MECHANISMS OF REDOX REACTIONS OF SIMPLE CHEMISTRY

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I. Introduction

The principal concern in this chapter will be the mechanism of reaction of metal ions in which a change of oxidation state takes place on reaction. These reactions, of which

$$Fe^{++} + Ce(IV) \rightarrow Fe^{+++} + Ce^{+++} \qquad (1)$$

may be taken as typical, are part of the material of instruction in general and analytical chemistry and as such are familiar to anyone with training in chemistry. Nevertheless, fundamental questions as to the means by which the change in oxidation state takes place were until recently not formulated, let alone answered.

The general subject includes as a proper part problems of specific chemistry such as are encountered in the reaction, for example, of Fe^{++} with MnO_4^-: What are the steps by which the system proceeds to the final products, and what are the properties of the intermediate oxidation states of Mn (or of Fe) which must be involved for such a complex over-all reaction? Important for inorganic chemistry as such questions are, for the most part they have been set aside, and attention is directed rather to the description of the individual steps. Given a process of simple order, we shall consider questions such as these: What is the closest distance of approach of oxidant and reductant? What is the arrangement of other groups besides the reactant metal ions in the activated complex? What motions of these groups are necessary to consummate the reaction? How are the rates dependent on the nature of the metal ions and on the other groups which may be present in the activated complex? These questions will be given a more specific formulation when we consider the various proposals which have been made describing the "electron transfer" process.

II. Electron Transfer in the Gas Phase

It is instructive to consider some features of the data on charge-transfer processes in the gas phase between simple molecules before considering the systems as they are complicated by the interactions of the central atoms with molecules of the solvent or other groups. The earliest experimental evidence for the occurrence of electron transfer between species in the gas phase was obtained from mass spectroscopic measurements (*120*). Data on the cross sections for such reactions are derived principally from two sources: measurement of the drift velocity of ions in various gases and measurements of the attenuation of ion beams brought about by inelastic collisions with molecules. The cross section for charge transfer is dependent on the kinetic energy of ions, so that the data on the drift velocity, involving speeds more nearly those of thermal energies, will be considered first.

The subject of drift velocities, particularly as it pertains to inert gas systems, was discussed by Hornbeck (*58*) (experimental results) and Holstein (*57*) (theoretical) as part of the program for a symposium on Electron Transfer Processes in general, held at Notre Dame in 1952. The significant observation is that the drift velocity of an ion such as He^+ is much less than is expected if account is taken only of the usual processes for energy transfer, including polarization of He by the positive ion. Similar effects are noted for the other inert gas ions and have been recorded also for N_2^+ in N_2 (*90*). The effective collision cross section is increased by symmetry effects which include electron transfer as a component. Table I presents the data taken from Hornbeck's paper comparing the cross section for charge transfer with the "normal" cross section for ion-molecule interaction including atom polarization. T_i considerably exceeds T_a, and

TABLE I

COMPARISON OF CROSS SECTION FOR ELECTRON TRANSFER T_i WITH GAS KINETIC CROSS SECTION T_a

	$T_i \times 10^{16}$ (cm²)	$T_a \times 10^{16}$ (cm²)
He	54	15
Ne	65	21
A	134	42

is large enough so that electron transfer over nuclear separations as large as 5-8 Bohr radii must be invoked. For N_2^+ in N_2 the effect on drift velocity is smaller than is observed for the inert gases, and the mobility is only 7.5% less than the normal gas kinetic mobility. The difference between an inert gas on the one hand and a more complex molecule on the other can be attributed to the circumstance that the equilibrium internuclear separations for N_2^+ and N_2 are different, as are the separations of the vibrational levels. Since the electron transfer process is adiabatic, the energies at the two sites must match closely to make transfer possible.

During the Notre Dame Symposium, Muschlitz and Simons (*93*) summarized work on the cross sections for inelastic scattering of protons by various gases. The cross sections for 100-volt protons on He, Ne, Kr, and A are in the ratios 0, 1.5, 48, and 28 (*52*); for a complex molecule such as C_2H_6, a value of 112 is observed; there is a decrease in the cross section for inelastic scattering as the kinetic energies of the ions increase (*118*). The interesting qualitative features are: the maximum in the cross section for the inert gas as atomic number increases and the large cross section for C_2H_6 (and other complex molecules). Presumably, the large cross section for complex molecules undergoing electron transfer to H^+ comes about because, by using vibrational states, these molecules can provide many ways of bringing about the energy matching.

Since shielding by other electrons at large distances for a test electron is complete, and since the cross sections for electron transfer when simple atoms are involved are large compared to atomic dimensions, hydrogen-like wave functions can be used to describe the electron distribution at the large radii in question. Thus calculations of the probability of electron transfer, at least in simple cases, meet with a fair degree of success. Such calculations have been made by Holstein (*57*) for the symmetrical inert gas systems, using Hartree-Fock wave functions for the outermost shells. Gurnee and Magee (*48*), dealing with the same systems, have used the Slater wave functions (*119*) and have chosen in each case a value for the parameter α (which in the hydrogen-like case would be $(2I)^{1/2}$ where I is the ionizing potential) such that the one-electron wave function is approximately satisfied for the range of distances in question. Satisfactory agreement of calculated and experimental cross sections for $Ne + Ne^+$ and $He + He^+$ is obtained. The treatment of Gurnee and Magee also includes double charge transfer reactions; the theory and observations made for such reactions (*141*) are germane to the issue of 1 *versus* 2*e* changes in redox reactions. Experimentally, the cross section for $Ne^{++} + Ne = Ne + Ne^{++}$ is about ¼ of that for the 1*e* process in the same system, while for A, the ratio is about ½. Theory (*48*) suggests a ratio of about ½ for both sets of reactants. For the discussion of charge transfer in diatomic molecules, Gurnee and Magee used Heitler-London functions for the electronic part of the wave functions and harmonic oscillator and rigid rotator functions for the internal motions. Of the internal motions, only the vibrational part affects the probability of electron transfer. Gurnee and Magee have tabulated values of the vibrational overlap integrals for H_2-H_2^+, HD-HD^+, D_2-D_2^+, and N_2-N_2^+—these range from 0.195 for D_2-D_2^+ to 0.940 for N_2-N_2^+. The case of widest application is that for which the energies of the initial and final states differ. At small relative velocities, the probability of transfer decreases sharply as the energy difference increases; for an energy difference as small as 0.05 ev, electron transfer is possible only when relative velocities are of the order of 10^6 cm sec^{-1} or larger (*48*).

