reactions so far studied the rate law is of the form:

$$\text{Rate} = k_{obs}[Pt^{II}][Pt^{IV}][X^-] \tag{75}$$

In the reaction of $Pt(NH_3)_4^{2+}$ with *trans*-$Pt(NH_3)_4Cl_2^{2+}$ in the presence of free (and labeled) chloride, small equilibrium concentrations of a penta-coordinated platinum(II) complex are believed to be formed in a rapid first step:

$$Pt(NH_3)_4^{2+} + {}^*Cl^- \overset{K_a}{\rightleftharpoons} Pt(NH_3)_4{}^*Cl^+ \tag{76}$$

These subsequently interact with the platinum(IV) with the formation of a symmetrical activated complex:



$$\left[\begin{array}{c} (NH_3)_2 \quad (NH_3)_2 \\ | \qquad\qquad | \\ Cl^*{-}Pt\cdots Cl\cdots Pt{-}Cl \\ | \qquad\qquad | \\ (NH_3)_2 \quad (NH_3)_2 \end{array}\right]^{3+}$$

Two electrons are transferred and when the activated complex breaks down the chloride bridge remains, attached to the newly formed platinum(IV). The net effect of the exchange therefore is the substitution of a labeled chloride ion into the coordination sphere of the $Pt^{IV}$. The experimental rate constant $k_{obs}$ is equal to $kK_a$ (where $K_a$ is as defined in Eq. 76). Values for $k_{obs}$ vary a good deal depending on the ligands present (Table IX). That there is no detectable exchange between *trans*-$Pt(tetrameen)_2Cl_2^{2+}$ and $Pt(tetrameen)_2^{2+}$ over 14 days seems reasonable in view of the bulky nature of the tetramethylethylenediamine ligand, which prevents a sufficiently close approach of the two reactants. In the reaction of $Pt(NH_3)_4^{2+}$ with $Pt(NH_3)_5Cl^{3+}$, slower rates are to be expected since a Pt—$NH_3$ bond has to be broken:

$$Pt(NH_3)_4^{2+} + Pt(NH_3)_5Cl^{3+} + Cl^- \rightarrow trans\text{-}Pt(NH_3)_4Cl_2^{2+} + Pt(NH_3)_4^{2+} + NH_3 \tag{77}$$

Although the chloride forms a bridging group the transfer of two electrons cannot be accounted for by a mechanism involving chlorine-atom transfer. The transfer of $Cl^+$ would seem even less likely. The exchange of $Pt(NH_3)_4^{2+}$ with *trans*-$Pt(NH_3)_4Cl_2^{2+}$ in the presence of thiocyanate ions provides a useful method for the preparation of *trans*-$Pt(NH_3)_4(SCN)_2^{2+}$.

The exchange between tin(II) and tin(IV) has to be studied in a complexing medium to avoid precipitation of hydroxotin(IV) species. In dilute hydrochloric acid a variety of complexed ions are present, but in the concentrated acid the exchanging species are probably $SnCl_4^{2-}$ and $SnCl_6^{2-}$. At 25° the rate constants in 9.0, 10.0, and 11.0 *N* acid are 0.38, 0.55, and 0.73 l·mole$^{-1}$ sec$^{-1}$, respectively (*64*). The activation energy of 10.8 kcal mole$^{-1}$ in 10 *N* HCl is some 10 kcal mole$^{-1}$ less than values obtained for the exchange between $SnCl_2$ and $SnCl_4$ in ethyl (*264*) and methyl (*265*) alcohol, and a different mechanism seems likely. Unlike other systems which are considered below, the exchange remains first order in both the reactants. The exchange has also been studied in sulfuric acid (*155*).

TABLE IX

RATE OF EXCHANGE BETWEEN PLATINUM(II) AND PLATINUM(IV) COMPLEXES IN THE PRESENCE OF CHLORIDE AT 25°

| Reaction | $k_{obs}$ ($l^2 \cdot mole^{-2}\, sec^{-1}$) |
|---|---|
| $Pt(NH_3)_4^{2+}$ + *trans*-$Pt(NH_3)_4Cl_2^{2+}$ + $Cl^-$ | 6.5 |
| $Pt(en)_2^{2+}$ + *trans*-$Pt(en)_2Cl_2^{2+}$ + $Cl^-$ | 15.0 |
| $Pt(NH_3)_4^{2+}$ + *trans*-$Pt(en_2)Cl_2^{2+}$ + $Cl^-$ | 3.3 |
| $Pt(NH_3)_4^{2+}$ + *cis*-$Pt(NH_3)_4Cl_2^{2+}$ + $Cl^-$ | $2.7 \times 10^{-3}$ |
| $Pt(NH_3)_4^{2+}$ + $Pt(NH_3)_5Cl^{3+}$ + $Cl^-$ | $6.5 \times 10^{-4}$ |
| $Pt(NH_3)_4^{2+}$ + *trans*-$Pt(NH_3)_3Cl_3^+$ + $Cl^-$ | 21.7 |

The rate of exchange of antimony(III) with antimony(V) increases steadily with increasing hydrochloric acid concentrations to a maximum value in approximately 9.3 *N* HCl and then decreases again between 9.3 *N* and 12.0 *N* (*61*, *85*, *275*). The complexity of the system can be explained in terms of slow interconversion among two or more forms of $Sb^V$ which exchange at different rates (*85*). In 9.5 *N* hydrochloric acid the predominant form of $Sb^V$ is $SbCl_6^-$ (or possibly $HSbCl_6$), while the most likely form of $Sb^{III}$ over a wide range of hydrochloric acid concentrations is thought to be $SbCl_4^-$ (*62*). In concentrated HCl the activation energy is 17.2 kcal mole$^{-1}$. Over a lower range of hydrochloric acid concentrations, Kambara *et al.* (*229*) report a maximum rate at about 2.0 *N* hydrochloric acid. There is no exchange in aqueous sulfuric acid solutions but this can be initiated by the addition of chloride ions. In carbon tetrachloride there are two paths for exchange (*44*), one involving the dissociation and subsequent recombination of $SbCl_5$,

$$SbCl_5 \rightleftharpoons SbCl_3 + Cl_2 \qquad (78)$$

and the other having an activated complex containing one $SbCl_3$ and two $SbCl_5$ molecules. With the addition of anhydrous hydrochloric acid as catalyst (*305*) there is a third term which appears to involve $SbCl_3$ and $HSbCl_6$ or $SbCl_6^-$. In the full rate law,

$$\text{Rate (sec}^{-1}) = 1.6 \times 10^{-3}[SbCl_5] + 1.8 \times 10^{-4}[SbCl_3][SbCl_5]^2 + 2.1 \times 10^{-5}[SbCl_3][HSbCl_6] \tag{79}$$

the third term becomes dominant for conditions $[HCl] > [SbCl_5]$.

Other exchange reactions which have been studied include that of arsenic(III) with arsenic(V) in 10.8 *N* hydrochloric acid (*24*), and that of $PCl_3$ with $PCl_5$ in carbon tetrachloride (*51*). The latter is first order in $PCl_5$ and zero order in $PCl_3$, which suggests a dissociation mechanism:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \tag{80}$$

The exchange between $[Hg^I]_2$ and $Hg^{II}$ is too fast to study by normal techniques (*404*). The most likely path is the disproportionation reaction

$$[Hg^I]_2 \rightleftharpoons Hg^0 + Hg^{II} \tag{81}$$

but a dissociation $Hg_2^{2+} \rightarrow 2Hg^+$ followed by the rapid exchange of $Hg^+$ and $Hg^{2+}$ ions is also possible.

## IV. Reactions in Which Binuclear Complexes Are Formed

Binuclear complexes have been identified as intermediates or final products in a number of redox reactions, and provide evidence for inner-sphere mechanisms. Typical cases are with chromium(II) or cobalt(II) complexes as the reducing agent, the chromium(III) or cobalt(III) ions which are formed capturing a nonlabile group attached to the other reactant in their inner-coordination spheres.

Newton and Baker (*279*) obtained evidence for the formation of at least one binuclear intermediate in the reaction of chromium(II) with uranium(VI). The intermediate reacts with thallium(III) and vanadium(IV) at rates which are first order in the intermediate but zero order in the concentration of oxidizing agent. In the absence of other reactants the intermediate decomposes to give $U^{IV}$, $U^{VI}$, and $Cr^{III}$ ions with half-lives ranging from 4 to 8 minutes at 0°. Gordon (*153*) has shown that the intermediate,

$$[(H_2O)_5Cr^{III}—O—U^V—O]^{4+}$$

which is first formed, undergoes a much slower reaction with a second $Cr^{2+}$ with the formation of a second intermediate,

$$[(H_2O)_5Cr—O—U—O—Cr(H_2O)_5]^{6+}$$

The latter then decomposes to give mononuclear products, the net reaction being

$$2Cr^{2+} + UO_2^{2+} \xrightarrow{4H^+} 2Cr^{3+} + U^{4+} + 2H_2O \tag{82}$$

Experiments in which the $UO_2^{2+}$ was labeled with oxygen-18 have shown that there is oxygen-atom transfer to the hexaquochromium(III) product.

In the reaction of chromium(II) with neptunium(VI) a binuclear complex,

$$[(H_2O)_5Cr^{III}—O—Np—O]^{4+}$$

is formed, and this has been separated by ion-exchange techniques (*351*). The specific rate of decomposition for the complex is $2.32 \times 10^{-6}$ sec$^{-1}$ at 25° and in 1.0 *M* perchloric acid. A value of the equilibrium constant

$$K = \frac{[Cr^{III} \cdot Np^V]}{[Cr^{III}][Np^V]} \tag{83}$$

of $2.62 \pm 0.48$ l·mole$^{-1}$ has been determined at 25° by a spectrophotometric method (*352*).

The reaction of $VO^{2+}$ and $Cr^{2+}$ proceeds by way of a binuclear intermediate $VOCr^{2+}$, which has been identified spectroscopically (*124*). The binuclear ion is formed rapidly ($k > 3 \times 10^3$ l·mole$^{-1}$ sec$^{-1}$ at 5°) and in relatively high concentrations providing $[Cr^{II}] \leqslant [V^{IV}]$. The green intermediate decays to vanadium(III) and chromium(III) in a pseudo-first-order reaction with a hydrogen-ion dependence indicating the presence of protonated and unprotonated forms of the intermediate. There is also evidence for the formation of a binuclear ion in the reaction of $Cr^{2+}$ with $VO_2{}^+$ (*279*), but details of this reaction have not yet been studied. In Table X a list of data for the decomposition of various binuclear complexes is given.

When vanadium(II) and vanadium(IV) are mixed in acid perchlorate solutions a brown colored intermediate is observed, which has been shown to be a dimeric form of vanadium(III) (*282*). It has been possible to assign a formula $VOV^{4+}$ to this intermediate (*282*). The rates of formation and decomposition of the dimer have been studied at the 425 m$\mu$ maxima ($\epsilon = 6.8 \pm 0.8 \times 10^3$). The rate of formation is given by $k_1[V^{2+}][VO^{2+}]$ and its rate of decomposition by the two terms $(k_2 + k_3[H^+])[VOV^{4+}]$. At 0° and ionic strength $\mu = 1.0$ *M*, $k_1$ is about 0.067 l·mole$^{-1}$ sec$^{-1}$, $k_2$ is very small and of the order of 0.003 sec$^{-1}$, and $k_3$ is 0.330 l·mole$^{-1}$ sec$^{-1}$. The reaction can also be studied by following the disappearance of vanadium(IV) at 760 m$\mu$ (*281*), since the dimeric species does not absorb at this wavelength. The rate law is of the form

$$-d[V^{IV}]/dt = (k_4 + k_5[H^+])[V^{II}][V^{IV}] \tag{84}$$

and $k_4$ (0.106 l·mole$^{-1}$ sec$^{-1}$ at 0°) accounts for nearly all of the rate. By comparing $k_1$ and $k_4$ it can be concluded that about 65% of the overall reaction involves the intermediate, and the rest of the reaction proceeds directly to the final products, probably by way of an outer-sphere activated complex. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ corresponding to $k_4$ are 12.3 kcal mole$^{-1}$ and −16.5 eu, respectively.

TABLE X

A COMPARISON OF DATA FOR THE DECOMPOSITION OF BINUCLEAR COMPLEXES (*124*)

| Mode of formation | Binuclear ion[a] | $k_{obs}$ (sec$^{-1}$) at 25° | Reference |
|---|---|---|---|
| $Cr^{II} + V^{IV}$ | $CrOV^{4+}$ | $0.018 + 0.645[H^+]$ | (*124*) |
| $V^{II} + V^{IV}$ | $VOV^{4+}$ | $0.03 + 1.54[H^+]$ | (*282*) |
| $Fe^{II} + Fe^{IV}$ | $FeOFe^{4+}$ | $0.35 + 3.5[H^+]$ | (*93*) |
| $Cr^{II} + Cr^{IV}$ | $CrOHCr^{5+}$ [b] | $1.5 \times 10^{-6}$ | (*92*) |
| $Cr^{II} + Np^{VI}$ | $CrONpO^{4+}$ | $2.3 \times 10^{-6}$ | (*351*) |

[a] In a number of cases the formula of the binuclear complexes is uncertain. Possibilities are $M(OH)_2M'$, $M(OH)M'$, and $MOM'$.

[b] The double-bridged complex $Cr(OH)_2Cr^{4+}$ is known to be formed by the direct reaction of $Cr^{II}$ with $Cr^{IV}$ (*228*). In the decomposition of this dimer the monobridged complex, $CrOHCr^{5+}$, is the immediate precursor of $Cr^{3+}$ (*92, 382*).

In the reaction of chromium(II) with thallium(III) the chromium(III) product is in the form of a binuclear complex (*27*), which suggests that chromium(IV) is formed in the first step:

$$Cr^{II} + Tl^{III} \rightarrow Cr^{IV} + Tl^{I} \tag{85}$$

$$Cr^{II} + Cr^{IV} \rightarrow (Cr^{III})_2 \tag{86}$$

The binuclear complex has been shown to have the formula $(H_2O)_4Cr(OH)_2Cr(H_2O)_4^{4+}$ (*228*). A single-bridged dimer, $(H_2O)_5Cr\cdot OH\cdot Cr(H_2O)_5^{5+}$, is formed as an intermediate in the slow decomposition of the double-bridged complex (*92*).

A binuclear iron(III) complex (*266*) is also formed in the two-equivalent oxidation of iron(II) with HOCl and $O_3$ (*93*). Again this suggests that iron(IV) is being formed and the kinetic data are consistent with a reaction sequence:

$$Fe^{II} + Ox_2 \rightarrow Fe^{IV} + red_2 \tag{87}$$

$$Fe^{II} + Fe^{IV} \rightarrow (Fe^{III})_2 \tag{88}$$

Decomposition of the dimer is rapid and has to be studied by flow techniques.

The binuclear ions $(NC)_5Co\cdot O_2\cdot Co(CN)_5^{6-}$ and $(NC)_5Co\cdot NC\cdot Fe(CN)_5^{6-}$ have been prepared (*179*) by oxidation of the pentacyano complex of cobalt(II) with $O_2$ and $Fe(CN)_6^{3-}$, respectively:

$$2Co(CN)_5^{3-} + O_2 \rightarrow (NC)_5Co\cdot O_2\cdot Co(CN)_5^{6-} \tag{89}$$

$$Co^{II}(CN)_5^{3-} + Fe^{III}(CN)_6^{3-} \rightarrow (NC)_5Co^{III}\cdot NC\cdot Fe^{II}(CN)_5^{6-} \tag{90}$$

That small amounts of $Fe(CN)_6^{4-}$ are formed in reaction (90) suggests that a second path occurring by an outer-sphere mechanism may be effective. Alternatively, significant amounts of $(NC)_5Co^{III}\cdot NC\cdot Fe^{III}(CN)_5^{5-}$ and $Fe(CN)_6^{4-}$ may be formed in the reaction:

$$(NC)_5Co^{III}\cdot NC\cdot Fe^{II}(CN)_5^{6-} + Fe(CN)_6^{3-} \rightarrow (NC)_5Co^{III}\cdot NC\cdot Fe^{III}(CN)_5^{5-} + Fe(CN)_6^{4-} \tag{91}$$

The $Co^{III}\cdot Fe^{II}$ complex can be oxidized to the $Co^{III}\cdot Fe^{III}$ complex with iodine. Taube and Myers (*379*) have suggested that the reaction between $Cr^{2+}$ and $Fe(CN)_6^{3-}$ occurs via a bridged activated complex with the cyanide bridge persisting in the insoluble product. The oxidation of $Co^{II}(EDTA)^{2-}$ by $Fe(CN)_6^{3-}$ (*5*), while giving $Co^{III}(EDTA)^-$ and $Fe(CN)_6^{4-}$ as the final products, also occurs with the formation of an intermediate $(EDTA)Co^{III}\cdot NC\cdot Fe^{II}(CN)_5^{5-}$. Wilkins and Hutchital (*402*) have determined the rates of the various processes involved, using temperature-jump and stopped-flow techniques. Another intermediate, $(EDTA)Co^{III}\cdot NC\cdot Fe^{III}(CN)_5^{4-}$, which is formed as a result of the rapid oxidation of the first intermediate with $Fe(CN)_6^{3-}$, must also be considered for a full description of the system (*422*). The reaction of $Co^{II}(EDTA)^{2-}$ with $IrCl_6^{2-}$ has also been studied (*119*), but as yet there is no evidence for an intermediate.

In a number of reactions a more complex hydrogen-ion dependence is the only evidence for the formation of a binuclear intermediate. In such cases the intermediate is of transitory nature and cannot be identified by spectrophotometric methods. A good example is the chromium(II) reduction of vanadium(III) (*125, 174a, 370*). The reaction is first order in both reactants,

$$\text{Rate} = k_{obs}[Cr^{II}][V^{III}] \tag{92}$$

where $k_{obs}$ shows a hydrogen-ion dependence of the form

$$k_{obs} = a/(c + [H^+]) \tag{93}$$

To fit this equation a mechanism of the type

$$Cr^{2+} + V^{3+} \rightleftharpoons CrOHV^{4+} + H^+ \tag{94}$$

$$CrOHV^{4+} \rightarrow CrOH^{2+} + V^{2+} \tag{95}$$

was suggested (*125*). This was unsatisfactory however because it appeared to exclude reactions of $VOH^{2+}$ (*370*). Haim (*174a*) has considered a number of alternative mechanisms and one of these

$$Cr^{2+} + VOH^{2+} \rightleftharpoons CrOHV^{4+} \tag{96}$$

$$CrOHV^{4+} + H^+ \rightarrow Cr^{3+} + V^{2+} + H_2O \tag{97}$$

seems more satisfactory, particularly as recent work (*371*) has confirmed Eq. (93). Other reactions of chromium(II) show a strong preference for paths involving a hydroxide ion, and although it is perhaps surprising that the reaction of $Cr^{2+}$ with $V^{3+}$ appears to make no contribution, this is more reasonable than the alternative in which the $Cr^{2+}$—$VOH^{2+}$ reaction makes no contribution.

The kinetics of the reaction

$$Fe^{II} + Pu^{VI} \rightarrow Fe^{III} + Pu^{V} \tag{98}$$

have been studied in 0.05–2.0 $N$ perchloric acid solution, $\mu = 2.0\ M$ (*280*). The rate conforms to an empirical equation

$$\frac{-d[Pu^{VI}]}{dt} = [Pu^{VI}][Fe^{II}]\left(A + \frac{1}{B + C[H^+]}\right) \tag{99}$$

which can only be accounted for by considering the formation of a metastable binuclear intermediate $Pu^{V} \cdot Fe^{III}$ having the same composition as the activated complex. Thus reaction can occur in the normal way,

$$Fe^{2+} + PuO_2^{2+} \rightarrow Fe^{3+} + PuO_2^{+} \tag{100}$$

but in addition a binuclear intermediate is formed:

$$Fe^{2+} + PuO_2^{2+} \rightleftharpoons [Fe \cdot O \cdot PuO]^{4+} \tag{101}$$

The latter (and its hydrolyzed form) subsequently decomposes to give products:

$$[Fe \cdot O \cdot PuO]^{4+} \rightarrow Fe^{3+} + PuO_2^{+} \tag{102}$$

$$[HOFe \cdot O \cdot PuO]^{3+} \rightarrow FeOH^{2+} + PuO_2^{+} \tag{103}$$

Using the steady-state approximation for the concentration of the intermediate, a hydrogen-ion dependence of the required form is obtained. The reaction of iron(II) with plutonium(IV) has also been studied (*286*),

$$Fe^{II} + Pu^{IV} \rightarrow Fe^{III} + Pu^{III} \tag{103}$$

and is relatively straightforward. The most important path is the one having an inverse hydrogen-ion dependence, which is consistent with a reaction of $Fe^{2+}$ with $PuOH^{3+}$.