III. Interaction of Reactant Ions with Environment

For the systems with which we are concerned, other molecules are always in close proximity to the species undergoing charge transfer. Since even in a solvent of low dielectric constant the energy of interaction with the medium of a charge residing on a sphere of atomic dimensions amounts to several tens of kilocalories per mole, and since a redistribution of charge always occurs in the reactions of present interest, due consideration must be given to these interactions. These interactions are often discussed in a way that glosses over structural features, as is done for example in the application of the Born equation. But from a chemist's point of view it is necessary to inquire into the structure of the solvent surrounding the ions, especially in a solvent containing polar molecules, and in particular to distinguish groups in the first coordination sphere from those further out which may also be influenced by the electric field of the central ions. This distinction is natural, not only because the forces binding the first layer are greater than for those further out, but also because the residence time for a solvent molecule adjacent to a cation of high charge may be considerably greater than for solvent having only solvent as neighbor. The forces that give individuality to the different ions, whether we consider the influence of the ligands on the central ion or vice versa, are largely expended in the first coordination sphere, so that differences in the interaction which two ions such as $Al(OH_2)_6^{+++}$ and $Fe(OH_2)_6^{+++}$, having the first coordination spheres completed, have with the surrounding medium can be understood largely as differences that arise from the slightly different radii of the two central ions. The distinction between groups in the first coordination sphere and other groups may become unsharp in certain cases [of which $Cr(H_2O)_6^{++}$ may be an example] in which not all the groups in the first coordination sphere are equivalent. However, even in most such cases, the less firmly bound solvent molecules experience a much greater electric field than do those in the second sphere of coordination, so that the distinction can still be maintained.

Several aspects of solvation phenomena will be considered: solvation of cations, interaction of cations with other groups, and phenomena of electrolytic dissociation. The essential general features will be covered if we consider on the one hand a solvent of high dielectric constant, such as water, and on the other, remark on the differences in the state of an electrolyte produced by dissolving it in solvents of low dielectric constant. Special emphasis will be given to the subject of hydration of ions, because most of the work on redox reactions has been done with water as solvent.

Over the last 15 years great progress has been made in understanding hydration of cations. The existence of well-defined hydrates of cations in crystals leads naturally to the supposition that cations in solutions will also be hydrated. Certainly the energies of hydration of cations with water are great enough (ranging from approximately 60 kcal mole^{-1} (*73*) for Cs^+ to $> 10^3$ kcal for a tripositive cation such as Al^{+++}) so that it is *not unreasonable to* expect cations and water in the first sphere of coordination to constitute definite chemical species. In spite of the force which such general considerations may have, hydrated cations have not been part of the careful chemist's vocabulary of molecules, and for good reasons. With only evidence of the kind cited for the existence of hydrated ions in solution, questions can be raised as to their existence as definite species. In the solid, species of particular formula may be stabilized by the forces producing the ordered arrangement. In the liquid, several different configurations may have approximately the same energy; even when the energy differences for different configurations are appreciable, the residence time of a particular set of water molecules in the first coordination sphere may be so short that the concept of the hydrated cation as a molecule loses significance. In a program for the study of hydration of ions, the experimenter seeks to establish the formulae of the hydrated ions, their labilities and the energy differences between states of different coordination numbers.

Most of the classical physicochemical methods for the study of hydration of ions fail to distinguish between water in the first coordination sphere and water more remote from the central ion which also comes under the influence of its charge. Some of the methods more recently applied have provided a clearer picture. The oxygen isotope exchange method, where applicable, not only can define the composition of the first coordination sphere but also can be used to measure the lability of the aquo ion. Thus it has served to establish $Cr(OH_2)_6^{+++}$ (*64*); $(NH_3)_5Co(OH_2)^{+++}$ (*114*); and $(NH_3)_4Co(OH_2)_2^{+++}$ (*105*) as well-defined species in solution and also to fix the half-time for exchange of these species ($t_{1/2}$ of the order of 20 to 40 hr at 25°). In a further development (*10*) of this method, which makes accessible shorter sampling times, it has been shown that $Al^{+++}aq.$ can indeed be represented as $Al(OH_2)_6^{+++}$, and that the half-time for the exchange of bound water exceeds 0.005 sec. Experiments on the effect which cations exert on the relative fugacities of H_2O^{16} and H_2O^{18} have served to indicate that even cations which form labile hydrates (for example, $H^+aq.$) nevertheless form definite hydrates (*40*).

Perhaps the greatest progress has been made in the subject of hydration of cations by the studies of the electronic spectra of transition metal ions. The theoretical developments on the influence of ligand fields on the energy levels of ions, which culminated in the work of Penney and Schlapp (*102*) and of Van Vleck (*133*) on magnetic properties of ions, have been applied by Hartmann and co-workers (*51, 65*), as well as others (*91*), to the problem at hand. The theoretical ideas can be applied in two ways. In one application the spectrum of an ion in solution is compared with that in a solid in which the composition and constitution of the hydrated ion are known. However unsatisfactory the simple application of crystal field theory may be in predicting quantitatively the energy levels of the ion in a hydrate, it can in many cases nevertheless be trusted to indicate the magnitude of the changes in spectrum which can be expected to accompany a change in coordination number. In another application, less empirical but also less dependable, an analysis of the spectrum of the ion, applying the principles of crystal field theory, can be used to determine the symmetry of the ligand field. Difficulties can be encountered in the second application arising from the incomplete resolution of the electronic bands and from unresolved questions of intensities. The work on the electronic spectra has, however, served to establish the formulae of the hydrates of most colored transition metal ions in water.

A relatively new technique (*139*) for measuring the substitution labilities of hydrated paramagnetic cations is observation of the line broadening of the nuclear magnetic resonance absorption of ligand nuclei caused by the central ion. The effect of the line broadening is particularly marked for ions which permit rapid exchange of water in the first coordination sphere and is much weaker for an ion such as $Cr(H_2O)_6^{+++}$. This technique has been applied by Wertz (*139*) to Cl^- substitution and by Connick (*30*) to H_2O substitution in hydrated cations. There has been a revival of interest (*22*) in the application of X-ray diffraction to a study of aqueous solutions, and further significant progress can be expected in the near future using this technique.

Specific hydration of anions is not dealt with here, not because the energy of hydration is not large but because there is greater question of the existence of definite species in the sense implied in the discussion of the cations. The hydration of anions is different in this sense, that simple ion dipole (hydrogen bond) interactions come into question, and it is likely that the residence time of a particular water molecule adjacent to an anion will not be much longer than for water adjacent to water.

Conventional physicochemical methods, the most powerful of which depend on the application of the mass law, can be used to establish the composition of a complex ion with respect to a nonsolvent ligand. Even when the composition with respect to nonsolvent ligands is established, many questions remain which are particularly hard to answer for substitution labile systems. Thus when an ion of formula $FeCl_4^-$ is proposed, one can ask, how many molecules of water in addition to the Cl^- comprise the first coordination sphere? If the formula is $FeCl_4(H_2O)_2^-$, what is the ratio of the *cis* to *trans* form at equilibrium? Furthermore, for oppositely charged ions of high charge, the distribution between two forms must be considered, in only one of which is there a direct bond of the ligand to central ions. Thus the studies on hydration of cations need to be extended also to complex ions which are coordinatively unsaturated with respect to nonsolvent ligands. Studies with complex ions which are not labile to substitution help greatly in assessing the importance of outer-sphere[1] forms. For the system $(NH_3)_5CoOH_2^{+++} + SO_4^{=}$, inner-sphere and outer-sphere forms are of about equal stability (*131*). The outer-sphere affinity of $Cr(H_2O)_6^{+++}$ for Cl^- is very small. This latter conclusion, based on the careful work of Gates and King (*43*), casts doubt on the strong outer-sphere association of halides and tripositive ions indicated by the work of Linhard (*78*) and of Evans and Nancollas (*39*).

The incomplete dissociation of ion pairs which are coordinatively independent, observed for ions of opposite and high charge, even in water, is a common phenomenon in solvents (*71*) of low dielectric constant (D). In liquid NH_3 with $D = 27$ at $-60°$, strong electrolytes such as $NaNO_3$ or NH_4Cl have dissociation constants of the order of 10^{-3}. When dioxane is the solvent ($D = 2.18$), a salt such as Bu_4NClO_4, though comprised of large ions of low charge, has a dissociation constant of the order of 10^{-18}. For such solutions the model of an ion atmosphere surrounding each ion collapses to one in which the electrolyte exists as ion pairs, but with the further complication that at reasonable concentrations of electrolyte association of the ion pairs takes place (*41*).

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[1] The term requires definition. It refers to regions beyond the first coordination sphere of a cation considered as center, but not to anions considered as centers. Thus, for the system Al^{+++} aq. — Cl^- aq., the distinction is between $AlCl^{++}$ aq. and $Al(OH_2)_6^{+++} \cdot Cl^-$, and the question of the hydration of Cl^- is not raised (for example, no distinction is made between structures such as $Al^{+++}(OH_2)_6\ Cl^-$ and $Al^{+++}(OH_2)_6\ (OH_2)_n\ Cl^-$).

IV. General Consideration of the Electron Transfer Process in Solution

Let us consider first some general features of electron transfer between ions in solution without specific, detailed discussions of individual systems. The conditions which must be met to make electron transfer between two ions possible are matching the energy of the electron at the two sites and sufficient orbital overlap between the two sites to provide for a reasonable probability of transfer (*76, 104*). Various factors are involved in meeting these conditions, and these are considered qualitatively in the present section discussing mainly reactions in media of high dielectric constant but also referring briefly to media of low dielectric constant.

The mechanism of the electron transfer itself has been given considerable discussion, and attention has been directed to it as a barrier penetration phenomenon (*84, 104, 137*). This emphasis is justified only to the extent that other reasonable possibilities exist. Let us examine at the outset one such alternative process which has also come up for consideration, namely one in which the electron spends sufficient time in the solvent to be solvated. For a reaction with Fe^{++} as reducing agent, the mechanism corresponding to this process would be formulated as follows:

$$\mathrm{Fe^{++}\ aq.} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Fe^{+++}\ aq.} + e^-\ \mathrm{aq.} \tag{2}$$

$$\text{Oxidizing agent} + e^-\ \mathrm{aq.} \xrightarrow{k_2} \text{products.} \tag{3}$$

A mechanism of this kind, consisting of discrete steps, can be rejected on the basis of kinetic evidence for all systems which have thus far been studied in detail (although it would be dangerous to reject it as a possibility for very powerful reducing agents in water or liquid ammonia). For if reaction (2) forward is slow compared to (3), the rate of reaction will be independent of the concentration of oxidizing agent, while if (2) is maintained as an equilibrium with (3) rate determining, the rate of reaction will be inverse in the concentration of Fe^{+++}. Such rate laws have not been observed for the systems of simple chemistry which we are discussing. However, the feature that the rates can be inverse in the concentration of the product formed from the reducing agent has frequently been observed for systems of complex chemistry. In every such case, this kinetic feature can reasonably be attributed to the formation of an intermediate oxidation state.

If the model is modified by postulating that the electron is strongly affected by the presence of the oxidizing agent, the conditions for barrier penetration are also met, and it is difficult to see what experimental criteria would distinguish the two cases, whether the electron surmounts a barrier the shape and magnitude of which is affected by the reactant ions, or whether it penetrates such a barrier. An answer would be given if the energy levels of the electron in the activated complex were known and if the shape and height of the barrier could be calculated. Knowledge of the distribution of electrons in the complex molecules in question is not sufficiently quantitative to settle the issue at present.