The reaction between vanadium(III) and uranium(VI) has also been studied (*285*), using the catalysis of the vanadium(III)–iron(III) reaction by uranium(VI). Without regard to the hydrogen-ion concentration, the mechanism is:

$$V^{III} + U^{VI} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} V^{IV} + U^{V} \tag{105}$$

$$U^{V} + Fe^{III} \xrightarrow{k_2} U^{VI} + Fe^{II} \tag{106}$$

The hydrogen-ion dependence of $k_1$ is not consistent with a single rate-determining step or with a set of such steps occurring in parallel. The dependence is consistent with consecutive reactions and the formation of a binuclear intermediate which is present as $[HOV{\cdot}O{\cdot}UO]^{4+}$ and $[OV{\cdot}O{\cdot}UO]^{3+}$. In the analogous reaction between vanadium(III) and plutonium(VI), (*310*), there is as yet no evidence for an intermediate.

## V. Other One-Equivalent Reactions between Metal Ions

For the series of reactions of $Cr^{2+}$ with $Co^{III}(NH_3)_5X^{2+}$ complexes, there is transfer of the $X^-$ ligand to the newly formed chromium(III) (*272*):

$$Cr^{2+} + Co(NH_3)_5X^{2+} \xrightarrow{5H^+} CrX^{2+} + Co^{2+} + 5NH_4^+ \tag{107}$$

As in the reactions of $Cr^{2+}$ with $Cr^{III}X^{2+}$, the only satisfactory explanation is that inner-sphere activated complexes

$$[(H_2O)_5Cr^{II}\text{—}X\text{—}Co^{III}(NH_3)_5]^{4+}$$

are formed. Some of the results obtained for such reactions are shown in Table XI.[2] The order of effectiveness of the halide ions, $I^- > Br^- > Cl^- > F^-$, is of particular interest (*76*). The same order is found with $Co(CN)_5^{3-}$ (*78*) and H-atoms (*20*, *189*, *274*) as the reducing agent [and also in the outer-sphere reactions with $V^{2+}$ (*79*, *104a*), $Cr(bipy)_3^{2+}$ (*76*, *413*), $Ru(NH_3)_6^{2+}$ (*122*)], and may be termed the "normal" order of bridging efficiency. In the reactions with $Fe^{2+}$ (*104a*, *126*) and $Eu^{2+}$ (*79*) (which are of uncertain mechanism), an inverted order, $F^- > Cl^- > Br^- > I^-$, is observed (Fig. 1). The normal order is also found in the reactions of $Cr^{2+}$ with $Cr(NH_3)_5X^{2+}$ (*291*) and $CrX^{2+}$ (*40*), and the inverted order when $Fe^{2+}$ reacts with $FeX^{2+}$ complexes. The bridging

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[2] Here and elsewhere, for convenience, $X^-$ is used to denote ligands which in most cases have a unit negative charge, but which may also be $H_2O$, $SO_4^{2-}$, etc.

efficiency thus seems to depend primarily upon the nature of the reducing agent and to a lesser extent on the nature of the oxidizing agent. Sutin has pointed out (*361*) that the ratio of stability constants $K_{F^-}/K_{I^-}$ is about $2 \times 10^2$ for the pentamminecobalt(III) complexes, and, since $K_{F^-}/K_{Br^-}$ is $6 \times 10^6$ and $3 \times 10^5$ for the aquochromium(III) and aquoiron(III) complexes, respectively, the standard free energy change is consistent with the inverted order for the reactions of both $Cr^{2+}$ and $Fe^{2+}$ with $Co(NH_3)_5X^{2+}$. The polarizabilities of the halide ions favor the normal order, and the observed order might therefore reflect some compromise between these two factors. Free energy considerations are not able to explain why the normal order is observed for the exchange of $Cr^{2+}$ with $CrX^{2+}$, and the inverted order for the exchange of $Fe^{2+}$ with $FeX^{2+}$.

TABLE XI

KINETIC DATA FOR $Cr^{2+}$–$Co(NH_3)_5X^{2+}$ REACTIONS AT 25°

| Cobalt complex | $k$ (l·mole$^{-1}$ sec$^{-1}$) | $\Delta H^\ddagger$ (kcal mole$^{-1}$) | $\Delta S^\ddagger$ (eu) | Ref. |
|---|---|---|---|---|
| $Co(NH_3)_5H_2O^{3+}$ (20°) | 0.5 | 2.9 | −52 | (*412*) |
| $Co(NH_3)_5OH^{2+}$ (20°) | $1.5 \times 10^6$ | 4.6 | −18 | (*412*) |
| $Co(NH_3)_5F^{2+}$ | $2.5 \times 10^5$ | — | — | (*76*) |
| $Co(NH_3)_5Cl^{2+}$ | $6 \times 10^5$ | — | — | (*76*) |
| $Co(NH_3)_5Br^{2+}$ | $1.4 \times 10^6$ | — | — | (*76*) |
| $Co(NH_3)_5I^{2+}$ | $3 \times 10^6$ | — | — | (*76*) |
| $Co(NH_3)_5N_3^{2+}$ | $\sim 3 \times 10^5$ | — | — | (*79*) |
| $Co(NH_3)_5NCS^{2+}$ | 19 | 6.9 | −29 | (*79*) |
| $Co(NH_3)_5SO_4^+$ | 18 | 6.2 | −32 | (*79*) |
|  | 22 | 8.3 | −25 | (*301*) |
| $Co(NH_3)_5SO_3^+$ | 18.6 | 8.3 | −26 | (*301*) |
| $Co(NH_3)_5S_2O_3^+$ (O) | 13.3 | 4.2 | −39 | (*301*) |
| $Co(NH_3)_5S_2O_3^+$ (S) | 0.18 | 24.6 | −3 | (*301*) |
| $Co(NH_3)_5SeO_3^+$ | > 100 | — | — | (*270*) |
| $Co(NH_3)_5SeO_4^+$ | 360 | — | — | (*270*) |
| $Co(NH_3)_5NO_3^{2+}$ | ~ 90 | — | — | (*79*) |
| $Co(NH_3)_5PO_4$ | $5 \times 10^9$ | — | — | (*79*) |
| $Co(NH_3)_5CN^{2+}$ (15°) | 61 | — | — | (*129*) |

Halpern and Rabani (*189*) have suggested that for reactions

$$\text{Co—X} + \text{red} \rightarrow \text{Co} + \text{X—red} \tag{108}$$

the reactivity order is determined by the strength of the bond being broken (Co—X), and the bond being formed (X—red). For the oxidants and reductants in question the trend is almost certainly for bond strengths to increase in the order, $I^- < Br^- < Cl^- < F^-$. Since the influence of bond making is expected to be of less importance than bond breaking for highly reactive reductants, the reactivity order should follow the sequence $Co(NH_3)_5I^{2+} > Co(NH_3)_5Br^{2+} > Co(NH_3)_5Cl^{2+} > Co(NH_3)_5F^{2+}$. For reductants of low reactivity, on the other hand, stabilization of the transition state by bond making to the reductant is expected to assume greater importance, and the reactivity order should thus be influenced to a greater degree by the strength of the bond being formed, i.e., $F^- > Cl^- > Br^- > I^-$. The observed reactivity orders are consistent with this interpretation; thus the rate constants for the reactions with $Co(NH_3)_5Cl^{2+}$ are H ($1.6 \times 10^9$) > $Co(CN)_5^{3-}$ ($2 \times 10^7$) > $Cr^{2+}$ ($2.6 \times 10^6$) > $Eu^{2+}$ ($3.9 \times 10^2$) > $Fe^{2+}$ ($1.4 \times 10^{-3}$), the values in parentheses being the rate constants in l·mole$^{-1}$ sec$^{-1}$ at 25°. Diebler and Taube (*104a*) have suggested that electron transfer may proceed by means of $\sigma$-interactions when chromium(II) is the reducing agent, and

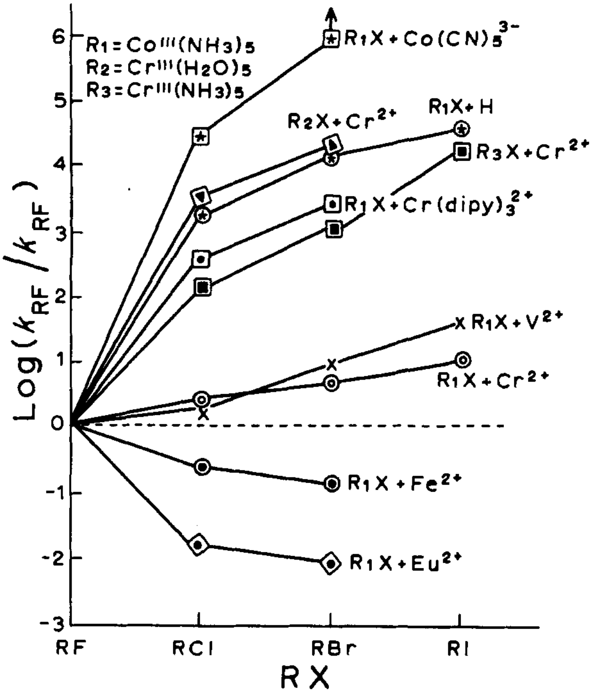


FIG. 1. Showing the trend in rate constants, $\log(k_{RX}/k_{RF})$, for reactions of fluoro, chloro, bromo, and iodo complexes. [Reproduced with permission from Halpern (*182*) with additional data from Halpern and Rabani (*189*).]

that $\pi$-interactions may be more important than $\sigma$-interactions when iron(II) is involved.

The relative rates observed with azide and thiocyanate ions as bridging groups are important. As in the corresponding $Cr^{2+}$–$CrX^{2+}$ reactions, electron transfer is believed to proceed through a polyatomic bridged activated complex $[Cr{-}N{=}N{=}N{-}Co]^{4+}$, the much lower rate observed with $Co(NH_3)_5NCS^{2+}$ being attributed to the unsymmetrical nature of the NCS-bridged intermediate, which results in the formation of the less stable $CrSCN^{2+}$. As a general rule, provided transfer of the bridging group occurs in the inner-sphere activated complex and provided the nitrogen-bonded thiocyanate is the stable isomer, the inner-sphere reaction should proceed faster when the bridging group is azide than when it is thiocyanate. Using this criterion, the reactions of $Fe^{2+}$ with $FeN_3^{2+}$ and $FeNCS^{2+}$ are probably inner-sphere reactions, while the similarity in rates for the reaction of $V^{2+}$ with $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)NCS^{2+}$ suggests that these reactions are outer-sphere (*79*, *361*). The absence of a discrimination between azide and thiocyanate in the reductions of $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5NCS^{2+}$ by $Co(CN)_5^{3-}$ (*78*) (which are inner-sphere) is due to the fact that the sulfur-bonded form $Co(CN)_5SCN^{3-}$ is the more stable form (*182*). With $Cr(bipy)_3^{2+}$, which reacts via an outer-sphere path, the rates with $Co(NH_3)_5N_3^{2+}$ and $Co(NH_3)_5NCS^{2+}$ are comparable (*79*). The reactions of $Co(NH_3)_5CN^{2+}$ with $Cr^{2+}$ (*129*) and $Co(CN)_5^{3-}$ (*186*) result in the formation of $CrNC^{2+}$ and $Co(CN)_5NC^{3-}$, respectively. The latter undergoes first-order decay to $Co(CN)_6^{3-}$ with a half-life of 1.6 sec (*186*). The reduction of pentammine cobalt(III) complexes $Co(NH_3)_5NO_2^{2+}$, $Co(NH_3)_5ONO^{2+}$, and $(NH_3)_5Co{\cdot}(NO)_2{\cdot}Co(NH_3)_5^{4+}$ (containing nitro, nitrito, and hyponitrito ligands) with $Cr^{2+}$, and of $Cr(NH_3)_5NO_2^{2+}$ with $Cr^{2+}$, has been studied (*137*). In all cases the first step is the reduction of the cobalt(III) center and not the ligand. If ligand reduction were the first step, the reaction scheme, with for example nitropentammine cobalt(III) complex, would be

$$Co^{III}NO_2 + Cr^{II} \longrightarrow Co^{III}NO_2^{\cdot} + Cr^{III} \qquad (109)$$

$$Co^{III}NO_2^{\cdot} + Cr^{II} \longrightarrow Co^{III}NO + Cr^{III} \qquad (110)$$

$$Co^{III}NO + Cr^{II} \longrightarrow Co^{II} + ONCr^{III} \qquad (111)$$

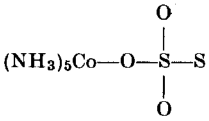
but this is inconsistent with experimental observations. The suggested mechanism is:

$$Co^{III}NO_2 + Cr^{II} \longrightarrow Co^{II} + ONOCr^{III} \qquad (112)$$

$$Cr^{III}ONO + Cr^{II} \longrightarrow Cr^{III} + {}^{\cdot}O_2NCr^{III} \qquad (113)$$

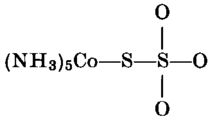
$$Cr^{III}NO_2^{\cdot} + Cr^{II} \xrightarrow{2H^+} Cr^{III}NO + H_2OCr^{III} \qquad (114)$$

Peters and Fraser (*301*) find that both isomers of thiosulfatopentamminecobalt(III) are stable, the usual method of preparation yielding mainly the oxygen-bonded species (I). In the reactions with chromium(II) the oxygen-bonded isomer reacts about 70 times faster than



$(NH_3)_5Co{-}O{-}\overset{O}{\underset{O}{S}}{-}S$

(I)



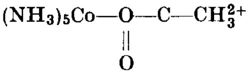
$(NH_3)_5Co{-}S{-}\overset{O}{\underset{O}{S}}{-}O$

(II)

the sulfur-bonded form. The rate constant for the former is comparable to those observed for the sulfato and sulfito complexes. The similarity of the rate constants and activation parameters for the sulfato and sulfito reactions can be explained by considering the bonding of the ligands. Since the bonding in the sulfito complex is Co—S and that of the sulfato complex Co—O—S, both ligands possess three oxygens which are not bound to the cobalt.

Fraser and colleagues have also studied the effect which different oxyanion complexes of pentammine and tetramminecobalt(III) have on rate constants of reactions with chromium(II), vanadium(II), europium(II), and titanium(III) (*270*). The complexes studied include the metaborato, carbonato, nitro, nitrito, nitrato, selenito, selenato, and phosphate complexes. Rates are found to increase when the sulfur atom is replaced by selenium. Candlin *et al.* (*79*) have also studied the reduction of the phosphatopentamminecobalt(III) complex with chromium(II), vanadium(II), and europium(II). In these reactions $Co(NH_3)_5PO_4$ and the protonated species $Co(NH_3)_5PO_4H^+$, $Co(NH_3)_5PO_4H_2^{2+}$, and $Co(NH_3)_5PO_4H_3^{3+}$ are effective.

Reactions of $Cr^{2+}$ with pentamminecobalt(III) complexes $Co(NH_3)_5X^{2+}$, where $X^-$ is a carboxylate group, have been extensively studied. In the case in which $X^-$ is an acetate group (*333*)



$(NH_3)_5Co{-}O{-}\underset{\overset{\|}{O}}{C}{-}CH_3^{2+}$

the product is $Cr^{III}OOCCH_3^{2+}$, and attack must therefore be at one of the oxygen atoms [contrary to one report (*138*), the two oxygens are not equivalent (*134*)]. It is not known whether $Cr^{2+}$ attacks the carbonyl or the Co—O—C oxygen, although the former would seem the most likely since it is sterically less hindered. As Taube has suggested, it is possible that in one series of complexes, those of the simple carboxylate ions for example, attack is at one of these positions, but when a chelate function is introduced the position of attack changes (*378*). The reactions are not very rapid unless the bridging ligand contains (a) a conjugate bond system, or (b) a second group capable of binding the reducing agent. There are three types of reaction to consider: first, *adjacent attack*; second, *adjacent attack with chelation*; and third, *remote attack*.

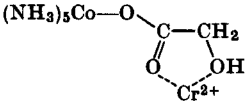
Table XII summarizes kinetic data for the reactions of chromium(II) with carboxylatopentammine complexes containing ligands which do not chelate the reducing agent or favor reaction by remote attack. That the rate constants vary so little (if the formato complex is excluded, they all lie within the range 0.04–0.21 l·mole$^{-1}$ sec$^{-1}$) (*70*, *140*, *333*) deserves further comment. The ligands differ markedly in physical properties, and there is a large variation of $10^4$–$10^5$ for the dissociation constants of the corresponding organic acids (*378*). Since the $Cr^{2+}$ attacks an oxygen of the carboxyl group, the rates might be expected to reflect the availability of unshared electrons on the oxygen atoms (i.e., the basicity of the organic acids). A decrease in rate constants is in fact noted for the series $CH_3COO^-$, $ClCH_2COO^-$, and $Cl_2CHCOO^-$, but the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values are such that at a higher temperature the rate constants will not lie in this same order (*378*). Furthermore, the formate ion is less basic than acetate and yet the reduction of the formato complex is much faster (*70*). Fraser (*141*) had indicated the importance of steric effects in these

TABLE XII

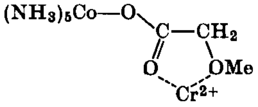
DATA (AT 25°) FOR $Cr^{2+}$–$Co(NH_3)_5X^{2+}$ REACTIONS INVOLVING ADJACENT ATTACK OF THE $Cr^{2+}$

| Ligand | $k$ (l·mole$^{-1}$ sec$^{-1}$) | $\Delta H^\ddagger$ (kcal mole$^{-1}$) | $\Delta S^\ddagger$ (eu) | $\Delta G^\ddagger$ (kcal mole$^{-1}$) | Ref. |
|---|---|---|---|---|---|
| Acetate | 0.18 | 3.5 | −50 | 18.5 | (*333*) |
| Monochloroacetate | 0.10 | 7.9 | −37 | 19.0 | (*139*) |
| Dichloroacetate | 0.074 | 2.5 | −55 | 19.0 | (*139*) |
| Trifluoroacetate | 0.052 | — | — | — | (*164*) |
| Benzoate | 0.14 | 4.9 | −46 | 18.7 | (*139*) |
| *o*-Chlorobenzoate | 0.074 | 6.0 | −43 | 18.9 | (*139*) |
| *p*-Chlorobenzoate | 0.21 | 10.0 | −28 | 18.4 | (*139*) |
| *m*-Phthalate | 0.13 | 2.1 | −56 | 18.9 | (*333*) |
| Propionate | 0.081 | — | — | — | (*376*) |
| Cyclo-$C_3H_5COO^-$ | 0.125 | 7.3 | −38 | 19.0 | (*140*) |
| Cyclo-$C_5H_9COO^-$ | 0.072 | 9.2 | −33 | 19.0 | (*140*) |
| Cyclo-$C_6H_{11}COO^-$ | 0.040 | 12.4 | −23 | 19.0 | (*140*) |
| Formate | 7.0 | — | — | — | (*70*) |

reactions, and this would seem to be particularly important in explaining the high rate constant for the formate complex. The variation in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (but not $\Delta G^{\ddagger}$) in Table XII is difficult to explain and suggests that several factors may be important. Questions which arise are why the $\Delta S^{\ddagger}$ terms should be so favorable, why the $\Delta S^{\ddagger}$ term should vary as it does for the acetate, chloroacetate, and dichloroacetate complexes, and why $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ should be so affected by remote substituents (*378*) (compare the values for the benzoate and *p*-chlorobenzoate reactions).



(III)

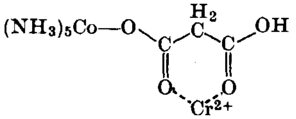


(IV)

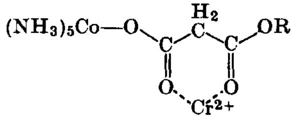
On the other hand, a systematic trend in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values is observed in the reactions of the cyclopropane, cyclopentane, and cyclohexane carboxylato complexes. That noncarboxylated complexes derived from imidazole, pyridene, and dimethylformamide react much more slowly than these bound through carboxyl emphasizes the effectiveness of the bound carboxyl group as a bridge for electron transfer (*162*).

The effect of chelation of the reducing agent is illustrated by the reaction of chromium(II) with the pentamminecobalt(III) complexes of α-hydroxy acids, e.g., glycolate and lactate (*70*). With glycolate as the bridging ligand the rate is about 16 times faster than when it is acetate. This is consistent with the view that chelation of the $Cr^{2+}$ by glycolate (III) takes place in the activated complex. The initial chromium(III) product is metastable and reverts (half-life ~ 22 hours) to a species identical with the glycolatopentaquochromium(III) ion as prepared by conventional methods (*70*). This evidence together with the fact that the initial chromium(III) product has a higher extinction coefficient indicates that the chromium is chelated by the bridging group in the activated complex. The rate is independent of the hydrogen-ion concentration over the range 0.05–1.0 *N* (Table XIII). When the hydrogen of the OH group is replaced by a methyl group (IV) (methoxyacetate ligand), a steric factor is believed to be effective, and the benefit from chelation is less than for the glycolate. The higher rate for α- as opposed to β-malate ($HO_2C \cdot CH(OH) \cdot CH_2 \cdot CO_2H$) could mean that this is the form which has the OH linked α to the carboxyl on the $Co^{III}$. The effectiveness of OH in chelation should diminish as this group becomes further removed from the adjacent carboxyl (*70*).