The suggestion (*34*) analogous to that contained in Eqs. (2) and (3), but having the oxidizing agent remove electrons from the solvent, can be rejected in many systems for reasons similar to those advanced for the electron in the solvent. In any case, such processes would seem to be reasonable possibilities only for the strongest oxidizing agents—for $H_2O = HO + H^+ + e^-$ lies at approximately -2.8 volts (*72*)—and there is no evidence that an oxidizing agent such as Co^{+++}aq. with E^0 at -1.8 volts makes use of a solvent-hole mechanism.

The limited conclusions reached in the preceding paragraph should not be taken to imply that the description of these processes as barrier penetration phenomena is always apt. It is useful to consider the extreme mechanisms: in one the geometries of the oxidized and reduced forms, at least as regards the first sphere of coordination, are the same, and substitutions in the first coordination sphere are not readily accepted; in the other there are important changes in the first coordination sphere accompanying the electron transfer, and further, at least one of the species readily accepts substitution, and the coordination spheres interpenetrate in the activated complex. It will be noted that more than one condition has been specified for each case. The conditions are not necessarily combined as they appear here, and other cases can arise. The particular combinations have been chosen to provide the greatest contrast in behavior which can be expected.

The systems of the first class afford the closest approach to a simple barrier penetration process, and perhaps they more readily respond to a theoretical analysis. It can reasonably be supposed that for these systems orbital overlap for the two ions is small, so that the frequency of the electronic transition is small, and there is no substantial binding between the two exchanging centers. A model of this kind presumably corresponds to the "weak overlap" cases as defined and discussed by Marcus (*82*). In attempting to calculate the rates of these reactions, besides the problem of the shape and height of the barrier for the electron transfer, electrostatic interaction of the reactants must be dealt with and the energy necessary to distort the solvent and ionic atmosphere about each ion to make the energy of the electron equal at the two sites. Different workers have emphasized different ones of these factors, and serious differences of opinion are recorded.

The electrostatic interactions are allowed for in the various treatments of the problem (*82,84,137*), but the quantitative validity of the treatments covering close distances of approach has been correctly questioned (*104*). In discussing the frequency of electronic transition, Libby (*76*) uses the radial dependence of hydrogen-like wave functions, with due regard for the charges of the ions, and discusses electron exchange between transition metal ions over distances of several Ångstrom units; Zener (*142*), in discussing the overlap of *d* electrons of nearest neighbor transition metal cations (nearest neighbor Mn cations are separated by $O^=$) in a solid such as $LaMnO_3$, states, ". . . Mn^{+3} ions are sufficiently far apart as to have no appreciable overlapping." Marcus (*82*) considers the ions, including the first coordination shell, as conducting spheres, takes the distance of approach for electron transfer to be the sum of the radii of the spheres and concludes that factors other than the frequency of transition of the electron determine the rate of reaction. Marcus *et al.* (*84*) leave the probability of the electron transfer, depending as it does on distance, as a running parameter, balancing the increasing electrostatic repulsion on close approach against the greater probability for barrier penetration under these circumstances. The assumption of the complex ion as a conducting sphere, necessary because knowledge of the electron distribution in such ions is so little understood, does, however, gloss over the extraordinary differences in rate observed for different ligands, and no theory can be considered satisfactory that does not make allowance for the chemical individualities of the systems.

For reactions in which there are no changes in the first coordination sphere, the effects arising from the requirement for nonequilibrium polarization of the surroundings are relegated to regions beyond the first sphere of coordination, but they are nevertheless important. Marcus (*82*) has given a mature discussion of the contribution made to the free energy of activation of these processes by the requirement for solvent reorganization. Electrolyte effects also exist, for the transfer of an electron from one site to another requires the eventual redistribution of ions; as in the case of dipole interactions, the changes must occur prior to the electron transfer as part of the requirement that no energy change accompany electron transfer. There may in fact be an interplay between the solvent dipole and ion atmosphere contributions, and it is conceivable that the transfer of a single ion from one site to another can make up a large part of the total energy requirement of the activation of the environment. A specific mechanism (*33, 112*) of this type which has been suggested is a proton shift from the coordination shell of the reducing agent to that of the oxidizing agent on electron transfer (or described as H-atom transfer).

To make the discussion concrete, let us take as the activated complex for the reactions of the second type a species of geometry: $L_5M^{+n+1}X$ $M^{+n}W_5$, where L, X, and W are ligand groups which may all be alike, and the M's are metal ions. In arriving at a configuration having X as a bridging group, either M^{+n+1} or M^{+n} (or both) has undergone substitution in the first coordination sphere. We will also assume that the electronic transfer or redistribution of the electron itself is extremely rapid. This is an independent assumption which does not follow from the assumed geometry, but it seems to be required to explain why certain systems adopt this kind of activated complex in undergoing electron transfer reactions. Important differences as compared to the previous class are realized for these systems. The electron is effectively distributed over the two sites, and the binding resulting therefrom lowers the energy needed for the formation of the activated complex. Whereas in the previous case the electron waits for an appropriate fluctuation without being able to influence the changes required in the site to which it will transfer, in the case under present discussion it affects the energy required to produce the fluctuation there. Presumably the reaction is consummated by some fluctuation which causes the separation of M^{n+1} and M^n, and may require other changes in the coordination spheres as well. If, for example, the fluctuation in question is the transfer of X from an equilibrium position close to the oxidizing cation to one close to the reducing cation, the redistribution of the electron affects the energy that is necessary to stretch the M^{n+1}-X bond and to compress the M^n-X bond.

A feature of the bridged activated complex is that the bridging group may move from the oxidizing agent to the reducing agent, that is, in the direction opposite to that of the electron. When the bridging group is negatively charged, the process is electrically equivalent to the transfer of an atom from the oxidizing agent to the reducing agent, and thus the demand for reorientation of solvent is less than in the previous mechanism. This feature also operates to encourage traffic by a path which in certain other respects appears to be highly unfavorable to reaction.

For reactions of this class, even less than for those discussed earlier, is it possible to account quantitatively for the rates. In fact, it can be considered an ambitious goal even to predict whether in a particular instance substitution to form the binuclear complex is rate determining or whether, as was assumed in the foregoing discussion, equilibrium to form the binuclear complex is established rapidly, and the slow step is disruption of the binuclear complex. For a quantitative discussion, the energy of interaction in such a binuclear complex must be assessed. This energy will depend greatly on the electronic structures of the metal ions, on the properties of the bridging group, and on the properties of the other ligands. Similarly, the energies required to produce the changes in coordination sphere necessary to complete the reaction will be dependent on the same factors. At the present time, far from being able to treat these factors quantitatively, we still lack a full description of the activated complexes for systems of the widely different electronic structures which must be considered.

In solvents of low dielectric constant the differences between the two types of activated complex become less pronounced. Thus, considering for example the system involving electron exchange between ClO_2 and ClO_2^-, when the solvent is water the mechanism would fairly clearly be of the first type; however, in a solvent of low dielectric constant, free ClO_2^- does not exist, but it will always be in association with the counter cation. When the dipole moment of the solvent is low, the only mechanism for bringing about the matching of energy of the electron at two sites is the motion of the cation, and we thus have the parsimony of atomic readjustments characteristic of the second class. The electron will follow the motion of the cation from ClO_2^- to ClO_2, and the activated complex can be considered to be of the bridged type $[ClO_2NaClO_2]$ in the case under present discussion.

The two types of activated complex that have been discussed present the gross geometrical features of two types which have been experimentally delineated; however, the types that are observed do not necessarily present the other features which were referred to in the cases chosen for the qualitative theoretical discussion. In the next two sections the experimental evidence on the nature of "outer sphere" and "bridged" activated complexes is discussed (the terms have no connotations other than the geometry of the activated complexes implied by them), and the general observations relating to the kinetic behavior of the corresponding systems will be outlined.

V. The Outer-Sphere Activated Complex

The discussion of experimental methods which opens this section applies equally well to the next two sections. The development of new methods of measurements of rates has been an important part of the progress in this field. The majority of the kinetic work done has been for systems in which there is no net chemical change. The reasons for this choice of problem are understandable; they arise in part from the desire to have the chemistry simple and partly from the novelty and excitement of using isotopic tracers to measure rates of reactions, which until recently could not be measured by any other means. In fact, when the significance of isotopic methods in this field is appraised, it becomes obvious that of principal importance is the fact that the new methods attracted many capable workers who otherwise might not have developed an interest in this area of chemistry.

The principal method for measuring the rate of exchange in a system in which there is no net chemical exchange is to observe the redistribution of nuclei between the two forms. In such applications separations of the oxidation states after various intervals of time are made. These can involve, singly or in combination, precipitation, complex ion formation, solvent extraction, ion exchange, and separation by diffusion. The method of quenching and making separations by precipitation, in combination with a flow technique for mixing, has been applied particularly successfully by Wahl and his students. An indirect method which does not require separation of the species undergoing electron exchange has been used in the special case of the $Cr^{++}aq.$-$Cr(OH_2)_6^{+++}$ system (*103*): exchange of electrons between these two forms provides a path for rapid water exchange of the ion $Cr(OH_2)_6^{+++}$. A powerful new technique involves paramagnetic resonance measurements; the lifetime of the paramagnetic state which is being observed is reduced by electron exchange with the reaction partner, resulting in line broadening (*135*). Another new approach depends on the broadening of the magnetic resonance absorption of a nucleus, caused by the presence of the exchange partner. (*80*)

A very ingenious method which in essence satisfies the conditions of no net change, and which can be applied to ions that exist in *d-l* forms, was introduced by Dwyer and Gyarfas (*36*). This method exploits the change in the rotatory power of a system in which a net change of the following kind is taking place:

$$d\text{-}MC_3^{++} + l\text{-}MC_3^{+++} \rightarrow d\text{-}MC_3^{+++} + l\text{-}MC_3^{++}. \qquad (4)$$

It is regrettable that with all the activity that has developed in measuring rates of virtual changes there has been so little acceleration of the work for systems involving net chemical changes. Many of the important questions of mechanism which are posed can be answered as well by the study of orthodox reactions as they can by that of more exotic ones and, in most instances, by the expenditure of much less effort. The techniques which have been used are conventional, but for many of the important reactions further development of methods for the measurements of rates of rapid reactions is called for. Many of the systems of interest here involve intensely colored ions, so that the flow spectrophotometric method can often be applied.

Among the reagents for which electron transfer can take place without net rearrangement of the coordination sphere are the following[2]: MnO_4^-

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[2] The abbreviation phen represents 1,10-phenanthroline, and dip represents 2,2′-bipyridine.

– $MnO_4^=$, $IrCl_6^{\equiv}$ – $IrCl_6^=$, $Fe(CN)_6^{4-}$ – $Fe(CN)_6^{\equiv}$, $Mo(CN)_8^{\equiv}$ – $Mo(CN)_8^=$, $Fe(phen)_3^{++}$ – $Fe(phen)_3^{+++}$, $Fe(dip)_3^{++}$ – $Fe(dip)_3^{+++}$, $Os(dip)_3^{++}$ – $Os(dip)_3^{+++}$, $Co(dip)_3^{++}$ – $Co(dip)_3^{+++}$. The list is not intended to be exhaustive but only to provide an introduction to reagents of this class. Oxyions, CN^- and halide complexes are represented, various central metal ions, cations and anions, and species of coordination number 4, 6, and 8.

Both members of each couple are substitution inert, and for all $1e^-$ redox reactions which are possible for mixtures within this group, whether involving virtual or net chemical changes, electron transfer takes place much more rapidly than does substitution in the first coordination sphere. Thus, even in the absence of direct proof that no labilization of the coordination sphere occurs in the activated complex, it is almost certain that no interpenetration of the coordination spheres occurs. The outer sphere activated complexes are not necessarily restricted to reagents of this kind, but it is only for them that it is possible to assert with some confidence that this type of activated complex operates. It is also characteristic of the molecules in this group that the change in oxidation state takes place with little change in the dimensions of the molecule; thus these systems approach fairly closely the conditions which were chosen for the first class which was given theoretical discussion in the previous section.