The complexes so far considered are all of the α-hydroxy acid class. A second carboxylate group can also serve to chelate the chromium(II) reactant. When the bridging ligand is malonate as in (V), the reaction rate is approximately twice that when it is acetate. Analysis of the reaction mixture by an ion-exchange technique (*210*) has shown that well over 85% of the product is in the chelate form. The hydrogen-ion dependence is:



(V)



(VI)

$$k_{obs} = k_1 + k_2[H^+]^{-1} + k_3[H^+] \tag{115}$$

With ethyl malonate and other derivatives obtained by substitution at the methylene center, there is no $k_3$ term. With methyl and ethyl half-ester derivatives (VI), on the other hand, there appears to be a $k_3$ term but no $k_2$ term (*211*). Alternative explanations are possible to account for this variation (*70*, *211*).

TABLE XIII

DATA (25°) FOR $Cr^{2+}$–$Co(NH_3)_5X^{2+}$ REACTIONS BELIEVED TO INVOLVE CHELATION

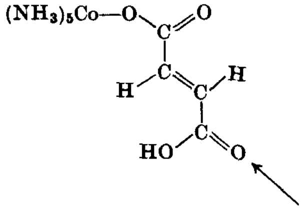
| Ligand | $k$ (l·mole$^{-1}$ sec$^{-1}$) | $\Delta H^‡$ (kcal mole$^{-1}$) | $\Delta S^‡$ (eu) | Ref. |
|---|---|---|---|---|
| Glycolate | 3.06 | 9.0 | −26 | (*70*) |
| Methoxyacetate | 0.42 | 11.3 | −23 | (*70*) |
| Lactate | 6.65 | — | — | (*70*) |
| Methyl lactate | 11.5 | 9.1 | −24 | (*70*) |
| *d*-Tartrate[a] | 1.49 | — | — | (*70*) |
| α-Malate[a] | 2.7 | — | — | (*70*) |
| β-Malate[a] | 0.36 | — | — | (*70*) |
| Malonate[a,b] | 0.29 | — | — | (*70*) |
| Ethyl malonate[a] | 0.18 | — | — | (*70*) |
| Benzyl malonate[a] | 0.99 | — | — | (*70*) |
| Dimethyl malonate[a] | 0.070 | — | — | (*70*) |
| Methyl malonate (half-ester)[b] | 0.41 | 10.1 | −26 | (*211*) |
| Ethyl malonate (half-ester)[b] | 0.50 | 9.6 | −27.5 | (*211*) |

[a] There is also an inverse hydrogen ion-dependent path.

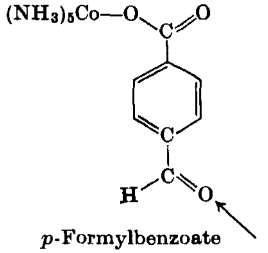
[b] There is also a direct hydrogen ion-dependent path.

An investigation has been made of the product distribution in the reactions with the methyl and ethyl malonate complexes. In each case, ester hydrolysis accompanies the oxidation-reduction process (*211*). For the former complex about 50% of the bridging ligand appears as the chelated product and for the latter about 67 %. The alcohol corresponding to the amount of chelated product formed is found free in solution. The remainder of the ligand appears as the unchelated ester malonato complex of chromium(III). This suggests that there are parallel paths for the reaction, one corresponding to the simple adjacent attack leading to the monodentate half-ester complex, and the other to an intermediate in which both ends of the ligand are trapped in the chromium (III) coordination sphere. With vanadium(II) and europium (II) no hydrolysis results, and (contrary to a previous report) ester hydrolysis does not occur in the reaction of the succinate half-ester complex with any of the three reducing agents, $Cr^{2+}$, $V^{2+}$, and $Eu^{2+}$ (*211*). The implication may be that there is no chelation in the case of the succinate half-ester. The effectiveness of *o*-phthalate (*333*) and salicylate ligands (*139*, *164*, *363*) has also been studied. Chelation can also occur through a sulfur atom (*162*), and appears to be important in the reduction of some pyridine- and pyrazinecarboxylato complexes (*162*).

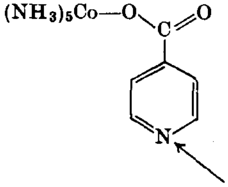
Remote attack occurs when complexes having a ligand with a conjugate-bond system extending from a remote polar group (e.g., carboxyl, carbonyl, or the nitrogen of an aromatic ring system) are reduced. The reducing agent attacks the bridging ligand at the polar group remote from the coordinated carboxyl group, the continuous pathway of double bonds providing an efficient means of electron transport between the two metal ions. For most systems the evidence for remote attack is simply that rates are larger than those observed for normal adjacent attack, and that chelation is absent. A feature of the reactions (Table XIV) is a term first order in hydrogen-ion concentration:



H-fumarate



*p*-Formylbenzoate



Pyridine-4-carboxylate

$$k_{obs} = k_1 + k_2[\mathrm{H}^+] \qquad (116)$$

It has been suggested that the addition of a proton to the carboxyl group adjacent to the cobalt(III) may improve conjugation between the two polar groups. In addition, the complexes of pyridine-4-carboxylate and pyridine-2-carboxylate (and possibly cinnoline-4-carboxylate) are rapidly reduced by $Cr^{2+}$, at least in the forms which present nitrogen without an associated proton. The *p*-phthalate complex has now been shown to be reduced at the normal rate of 0.20 $l \cdot mole^{-1} sec^{-1}$ (which is of the same order as for the *ortho* and *meta* derivatives), thus ruling out any appreciable contribution by remote attack (*162*). Earlier evidence, which suggested that ester hydrolysis accompanies remote attack of the methyl fumarate complex, has recently been questioned (*378*). The specific rates for the methyl fumarate (*333*) and phenyl fumarate (*143*) half-ester complexes (1.4 and 1.3 $l \cdot mole^{-1} sec^{-1}$, respectively) are not very different from the rate of the reaction with the fumarate complex (1.3 $l \cdot mole^{-1} sec^{-1}$) (*333*). Manning *et al.* (*252*) have concluded that the chlorofumarate isomer, which reacts the more rapidly (Table XIV), has the halogen remote from the carboxyl group attached to the cobalt atom. The halogen is thought to interfere more with the coplanarity of the carboxyl group when it is in the $\beta$ position than when it is in the $\alpha$ position. It would now seem that remote attack may occur (with conjugate systems) only when the ligand is reducible (*162*, *164*). For example, uncomplexed malic, oxalic, and pyruvic acids are readily reduced to a radical ion by $Cr^{2+}$, but phthalic acid is not. The maleato complex is partially isomerized to fumarate when the maleato complex is reduced (*143*). In the case of the *p*-formylbenzoate complex, the ligand is not bound to the chromium(III) product. This provides additional evidence for remote attack in this instance since, when the chromium(III) complex coordinated to *p*-formylbenzoate through the carboxylate group is

TABLE XIV

RATE CONSTANTS (AT 25°) FOR $Cr^{2+}$–$Co(NH_3)_5X^{2+}$ REACTIONS BELIEVED TO PROCEED BY REMOTE ATTACK

| Ligand | $k_1$ ($l \cdot mole^{-1} sec^{-1}$) | $k_2$ ($l^2 \cdot mole^{-1} sec^{-1}$) | References |
|---|---|---|---|
| H-fumarate | 1.3 | 3.5 | (*333*) |
| H-chlorofumarate[a] | 1.3 | 1.2 | (*252*) |
| | 0.09 | 0.5 | (*252*) |
| H-maleate | 200 | 100 | (*143*) |
| H-butadienedicarboxylate | 2.2 | 15.0 | (*162*) |
| *p*-Formylbenzoate | 40 | $4 \times 10^2$ | (*142, 162*) |
| Pyruvate | $2.1 \times 10^3$<br>($[H^+] = 0.1$ *N*) | ? | (*70*) |
| Cinnoline-4-carboxylate | > 1100 | ? | (*162*) |
| Pyridine-4-carboxylate | $1.5 \times 10^3$ | 1.3 | (*164*) |

[a] Isomeric forms, see text.

prepared, the rate of dissociation is slow (*142*, *162*). It is reasonable to suppose that the position of attack is at the carbonyl group, since such a group attached to chromium(III) is expected to be lost rapidly by aquation.

More recently Gould (*163*) has extended his work on electron transfer through organic structural units to include the effect of chain branching and nitro and thia substituents. As in earlier studies, the enhancement of rates through remote attack of ligands having conjugate bonding is confined to those ligands which are readily reducible. Jordan *et al.* (*226*) have studied the $Cr^{2+}$ reduction of nitrilo and related pentammine complexes $Co(NH_3)_5NCCH_3^{3+}$, $Co(NH_3)_5NCCH{=}CH_2^{3+}$, $Co(NH_3)_5NCCH_2CN^{3+}$, and $Co(NH_3)_5NC_5H_5^{3+}$.

The reaction of chromium(II) with the hexammine complex $Co(NH_3)_6^{3+}$ is believed to be an outer-sphere reaction, since there is no inverse hydrogen-ion dependence (thus excluding amide bridging) (*414*). Manning and Jarnagin (*251*) have studied the catalysis by chloride and bromide,

$$k_{obs} = k_1 + k_2[X^-] \qquad (117)$$

using relatively large (> 0.1 *M*) concentrations of the halide ions. They compare $k_1$ and $k_2$ values with those obtained for the $Cr^{2+}$–$Co(NH_3)_5OAc^{2+}$ and $Cr^{2+}$–$Co(NH_3)_5FuH^{2+}$ reactions (*333*) (where Fu = fumarate). These reactions are known to be inner-sphere and, since both the halide and organic ligand have been detected in the inner-coordination sphere of the chromium(III) produced, it can be concluded that the activated complexes are $[(NH_3)_5Co{\cdot}OAc{\cdot}CrX(H_2O)_4]^{3+}$ and $[(NH_3)_5Co{\cdot}FuH{\cdot}CrX(H_2O)_4]^{3+}$, respectively. They find that $Cl^-$ is about 2.5 times more effective than $Br^-$ in all three cases. It seems likely that in both inner- and outer-sphere reactions the $Cr^{2+}$ reactant brings the halide into the transition complex. The role of the halide ion would appear to be either or both (a) to make the relaxation time of the ligand vibrations more rapid and (b) to raise the energy of the electron which is to be transferred, as Zwickel and Taube have suggested (*414*). Pyrophosphate accelerates the reduction of $Co(NH_3)_5Cl^{2+}$ by $Cr^{2+}$ and the chromium(III) product contains both the chloride and pyrophosphate in its inner-coordination sphere (*120*, *375*). Chloride ions accelerate the $Cr^{2+}$ reduction of $Co(NH_3)_5H_2O^{3+}$ presumably by a similar nonbridging mechanism (*244*).

While outer-sphere reactions are the exception with chromium(II), the converse may be the case with vanadium(II). It is perhaps significant that the reaction of $V^{2+}$ with $Co(NH_3)_6^{3+}$ ($k = 4.4 \times 10^{-3}$ l·mole$^{-1}$ sec$^{-1}$ at 25°) is faster than that of $Cr^{2+}$ with $Co(NH_3)_6^{3+}$ ($k = 9 \times 10^{-5}$ l·mole$^{-1}$

$\text{sec}^{-1}$), although the redox potential is much more favorable for $Cr^{2+}$ (*414*). The reaction of $V^{2+}$ with the binuclear complex $(NH_3)_5Co \cdot NH_2 \cdot Co(NH_3)_5^{5+}$ takes place in one-equivalent steps (*109*),

$$V^{2+} + (NH_3)_5Co \cdot NH_2 \cdot Co(NH_3)_5^{5+} \xrightarrow{H^+} V^{3+} + Co(NH_3)_6^{3+} + Co^{2+} + 5NH_3 \quad (118)$$

$$V^{2+} + Co(NH_3)_6^{3+} \longrightarrow V^{3+} + Co^{2+} + 6NH_3 \quad (119)$$

and not with intermediate formation of vanadium(IV). That reaction (118) is some 30 times faster than reaction (119) is due to the difference in activation entropies. Similar results have been obtained with $Cr^{2+}$ as the reducing ion. In the reaction of $V^{2+}$ with $Co(NH_3)_5H_2O^{3+}$, rate constants are independent of hydrogen-ion concentrations over the range $10^{-4}$ to 1.0 *N* (*107*), and the path involving $Co(NH_3)_5OH^{2+}$ appears to play no significant role as it does in the $Cr^{2+}$ reaction. Dodel and Taube (*107*) have also studied the effect of $Cl^-$, $SO_4^{2-}$, and $F^-$ on the rates of the $V^{2+}$–$Co(NH_3)_6^{3+}$ and $V^{2+}$–$Co(NH_3)_5H_2O^{3+}$ reactions, and find the ratios of $k_2$ (for the catalyzed reaction) to $k_1$ (for the uncatalyzed reaction) to be 8.0, 1930, and 21,000, respectively, in the one case, and 8.5, 1830, and 18,300 in the second case. They conclude that the $V^{2+}$–$Co(NH_3)_5H_2O^{3+}$ reaction, like the $V^{2+}$–$Co(NH_3)_6^{3+}$ reaction, is outer-sphere. The similarity of the rates for the vanadium(II) reduction of $Co(NH_3)_5N_3^{2+}$ (18.0 $l \cdot \text{mole}^{-1}\ \text{sec}^{-1}$) and $Co(NH_3)_5NCS^{2+}$ (0.3 $l \cdot \text{mole}^{-1}\ \text{sec}^{-1}$) suggests that these reactions are outer-sphere (*79*), but similar rates might also be expected here if substitution into the $V^{2+}$ coordination sphere were rate determining. Other reasoning suggests that the reaction of $V^{2+}$ with $FeNCS^{2+}$ and $FeCl^{2+}$ are outer-sphere (*36*). Thus the two rates are similar and are more rapid than rates which are generally observed for the replacement of a water molecule in the inner-coordination sphere of $V^{2+}$. Other related studies have been reported (*416*, *419*).

Candlin *et al.* (*79*) have compared kinetic data for the reduction of a wide range of pentamminecobalt(III) complexes with $Cr^{2+}$, $V^{2+}$, $Eu^{2+}$, and $Cr(bipy)_3^{2+}$. The variation in rate with $V^{2+}$ as the reductant was found to be much smaller than with $Cr^{2+}$, and to show sufficient similarity to the variation in rates observed with $Cr(bipy)_3^{2+}$ to suggest that $V^{2+}$ and $Cr(bipy)_3^{2+}$ react by an outer-sphere mechanism. In contrast, the reactivity of $Eu^{2+}$ toward the halopentamminecobalt(III) complexes (*79*) was found to decrease: $Co(NH_3)_5F^{2+} > Co(NH_3)_5Cl^{2+} > Co(NH_3)_5Br^{2+} > Co(NH_3)_5I^{2+}$, a trend which has been interpreted in terms of an inner-sphere mechanism. A similar trend is observed in the reactions of $Fe^{2+}$ with $Co(NH_3)_5X^{2+}$ complexes (Fig. 1).

Candlin and Halpern (*77*) have examined volumes of activation for a number of $Fe^{2+}$ reactions with cobalt(III) complexes as a possible means of distinguishing between inner- and outer-sphere mechanisms. In the inner-sphere reaction, but not in the outer-sphere reaction, a coordinated water molecule is set free. Since the effective volume of the water molecule in the liquid is almost certainly larger than that when coordinated, more positive $\Delta V^{\ddagger}$ values should be observed for the inner-sphere process. The $\Delta V^{\ddagger}$ values observed range from 2.2 to 14 cc/mole and are consistent with inner-sphere mechanisms. Until a number of reactions of known mechanisms have been examined, however, this conclusion must be considered tentative.

Endicott and Taube (*122*) have studied the reactions of $Ru(NH_3)_6^{2+}$ with pentammine and tetrammine cobalt(III) complexes. Since $Ru(NH_3)_6^{2+}$ undergoes substitution very slowly compared to the rate at which it is oxidized, and the product is $Ru(NH_3)_6^{3+}$ (*121*), there can be little doubt that these reactions are of the outer-sphere type. The redox potential for the $Ru(NH_3)_6^{2+}/Ru(NH_3)_6^{3+}$ couple was found to be 0.214 volt by measuring the position of the equilibrium (*122*, *123*):

$$Ru(NH_3)_6^{2+} + Cu^{2+} \rightleftharpoons Ru(NH_3)_6^{3+} + Cu^{+} \qquad (120)$$

It is of interest that the $Co(NH_3)_6^{2+}/Co(NH_3)_6^{3+}$ couple (0.055 volt), but not the $Co^{2+}/Co^{3+}$ couple (1.95 volts), is less than this value. The reaction of $Ru(NH_3)_6^{2+}$ with $Co(NH_3)_6^{3+}$ is effective therefore only because $Co(NH_3)_6^{2+}$ is labile and is in effect removed from the equilibrium:

$$Ru(NH_3)_6^{2+} + Co(NH_3)_6^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(NH_3)_6^{3+} + Co(NH_3)_6^{2+} \qquad (K = 1.4 \times 10^{-2}) \qquad (121)$$

(Similar considerations also apply for other reactions in which cobalt(III) ammines are reduced, e.g., with $Fe^{2+}$.) In view of the unfavorable free energy change it is surprising that this reaction is as rapid as it is ($k_1 = 1 \times 10^{-2}$ l·mole$^{-1}$ sec$^{-1}$ at 25°). The reaction does not conform to the equation derived by Marcus for outer-sphere reactions (*122*). In the reaction of $Ru(NH_3)_6^{2+}$ with $Co(NH_3)_5N_3^{2+}$ complicated behavior is observed, the most likely explanation being that uncomplexed azide ion can also oxidize $Ru(NH_3)_6^{2+}$. The complex $Co(NH_3)_5H_2O^{3+}$ ($k = 3.0$ l·mole$^{-1}$ sec$^{-1}$) reacts faster than the hydroxy complex $Co(NH_3)_5OH^{2+}$ ($k = 0.04$ l·mole$^{-1}$ sec$^{-1}$). It should be noted that for reactions in which $Co(NH_3)_5OH^{2+}$ does not react appreciably faster than $Co(NH_3)_5H_2O^{3+}$, i.e., with $V^{2+}$, $Cr(bipy)_3^{2+}$, and $Ru(NH_3)_6^{2+}$, outer-sphere mechanisms are involved. In the reduction of $Ru(NH_3)_6^{3+}$, $Ru(NH_3)_5Cl^{2+}$, and $Ru(NH_3)_5H_2O^{3+}$ by $Cr^{2+}$ (*123*), the net changes are

$$Ru(NH_3)_6^{3+} + Cr^{2+} \rightarrow Ru(NH_3)_6^{2+} + Cr^{3+} \qquad (122)$$

$$Ru(NH_3)_5Cl^{2+} + Cr^{2+} \rightarrow Ru(NH_3)_5^{2+} + CrCl^{2+} \qquad (123)$$

$$Ru(NH_3)_5H_2O^{3+} + Cr^{2+} \rightarrow Ru(NH_3)_5^{2+} + Cr^{3+} \qquad (124)$$

where in Eqs. (123) and (124) a water molecule probably completes the coordination sphere of $Ru(NH_3)_5^{2+}$.

The pentacyanocobalt(II) complex is a strong reducing agent (*183*) which is now thought to have a square pyramidal (*415*), or octahedral $Co(CN)_5H_2O^{3-}$ structure (*425*). In the oxidation of $Co^{II}(CN)_5^{3-}$ by pentamminecobalt(III) complexes in the presence of free cyanide ions, there is evidence for both inner- and outer-sphere mechanisms (*78*, *187*). With $X^- = Cl^-$, $N_3^-$, $NCS^-$, and $OH^-$, the rate law is of the form

$$\text{Rate} = k_i[Co^{II}(CN)_5^{3-}][Co^{III}(NH_3)_5X^{2+}] \tag{125}$$

and, since $Co^{III}(CN)_5X^{3-}$ ions are formed, it is concluded that the reactions proceed with the formation of an inner-sphere activated complex:

$$[(CN)_5Co^{II}XCo^{III}(NH_3)_5]^-$$

With $X^- = PO_4^{3-}$, $CO_3^{2-}$, $SO_4^{2-}$, $NH_3$, and $OAc^-$, on the other hand, the reaction follows a different course and $Co^{III}(CN)_6^{3-}$ is formed. The rate law shows a direct dependence on the concentration of cyanide ions,

$$\text{Rate} = k_o[Co^{II}(CN)_5^{3-}][Co^{III}(NH_3)_5X^{2+}][CN^-] \tag{126}$$

and reactions are thought to proceed by an outer-sphere mechanism involving $Co^{III}(NH_3)_5X^{2+}$ and $Co^{II}(CN)_6^{4-}$, where the latter is presumed to exist in equilibrium with $Co^{II}(CN)_5^{3-}$:

$$Co^{II}(CN)_5^{3-} + CN^- \rightleftharpoons Co^{II}(CN)_6^{4-} \tag{127}$$

In two cases, with $X^- = F^-$ and $NO_3^-$, both inner- and outer-sphere paths are observed, and these can be made to predominate in turn by varying the concentration of cyanide ions. From the data in Table XV it can be seen that, for the outer-sphere reactions, there is only a relatively small variation in rate constants as $X^-$ is varied.