The group considered here has been restricted to molecules which can reasonably be regarded as coordinatively saturated. There are numerous molecules, some of which are particularly important, for which certain elements only of the structure of the first coordination sphere are known to be preserved on electron transfer. These include[3]: ClO_2^- – ClO_2, UO_2^+ – UO_2^{++}, etc., $Fe(cpn)_2$ – $Fe(cpn)_2^+$, etc., Fe^{II}(porphyrin) – Fe^{III} (porphyrin), etc. Here the ligands specified in the formulas do not provide for coordinative saturation of the molecule. In UO_2^{++}, for example, the oxygens are colinear with the U atom, and groups held around the girdle of this molecule are readily replaced; furthermore, it is not known whether changes in the girdle coordination accompany electron transfer. On the basis of structures of the reactants alone, no conclusions as to the geometries of the activated complexes can be reached for this class of reagents.

The system among those of present interest which has been most thoroughly studied is exchange between MnO_4^- and $MnO_4^=$. A number of workers (*21, 61, 77, 115*) have done experiments with this reaction, but the most successful and complete study is that of Sheppard and Wahl (*115*). The rate of the reaction has been proved to be first order in each of the reactants, as was tacitly assumed in the earlier discussion of reactions of this class. The specific rate at 0° is reported as 710 M^{-1} sec^{-1}, E as

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[3] The abbreviation cpn represents the cyclopentadiene radical, C_5H_5.

10.5 kcal mole^{-1} and $\Delta S^‡$ as −9 e.u., for a medium which contains NaOH at 0.16 *M*. There is fairly direct evidence that in the $MnO_4^=$ – MnO_4^- reaction there is no interpenetration of coordination spheres. Symons (*124*) has shown that when MnO_4^- is reduced to $MnO_4^=$ by labelled water containing OH^-, the isotopic composition of MnO_4^- is unaltered. This reaction cannot occur without accompanying electron transfer between MnO_4^- and $MnO_4^=$. If, for example, the electron transfer were to take place by an activated complex such as $[O_3MnOMnO_3]^-$, MnO_4^- would be brought into rapid exchange with the solvent. Some exchange does occur if $MnO_4^=$ is allowed to accumulate, but this is attributable to exchange of $MnO_4^=$ rather than to oxygen exchange in the act of electron transfer.

TABLE II

SALT EFFECTS IN THE MnO_4^- – $MnO_4^=$ EXCHANGE REACTION
(TEMPERATURE, 0°)

Medium (electrolyte, molarity)	k (M^{-1} sec^{-1})
NaOH, 0.16	730
NaOH, CsOH, each 0.08	1730
CsOH, 0.16	2470
NaOH, 0.16, $Co(NH_3)_6Cl_3$, 0.001	1860
NaOH, 0.16, $Na_3Fe(CN)_6$, 0.001	1180

The data obtained by Sheppard and Wahl for the MnO_4^- – $MnO_4^=$ reaction feature some interesting salt effects. Table II contains a summary of the salient data reported by them.

Two effects are to be looked for in considering the influence of salts in reaction rate: a general ion-atmosphere effect and, when ions of high charge are involved, ion-pairing effects. Both appear to be illustrated by the data of Table II. The equilibrium ion-atmosphere distribution is unfavorable to the electron transfer so that a readjustment of these atmospheres must occur prior to the transfer. This readjustment may actually involve an anion moving in a direction opposing that of electron transfer, or a cation in the same direction. The difference in rate brought about by changing the electrolyte from 0.16 *M* NaOH to 0.16 *M* CsOH seems very large for an ordinary ion-atmosphere effect. The direction of change is such as to suggest that the mobility of the cation is an important factor in the electron transfer. In the present system, this may well be the case in spite of the high mobility of the OH^-; for an activated complex of negative charge, cations will predominate in the ion atmosphere, and a special sensitivity to cation influences will prevail. Even though the equilibrium properties are determined by a general ion atmosphere distribution, for the rate process it may be economical of time to provide for energy matching at the two sites by specific motion of a few ions rather than by small readjustments for many. Such a means for electrostatic readjustment is all the more likely when there is strong ion pairing. Thus when $Co(NH_3)_6^{+++}$ is added to the $MnO_4^- - MnO_4^=$ solution, a substantial fraction may be present as the outer sphere complex $Co(NH_3)_6^{+++}$ $MnO_4^=$. The electron then can follow the motion of the tripositive cation from $MnO_4^=$ to MnO_4^-. Thus it is not a foregone conclusion for these systems that electron transfer will be more rapid for the so-called free ions than it is, for example, when one of the ions is present as part of a complex. For example, the pair $HClO_2 - ClO_2$ may undergo electron exchange as rapidly as $ClO_2^- - ClO_2$; this relationship is actually indicated by the incomplete data which were obtained for this system (*31*). Whatever advantage, in respect to energy of activation, the system may lose in changing from ClO_2^- to $HClO_2$, may be made up in the greater economy of motion needed in the latter case, therefore leading to a more favorable entropy of activation.

The acceleration in reaction rate produced by low concentrations of $Fe(CN)_6^{\equiv}$ may be a result of catalysis by the $Fe(CN)_6^{4-} - Fe(CN)_6^{\equiv}$ couple, and the specific rate indicated for the reaction of $MnO_4^=$ with $Fe(CN)_6^{\equiv}$ is of the order of 10^3 M^{-1} sec^{-1} (*115*).

Wahl and Deck (*134*) have succeeded in getting an estimate of the specific rate for electron exchange between $Fe(CN)_6^{4-} - Fe(CN)_6^{\equiv}$; they report for the rate coefficient at 4°, 1×10^3 M^{-1} sec^{-1}.

For the majority of the systems which have been investigated, only lower limits on the rates have been established. George and Irvine (*44*) report for the reactions: $Fe(dip)_3^{++} - Fe(phen)_3^{+++}$, $Fe(dip)_3^{++} - Ru(dip)_3^{+++}$, $Fe(CN)_6^{4-}$ with $Fe(phen)_3^{+++}$, $Ru(dip)_3^{+++}$ or $IrCl_6^=$, $Mo(CN)_6^{4-} - IrCl_6^=$, a lower limit for the specific rates of 10^5 M^{-1} sec^{-1} at 18°. Since for these systems involving net changes no question of separation-induced exchange can be raised, the lower limit for the specific rate reported can be regarded as established. Other reactions to which the same remarks apply, and for which the minimum specific rate has been set even higher ($k > 2 \times 10^6$ M^{-1} sec^{-1} at 0°), are: $Os(dip)_3^{++}$ with $Fe(phen)_3^{+++}$, $Fe(dip)_3^{++}$, and $Fe(phen)_3^{++}$ with $Ru(dip)_3^{+++}$ (*37*). Eichler and Wahl repeated the experiment of Dwyer and Gyarfas (*36*) with the $Os(dip)_3^{++} - Os(dip)_3^{+++}$ system, but the results do not agree quantitatively. Whereas Dwyer and Gyarfas report that with solutions at 5×10^{-4} M at 5°, more than a minute is required for complete reaction, Eichler and Wahl find that the reaction is complete in 15 sec, even when the concentrations are reduced to 10^{-4} M. From the work of the latter authors, the specific rates of this reaction can be set as $> 10^5$ M^{-1} sec^{-1}. The electronic paramagnetic resonance (EPR) method has been used to set an upper limit of 4×10^8 M^{-1} sec^{-1} on the rate of electron exchange for the $W(CN)_8^{4-} - W(CN)_8^{\equiv}$ (*138*).

A number of other reactions have been studied using orthodox isotopic tracer techniques for which complete exchange in the time of separation was observed. The lower limits for the specific rates that can be calculated are considerably smaller than those to which we have referred, and since in many cases no proof could be adduced that the separation method did not cause the exchange, these results are not reported. The review by Amphlett (*5*) gives references to many of the literature reports on these and other reactions in the entire field.

For the systems which will be discussed now, it is not as certain as for those already discussed that the activated complexes are of the outer-sphere type. These systems differ in that one reaction partner is substitution labile (this is not so certain for $Co(phen)_3^{++}$ but is certain[4] for the $Co(NH_3)_6^{++}$ and $Co(en)_3^{++}$ complexes), so that the coordination sphere of the reducing cation can readily be entered. However, because the data indicate that enough amine appears in the activated complex to complete the coordination sphere of the reducing agent, and because no suitable bridging group is present on the oxidizing agent, it seems almost certain that the electron moves through the coordination spheres of both reaction partners. The results on rates and energetics of the activated complexes are summarized in Table III.

TABLE III

RATES OF ELECTRON EXCHANGE FOR SOME COBALT COMPLEXES

	μ	Temperature (°C)	k (M^{-1} sec^{-1})	E (kcal)	Reference
$Co(phen)_3^{++} - Co(phen)_3^{+++}$	—	~0	3.5	—	*38*
$Co(en)_3^{++} - Co(en)_3^{+++}$[a]	0.98	25	6×10^{-4}	~14	*75*
$Co(NH_3)_6^{++} - Co(NH_3)_6^{+++}$	0.98	45	$<7 \times 10^{-6}$	—	*75*
$Co(en)_3^{++} - Co(NH_3)_6^{+++}$	0.98	25	2×10^{-2}	—	*75*

[a] No specific effect of Cl^- at 1-M level.

Not enough systematic work has been done to evaluate the various factors that affect the rates for the class of reactions which has been considered, but a few general observations may be in order. Contributing to the high rates which are observed for most of them is the circumstance that because of the electronic structures, very little change in geometry takes place in the first coordination sphere on electron transfer, and such

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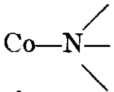
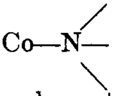
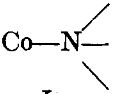
[4] The abbreviation en represents ethylenediamine.

rearrangements as are necessary are relegated to outer spheres where the intensities of the interactions are much reduced. The factors that contribute to the remarkable result that for many of these ions an electron can be accepted without much increase in internuclear distance are fundamental to understanding the results on electron transfer. For most members of the class the electron population is such that the electrons can avoid the ligands (the exceptions are in the Co^{++} complexes), but this is not a sufficient condition. Thus, while in the couple $V(OH_2)_6^{++} - V(OH_2)_6^{+++}$ the electrons can also avoid the six ligands around each ion, a considerable expansion in the first coordination sphere results when V^{+++} absorbs an electron. Strong π interactions of the $d\epsilon$ electrons with ligand orbitals must be invoked, but to explain the observations it must further be supposed that the $d\epsilon$ electrons of the metal are bonding rather than antibonding (*100, 111*). One is led to conclude that bonding of this type for $d\epsilon$ electrons is particularly effective when the ligands have multiple bonds or conjugated multiple bonds, but it may not be limited to such cases. Thus in terms of the geometrical features which have been considered, $IrCl_6^{\equiv} - IrCl_6^{=}$ probably does not differ from $Fe(CN)_6^{4-} - Fe(CN)_6^{\equiv}$, for example, but when a parallel case for the first row transition series is considered, for example VCl_2 *versus* VCl_3, a large change in dimension again results on change in oxidation number.

Besides the influence that the ligand has in determining the geometrical and electronic structure of the complex, there may also be the direct (but related) influence of affecting the distribution of the d electrons in the complex and thus the probability of barrier penetration. Unfortunately, there are no observations which expose separately the geometrical and "conductivity" factors, but the second factor will readily be discernible in some of the systems discussed in the next section.

The slower rates for the Co systems, summarized in Table III compared to those for systems described earlier, can be attributed to the circumstance that large readjustments of the bonds must be made to provide sites equally favorable to occupancy by the electron. This circumstance is itself a result of the electronic structure. The seven d electrons of Co^{++} can not all be accommodated in the $d\epsilon$ orbitals and so prevent the close approach of ligands to the metal; when there are only six d electrons, as in Co^{+++}, these can be accommodated in the $d\epsilon$ set of orbitals and thus do not interfere as markedly with the close approach of the ligands to the central ion. The difference in dimensions of Co(III) and Co(II) complexes is probably much less marked for the Co(phen) complexes than it is for those of the  $\mathrm{Co{-}N}\!<$ type. Although $Co(phen)_3^{++}$ has a magnetic moment of 5.2 Bohr magnetons (*38*), the complex probably has a configuration close to that which would make the electronic state with one unpaired electron the ground state. Thus the readjustment required in the Co(phen) system preceding electron transfer is probably a great deal less than it is for the  systems. The role of the conjugated system of double bonds in phenanthroline in bringing the *d* electrons to the surface of the complex ion may also be important in causing a greater rate of electron transfer for the Co(phen) as compared to  case.