Pentacyanocobalt(II) also reacts with organic halides in aqueous solution to form pentacyanoorganocobaltate(III) compounds according to the reaction:

$$2Co(CN)_5^{3-} + RX \rightarrow Co(CN)_5R^{3-} + Co(CN)_5X^{3-} \tag{128}$$

Halpern and Maher (*185*) have studied the kinetics of such reactions with a number of organic halides, and in each case found the reaction to be first order in $Co(CN)_5^{2-}$ and the halide. The results are interpreted in terms of the stepwise mechanism:

$$Co(CN)_5^{3-} + RX \longrightarrow Co(CN)_5X^{3-} + R \tag{129}$$

$$Co(CN)_5^{3-} + R \xrightarrow{\text{fast}} Co(CN)_5R^{3-} \tag{130}$$

Second-order rate constants at 25° range from $2.5 \times 10^{-4}$ l·mole$^{-1}$ sec$^{-1}$ for $ClCH_2CO_2^-$ to $9 \times 10^4$ l·mole$^{-1}$ sec$^{-1}$ for $ICH_2CO_2CH_3$, the general trend reflecting an inverse dependence of the rate constant on the carbon-halogen bond strength.

TABLE XV

KINETIC DATA FOR INNER-SPHERE ($k_i$) AND OUTER-SPHERE ($k_o$) $Co^{II}(CN)_5^{3-}$–$Co^{III}(NH_3)_5X^{2+}$ REACTIONS (AT 25°, $\mu = 0.2$) (*78*, *187*)

| $X^-$ | $k_i$ (l·mole$^{-1}$ sec$^{-1}$) | $k_o$ (l$^2$·mole$^{-2}$ sec$^{-1}$) |
|---|---|---|
| $Br^-$ | $> 2 \times 10^9$ | — |
| $Cl^-$ | $\sim 5 \times 10^7$ | — |
| $N_3^-$ | $1.6 \times 10^6$ | — |
| $NCS^-$ | $1.1 \times 10^6$ | — |
| $ONO^-$ [a] | $4.2 \times 10^5$ | — |
| $OH^-$ | $9.3 \times 10^4$ | — |
| $NO_2^-$ [a] | $3.4 \times 10^4$ | — |
| $NH_3$ | — | $9 \times 10^4$ |
| $SO_4^{2-}$ | — | $3.6 \times 10^4$ |
| $OAc^-$ | — | $1.1 \times 10^4$ |
| Fumarate$^{2-}$ | — | $1.2 \times 10^4$ |
| Oxalate$^{2-}$ | — | $1.0 \times 10^4$ |
| Maleate$^{2-}$ | — | $7.5 \times 10^3$ |
| Succinate$^{2-}$ | — | $6 \times 10^3$ |
| $CO_3^{2-}$ | — | $\sim 1 \times 10^3$ |
| $PO_4^{3-}$ | — | $5.2 \times 10^2$ |
| $F^-$ | $1.8 \times 10^3$ | $1.7 \times 10^4$ |
| $NO_3^-$ | $\leqslant 1.0 \times 10^4$ | $2.4 \times 10^5$ |

[a] The nitro and nitrito complexes both give $Co(CN)_5NO_2^{3-}$ as the final product. In the former, $Co(CN)_5ONO^{3-}$ has been detected as an intermediate (*186*).

In the reactions of H-atoms with a variety of cobalt(III) ammine complexes, the ligands of the complex are inert toward the H-atoms with the possible exception of the complexes $Co(NH_3)_5NO_2^{2+}$, $Co(NH_3)_5N_3^{2+}$, $Co(NH_3)_5(O_2CCH{=}CHCO_2H)^{2+}$, and $Co(NH_3)_5NCS^{2+}$, and reactions proceed with the reduction of cobalt(III) to cobalt(II). There is only general agreement between the rate constants determined by Halpern and Rabani (*189*), Anbar and Meyerstein (*20*), and Navon and Stein (*274*), and numerical values for any one reaction differ by as much as two powers of ten. The nature of the reductant, its low reactivity toward $Co(NH_3)_6^{3+}$, and the very drastic solvation change associated with the direct outer-sphere oxidation of H-atoms to $H_3O^+$ (which will be more extensively solvated), tend to favor attack of the H-atom on the anionic ligand (*189*):

$$(NH_3)_5Co^{III}X^{2+} + H \rightarrow [(NH_3)_5Co^{II}XH)]^{2+} \rightarrow Co^{II} + HX + 5NH_3 \qquad (131)$$

The reactivity pattern, $Co(NH_3)_5I^{2+} > Co(NH_3)_5Br^{2+} > Co(NH_3)_5Cl^{2+} > Co(NH_3)_5^{2+}$, is the same as that observed with $Cr^{2+}$ and $Co(CN)_5^{3-}$ as reductant, but the reverse of that observed for $Eu^{2+}$ and $Fe^{2+}$ (Fig. 1).

Recent studies of the reduction of $Co(en)_2NCSX^+$ complexes by chromium(II) (*177*) and of $Co(en)_2ClX^+$ complexes by iron(II) (*56*) ($X^- = H_2O$, $NH_3$, $Cl^-$, and $SCN^-$) have shown that cis and trans isomers differ considerably in reactivity. Although the chromium(II) reactions proceed via thiocyanate-bridged activated complexes, while the iron(II) reactions are believed to proceed via chloride-bridged activated complexes (with the possible exception of $Co(en)_2ClN_3{}^+$), the same sort of general pattern emerges in both series of reactions. First of all, for $X^- = NH_3$ or $NCS^-$, only minor differences between the rates of the *cis* and trans isomers are observed. Second, replacement of $NH_3$ by $NCS^-$ in either the cis or trans position results in a modest increase in rate. Third, replacement of $NH_3$ by $H_2O$ results in a large increase in rate, especially for the trans compound. The observed nonbridging ligand effects have been discussed (*56*) in terms of the models proposed by Orgel (*292*) and Taube (*376*, *377*) (see also page 166). Green *et al.* (*165*) have investigated the extent to which the stretching of Co—$NH_3$ bonds is important in the reactions of $Co(NH_3)_5H_2O^{3+}$, $Co(NH_3)_5Cl^{2+}$, $Co(en)_2NH_3Cl^{2+}$, and $Co(en)_2(NH_3)H_2O^{2+}$ with $Cr^{2+}$. The kinetic fractionation factors $d(\ln[^{14}N])/d(\ln[^{15}N])$ are very small (1.002 and 1.001) for the first two complexes, and identical with $NH_3$ *cis* or *trans* to the bridging group in the ethylenediamine complexes. It is concluded that in these reactions at least there is little change in Co—$NH_3$ bond lengths attendant on electron transfer.

Kruse and Taube (*245*) have shown that, in the reaction of $Cr^{2+}$ with *cis*-$Co(en)_2(H_2O)_2^{3+}$, only one oxygen atom is transferred to the chromium atom. This demonstrates that electron transfer proceeds via a singly bridged activated complex. The reductions of *cis*- and *trans*-diaquo and aquoamminebis(ethylenediamine)cobalt(III) complexes by $Cr^{2+}$ have been studied by Cannon and Earley (*80*) and found to obey the rate law:

$$\text{Rate} = k[Co^{III}][Cr^{II}][H^+]^{-1} \qquad (132)$$

At 25° second-order rate constants $\times 10^{-6}$ ($l \cdot mole^{-1}\ sec^{-1}$) and activation energies (kcal $mole^{-1}$) for the reduction of the hydroxo complexes are: aquo complexes, cis 0.79, 6.4; trans 2.6, 2.6; ammine complexes, cis 0.20, 6.2; trans 0.22, 2.4. Outward motion of the ligand trans to the bridging group at the time of electron transfer is probably much less important in these reactions. The variation in activation energies may be due to reorganization requirements within the binuclear complex, or enthalpy requirements for the formation of the binuclear complex.

Haim (*172*) has compared the rates of reduction of *cis*- and *trans*-$Co(NH_3)_4(N_3)_2^+$ and $Co(NH_3)_5N_3^{2+}$ by $Fe^{2+}$ (Table XVI). All three reactions show a first-order dependence on each of the reactants, but, whereas the reactions of $Co(NH_3)_5N_3^{2+}$ and *cis*-$Co(NH_3)_4(N_3)_2^+$ are independent of the hydrogen-ion concentration, that of *trans*-$Co(NH_3)_4(N_3)_2^+$ shows a strong direct dependence:

TABLE XVI

RATE CONSTANTS $k_1$ AND $k_2$ FOR THE REACTION OF $Fe^{2+}$ WITH AZIDE COMPLEXES OF $Co^{III}$ (AT 25°)

| $Co^{III}$ complex | $k_1$ ($l \cdot mole^{-1} sec^{-1}$) | $k_2$ ($l^2 \cdot mole^{-2} sec^{-1}$) |
|---|---|---|
| $Co(NH_3)_5N_3^{2+}$ | 0.009 | — |
| *trans*-$Co(NH_3)_4(N_3)_2^+$ | 0.073 | 1.36 |
| *cis*-$Co(NH_3)_4(N_3)_2^+$ | 0.186 | — |
| *trans*-$Co(NH_3)_4(H_2O)N_3^{2+}$ | 24.0 | — |
| *cis*-$Co(NH_3)_4(H_2O)N_3^{2+}$ | 0.355 | — |

$$k_{obs} = k_1 + k_2[H^+] \tag{133}$$

Because of the substitution lability of the $Fe^{III}$ product, it cannot be ascertained whether these reactions proceed *via* a bridged or outer-sphere activated complex. Assuming that bridged activated complexes are formed, reasonable explanations can be advanced for the relative rates of these reactions. The increased reactivity of *trans*-$Co(NH_3)_4(N_3)_2^+$ as compared to $Co(NH_3)_5N_3^{2+}$ is as expected, but the reaction of the *cis* complex is faster still. In the latter case the most probable explanation is that both azide ligands bridge the reactants in the activated complex. With the trans isomer, one of the azide ions is non-bridging and protonation of this ligand facilitates electron transfer. Haim (*173*) has also studied the reduction of *cis*- and *trans*-$Co(NH_3)_4(H_2O)N_3^{2+}$ with iron(II). The enhanced rate with a water molecule in the *trans* position is again noted.

Kopple and Miller (*240*) have determined the rates of reaction of a number of tetramminecobalt(III) complexes with chromium(II). With *trans*-$Co(NH_3)_4(OAc)_2^+$ there is a direct hydrogen-ion dependence

($k = 15 + 50[H^+]$ l·mole$^{-1}$ sec$^{-1}$ at 25°) and the reaction is appreciably faster than the reaction of $Co(NH_3)_5OAc^{2+}$ ($k = 0.18$ l·mole$^{-1}$ sec$^{-1}$), which has no hydrogen-ion dependence. In the case of the *cis*-$Co(NH_3)_4(H_2O)OAc^{2+}$ complex there is an inverse hydrogen-ion dependence ($k = 47 + 2.8[H^+]^{-1}$ l·mole$^{-1}$ sec$^{-1}$), and since $CoOAc^{2+}$ is the product a part of the reaction at least probably proceeds by a di-bridged activated complex with bridging hydroxo and acetato ligands. Similar reasoning applies in the reaction of *cis*-$Co(NH_3)_4(H_2O)SO_4^+$ with $Cr^{2+}$ (*269*), although in this instance the hydrogen-ion dependence is more complex:

$$k_{obs} = 1.1[H^+]^{-1} + 3.0 + 8.5[H^+]$$

In the reduction of $Co^{III}EDTA^-$ (which may be written $CoY^-$) and related complexes with $Fe^{2+}$ (*303*, *406*) and $Cr^{2+}$ (*405*), it is concluded that both series of reactions are of the inner-sphere type. One or two carboxylate groups of the chelate ligand are believed to form bridging groups, except in the case of $Co^{III}(HY)Cl^-$ and $Co^{III}(YOH)OH$. In the latter the bridging ligands are the chloro and hydroxo groups, respectively. In the reduction of $CoY^-$ and $Co(C_2O_4)_3^{3-}$ in weak acid solutions, some of the chromium(III) product is coordinated to three carboxylato groups (*405*). It now seems doubtful whether more than two carboxylate groups are transferred in the initial step (*407*).

At 0° the rate equation for the reaction of iron(II) and cobalt(III) aquo ions (*53*) is of the form:

$$\text{Rate (sec}^{-1}) = 10[Fe^{2+}][Co^{3+}] + 6500[Fe^{2+}][CoOH^{2+}] \qquad (134)$$

That the rate is some $10^5$ times slower than that predicted by the Marcus theory is probably due to spin restrictions of the cobalt(III) reactant. With $CoCl^{2+}$ as the oxidant it has been established that the reaction is of the inner-sphere type (*94*),

$$Fe^{2+} + CoCl^{2+} \rightarrow [FeClCo]^{4+} \rightarrow FeCl^{2+} + Co^{2+} \qquad (135)$$

and high intermediate concentrations of $FeCl^{2+}$ have been detected. Other $Fe^{II}$–$Co^{III}$ reactions are of the inner-sphere type (*421*).

Kirwin *et al.* (*238*) find that the reaction of cobalt(III) with silver(I) consists of a rapid equilibrium,

$$Co^{III} + Ag^{I} \rightleftharpoons Ag^{II} + Co^{II} \qquad (136)$$

followed by the reaction of $Ag^{II}$ with water. The latter reaction has been studied separately (*237*) and the rate law is of the form,

$$\text{Rate} = k[Ag^{II}]^2[Ag^{I}]^{-1} \qquad (137)$$

which is consistent with a mechanism:

$$\mathrm{Ag^{II}} \rightleftharpoons \mathrm{Ag^{I}} + \mathrm{Ag^{III}} \tag{138}$$

$$\mathrm{Ag^{III}} + \mathrm{H_2O} \rightarrow \text{products} \tag{139}$$

It can be concluded therefore that the $\mathrm{Ag^{III}}$ and not the $\mathrm{Ag^{II}}$ oxidizes water.

Dulz and Sutin (*116*) have used flow techniques to study the kinetics of the reaction of $\mathrm{Cr^{2+}}$ with $\mathrm{Fe^{3+}}$ in the presence of chloride ions. The rate equation is

$$\text{Rate} = k_1[\mathrm{Cr^{2+}}][\mathrm{Fe^{3+}}] + k_2[\mathrm{Cr^{2+}}][\mathrm{FeOH^{2+}}] + k_3[\mathrm{Cr^{2+}}][\mathrm{FeCl^{2+}}] + k_4[\mathrm{Cr^{2+}}][\mathrm{Fe_3{}^{+}}][\mathrm{Cl^{-}}] \tag{140}$$

and, at 25° and $\mu = 1.0\ M$, $k_1 = 2.3 \times 10^3$ l·mole$^{-1}$ sec$^{-1}$, $k_2 = 3.3 \times 10^6$ l·mole$^{-1}$ sec$^{-1}$, $k_3 = 2.0 \times 10^7$ l·mole$^{-1}$ sec$^{-1}$, and $k_4 = 2.0 \times 10^4$ l$^2$·mole$^{-2}$ sec$^{-1}$. It is possible to identify the two chloride paths since observed rates are different if, in the one case, a $\mathrm{Cr^{2+}} + \mathrm{Cl^{-}}$ solution is allowed to react with $\mathrm{Fe^{3+}}$ and, in the other, both the $\mathrm{Cr^{2+}}$ and $\mathrm{Fe^{3+}}$ solutions are premixed with equivalent amounts of chloride. The reaction path $k_3$ is of the inner-sphere type, but the activated complex for $k_4$, which also involves chloride, is less certain. In similar experiments using thiocyanate instead of chloride, Haim and Sutin (*176*) have shown that $\mathrm{CrSCN^{2+}}$ (35%) and $\mathrm{CrNCS^{2+}}$ (65%) are both produced (see page 165).

A quenching method has been used by Adamson *et al.* (*9*) to study the kinetics of the oxidation of iron(II) by cerium(IV):

$$-d[\mathrm{Fe^{II}}]/dt = k[\mathrm{Fe^{II}}][\mathrm{Ce^{IV}}] \tag{141}$$

Both reactants were in the micromolar concentration range, the overall rate constant $k$ being of the order of $10^3$ l·mole$^{-1}$ sec$^{-1}$ at 0.3°. The hydrogen-ion dependence is of the approximate form

$$k = a[\mathrm{H^+}] + b + c[\mathrm{H^+}]^{-1} \tag{142}$$

and, since the principal $\mathrm{Ce^{IV}}$ species is $\mathrm{CeOH^{3+}}$ and not $\mathrm{Ce^{4+}}$, this corresponds to reaction steps $\mathrm{Ce^{4+}} + \mathrm{Fe^{2+}}$, $\mathrm{CeOH^{3+}} + \mathrm{Fe^{2+}}$, and $\mathrm{Ce(OH)_2^{2+}} + \mathrm{Fe^{2+}}$, respectively. The reaction is catalyzed by bisulfate and fluoride, but not by chloride.

The reaction of iron(II) with manganese(III)

$$\mathrm{Fe^{II}} + \mathrm{Mn^{III}} \rightarrow \mathrm{Fe^{III}} + \mathrm{Mn^{II}} \tag{143}$$

has been studied by Diebler and Sutin (*104*) using a flow technique, and by Nicol and Rosseinsky (*289*) using a polarographic method. At 25°, $k_{obs}$ is of the order of $10^4$ l·mole$^{-1}$ sec$^{-1}$, where

$$k_{obs} = k_1 + k_2[\mathrm{H^+}]^{-1} \tag{144}$$

Activation parameters for $k_1$ are $\Delta H^\ddagger = 12.1$ kcal mole$^{-1}$ and $\Delta S^\ddagger = -1.3$ eu. The one-equivalent reaction of manganese(II) with cobalt(III) ($k_{obs} \sim 10^2$ l·mole$^{-1}$ sec$^{-1}$ at 25°) has been studied in less detail (*104*). Oxidation of manganese(II) with cerium(IV) (*32*) in 4.5 *M* sulfuric acid proceeds to an equilibrium

$$\mathrm{Mn^{II} + Ce^{IV} \rightleftharpoons Mn^{III} + Ce^{III}} \tag{145}$$

the equilibrium constant being 0.015 at ~ 20°.

Rosseinsky and Higginson (*327*) have studied the reaction of vanadium(IV) with cobalt(III),

$$\mathrm{V^{IV} + Co^{III} \rightarrow V^{V} + Co^{II}} \tag{146}$$

and in addition the reaction of vanadium(III) with cobalt(III). In the latter the full reaction sequence is

$$\mathrm{V^{III} + Co^{III} \longrightarrow V^{IV} + Co^{II}} \tag{147}$$

$$\mathrm{V^{IV} + Co^{III} \longrightarrow V^{V} + Co^{II}} \tag{148}$$

$$\mathrm{V^{III} + V^{V} \xrightarrow{fast} 2V^{IV}} \tag{149}$$

rate constants for the hydrogen ion-independent paths in Eqs. (147) and (148) being 0.192 and 0.260 l·mole$^{-1}$ sec$^{-1}$, respectively, at 0°. The reaction of vanadium(III) and iron(III) follows a similar sequence (*200*),

$$\mathrm{V^{III} + Fe^{III} \longrightarrow V^{IV} + Fe^{II}} \tag{150}$$

$$\mathrm{V^{IV} + Fe^{III} \rightleftharpoons V^{V} + Fe^{II}} \tag{151}$$

$$\mathrm{V^{III} + V^{V} \xrightarrow{fast} 2V^{IV}} \tag{152}$$

the overall reaction being represented by Eq. (150). Although the equilibrium in reaction (151) lies well to the left ($K \sim 10^{-6}$), reaction (152) is sufficiently fast to make the path provided by reactions (151) and (152) effective in the absence of large amounts of Fe$^{\mathrm{II}}$. Copper(II) catalyzes the reaction, and with Cu$^{\mathrm{II}}$ concentrations at least equivalent to those of Fe$^{\mathrm{III}}$ the catalyzed reaction predominates. Under those conditions the rate is independent of Fe$^{\mathrm{III}}$,

$$\text{Rate} = k_{cat}[\mathrm{V^{III}}][\mathrm{Cu^{II}}] \tag{153}$$

which is consistent with a mechanism:

$$\mathrm{V^{III} + Cu^{II} \longrightarrow V^{IV} + Cu^{I}} \tag{154}$$

$$\mathrm{Cu^{I} + Fe^{III} \xrightarrow{fast} Cu^{II} + Fe^{II}} \tag{155}$$

The vanadium(III)–vanadium(V) reaction has been studied by making use of the high vanadium(V) absorption in the 300–350 m$\mu$

region, and by using low reactant concentrations (*101*). A feature of the reaction is the complex hydrogen-ion dependence:

$$k_{obs} = k_1[H^+] + k_2 + k_3[H^+]^{-1} + k_4[H^+]^{-2} \tag{156}$$

The reaction of vanadium(V) with iron(II),

$$Fe^{II} + V^{V} \rightarrow Fe^{III} + V^{IV} \tag{157}$$

has been studied by two different methods (*100*, *288*). Again there is a direct and an inverse hydrogen ion-dependent path, which suggests that the vanadium(V) ion $VO_2^+$ can bring either a proton or an $OH^-$ into the activated complex.

That the reaction of europium(II) with vanadium(III) (*10*) is slower than the corresponding chromium(II)–vanadium(III) reaction is at least in part due to the difficulty in transferring *f* electrons. In the reaction of europium(II) with chromium(III) there is incomplete reaction, the equilibrium constant $K$ being ~ 2. The following reactions have been studied,

$$\begin{tikzcd}
Eu^{2+} + Cr^{3+} \arrow[r, "+Cl^-"] \arrow[dd, shift left, "k_1"] & Eu^{2+} + Cr^{3+} + Cl^- \arrow[rr, "slow"] \arrow[dr, "as\ k_1"'] & & Eu^{2+} + CrCl^{2+} \arrow[dl, shift left, "k_2"] \\
& & Eu^{3+} + Cr^{2+} + Cl^- \arrow[ur, shift left, "k_{-2}"] & \\
Eu^{3+} + Cr^{2+} \arrow[uu, shift left, "k_{-1}"] & & &
\end{tikzcd} \tag{158}$$

$k_1$ and $k_{-1}$ being of the order of $10^{-5}$ l·mole$^{-1}$ sec$^{-1}$ and $k_2$ around $10^{-3}$ l·mole$^{-1}$ sec$^{-1}$ at 25°.

The effect which chloride ions have on a number of titanium(III) reactions is of interest. Thus with iron(III) there is a marked catalysis (*97*) but with plutonium(IV) (*315*) there is little or no effect [contrast the large effect which chloride has on the $Fe^{II}$–$Pu^{IV}$ reaction (*286*)] and, with mercury(II), chloride ions inhibit the reaction (*97*). Chloride ions have little or no effect on the plutonium(IV) oxidation of vanadium(III) and uranium(IV) (*316*), but inhibit the reaction of iron(II) with thallium(III), and the thallium(I)–thallium(III) exchange (*147*, *191*). There is a first-order dependence on metal ion concentrations in the reaction between titanium(III) and mercury(II) (*97*). The first step

$$Ti^{III} + Hg^{II} \rightarrow Ti^{IV} + Hg^{I} \tag{159}$$

is rate-determining, and is presumably followed by

$$Ti^{III} + Hg^{I} \xrightarrow{fast} Ti^{IV} + Hg^{0} \tag{160}$$

$$Hg^{0} + Hg^{II} \xrightarrow{fast} (Hg^{I})_2 \tag{161}$$

Unless mercury(II) is in excess of the titanium(III), mercury is precipitated. Similar mechanisms are observed with chromium(II) and europium(II) as the reducing ion (*371*). In the mercury(II) oxidation of vanadium(III) the rate equation is complex (*197*). The oxidation of iron(II) by mercury(II) is very slow (*7*).

The oxidation of tantalum clusters, $Ta_6Cl_{12}^{2+}$, with iron(III) proceeds stepwise (*132*):

$$Ta_6Cl_{12}^{2+} + Fe^{3+} \rightarrow Ta_6Cl_{12}^{3+} + Fe^{2+} \tag{162}$$

$$Ta_6Cl_{12}^{3+} + Fe^{3+} \rightleftharpoons Ta_6Cl_{12}^{4+} + Fe^{2+} \tag{163}$$

The equilibrium constant for the second stage is less than unity, and iron(III) concentrations greater than ca. 0.01 $M$ are required to effectively convert $10^{-5}$ $M$ $Ta_6Cl_{12}^{2+}$ to $Ta_6Cl_{12}^{4+}$. With initial concentrations of iron(III) of around $10^{-4}$ $M$, the rate constant for reaction (162) can be determined and is found to be 620 $l\cdot mole^{-1}$ $sec^{-1}$ at 15° and $\mu = 0.02$ $M$.

When vanadium(II) and uranium(VI) are mixed (*283*), the first step

$$V^{II} + U^{VI} \rightarrow V^{III} + U^{V} \tag{164}$$

is followed by

$$V^{II} + U^{V} \rightarrow V^{III} + U^{IV} \tag{165}$$

$$2U^{V} \rightarrow U^{IV} + U^{VI} \tag{166}$$

$$V^{III} + U^{V} \rightarrow V^{IV} + U^{IV} \tag{167}$$

The rates observed for reactions (165), (166), and (167) are such that it is difficult to determine directly the rate of reaction (164) but, if an excess of vanadium(IV) is added, the reaction

$$V^{IV} + U^{V} \rightarrow V^{III} + U^{VI} \tag{168}$$

is much faster than reactions (165), (166), and (167). Under these conditions the uranium(VI) in effect catalyzes the reaction of vanadium(II) with vanadium(IV). The only term in the rate law is

$$\text{Rate} = k_1[V^{II}][U^{VI}] \tag{169}$$

and $k_1$ is essentially independent of the hydrogen-ion concentration. The activation parameters for $k_1$ are $\Delta H^\ddagger = 7.1$ kcal $mole^{-1}$ and $\Delta S^\ddagger = -26.1$ eu. The reaction of vanadium(III) and uranium(VI) has already been referred to (page 188).

The reaction of vanadium(III) with neptunium(V) (*25*)

$$V^{III} + Np^{V} \xrightarrow{k_1} V^{IV} + Np^{IV} \tag{170}$$

proceeds only in part by the direct route. The rate law is of the form

$$-d[NpO_2^+]/dt = [NpO_2^+][V^{3+}](k_1 + k_3K_2[Np^{4+}][VO^{2+}]^{-1}) \tag{171}$$

which is consistent with additional steps:

$$\mathrm{V^{III}} + \mathrm{Np^{IV}} \underset{\text{fast}}{\overset{K_2}{\rightleftharpoons}} \mathrm{V^{IV}} + \mathrm{Np^{III}} \tag{172}$$

$$\mathrm{Np^{III}} + \mathrm{Np^{V}} \xrightarrow{k_3} 2\mathrm{Np^{IV}} \tag{173}$$

The rate constant $k_3$ can be obtained independently, and $K_2$ for the equilibrium in reaction (172) can be determined directly by mixing solutions of vanadium(III) and neptunium(IV). The first stage, Eq. (170), differs from other reactions involving oxycations in that the rate law does not have a direct hydrogen-ion dependence. This suggests that there is oxygen-atom bridging,

$$\mathrm{V^{3+}} + \mathrm{NpO_2^{+}} \rightarrow [\mathrm{ONpOV}]^{4+} \rightarrow \mathrm{VO^{2+}} + \mathrm{NpO^{2+}} \tag{174}$$

where the $\mathrm{NpO^{2+}}$ subsequently equilibrates with $\mathrm{H^+}$ ions. The activation parameter corresponding to $k_1$ and $\Delta H^\ddagger = 14.6$ kcal mole$^{-1}$ and $\Delta S^\ddagger = -12.3$ eu. In the reduction of neptunium(VI) by vanadium(III) (*336*), there is an inverse hydrogen-ion dependence:

$$\text{Rate} = [\mathrm{Np^{VI}}][\mathrm{V^{III}}](k_1 + k_2[\mathrm{H^+}]^{-1}) \tag{175}$$

Activation parameters for $k_1$ are $\Delta H^\ddagger = 18.6$ kcal mole$^{-1}$ and $\Delta S^\ddagger = 5$ eu.

The vanadium(III) reductions of plutonium(IV) (*277*) and plutonium(VI) (*310*) have been studied, and are relatively straightforward. In both instances single-stage one-equivalent reactions are observed, and the hydrogen-ion dependence is of the form:

$$k_{obs} = k_1[\mathrm{H^+}]^{-1} + k_2[\mathrm{H^+}]^{-2} \tag{176}$$

With titanium(III) as the reducing ion both the plutonium(IV) (*315*) and plutonium(VI) (*314*) reactions have just one inverse hydrogen ion-dependent path.

A feature of reactions in which the extent of hydrolysis of one of the reactants increases markedly in going to products is the large inverse hydrogen-ion dependence. In the oxidation of neptunium(IV) to neptunium(V), for example, the overall equation (*214*) being

$$\mathrm{Np^{4+}} + \mathrm{Fe^{3+}} + 2\mathrm{H_2O} \rightarrow \mathrm{NpO_2^{+}} + \mathrm{Fe^{2+}} + 4\mathrm{H^+} \tag{177}$$

the rate law is

$$-d[\mathrm{Np^{IV}}]/dt = k[\mathrm{Np^{IV}}][\mathrm{Fe^{III}}][\mathrm{H^+}]^{-3} \tag{178}$$

and the reaction is more favorable when the hydrolysis of $\mathrm{Np^{4+}}$ approaches that of the products. In the corresponding reaction of iron(III) with uranium(IV) (*58*), uranium(VI) is the final product,

$$\mathrm{U^{4+}} + 2\mathrm{Fe^{3+}} + 2\mathrm{H_2O} \rightarrow \mathrm{UO_2^{2+}} + 2\mathrm{Fe^{3+}} + 4\mathrm{H^+} \tag{179}$$

and the first step in which uranium(V) is formed is rate-determining. Betts (*58*) reports a hydrogen-ion dependence:

$$-d[\mathrm{U^{IV}}]/dt = [\mathrm{U^{IV}}][\mathrm{Fe^{III}}](k_1[\mathrm{H^+}]^{-1} + k_2[\mathrm{H^+}]^{-2}) \qquad (180)$$

The reaction has also been studied in sulfuric and hydrochloric acid solutions (*135*). Similar kinetics are observed for the reaction with cerium(IV) (*39*), the rate equation being

$$-d[\mathrm{U^{IV}}]/dt = k[\mathrm{U^{IV}}][\mathrm{Ce^{IV}}][\mathrm{H^+}]^{-2} \qquad (181)$$

The disproportionation of uranium(V)

$$\mathrm{U^{V} + U^{V} \rightarrow U^{IV} + U^{VI}} \qquad (182)$$

is rapid (*219a*), the rate law showing a direct hydrogen-ion dependence,

$$\text{Rate (sec}^{-1}) = 436[\mathrm{UO_2}^+]^2[\mathrm{H^+}] \qquad (183)$$

which is as expected since there is a conversion of $UO_2^+$ to $U^{4+}$. Newton and Baker (*284*) have shown that the disproportionation is much slower in the presence of uranium(VI) due to the formation of a binuclear complex:

$$\mathrm{UO_2^+ + UO_2^{2+} \rightarrow U_2O_4^{3+}} \qquad (184)$$

The disproportionation of plutonium(V) (*309*) is much slower than that of uranium(V),

$$\text{Rate (sec}^{-1}) = 3.6 \times 10^{-3}[\mathrm{PuO_2}^+]^2[\mathrm{H^+}] \qquad (185)$$

the activation energy (19 kcal $\text{mole}^{-1}$) being twice that for the uranium reaction. Sullivan *et al.* (*354*) have obtained data for the disproportionation of neptunium(V) by studying the reverse reaction (*203*):

$$\mathrm{Np^{IV} + Np^{VI} \rightarrow 2Np^{V}} \qquad (186)$$

In the disproportionation of americium(V) (*88*), the net reaction is

$$\mathrm{3AmO_2^+ + 4H^+ \rightarrow 2AmO_2^{2+} + Am^{3+} + 2H_2O} \qquad (187)$$

The rate equation for $\mu = 2.0\ M$ perchlorate solutions is

$$-d[\mathrm{AmO_2}^+]/dt = k_1[\mathrm{AmO_2}^+]^2[\mathrm{H^+}]^2 + k_2[\mathrm{AmO_2}^+]^2[\mathrm{H^+}]^3 \qquad (188)$$

and, at 25°, $k_1 = 7.0 \times 10^{-4}\ \mathrm{l^3 \cdot mole^{-3}\, sec^{-1}}$ and $k_2 = 4.6 \times 10^{-4}\ \mathrm{l^4 \cdot mole^{-4}\, sec^{-1}}$. Although the acid dependence is lower than the fourth-power dependence previously reported (*180*, *345*), it remains higher than for the other disproportionations. This difference in behavior is difficult to explain.

The reaction of neptunium(III) with neptunium(V) has been studied (*202*),

$$\mathrm{Np^{3+} + NpO_2^+ + 4H^+ \rightarrow 2Np^{4+} + 2H_2O} \qquad (189)$$

and the rate law is

$$\text{Rate (sec}^{-1}) = 43[\text{Np}^{3+}][\text{NpO}_2{}^{+}][\text{H}^{+}]$$

A slower rate is observed for the corresponding plutonium(III)–plutonium(V) reaction (*308*):

$$\text{Rate (sec}^{-1}) = 0.04[\text{Pu}^{3+}][\text{PuO}_2{}^{+}][\text{H}^{+}] \qquad (190)$$

With plutonium(III) and plutonium(VI) (*313*), the reactants and products are in the same hydrolyzed state and there is no hydrogen-ion dependence:

$$\text{Pu}^{3+} + \text{PuO}_2^{2+} \rightarrow \text{Pu}^{4+} + \text{PuO}_2{}^{+} \qquad (191)$$

The rate-determining step in the reaction (*356*)

$$2\text{Np}^{\text{VI}} + \text{U}^{\text{IV}} \rightarrow 2\text{Np}^{\text{V}} + \text{U}^{\text{VI}} \qquad (192)$$

corresponds to a change,

$$\text{Np}^{\text{VI}} + \text{U}^{\text{IV}} \rightarrow \text{Np}^{\text{V}} + \text{U}^{\text{V}} \qquad (193)$$

and the rate law (in $\text{sec}^{-1}$) is

$$d[\text{NpO}_2{}^{+}]/dt = 21.35[\text{U}^{4+}][\text{NpO}_2^{2+}][\text{H}^{+}]^{-1} \qquad (194)$$

Newton has studied the reactions of uranium(IV) with plutonium(IV) (*277*) and plutonium(VI) (*276*). The reaction of neptunium(V) with uranium(IV) is complex (*335*).

## VI. Noncomplementary and Two-Equivalent Reactions

Noncomplementary reactions are those occurring between one- and two- or three-equivalent reagents. A good example is the reaction of tin(II) with iron(III):

$$\text{Sn}^{\text{II}} + 2\text{Fe}^{\text{III}} \rightarrow \text{Sn}^{\text{IV}} + 2\text{Fe}^{\text{II}} \qquad (195)$$

This reaction is slow in perchloric acid solution but is strongly catalyzed by chloride ions (*161*), which serve to complex (and keep in solution) the tin(IV) which is formed. At high iron(III) to tin(II) ratios the rate law is of the form,

$$-d[\text{Fe}^{\text{III}}]/dt = k_{obs}[\text{Fe}^{\text{III}}][\text{Sn}^{\text{II}}] \qquad (196)$$

where $k_{obs}$ is strongly dependent on the chloride concentration. To account for data over a wide range of conditions, Weiss (*397*) proposed the mechanism:

$$\text{Sn}^{\text{II}} + \text{Fe}^{\text{III}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Sn}^{\text{III}} + \text{Fe}^{\text{II}} \qquad (197)$$

$$\text{Sn}^{\text{III}} + \text{Fe}^{\text{III}} \xrightarrow{k_2} \text{Sn}^{\text{IV}} + \text{Fe}^{\text{II}} \qquad (198)$$

Applying stationary-state kinetics for the unstable $\mathrm{Sn^{III}}$ state, it can be shown that

$$\frac{-d[\mathrm{Fe^{III}}]}{dt}=\frac{2k_1\,k_2[\mathrm{Fe^{III}}]^2\,[\mathrm{Sn^{II}}]}{k_{-1}[\mathrm{Fe^{II}}]+k_2[\mathrm{Fe^{III}}]} \tag{199}$$

On adding quantities of $\mathrm{Fe^{II}}$ initially so that $k_{-1}[\mathrm{Fe^{II}}] \gg k_2[\mathrm{Fe^{III}}]$, this reduces to an equation of the type

$$\frac{-d[\mathrm{Fe^{III}}]}{dt}=\frac{a[\mathrm{Fe^{III}}]^2[\mathrm{Sn^{II}}]}{[\mathrm{Fe^{II}}]} \tag{200}$$

which is the form of the rate law found by Noyes (*290*). Duke and Pinkerton (*112*) have studied the chloride-ion dependence and found this to be complex. More recently (*398*), using a cobalt(III) complex as substrate, it has been possible to show that a strongly reducing intermediate is formed in 1.0 $N$ hydrochloric acid solutions, and the results of a brief kinetic study are in good agreement with the mechanism outlined above. Other reaction sequences, in which there is intermediate formation of $[\mathrm{Fe \cdot Sn}]^{\mathrm{V}}$ or $\mathrm{Fe^{I}}$, would show different kinetic behavior.

The induced reduction of cobalt(III) complexes has also been used to test for the formation of tin(III) in other reactions of tin(II) (*398*). In the reactions with cerium(IV), chromium(VI), and manganese(VII), it has been concluded that tin(III) or a related reducing intermediate is formed. Thus in the reaction with cerium(IV) the most likely mechanism is

$$\mathrm{Sn^{II} + Ce^{IV} \rightarrow Sn^{III} + Ce^{III}} \tag{201}$$

$$\mathrm{Sn^{III} + Ce^{IV} \rightarrow Sn^{IV} + Ce^{III}} \tag{202}$$

with the additional step

$$\mathrm{Sn^{III} + Co^{III} \rightarrow Sn^{IV} + Co^{II}} \tag{203}$$

but without a full kinetic study the alternative mechanism

$$\mathrm{Sn^{II} + Ce^{IV} \rightleftharpoons [Sn \cdot Ce]^{VI}} \tag{204}$$

$$\mathrm{[Sn \cdot Ce]^{VI} + Ce^{IV} \rightarrow 2Ce^{III} + Sn^{IV}} \tag{205}$$

$$\mathrm{[Sn \cdot Ce]^{VI} + Co^{III} \rightarrow Sn^{IV} + Ce^{III} + Co^{II}} \tag{206}$$

cannot be entirely eliminated. In the reactions with mercury(II) and thallium(III) (and hydrogen peroxide, bromine, and iodine), tin(III) does not appear to be formed as an intermediate (*398*). Thus the reaction with thallium(III) appears to be of the single-stage two-equivalent type,

$$\mathrm{Sn^{II} + Tl^{III} \rightarrow Sn^{IV} + Tl^{I}} \tag{207}$$

and on balance a two-equivalent first step is highly probable in the tin(II)–mercury(II) reaction:

$$\mathrm{Sn^{II} + Hg^{II} \rightarrow Sn^{IV} + Hg^{0}} \qquad (208)$$

$$\mathrm{Hg^{0} + Hg^{II} \rightarrow (Hg^{I})_2} \qquad (209)$$

Both these reactions are rapid.

That the reduction of plutonium(VI) with tin(II) in mixed chloride-perchlorate media (*317*)

$$\mathrm{Sn^{II} + Pu^{VI} \rightarrow Sn^{IV} + Pu^{IV}} \qquad (210)$$

is much more rapid than the reduction of plutonium(V) with tin(II) has been interpreted as evidence that reaction (210) proceeds in a single step involving the transfer of two equivalents of charge. The reduction of plutonium(IV) by tin(II) becomes appreciable at chloride concentrations in the 1.5–2.0 *M* range (*311*),

$$\mathrm{Sn^{II} + 2Pu^{IV} \rightarrow Sn^{IV} + 2Pu^{III}} \qquad (211)$$

and tin(III) is probably involved as an intermediate. That reaction (211) should be so much more susceptible to chloride catalysis than reaction (210) is reasonable since the plutonium(IV) is present as $Pu^{4+}$.

The two-equivalent reaction between uranium(IV) and thallium(III)

$$\mathrm{U^{IV} + Tl^{III} \rightarrow U^{VI} + Tl^{I}} \qquad (212)$$

has been extensively studied. Harkness and Halpern (*192*) report a first-order dependence on both reactants, but this gives no information regarding the possible intermediate formation of $U^{V}$ and $Tl^{II}$. Thus, a first step

$$\mathrm{U^{IV} + Tl^{III} \rightarrow U^{V} + Tl^{II}} \qquad (213)$$

followed by the fast reaction

$$\mathrm{U^{V} + Tl^{II} \rightarrow U^{VI} + Tl^{I}} \qquad (214)$$

would give second-order kinetics, as would the mechanism involving simultaneous transfer of two electrons. Since the uranium(IV), (V), and (VI) oxidation states are predominantly $U^{4+}$, $UO_2{}^{+}$, and $UO_2^{2+}$, the increase in hydrolysis occurs in the first stage, $U^{IV} \rightarrow U^{V}$, of a two-stage process, and energetically this would not necessarily provide an easier route. More recently Wear (*394*) has examined the effect which a 2000-fold variation in the concentrations of reactants has on the kinetics. Although his results provide general support for the work of Harkness and Halpern (*192*), the orders with respect to $[U^{IV}]$ and $[Tl^{III}]$ have been found to change with concentration. The variations can be accounted for by considering a second term in $[U^{IV}]^2$ in the rate equation. Such a term can be explained by the polymerization of $U^{IV}$. Alternatively, a chain mechanism involving $Tl^{II}$ and $U^{V}$ can be used to provide a qualitative explanation of the data. However, since concentrations of $Tl^{II}$ and $U^{V}$ cannot as yet be determined, no quantitative treatment is possible. Quinn *et al.* (*306*) have noted small increases in rate constants in the presence of fumaric, malic, and malonic acids. It is interesting to note that with fumaric acid a maximum value in the rate constant is observed in solutions containing roughly equivalent amounts of fumaric acid and $U^{IV}$, and rates then decrease as more fumaric acid is added. The addition of oxalic and succinic acids results in a decrease in the rate. The reaction is complex in the presence of tartaric acid (*307*).

Reduction of vanadium(V) by an excess of tin(II) in dilute hydrochloric acid yields a mixture of vanadium(III) and vanadium(IV) (*110*). The dependence of the concentrations of these products upon reactant concentrations shows that the dominant initial step involves a two-equivalent change in oxidation states giving vanadium(III). Three distinct routes are postulated:

$$\mathrm{Sn^{II}+V^{V}} \longrightarrow [\mathrm{Sn.V}]^{\mathrm{VII}} \begin{array}{lr} \xrightarrow{k_1} \mathrm{Sn^{IV}+V^{III}} & (215)\\ \xrightarrow{k_2} \mathrm{Sn^{III}+V^{IV}} & (216)\\ \xrightarrow[+\mathrm{V^{V}}]{k_3} \mathrm{Sn^{IV}+2V^{IV}} & (217)\end{array}$$

Some of the $V^{III}$ formed in reaction (215) reacts further with $V^{V}$. The relative rates are $k_1 > k_2 > k_3$.

Product analysis has shown that, in concentrated hydrochloric acid, tin(II) and molybdenum(VI) react to give equimolar concentrations of molybdenum(V) and molybdenum(III) as initial products (*57*). This suggests that the reaction proceeds as follows,

$$\mathrm{Sn^{II} + Mo^{VI} \rightarrow Sn^{IV} + Mo^{IV}} \tag{218}$$

$$\mathrm{2Mo^{IV} \rightarrow Mo^{V} + Mo^{III}} \tag{219}$$

the first step being a two-equivalent change. The reaction of tin(II) with rhenium(V)

$$\mathrm{Sn^{II} + 2Re^{V} \rightarrow Sn^{IV} + 2Re^{IV}} \tag{220}$$

has also been studied (*42*).

Information regarding the mechanisms of noncomplementary reactions can often be obtained by the addition of reaction products. In the reaction,

$$\mathrm{2Fe^{II} + Tl^{III} \rightarrow 2Fe^{III} + Tl^{I}} \tag{221}$$

for example, curvature which second-order plots normally show after about 60% reaction becomes more pronounced with the addition of

$Fe^{III}$, but $Tl^{I}$ has no similar effect (*30*). This is consistent with a mechanism,

$$Fe^{II} + Tl^{III} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe^{III} + Tl^{II} \tag{222}$$

$$Fe^{II} + Tl^{II} \xrightarrow{k_2} Fe^{III} + Tl^{I} \tag{223}$$

but not the alternative:

$$Fe^{II} + Tl^{III} \rightleftharpoons Fe^{IV} + Tl^{I} \tag{224}$$

$$Fe^{II} + Fe^{IV} \longrightarrow 2Fe^{III} \tag{225}$$

Applying stationary-state kinetics for $Tl^{II}$ in reactions (222) and (223), the rate equation

$$\frac{-d[Fe^{II}]}{dt} = \frac{2k_1 k_2[Fe^{II}]^2[Tl^{III}]}{k_{-1}[Fe^{III}] + k_2[Fe^{II}]} \tag{226}$$

is obtained. Experimental data have been shown to fit the integrated form of this equation. In the presence of platinum metal, second-order plots are linear to at least 80% completion. Since the gradient is identical to that of the initial part of the plot in the absence of platinum, this suggests that there is no catalysis of reaction (222). There can therefore be no catalysis of the reverse of reaction (222), and reaction (223) is the only one which is catalyzed (*195*). The thallium(I)–thallium(III) exchange is also catalyzed by platinum metal (*148*). At an ionic strength $\mu = 3.0\ N$ the iron(II)–thallium(III) reaction is dependent on the inverse hydrogen-ion concentration, and there are terms corresponding to the inclusion of one and two $OH^-$ ions in the activated complex (*30*, *221*).

Reactions in which thallium(III) is reduced by vanadium(II), vanadium(III), and vanadium(IV) have been studied. The fastest of these is the reaction with vanadium(III),

$$2V^{III} + Tl^{III} \rightarrow 2V^{IV} + Tl^{I} \tag{227}$$

which has been studied in acid perchlorate solutions, 0.30–1.90 *M* in perchloric acid (*99*). The reaction is first order with respect to both vanadium(III) and thallium(III), and a mechanism involving thallium(II)

$$V^{III} + Tl^{III} \longrightarrow V^{IV} + Tl^{II} \tag{228}$$

$$V^{III} + Tl^{II} \xrightarrow{\text{fast}} V^{IV} + Tl^{I} \tag{229}$$

is in accordance with experiment. The data do not allow the hydrogen-ion dependence to be specified exactly, but the dependence is predominantly inverse power in $[H^+]$. At 0.5° and in 1.0 *M* perchloric acid, $k_{obs} = 353\ \text{l}\cdot\text{mole}^{-1}\ \text{sec}^{-1}$. A mechanism involving a two-equivalent first step is not compatible with experimental data (*99*, *197*). This is not unreasonable, since extensive changes in the degree of hydrolysis of the vanadium ion are required for the conversion of $V^{3+}$ to $VO_2^+$. The rate of the reaction of vanadium(II) with thallium(III) (*37*) is significantly less than that of vanadium(III), and the product is predominantly vanadium(IV). It is concluded (*37*) that there is in this instance a two-equivalent oxidation of the vanadium(II). At 0° and in 1.0 *M* perchloric acid, $k_{obs} \sim 68\ \text{l}\cdot\text{mole}^{-1}\ \text{sec}^{-1}$. The reaction of vanadium(IV) with thallium(III) is slow and has to be studied at elevated temperatures (*367*). Thallium(II) is believed to be formed as an intermediate.

In the outer-sphere reaction between $\text{Os(bipy)}_3^{2+}$ and thallium(III) (*220*), the mechanism is

$$\text{Os(bipy)}_3^{2+} + \text{Tl}^{\text{III}} \rightleftharpoons \text{Os(bipy)}_3^{3+} + \text{Tl}^{\text{II}} \tag{230}$$

$$\text{Os(bipy)}_3^{2+} + \text{Tl}^{\text{II}} \rightarrow \text{Os(bipy)}_3^{3+} + \text{Tl}^{\text{I}} \tag{231}$$

The rate increases only slightly as the hydrogen-ion concentration decreases, and $Tl^{3+}$ and $TlOH^{2+}$ must therefore react at about the same rate. Similar results have been obtained for the thallium(I)–thallium(III) exchange (*325*), and the implication may be that the latter is also outer-sphere. The addition of small concentrations of chloride produces a retardation as in other thallium(III) reactions. The reactions of the tris(1,10-phenanthroline), tris(bipyridyl), and bis(terpyridyl) complexes of ruthenium(II) with thallium(III) have also been studied (*268*). Thallium(II) is again formed as an intermediate:

$$\text{Ru(phen)}_3^{2+} + \text{Tl}^{\text{III}} \rightleftharpoons \text{Ru(phen)}_3^{3+} + \text{Tl}^{\text{II}} \tag{232}$$

$$\text{Ru(phen)}_3^{2+} + \text{Tl}^{\text{II}} \rightarrow \text{Ru(phen)}_3^{3+} + \text{Tl}^{\text{I}} \tag{233}$$

Reactions in which thallium(I) is oxidized to thallium(III) can also proceed with intermediate formation of thallium(II). Thus the mechanism of the reaction of thallium(I) with cobalt(III) (*31*) is

$$\text{Tl}^{\text{I}} + \text{Co}^{\text{III}} \rightleftharpoons \text{Tl}^{\text{II}} + \text{Co}^{\text{II}} \tag{234}$$

$$\text{Tl}^{\text{II}} + \text{Co}^{\text{III}} \rightarrow \text{Tl}^{\text{III}} + \text{Co}^{\text{II}} \tag{235}$$

At 53.9° and in 6.2 *N* nitric acid, the reaction of thallium(I) with cerium(IV) (*168*) follows a similar reaction sequence,

$$\text{Tl}^{\text{I}} + \text{Ce}^{\text{IV}} \rightleftharpoons \text{Tl}^{\text{II}} + \text{Ce}^{\text{III}} \tag{236}$$

$$\text{Tl}^{\text{II}} + \text{Ce}^{\text{IV}} \rightarrow \text{Tl}^{\text{III}} + \text{Ce}^{\text{III}} \tag{237}$$

but there are additional reactions involving hydroxyl radicals. The reaction has been studied in perchloric acid solutions at lower temperatures with silver(I) as catalyst (*197*), when the reaction sequence is:

$$\mathrm{Ag^{I} + Ce^{IV} \longrightarrow Ag^{II} + Ce^{III}} \tag{238}$$

$$\mathrm{Ag^{II} + Tl^{I} \longrightarrow Ag^{I} + Tl^{II}} \tag{239}$$

$$\mathrm{Tl^{II} + Ce^{IV} \xrightarrow{rapid} Tl^{III} + Ce^{III}} \tag{240}$$

Silver(I) and manganese(II) catalyze the oxidation of mercury(I) with cerium(IV) (*169*).

In the thallium(III) oxidation of chromium(II), thallium(II) does not appear to be formed as an intermediate (*27*). The reaction is first order in both the reactants, but a green binuclear chromium(III) complex is produced, and this suggests that a two-equivalent reaction

$$\mathrm{Cr^{II} + Tl^{III} \rightarrow Cr^{IV} + Tl^{I}} \tag{241}$$

followed by

$$\mathrm{Cr^{II} + Cr^{IV} \rightarrow (Cr^{III})_2} \tag{242}$$

is effective. The chloride dependence of the reaction has been studied at 25° (*114*). The reactant $\mathrm{TlCl^{2+}}$ produces about 50% hexaquochromium(III) and 50% monochlorochromium(III) ions, whereas $\mathrm{TlCl_2^{+}}$, $\mathrm{TlCl_3}$, and $\mathrm{TlCl_4^{-}}$ produce mainly monochlorochromium(III).

The rate of the reaction of the mercury(I) dimer with thallium(III) is inversely proportional to the concentration of mercury(II) (*28*, *29*), suggesting the mechanism:

$$\mathrm{[Hg^{I}]_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Hg^{0} + Hg^{II}} \tag{243}$$

$$\mathrm{Hg^{0} + Tl^{III} \xrightarrow{k_2} Hg^{II} + Tl^{I}} \tag{244}$$

The equilibrium first step is assumed to be rapid, and the reaction between $\mathrm{Hg^0}$ and $\mathrm{Tl^{III}}$ rate-determining. The resulting rate law is:

$$\frac{d[(\mathrm{Hg^{I}})_2]}{dt} = \frac{k_1 k_2[(\mathrm{Hg^{I}})_2][\mathrm{Tl^{III}}]}{k_{-1}[\mathrm{Hg^{II}}]} \tag{245}$$

Using an estimated value for $k_1/k_{-1}$ of $\sim 10^{-9}$ mole$^{-1}$, $k_2$ is of the order of $10^4$ l·mole$^{-1}$ sec$^{-1}$. The dismutation first step is also effective in the manganese(III) oxidation of the mercury(I) dimer (*326*). This is followed by a more complex reaction sequence in which manganese (IV) is involved:

$$\mathrm{(Hg^{I})_2 \overset{fast}{\rightleftharpoons} Hg^{0} + Hg^{II}} \tag{246}$$

$$\mathrm{2Mn^{III} \overset{fast}{\rightleftharpoons} Mn^{II} + Mn^{IV}} \tag{247}$$

$$\mathrm{Mn^{III} + Hg^{0} \longrightarrow Mn^{II} + Hg^{I}} \tag{248}$$

$$\mathrm{Mn^{III} + Hg^{I} \xrightarrow{fast} Mn^{II} + Hg^{II}} \tag{249}$$

$$\mathrm{Mn^{IV} + (Hg^{I})_2 \longrightarrow Mn^{II} + 2Hg^{II}} \tag{250}$$

In the cobalt(III) oxidation of the mercury(I) dimer, a different mechanism is observed (*327*). The rate is first order in both reactants but there are no other concentration terms. This is consistent with the mechanism:

$$(\mathrm{Hg^I})_2 + \mathrm{Co^{III}} \longrightarrow \mathrm{Hg^I} + \mathrm{Hg^{II}} + \mathrm{Co^{II}} \tag{251}$$

$$\mathrm{Hg^I} + \mathrm{Co^{III}} \xrightarrow{\text{fast}} \mathrm{Hg^{II}} + \mathrm{Co^{II}} \tag{252}$$

The dismutation reaction, as in reaction (243), appears to play no part in this reaction. The silver(II) oxidation of $(\mathrm{Hg^I})_2$ [in the silver(I)-catalyzed oxidations of $(\mathrm{Hg^I})_2$ (*197*)] may follow a similar mechanism, but requires further investigation.

The rate law for the reaction of chromium(VI) with iron(II) (*131*) is

$$\frac{-d[\mathrm{Fe^{II}}]}{dt} = [\mathrm{H^+}]^3 \frac{[\mathrm{Fe^{II}}]^2}{[\mathrm{Fe^{III}}]}(k_1[\mathrm{Cr^{VI}}] + k_2[\mathrm{Cr^{VI}}]^2) \tag{253}$$

where the $k_1$ term is for the reaction of mononuclear $\mathrm{Cr^{VI}}$ (which is predominant), and $k_2$ is for the reaction of binuclear chromium(VI). The mechanism is

$$\mathrm{Fe^{II}} + \mathrm{Cr^{VI}} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \mathrm{Fe^{III}} + \mathrm{Cr^{V}} \tag{254}$$

$$\mathrm{Fe^{II}} + \mathrm{Cr^{V}} \longrightarrow \mathrm{Fe^{III}} + \mathrm{Cr^{IV}} \tag{255}$$

$$\mathrm{Fe^{II}} + \mathrm{Cr^{IV}} \xrightarrow{\text{fast}} \mathrm{Fe^{III}} + \mathrm{Cr^{III}} \tag{256}$$

the second stage in which there is a reduction of $\mathrm{Cr^V}$ to $\mathrm{Cr^{IV}}$ being rate-determining. The latter is believed to correspond to a change in coordination number from four to six. In interpreting the data, ion pairing between $\mathrm{Fe^{3+}}$ and $\mathrm{CrO_4^{2-}}$ has to be taken into account. The analogous oxidation of tris(1,10-phenanthroline)iron(II) with chromium(VI) is not retarded by tris(1,10-phenanthroline)iron(III), and the first step is therefore not reversible (*131*). Fewer details of this reaction are obtained from the kinetic treatment. The kinetics of the reaction of vanadium(IV) with chromium(VI) resemble those of the iron(II) reaction (*127*). In the reaction of neptunium(V) with chromium(VI) (*353*), the series of one-equivalent steps

$$\mathrm{Np^V} + \mathrm{Cr^{VI}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Np^{VI}} + \mathrm{Cr^{V}} \tag{257}$$

$$\mathrm{Np^V} + \mathrm{Cr^{V}} \xrightarrow{k_2} \mathrm{Np^{VI}} + \mathrm{Cr^{IV}} \tag{258}$$

$$\mathrm{Np^V} + \mathrm{Cr^{IV}} \xrightarrow{\text{fast}} \mathrm{Np^{VI}} + \mathrm{Cr^{III}} \tag{259}$$

provides a reasonable mechanism for this reaction. In this case the first step is rate-determining and, assuming stationary-state kinetics for $\mathrm{Cr^V}$, a rate law

$$\frac{-d[\mathrm{Np^V}]}{dt} = 3k_1[\mathrm{Np^V}]\,[\mathrm{Cr^{VI}}]/(1 + k_{-1}[\mathrm{Np^{VI}}]/k_2[\mathrm{Np^V}]) \tag{260}$$

is obtained, which is in agreement with experiment.

The oxidation of chromium(III) with cerium(IV) (*385*)

$$3Ce^{IV} + Cr^{III} \rightarrow 3Ce^{III} + Cr^{VI} \qquad (261)$$

is too fast to be studied by conventional techniques in perchlorate solutions, but proceeds at a convenient rate in acid sulfate solutions. The rate law is of the form

$$\frac{-d[Cr^{VI}]}{dt} = \frac{k[Cr^{III}][Ce^{IV}]^2}{[Ce^{III}]} \qquad (262)$$

which is consistent with the mechanism:

$$Cr^{III} + Ce^{IV} \underset{k_{-1}}{\overset{k_1 \text{ fast}}{\rightleftharpoons}} Cr^{IV} + Ce^{III} \qquad (263)$$

$$Cr^{IV} + Ce^{IV} \xrightarrow{k_2} Cr^{V} + Ce^{III} \qquad (264)$$

$$Cr^{V} + Ce^{IV} \xrightarrow{\text{fast}} Cr^{VI} + Ce^{III} \qquad (265)$$

Again the slow step corresponds to the $Cr^{IV}$ to $Cr^{V}$ conversion.

The silver(I)-catalyzed oxidation of chromium(III) with cobalt(III) has been studied in 3 *M* perchloric acid (*239*). In the initial step, equilibrium concentrations of silver(II) are produced,

$$Ag^{I} + Co^{III} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ag^{II} + Co^{II} \qquad (266)$$

which can effect stepwise oxidation of the chromium(III) to chromium(VI):

$$Ag^{II} + Cr^{III} \xrightarrow{k_2} Ag^{I} + Cr^{IV} \qquad (267)$$

$$Ag^{II} + Cr^{IV} \longrightarrow Ag^{I} + Cr^{V} \qquad (268)$$

$$Ag^{II} + Cr^{V} \longrightarrow Ag^{I} + Cr^{VI} \qquad (269)$$

The rate constants $k_1$, $k_{-1}$, and $k_2$ have been evaluated. It is difficult to explain why the direct reaction between cobalt(III) and chromium(III) should be so slow.

In the reaction of silver(II) with thallium(I) in 6.18 *N* nitric acid (*117*), the nitrate radical is believed to be formed as an intermediate which then oxidizes the $Tl^{I}$ to $Tl^{II}$.

Sutcliffe and colleagues have also studied the kinetics of the reduction of lead(IV) by cerium(III) (*55*) and cobalt(II) (*54*) in acetic acid media. Lead(III) is believed to be formed as an intermediate in both instances, and there is evidence for a dimeric form of cobalt(II).

## VII. Outer-Sphere Reactions and Theoretical Considerations

The theoretical approach for outer-sphere reactions is relatively simple since no metal-ligand bonds are made or broken during the electron-transfer step, and arbitrary parameters which occur in theoretical studies of most other reactions in chemical kinetics are therefore absent. For reactions between two species differing only in oxidation states, there is no difference in the stability of products compared with reactants (i.e., $\Delta G^0 = 0$), and such reactions provide simple examples on which to base a theoretical treatment (*359*). A feature of outer-sphere reactions is that they are generally rapid. There are exceptions, however, and as a general rule the ligand type would seem to be important. Thus ligands such as water and ammonia appear to be much less effective in "conducting" electrons between metal ions than unsaturated ligands such as cyanide, phenanthroline, and bipyridine, the complexes of which are characterized by a high degree of $\pi$-bonding and electron delocalization. Reactions involving hexachloroiridate(IV) are also rapid, and again there is electron delocalization from the central metal atom (*166*).

The theoretical approach for the simplest electron-transfer reactions in solution is more complicated than that for electron-transfer reactions in the gas phase. This is because inner-coordination spheres of metal ions have to be taken into account, and other solvent or ion-pair interactions may also be important. In outer-sphere reactions, energy conservation requires that inner- and outer-coordination spheres of the reactants rearrange to some nonequilibrium configuration before electron transfer takes place. For an isotopic exchange reaction, this intermediate configuration is one in which the coordination spheres of the two reactants are identical. For reactions in which $\Delta G^0 \leqslant 0$, the coordination spheres of the reactants reorganize to a lesser extent and vibrational excitation energy of the products is probably liberated as part of the standard free energy change of the reaction. This means in effect that the structure of the activated complex tends to approach that of the reactants (*359*). A favorable free energy change serves therefore to decrease the free energy of activation, and there is a corresponding increase in rate. For outer-sphere reactions at least, electrostatic repulsion between the reactants has at the most only a small effect on the rate.

For a more detailed account of the theoretical approach, the reader is referred to articles by Marcus (*253*, *254*), Sutin (*359*, *361*), and Halpern (*181*). Of particular interest here are the correlations which have been possible using the Marcus equation,

$$k_{12} = (k_1 k_2 K_{12} f)^{1/2} \tag{270}$$

where

$$\log f = \frac{(\log K_{12})^2}{4 \log (k_1 k_2 / Z^2)} \tag{271}$$

In the above, $k_{12}$ and $K_{12}$ are the rate and equilibrium constants, respectively, for the redox reaction, and $k_1$ and $k_2$ are the rate constants for the corresponding exchange reactions. The collision frequency, $Z$, is for two uncharged molecules in solution and is assumed to have a value of $10^{11}$ l·mole$^{-1}$ sec$^{-1}$. In a number of instances when $K_{12} \rightarrow 1$, the $f$ term may be assumed to be unity [see, for example, Dulz and Sutin (*115*)]. Equation (270) can also be expressed in terms of activation free energies and the standard free energy change:

$$\Delta G^{\ddagger}_{12} = 0.5\Delta G_1^{\ddagger} + 0.50\Delta G_2^{\ddagger} + 0.5\Delta G^0_{12} - 1.15RT \log f \tag{272}$$

Equations (270) and (272) are applicable to outer-sphere reactions and are not in the first instance applicable to inner-sphere reactions.

For a series of reactions between $Fe^{2+}$ and substituted 1,10-phenanthroline complexes of iron(III), Ford-Smith and Sutin (*136*) have shown that there is a linear relationship between the free energy of activation, $\Delta G^{\ddagger}_{12}$, and the standard free energy change, $\Delta G^0_{12}$. The absence of specific steric effects suggests that the $Fe^{2+}$ has to some extent penetrated between the phenanthroline ligands. The reactions of $Fe^{2+}$ with the 2,2′-bipyridine and 2,2′,2″-tripyridine complexes of iron(III) have also been studied.

Other results of Sutin and colleagues have been discussed in terms of the Marcus approach. Thus the rates of the iron(II) reduction of $Ag(phen)_2^{2+}$, $Ag(bipy)_2^{2+}$, $Ru(bipy)_3^{3+}$, $Os(bipy)_3^{3+}$, and $IrCl_6^{2-}$ have been studied in perchloric and sulfuric acid solutions and shown to increase with the standard free energies of the reactions (*152*). A number of reactions between positively charged complexes, as well as those between oppositely charged complexes, have been shown to proceed with rate constants which are larger than $10^8$ l·mole$^{-1}$ sec$^{-1}$ (Table XVII). The rates for the oxidation of ferrocyanide ions by $IrCl_6^{2-}$, $MnO_4^-$, and $OsCl_6^{2-}$, on the other hand, are considerably slower and increase with the standard free energy change of the reaction (*152*).

The kinetics of the oxidation of a number of substituted tris(1,10-phenanthroline)iron(II) complexes by cerium(IV) in dilute sulfuric acid have been studied (*115*), and activation free energies are again related to the standard free energy change. In the oxidation of $Fe(bipy)_3^{2+}$, $Fe(bipy)_2(CN)_2$, $Fe(bipy)(CN)_4^{2-}$, and the corresponding phenanthroline complexes, oxidation of the mixed ligand complexes proceeds more rapidly than the oxidation of complexes containing identical ligands

(*74*). The kinetics of the oxidation of Ru(phen)$_3^{2+}$ by cerium(IV) (*267*), and of various substituted iron(II)-phenanthroline complexes by manganese(III) (*104*) and cobalt(III) (*74*), have also been studied. For other reactions involving a wide range of substitution-inert complexes, rate constants calculated from Eq. (270) are in good agreement with experimentally observed values (Table XVIII).

TABLE XVII

SECOND-ORDER RATE CONSTANTS FOR SOME OUTER-SPHERE REDOX REACTIONS AT 25° (*152*)

| Reaction[a] | Medium | $\Delta E^0$ (volts) | $k$ (l·mole$^{-1}$ sec$^{-1}$) |
|---|---|---|---|
| Os(bipy)$_3^{2+}$ + IrCl$_6^{2-}$ | 0.5 $N$ $HClO_4$ | 0.23 | $> 10^8$ |
| Fe(CN)$_6^{4-}$ + Fe(phen)$_3^{3+}$ | 0.5 $N$ $HClO_4$ | 0.23 | $> 10^8$ |
| Fe(CN)$_6^{4-}$ + Os(bipy)$_3^{3+}$ | 0.5 $N$ $HClO_4$ | 0.11 | $> 10^8$ |
| Fe(t-phen)$_3^{2+}$ + Ru(bipy)$_3^{3+}$ | 0.5 $N$ $H_2SO_4$ | 0.46 | $> 10^8$ |
| Os(bipy)$_3^{2+}$ + Ru(bipy)$_3^{3+}$ | 0.5 $N$ $HClO_4$ | 0.44 | $> 10^8$ |
| Os(bipy)$_3^{2+}$ + Fe(phen)$_3^{3+}$ | 0.5 $N$ $HClO_4$ | 0.23 | $> 10^8$ |
| Fe(p-phen)$^{2+}$ + Ru(bipy)$_3^{3+}$ | 0.5 $N$ $H_2SO_4$ | 0.19 | $> 10^8$ |
| Fe(t-phen)$_3^{2+}$ + Fe(d-bipy)$_3^{3+}$ | 0.5 $N$ $H_2SO_4$ | 0.14 | $> 10^8$ |
| Fe(d-bipy)$_3^{2+}$ + Fe(phen)$_3^{3+}$ | 0.5 $N$ $HClO_4$ | 0.11 | $> 10^8$ |
| Fe(CN)$_6^{4-}$ + IrCl$_6^{2-}$ | $H_2O$ | 0.66 | $1.2 \times 10^5$ |
| Fe(CN)$_6^{4-}$ + IrCl$_6^{2-}$ | 0.5 $N$ $HClO_4$ | 0.34 | $4.1 \times 10^5$ |
| Fe(CN)$_6^{4-}$ + $MnO_4^-$ | 0.1 $N$ NaOH | 0.10 | $1.34 \times 10^4$ |
| Fe(CN)$_6^{4-}$ + OsCl$_6^{2-}$ | $H_2O$ | 0.07 | $1.79 \times 10^{-1}$ |

[a] tripy = 2,2′,2″-tripyridine; d-dipy = 4,4′-dimethyl-2,2′-dipyridine; t-phen = 3,4,7,8-tetramethyl-1,10-phenanthroline; p-phen = 5-phenyl-1,10-phenanthroline.

The same theoretical approach has been considered for reactions between two hexaquo ions, although it is not yet known whether these proceed by inner- or outer-sphere mechanisms (*115*). With one or two notable exceptions, there is good agreement between calculated and experimental rate constants. In the case of the $Fe^{2+}$–$Co^{3+}$ reaction the discrepancy is ~ $10^5$, however (*115*). The reactions Fe(phen)$_3^{2+}$–$Co^{3+}$ (*74*) and $Ru(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ (*122*) are also exceptions, and it is perhaps significant that all three involve the cobalt(II)–cobalt(III) couple. It may be that spin-multiplicity restrictions (page 168) are responsible for the anomalous behavior of these systems. There is also a serious discrepancy between observed and calculated rate constants (700 and

$1.3 \times 10^6$ l·mole$^{-1}$ sec$^{-1}$, respectively, at 0°) for the reaction of $Fe^{2+}$ with $Ce^{4+}$ in 0.5 $N$ perchloric acid (*9*).

Favorable free energy changes are not always necessary for reactions to be fast, and rate constants approaching the diffusion-controlled limit of $\sim 2 \times 10^9$ l·mole$^{-1}$ sec$^{-1}$ have been observed for reactions in which the equilibrium constant $K$ is of the order of unity, and $\Delta G^0$ for the forward and back reactions $\sim 0$. The temperature-jump method is particularly useful for studying such reactions. A fairly large standard enthalpy change is desirable so that the temperature jump produces a significant change. One way in which this can be achieved is by having oppositely charged reactants (Table XIX).

TABLE XVIII

A COMPARISON OF OBSERVED AND CALCULATED RATE CONSTANTS FOR SOME OUTER-SPHERE REACTIONS (*74*)

| Reaction | $k_{12}$ (observed) (l·mole$^{-1}$ sec$^{-1}$) | $k_{12}$ (calculated) (l·mole$^{-1}$ sec$^{-1}$) |
|---|---|---|
| $W(CN)_8^{4-} + Ce^{IV}$ | $> 10^8$ | $6.1 \times 10^8$ |
| $Fe(CN)_6^{4-} + Ce^{IV}$ | $1.9 \times 10^6$ | $6.0 \times 10^6$ |
| $Mo(CN)_8^{4-} + Ce^{IV}$ | $1.4 \times 10^7$ | $1.3 \times 10^7$ |
| $W(CN)_8^{4-} + IrCl_6^{2-}$ | $6.1 \times 10^7$ | $8.1 \times 10^7$ |
| $Fe(CN)_6^{4-} + IrCl_6^{2-}$ | $3.8 \times 10^5$ | $5.7 \times 10^5$ |
| $Mo(CN)_8^{4-} + IrCl_6^{2-}$ | $1.9 \times 10^6$ | $1.0 \times 10^6$ |
| $W(CN)_8^{4-} + Mo(CN)_8^{3-}$ | $5.0 \times 10^6$ | $1.7 \times 10^7$ |
| $Fe(CN)_6^{4-} + Mo(CN)_8^{3-}$ | $3.0 \times 10^4$ | $2.7 \times 10^4$ |
| $W(CN)_8^{4-} + Fe(CN)_6^{3-}$ | $4.3 \times 10^4$ | $5.1 \times 10^4$ |

Sutin (*360*) has found that the rate constant for the inner-sphere reaction between $Cr^{2+}$ and $FeCl^{2+}$ can be calculated from Eq. (270). In this instance, the exchange rate constants $k_1$ and $k_2$ are for the reactions of $Cr^2$ with $CrCl^{2+}$ and $Fe^{2+}$ with $FeCl^{2+}$ (the chloride bridging paths only). The agreement of the observed log of the rate (7.3 l·mole$^{-1}$ sec$^{-1}$) with the calculated rate (8.5 l·mole$^{-1}$ sec$^{-1}$) is encouraging, and suggests that an equation of this form may also be applicable to inner-sphere reactions.

Free energy correlations of a different type have been proposed by Bächmann and Lieser (*34*). For the rate constants for electron exchange between different complexes of iron(III) and $Fe^{2+}$, the following relationship was found to hold:

$$\log_{10} k = 1.1 + 0.5\Delta \log_{10} K \qquad (273)$$

In this equation, $\Delta \log_{10} K$ is the difference between the logarithms of the stability constants for the iron(III) and iron(II) complexes with the same ligands. As far as stability constants are known, all the rate constants would seem to conform to this relationship.

Factors which determine entropy of activation of a redox reaction have also been considered. Newton and Rabideau (*287*) have reviewed the kinetics of aqueous oxidation-reduction reactions of uranium, neptunium, and plutonium, and shown that the entropies of the various activated complexes depend primarily on their charges. For activated complexes of charge +3, +4, +5, and +6, values of $S^\ddagger$, the entropy of the activated complex, were found to lie in the ranges 29–40, 63–81, 72–106, and 102–128 eu, respectively. Daugherty and Newton (*100*) have extended this approach to a consideration of reactions which do not involve actinide ions. Higginson *et al.* (*197*) have drawn attention to the linear correlation between $-\Delta S^\ddagger$ and the charge of the activated complex for a number of isotopic exchange reactions. Many reactions show deviations from this correlation in the direction of the entropy of reaction. For example, a number of reactions were found to have positive entropies of activation, when negative values might have been expected. The relationship may be summarized by the equation,

TABLE XIX

RATE CONSTANTS (l·mole⁻¹ sec⁻¹) FOR FORWARD ($k_f$) AND BACK ($k_b$) REACTIONS AS DETERMINED BY THE TEMPERATURE-JUMP METHOD

| Reaction[a] | Temp. (°C) | $k_f$ | $k_b$ | Ref. |
|---|---|---|---|---|
| $\mathrm{Os(bipy)_3^{2+} + Mo(CN)_8^{3-} \rightleftharpoons Os(bipy)_3^{3+} + Mo(CN)_8^{4-}}$ | 10 | $2.0 \times 10^9$ | $4.0 \times 10^9$ | (*75*) |
| $\mathrm{Fe(4,7\text{-}DMP)_3^{2+} + IrCl_6^{2-} \rightleftharpoons Fe(DMP)_3^{3+} + IrCl_6^{3-}}$ | 10 | $1.1 \times 10^9$ | $1.0 \times 10^9$ | (*184*) |
| $\mathrm{Fe(5,6\text{-}DMP)_3^{2+} + IrCl_6^{2-} \rightleftharpoons Fe(5,6\text{-}DMP)_3^{3+} + IrCl_6^{3-}}$ | 10 | $2.2 \times 10^8$ | $2.8 \times 10^9$ | (*217*) |
| $\mathrm{IrBr_6^{3-} + IrCl_6^{2-} \rightleftharpoons IrBr_6^{2-} + IrCl_6^{3-}}$ | 20 | $1.2 \times 10^7$ | $1.8 \times 10^6$ | (*218*) |
| $\mathrm{Fe(4,7\text{-}DMP)_3^{2+} + IrBr_6^{2-} \rightleftharpoons Fe(4,7\text{-}DMP)_3^{3+} + IrBr_6^{3-}}$ | 10 | $1.6 \times 10^8$ | $1.9 \times 10^9$ | (*217*) |
| $\mathrm{Fe(DMPY)_3^{2+} + IrCl_6^{2-} \rightleftharpoons Fe(DMPY)_3^{3+} + IrCl_6^{3-}}$ | 10 | $9.6 \times 10^8$ | $2.0 \times 10^8$ | (*217*) |
| $\mathrm{Ru(phen)_3^{2+} + RhCl_6^{2-} \rightleftharpoons Ru(phen)_3^{2+} + RhCl_6^{2-}}$ | 10 | $2.5 \times 10^9$ | $2.7 \times 10^8$ | (*217*) |

[a] DMP = 4,7-dimethyl-1,10-phenanthroline; DMPY = 4,4′-dimethyl-2,2′-bipyridine.

$$\Delta S^\ddagger = \Delta S_0^\ddagger + \alpha \Delta S^0 \tag{274}$$

where $\Delta S^\ddagger$ and $\Delta S^0$ refer to the redox reaction in which there is net chemical change, and $\Delta S_0^\ddagger$ is the corresponding entropy of activation (for similar charge types) from the correlation observed for isotopic exchange reactions. The coefficient $\alpha$ was found to have values ranging from 0.5 to 1.0. For reactions in which there are hydrolytic changes, for example reactions in which $V^{3+}$ is oxidized to $VO^{2+}$, entropy correlations suggest that at least partial hydrolysis occurs during the lifetime of the activated complex (*197*).

Other outer-sphere reactions, already referred to, include the $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$ (*234*, *339*), $Co(NH_3)_6^{2+}$–$Co(NH_3)_6^{3+}$ (*59*), and $MnO_4^{2-}$–$MnO_4^-$ (*273*) reactions. A number of $V^{2+}$ reactions are believed to be outer-sphere (*107*).

## VIII. Reactions of the Solvated Electron with Metal Ions

Recent application of the technique of pulse radiolysis (*108*), using short bursts of high-energy electrons (or X-rays), has led to a confirmation of the existence of the solvated electrons in water (*194*, *231*), methanol (*1*), ethanol (*374*), and dioxane (*48*). It has also enabled reactions of the solvated electron to be studied, and transient intermediates resulting from these reactions to be identified.

Reactions of the hydrated electron with metal ions are considered in this section. Water as a solvent is more dissociated ($K \sim 10^{-14}$ liter$^{-2}$ mole$^{2}$) than ammonia ($K \sim 10^{-30}$ liter$^{-2}$ mole$^{2}$), and reactions of the solvated electron with $H^+$ (or $H_3O^+$) (*159*)

$$e_{aq}^- + H^+ \rightarrow H \qquad (k = 2.4 \times 10^{10}\ l \cdot mole^{-1}\ sec^{-1}) \tag{275}$$

together with the reaction

$$e_{aq}^- + H_2O \rightarrow H + OH^- \qquad (k = 16 \pm 1\ l \cdot mole^{-1}\ sec^{-1}) \tag{276}$$

result in a much more rapid decay of $e_{aq}^-$. Reactions of the hydrated electron are studied by having solutes present in the sample of water which is irradiated, the decay of the $e_{aq}^-$ absorption at 700 m$\mu$ (*50*) being more rapid than would otherwise be observed. A necessary requirement is that the hydrogen-ion concentration be small, and values $< 10^{-5}\ N$ are generally used. For some reactions an allowance has to be made for the reaction $e_{aq}^- + e_{aq}^-$ ($k = 5 \times 10^9\ l \cdot mole^{-1}\ sec^{-1}$).

Alkali and alkaline-earth ions (with the possible exception of $Mg^{2+}$) do not affect the rate of decay of the electron absorption. The reaction with $Mg^{2+}$ is relatively slow and a rate constant $k < 10^5\ l \cdot mole^{-1}\ sec^{-1}$ has been observed (*18*). This is as expected in view of the standard electrode potential of around −2.5 volts for the hydrated electron. Baxendale and colleagues (*49*) have found that neutral solutions of $Cd^{2+}$, $Pb^{2+}$, $Co^{2+}$, and $Ni^{2+}$ are readily reduced by $e_{aq}^-$. With $Zn^{2+}$, $Fe^{2+}$, and $Mn^{2+}$, the rate constants are somewhat less (Table XX), the slower rate for $Mn^{2+}$ being reflected in the higher activation energy ($7.7 \pm 0.5$ kcal $mole^{-1}$) compared to that for $Co^{2+}$ ($5.7 \pm 0.5$ kcal $mole^{-1}$). Transient absorbing species with maxima at around 300 mμ have been detected in all but the $Fe^{2+}$ reaction, and it is concluded that these are due to the lower oxidation states $Cd^+$, $Pb^+$, $Co^+$, $Ni^+$, $Zn^+$, and $Mn^+$. The existence of $Zn^+$ and $Cd^+$ has been confirmed by ESR studies on irradiated ice containing $Zn^{2+}$ and $Cd^{2+}$, respectively (*271*). The decay of $Zn^+$ and $Ni^+$ has been followed in some detail (*49*). While $Zn^+$ appears to react by disproportionation,

TABLE XX

RATE CONSTANTS FOR THE REACTIONS OF $e^-_{aq}$ WITH METAL IONS (AT ROOM TEMPERATURE AND pH ~ 7) (*19*, *49*)

| Reactant | $k$ ($l \cdot mole^{-1} sec^{-1}$) | Reactant | $k$ ($l \cdot mole^{-1} sec^{-1}$) |
|---|---|---|---|
| $Cd^{2+}$ | $5.2 \times 10^{10}$ | $Ag^+$ | $3.2 \times 10^{10}$ |
| $Pb^{2+}$ | $3.9 \times 10^{10}$ | $Tl^+$ | $3.0 \times 10^{10}$ |
| $Co^{2+}$ | $1.2 \times 10^{10}$ | $Cu^{2+}$ | $2.9 \times 10^{10}$ |
| $Ni^{2+}$ | $2.2 \times 10^{10}$ | $Sn^{2+}$ (pH 11) | $3.4 \times 10^9$ |
| $Zn^{2+}$ | $1.5 \times 10^9$ | $Cr^{2+}$ | $4.2 \times 10^{10}$ |
| $Fe^{2+}$ | $1.6 \times 10^8$ | $Cr^{3+}$ | $6.0 \times 10^{10}$ |
| $Mn^{2+}$ | $4.0 \times 10^7$ | $Al^{3+}$ | $2.0 \times 10^9$ |

$$2Zn^+ \rightarrow Zn^0 + Zn^{2+} \tag{277}$$

the decay of $Ni^+$ is not as simple. The reductions of silver(I) and copper(II) ions are also rapid. With silver(I) there appear to be competing reactions,

$$Ag^+ + e^-_{aq} \rightarrow Ag^0 \tag{278}$$

$$Ag^+ + OH \rightarrow Ag^{2+} + OH^- \tag{279}$$

but with $\sim 10^{-3}$ $M$ solutions of copper(II) the reaction with $e^-_{aq}$ is predominant, and there is no transient absorption other than that of $e^-_{aq}$. At concentrations $> 5 \times 10^{-3}$ $M$ a transient absorption is produced which is attributed to the reaction:

$$Cu^{2+} + OH \rightarrow Cu^{3+} + OH^- \tag{280}$$

Anbar and Hart (*19*) report additional data for the reactions with $Sn^{II}$, $Cr^{II}$, $Cr^{III}$, and $Al^{III}$. On increasing the pH from 7 to 14 there is almost invariably a decrease in the observed rate constant. With aluminum(III) the decrease is from $2.0 \times 10^9$ to $5.5 \times 10^6$ $l \cdot mole^{-1} sec^{-1}$.

In the case of the permanganate and chromate oxyanions, fast rates are observed (*49*). With permanganate manganate ions are first formed,

$$MnO_4^- + e_{aq}^- \rightarrow MnO_4^{2-} \qquad (281)$$

and with higher dose rates further reduction to $MnO_4^{3-}$ can occur. Chromate differs from permanganate in that transient species are observed. Chromium(V) ions, $CrO_4^{3-}$ or $CrO_3^-$, are believed to be formed by reaction with $e_{aq}^-$ and H-atoms. They are quickly reoxidized to $CrO_4^{2-}$, however, probably by OH radicals.

Rate constants for reactions with a series of 3+ rare-earth ions are of the order of $10^8$ l·mole$^{-1}$ sec$^{-1}$ (*49*, *380*). Freshly made solutions appear to react more slowly than those which have been standing for some time. In the reaction of $Eu^{3+}$ with $e_{aq}^-$ the relatively stable $Eu^{2+}$ product has been identified (*160*). A linear correlation of reactivity with the $M^{2+}/M^{3+}$ redox potentials has been reported for the reactions of $Sm^{3+}$, $Yb^{3+}$, and $Eu^{3+}$ (*380*).

In other reactions, however, it can be concluded that the reactivity is not solely determined by the free energy change. Thus, the rate constants for the reactions of a number of ammine and aquo complexes having the same central metal atom have been shown to be similar (*19*), in spite of a quite pronounced variation in the oxidation-reduction potential. An explanation of relative rates in terms of electron affinity is also unsatisfactory, since the order of rate constants for 2 + transition metal ions (*21*) is

$$Mn^{2+} < Fe^{2+} < Zn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Cr^{2+}$$

and the order of electron affinities is

$$Mn^{2+} < Fe^{2+} < Cr^{2+} < Co^{2+} < Zn^{2+} < Ni^{2+} < Cu^{2+}$$

Anbar has suggested that the availability of a vacant *d* orbital on the central metal, and the gain in exchange energy on adding an electron are the major factors which determine the reactivity of transition metal ions (*15*). Thus addition of an electron to the $Cr^{2+}(t_{2g}^3 e_g^1)$ ion is particularly favorable since the electron spin is parallel to the four spins already present. With $Mn^{2+}(t_{2g}^3 e_g^2)$ on the other hand, a sixth electron must have its spin anti-parallel to the electrons already present and the reaction is less favorable. In the case of $Cu^{2+}$ the gain in energy is similar to that of $Cr^{2+}$, but $Zn^{2+}$ is expected to have a low reactivity since all the 3*d* orbitals are filled.

Ligands such as cyanide may affect the reactivity of the central atom by changing the ligand field and hence the electron density distribution. For example ferrocyanide with a $t_{2g}^6$ configuration is relatively unreactive

($k < 10^5$ l·mole$^{-1}$ sec$^{-1}$) (*16*). With low-spin Mn(CN)$_6^{4-}$, on the other hand, an electron is added to the last vacancy in the $t_{2g}$ level, and the complex is much more reactive ($k = 2.5 \times 10^{10}$ l·mole$^{-1}$ sec$^{-1}$) than Mn$^{2+}$ (*16*). Ligands such as the halide ions, which do not interact strongly with *d* orbitals, may affect the reactivity of a complex toward $e^-_{aq}$ by channeling the electron from the solvent to the central atom (*15*). From a rather limited series of rate constants, Anbar and Hart (*19*) have suggested that the efficiency of bridging groups is

$$I^- > Cl^- > F^- > H_2O > NH_3 \sim RNH_2 > CN^- > OH^-$$

Other results obtained by Baxendale *et al.* (*49*) for a series of cobalt(III) complexes are not entirely consistent with this order. The fact that the hydroxo complexes Al(OH)$_4^-$ and Zn(OH)$_4^{2-}$ are so inert is important (*19*). No *d* orbitals are involved in these two instances and it must be concluded that OH$^-$ is an extremely poor bridge for electrons. This is in accord with the observation that the rate of the outer-sphere reduction of, for example, Co(NH$_3$)$_5$OH$^{2+}$ with Ru(NH$_3$)$_6^{2+}$ is 100 times slower than with Co(NH$_3$)$_5$H$_2$O$^{3+}$ (*122*). The effectiveness of halide ions is similar to that observed for outer-sphere reactions. Marcus (*255*) has outlined assumptions, equations, and several applications of a recently formulated theory for the reactions of $e^-_{aq}$.

From the kinetics alone it can be concluded that the solvated electron is not an intermediate in electron-transfer reactions (*366*, *377*).

## IX. Reactions of Metal Ions with Compounds of Nonmetallic Elements

The reactions of molecular oxygen with Fe$^{II}$ (*146*), V$^{III}$ (*319*), Pu$^{III}$ (*278*), and U$^{IV}$ (*190*) in aqueous solutions (to give Fe$^{III}$, V$^{IV}$, Pu$^{IV}$, and U$^{VI}$, respectively) are believed to involve peroxide forms as intermediates. Thus, for the reaction

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad (282)$$

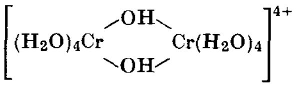
there is evidence for the mechanism:

$$Fe^{2+} + O_2 \overset{\text{fast}}{\rightleftharpoons} FeO_2^{2+} \qquad (283)$$

$$FeO_2^{2+} + Fe^{2+} + H_2O \longrightarrow FeO_2H^{2+} + HOFe^{2+} \qquad (284)$$

$$FeO_2H^{2+} + 2Fe^{2+} + 3H^+ \xrightarrow{\text{fast}} 3Fe^{3+} + 2H_2O \qquad (285)$$

With Cr$^{2+}$ (*27*, *114*), the dimer



is formed (*228*), and in ammoniacal solutions the final product is $(NH_3)_5Cr\cdot O\cdot Cr(NH_3)_5^{4+}$ (*227*). When oxygen is passed through ammoniacal cobalt(II) solutions, the complex $(NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5^{4+}$ can be isolated (*390*). That the brown vanadium(III) dimer is formed as an intermediate in the reaction of vanadium(II) with oxygen provides evidence for two-equivalent oxidation to vanadium(IV) in the first step (*365*). Substantial oxygen-atom transfer has been shown to occur in the ozone oxidation of manganese(II) and thallium(I) to manganese dioxide and thallium(III) oxide, respectively (*133*).

Zabin and Taube (*411*) have investigated the reactions of chromium(II) with the metal oxides $MnO_2$, $PbO_2$, $Tl_2O_3$, $Mn_2O_3$, $Co_2O_3$, and $CeO_2$, and found that $Cr(H_2O)_6^{3+}$ is the predominant form of the chromium(III) product. When the oxidizing agent has a higher oxygen content, as with $Pb_3O_4$ or $Ca_2PbO_4$, a chromium(III) dimer (or a higher polymer) is formed. There is no oxygen transfer from $PbO_2$ to Cr, but some does occur in the reactions with $MnO_2$, $Tl_2O_3$, and $Mn_2O_3$. The reactions are more rapid with those oxides containing metal ions which undergo two-electron changes (e.g., $MnO_2$, $PbO_2$, $Tl_2O_3$).

Halpern and colleagues (*241*, *302*, *395*) have shown that molecular hydrogen reacts homogeneously with a number of metal ions in aqueous solutions, reducing them to the metal or to a lower oxidation state. The reactions with $Cu^{2+}$, $Hg^{2+}$, $Hg_2^{2+}$, and $MnO_4^-$ all show a first-order dependence on both reactants. Silver(I) catalyzes the reduction of $Cr_2O_7^{2-}$ (*395*) and there are terms in $[Ag^+]$ and $[Ag^+]^2$ which correspond to rate-determining steps:

$$Ag^+ + H_2 \rightarrow AgH + H^+ \tag{286}$$

$$2Ag^+ + H_2 \rightarrow 2AgH^+ \tag{287}$$

The reduction of $Ag^I$ to metallic silver has also been studied (*396*).

The oxidation of chromium(II) solutions with halogens (*379*) provides with bromine and iodine a convenient means of preparing the 1 : 1 chromic halide complexes:

$$Cr^{2+} + X_2 \longrightarrow CrX^{2+} + X \tag{288}$$

$$Cr^{2+} + X \xrightarrow{\text{fast}} CrX^{2+} \tag{289}$$

With chlorine there is incomplete retention of the chloride, which suggests that the reaction might proceed at least in part via the labile chromium(IV) state. In the reactions of tin(II) with bromine and iodine (*398*), tin(III) was not detected as an intermediate. A full kinetic study has been made of the reaction between titanium(III) and iodine

(*222*), and iron(II) and chlorine (*96*). In the latter it was not possible to decide whether $Cl_2^-$ or Fe$^{IV}$ is formed as an intermediate. Solutions containing the cobalt(II)-EDTA complex are oxidized by bromine,

$$\mathrm{Co(EDTA)^{2-} + Br_2 \rightarrow [EDTACo{-}Br_2]^{2-} \rightarrow EDTACo{-}Br^{2-} + Br}$$

$$\mathrm{Co(EDTA)^{2-} + Br \xrightarrow{fast} EDTACo{-}Br^{2-}}$$

and the pentacyano cobalt(II) complex $CoCN_5^{2-}$ is likewise oxidized by halogens to Co$^{III}$(CN)$_5$X$^{3-}$, although there is only a poor yield with chlorine (*3*). The reactions of Fe$^{II}$ (*83*) and U$^{IV}$ (*154*) with bromine have also been studied.

Chlorine oxidation of $Co(en)_2XBr^+$ complexes (where $X^- = NH_3$, $Cl^-$, $Br^-$) results in the formation of $Co(en)_2XCl^+$ with retention of the configuration of the complex (*321*). Chlorine has also been used as a reagent for oxidizing the isothiocyanate ligand in $Cr(H_2O)_5NCS^{2+}$ (*384*) and $Cr(H_2O)_5SCN^{2+}$ (*176*, *177*). The products are $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5Cl^{2+}$, respectively. The cobalt-nitrogen bond is preserved in the oxidation of the isothiocyanato ligand of cobalt(III) complexes with $KIO_3$ and $H_2O_2$ (*332*):

$$\mathrm{Co(NH_3)_5NCS^{2+} \rightarrow Co(NH_3)_6^{3+}} \tag{290}$$

The oxidation of iron(II) (*43*) with hydrogen peroxide has been shown to conform reasonably well to the equation

$$\mathrm{2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + OH^-} \tag{291}$$

at hydrogen-ion concentration $> 0.01\ M$. The first-order dependence on both reactants under these conditions is consistent with the mechanism:

$$\mathrm{Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH + OH^-} \tag{292}$$

$$\mathrm{Fe^{2+} + OH \xrightarrow{fast} Fe^{3+} + OH^-} \tag{293}$$

Cahill and Taube (*71*) have suggested an alternative first step,

$$\mathrm{Fe^{II} + H_2O_2 \rightarrow Fe^{IV} + 2OH^-} \tag{294}$$

but recent experiments by Conocchioli *et al.* (*93*) seem to exclude this possibility. More complex behavior is observed under other conditions (*43*). Hydroxy radicals have been detected by ESR in the corresponding reaction with titanium(III) (*106*). In the reactions of hydrogen peroxide with Cr$^{II}$ (*23*) and V$^{II}$ (*365*) the products are the same as in the reactions with oxygen, and Cr$^{IV}$ and V$^{IV}$ are probably formed as intermediates. Chromium(III) is oxidized to chromium(VI) in alkaline solutions (*41*), there being a first-order dependence on both reactants. A $\mu$-peroxo-dicobalt(III) intermediate, EDTACo$\cdot$O$_2\cdot$CoEDTA$^{4-}$, is formed during the oxidation of the cobalt(II)-EDTA complex to cobalt(III) by hydrogen peroxide (*409*).

The reactions in which Fe$^{III}$ (*43*), Fe(CN)$_6^{3-}$ (*149*), Ce$^{IV}$ (*98*), and U$^{IV}$ (*38*) are reduced with hydrogen peroxide have also been studied. In the reaction with Fe$^{III}$, the initial step

$$Fe^{III} + H_2O_2 \rightarrow Fe^{II} + HO_2 + H^+ \tag{295}$$

is followed by

$$Fe^{III} + HO_2 \rightarrow Fe^{II} + O_2 + H^+ \tag{296}$$

The oxygen which is liberated has the same isotopic composition as the hydrogen peroxide (*69*). Again the kinetics are complex since the product also reacts with $H_2O_2$, as indicated above. Ardon and Bleicher (*26*) report the isolation of a new intermediate formed during the reduction of chromium(VI) with hydrogen peroxide. The compound may well have the structure $(H_2O)_5Cr\cdot O_2\cdot Cr(H_2O)_5^{5+}$. At 26.5° and hydrogen-ion concentration 0.2–4.0 $N$, the first-order rate constant for the decomposition of the complex is $\sim 1.4 \times 10^{-4}$ sec$^{-1}$. The complex is reduced by iodide and iron(II).

It now seems best to assume that the green complex $(NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5^{5+}$ is essentially two cobalt(III) ions bridged by a superoxide ion $O_2^-$ (*331*), whereas the brown complex $(NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5^{4+}$ contains two cobalt(III) ions bridged by a peroxide $O_2^{2-}$ ion (*387*). In acid solutions the latter is unstable. The 1 : 1 reductions of the green complex with Fe$^{II}$, V$^{IV}$, Sn$^{II}$, I$^-$, and $S_2O_3^{2-}$ (*368*) give two cobalt(II) ions and oxygen, the reaction sequence being:

$$(NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5^{5+} \rightarrow (NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5^{4+} \rightarrow 2Co^{2+} + O_2 + 10NH_3 \tag{297}$$

With sulfite and nitrite, on the other hand, 1 : 2 reactions are observed (*368*),

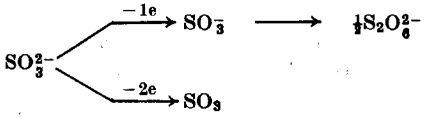
$$(NH_3)_5Co\cdot O_2\cdot Co(NH_3)_5^{5+} + 2SO_3^{2-} \rightarrow (NH_3)_5CoSO_4^{+} + Co^{2+} + 5NH_3 + SO_4^{2-} \tag{298}$$

and both bridging oxygen atoms may be transferred to the sulfate.

Different stoichiometries and products are observed in the oxidation of hydrazine, depending on whether one- or two-equivalent reagents are involved. The two reaction paths are (*198*, *199*, *201*, *236*):

$$\begin{tikzcd}
 & N_2H_3 \arrow[r] & \frac{1}{2}N_4H_6 \arrow[r] & \frac{1}{2}N_2+NH_3 & (299) \\
N_2H_4 \arrow[ur, "-e"] \arrow[dr, "-2c"'] & & & & \\
 & N_2H_2 \arrow[r, "-2e"] & N_2 & & (300)
\end{tikzcd}$$

One-equivalent reagents react by paths (299) and (300), and two-equivalent reagents exclusively by path (300). A similar distinction is possible in the reactions with sulfite (*196*):



**(301)**

**(302)**

One-equivalent reagents (e.g., $Ce^{III}$, $Co^{III}$, $Fe^{III}$, and $V^{V}$) react by paths (301) and (302) to give dithionate and sulfate (stoichiometry between 1.0 and 2.0), and two-equivalent reagents (e.g., $I_2$, $Br_2$, $Cl_2$, $IO_3^-$, $H_2O_2$, and $Tl^{III}$) by path (302) to give sulfate only (stoichiometry 2.0). No dithionate is produced in the oxidation of sulfite with $Fe(CN)_6^{3-}$, however (*388*). A mechanism,

$$Fe(CN)_6^{3-} + SO_3^{2-} \xrightarrow{\text{slow}} Fe(CN)_5SO_3^{4-} + CN^- \tag{303}$$

$$Fe(CN)_5SO_3^{4-} + Fe(CN)_6^{3-} \xrightarrow{\text{fast}} Fe(CN)_5SO_3^{3-} + Fe(CN)_6^{4-} \tag{304}$$

$$Fe(CN)_5SO_3^{3-} + H_2O \xrightarrow{\text{fast}} Fe(CN)_5^{3-} + H_2SO_4 \tag{305}$$

$$Fe(CN)_5^{3-} + CN^- \xrightarrow{\text{fast}} Fe(CN)_6^{4-} \tag{306}$$

in which the sulfite becomes coordinated in the inner-sphere, has been suggested. Other inert complexes, $Fe(CN)_5H_2O^{2-}$, $Fe(CN)_5NH_3^{2-}$, $Fe(bipy)_3^{3+}$, and $Co(C_2O_4)_3^{3-}$, show similar behavior, but with labile complexes such as $Fe^{3+}$ and $Fe(C_2O_4)_3^{3-}$, sulfate and dithionate are formed (*389*).

When hydroxylamine is reduced by titanium(III), $NH_2$ radicals and not OH radicals are produced in the first step (*102*):

$$Ti^{III} + NH_2OH \longrightarrow Ti^{IV} + NH_2 + OH^- \tag{307}$$

$$Ti^{III} + NH_2 \xrightarrow{H^+} Ti^{IV} + NH_3 \tag{308}$$

The oxidation of hydroxylamine by cerium(IV) (*393*) appears to involve prior coordination of $NH_2OH$ to the metal ion. The radical $NH_2O$, which is first formed, is oxidized further to $N_2O$ except at low $Ce^{IV}$ concentrations when $N_2$ is formed.

Parker and Spence (*297*) found that nitric oxide is a major product when molybdenum(V) is oxidized by nitrate ions. The molybdenum(V) is believed to be present predominantly as a dimer, the rate-controlling step being the reaction of mononuclear $Mo^{V}$ with nitrate ions. The reaction of cerium(III) with nitric acid is a reversible reaction,

$$Ce^{III} + HNO_3 + H^+ \rightleftharpoons Ce^{IV} + NO_2 + H_2O \tag{309}$$

which has been studied at 90–110° in 12–16 *N* nitric acid. The nitrite ion oxidations of molybdenum(V) (*344*) and iron(II) (*386*) have also been studied.

The kinetics of the reactions of bromide ions with $Ce^{IV}$ (*232*), and of iodide with neptunium(V) (*334*) and $(NH_3)_5Co \cdot O_2 \cdot Co(NH_3)_5^{5+}$ (*369*), fit the same sort of general pattern. Thus rate equations are of the type,

$$\text{Rate} = [Ce^{IV}](k_1[Br^-] + k_2[Br^-]^2) \tag{310}$$

which is consistent with a mechanism:

$$Ce^{IV} + Br^- \rightleftharpoons CeBr^{3+} \tag{311}$$

$$CeBr^{3+} + Br^- \rightarrow Ce^{III} + Br_2^- \tag{312}$$

$$CeBr^{3+} \rightarrow Ce^{III} + Br \tag{313}$$

Subsequent reactions of the radicals Br and $Br_2^-$ (with each other or the $Ce^{IV}$) are rapid. The rates of the reactions of $Fe^{III}$ (*372*) and $Fe(CN)_6^{3-}$ (*4*) with iodide also show first- to second-order dependence on iodide.

Perchlorate ions are reduced by $V^{II}$, $V^{III}$ (*235*), $Ti^{III}$ (*113*), $Ru(NH_3)_5^{2+}$, and $Ru(NH_3)_6^{2+}$ (*123*), but not by $Cr^{II}$ or $Eu^{II}$ (*10*). Gordon and Tewari (*158*) find that chlorite ions oxidize vanadium(II) to vanadium(III) and rule out the intermediate formation of vanadium(IV). Subsequent reactions are rapid as in the corresponding reaction with chromium(II) (*381*). In the latter it was found that chromium(II) reductions of chlorine dioxide, chlorite, hypochlorite, and chlorine were all at least $10^3$–$10^5$ times faster than the reaction with chlorate ($k = 39.0$ l·mole$^{-1}$ sec$^{-1}$ at 20°).

Peroxodisulfate ions have been shown to oxidize $Ce^{III}$ (*89*), $Cr^{III}$, and $V^{IV}$ (*410*) in the presence of $Ag^I$ as catalyst. Either $Ag^{II}$ or $Ag^{III}$ or both may be involved as intermediates in these reactions. The iron(III) oxidation of thiosulfate (*294–296*), cerium(IV) oxidation of hypophosphorus acid (*82*), and mercury(II) oxidation of carbon monoxide (*193*) have been studied.

Anbar (*17*) has recently reviewed the oxidation and reduction of ligands. The oxidation of an azide ligand with nitrite in complexes $Co(NH_3)_5N_3^{2+}$ (*178*), $Co(CN)_5N_3^{3-}$ (*175*), and *cis*- and *trans*-$Co(en)_2(N_3)_2^+$ (*248*) are of interest because five-coordination intermediates are believed to be formed:

$$Co(NH_3)_5N_3^{2+} + HNO_2 + H^+ \rightarrow Co(NH_3)_5H_2O^{3+} + N_2 + N_2O \tag{314}$$

In the presence of various anions ($X^- = F^-$, $Cl^-$, $Br^-$, $NO_3^-$, $SCN^-$, $H_2PO_4^-$, and $SO_4^{2-}$), Haim and Taube (*178*) have found that $Co(NH_3)_5X^{2+}$ complexes are formed as well as $Co(NH_3)_5H_2O^{3+}$, and conclude that $Co(NH_3)_5^{3+}$ is an intermediate. Pearson and Moore (*298*) have concluded that the intermediate in these oxidation-induced aquations are not the same as those produced in the spontaneous aquation of these complexes. The oxidation of $Co(NH_3)_5C_2O_4^+$ by two-equivalent oxidants ($H_2O_2/Mo^{VI}$ or $Cl_2$) produces $Co(NH_3)_5H_2O^{3+}$. With one-equivalent oxidants ($Ce^{IV}$, $Co^{3+}$, and $S_2O_8^{2-}/Ag^+$), on the other hand, $Co^{2+}$ is formed (*330*). When at 50° a solution of $Ag^I$ is added to an acid in solution of $S_2O_8^{2-}$ and $Co(NH_3)_5H_2O^{3+}$, a small fraction of the cobalt(III) complex is reduced to cobalt(II) (*383*).

Espenson (*128*) has found that oxidation of the coordinated iodide in $CrI^{2+}$ by iodate ions proceeds according to the rate law:

$$-d[CrI^{2+}]/dt = k[Cr^{2+}][I_2] \qquad (315)$$

The reaction rate is independent of the concentration of iodate, a reactant, and is directly dependent on the concentration of iodine, a product.

The oxidation of hydroxyethylenediaminetriacetic acid by vanadate(V) ions is largely suppressed when the ligand is coordinated to chromium(III) or cobalt(III). This result is consistent with a mechanism for the vanadate oxidation which requires the formation of a complex between the ligand and vanadate(V) prior to the electron-transfer step (*225*). Other reactions of metal ions with organic reagents (*399*) may proceed in a similar manner.

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