In summary of the work discussed in this section it can be said that the composition of the activated complex is known at least with respect to the exchanging species, and it is further known, at least for some systems, that reaction takes place without interpenetration of the coordination spheres. Important work which remains to be done is, an extension of the study of the salt effects, and the influence of ligand properties. Important fundamental questions which remain to be answered are: What is the optimum distance of approach for electron transfer? Precisely how is the energy matching brought about? How does the nature of the ligands and the solvent influence the probability of barrier penetration? Rough ideas as to the optimum distance of approach can perhaps be obtained from studies of the influence of ionic strength. If for a given salt concentration, the dimension of the ionic atmosphere is large compared to the separation of the ions undergoing reaction, a normal salt effect can be expected, but for the reverse case anomalies can be expected. If the distance of approach required for electron transfer is large, these anomalies will appear in dilute solution. It should be stressed that if the electron transfers over a large distance salt effects will be observed even for a reaction involving a neutral species, for example, $ClO_2 - ClO_2^-$, and it is precisely for such a system that there is the greatest hope of learning something about the geometry of the activated complex from study of the salt effects.

VI. The Bridged Activated Complex

The term "bridged" will be used to imply a configuration in which an atom or group of atoms is part of the coordination sphere of both cation partners in the redox reaction. The characteristic feature is that the coordination sphere of at least one of the partners has been entered, so that new bonds are established in making the activated complex. It is by no means necessary that this geometry correspond to the "strong overlap" (*82*) case, although, as will be adduced from the evidence for the cases which have been studied, strong electronic interaction between the cations must be invoked.

It is precisely the feature that bonds are broken and new bonds are formed in generating the activated complex that provides experimental access to some features of mechanism for these systems. In properly chosen systems, it can be expected that the new bonds formed in the process of activation will be retained when the metal ions separate to form products. In contrast to the systems discussed in the previous section, in which only the outer-sphere environment is changed on electron transfer, the inner coordination sphere is changed, and the substitution lability of the new combinations will in general be lower for the present cases. Even though generally lower labilities for the new rearrangements formed on electron transfer may actually obtain for the majority of systems, the substitutions are still so rapid compared to electron transfer that only the equilibrium configurations for the products are detected, leaving no hint as to the path by which they are arrived at.

Choosing as representative a system in which the bridged activated complex leads to net transfer of a group from oxidizing agent to reducing agent, it is seen that the conditions which must be met to make possible a conclusion about mechanism by examination of products are these: the oxidizing agent and the oxidized product must undergo substitution slowly compared to electron transfer, but the reducing agent must be labile with respect to substitution (to form the bridged activated complex, at least one partner must be labile to substitution). A variety of oxidizing agents qualify for such a test of mechanism, but of the aquo-ion reducing agents, only Cr^{++} satisfies the imposed conditions.

A typical system for which the bridged activated complex can readily be demonstrated is the following. When Cr^{++} is added to a solution containing $(NH_3)_5CoCl^{++}$ (this oxidizing agent is chosen because Cl^- is only very slowly replaced by H_2O or other groups), a rapid redox reaction takes place forming $CrCl^{++}$, Co^{++}, and NH_4^+. The significant observation is that $CrCl^{++}$ rather than $Cr(H_2O)_6^{+++}$ is formed. If electron transfer took place with the reaction partners widely separated, $Cr(OH_2)_6^{+++}$ would be the product, for once formed, $Cr(OH_2)_6^{+++}$ will not change to $CrCl^{++}$ rapidly enough for the formation of the latter by this route to come into question. Thus we can conclude that the Cr-Cl bond must have been formed prior to the electron transfer. An additional result which confirms the conclusion that Cl transfer is direct is the following: When the experiment is repeated with free radioactive Cl^- present, substantially none of this radioactivity appears in the product $CrCl^{++}$. Thus, it is shown that Cl^- transfer is not by way of loss and re-entry but rather that it is direct (*130*).

Complex ions of the series $(NH_3)_5Co^{III}L$ can be formed in great variety, and these are useful for the present purposes in providing a survey of groups which will act in the same capacity as Cl^-. Efficient transfer from $(NH_3)_5Co^{III}L$ to Cr^{++} is observed also for F^-, Br^-, I^-, $SO_4^=$ (*129*), N_3^-, CNS^-, carboxylic acids, $P_2O_7^{4-}$ (*125*), $PO_4^{\equiv}$, OH^- (*92*). Particularly significant is the fact that OH^- transfers, because a path involving the hydroxy complex is commonly observed in redox reactions of aquo cations with each other. In the reaction of $(NH_3)_5CoOH^{++}$ with Cr^{++}, transfer of oxygen is substantially quantitative, but for the equally important reaction of the aquo complex, the situation is much less clear. Some transfer, at least, is indicated, but the results are quite erratic. The experiments in which the aquo path predominates are difficult to perform, and various factors operate to reduce the apparent transfer (*92*). The results reported in reference *125* for the phosphate complex are wrong because the complex salt used was not really the inner sphere complex. The inner sphere form has since been prepared and shows normal transfer to Cr^{++}. The only oxidizing agent of this class for which net transfer has not been observed is $(NH_3)_5CoNO_3^{++}$. The reaction takes place rapidly, much more rapidly than with $(NH_3)_5CoOH_2^{+++}$, so that attack by Cr^{++} at NO_3^- is indicated; however, $CrNO_3^{++}$ is not observed. The failure to observe net transfer may simply be the consequence of a high substitution lability for $CrNO_3^{++}$.

The reaction

$$(NH_3)_5CoOH_2^{+++} + Cr^{++} \rightarrow \tag{5}$$

merits special discussion since it is a representative of the important class of reactions in which both members are aquo ions. The system has the useful and distinctive feature that a variety of tests of mechanism can be brought to bear, and definite conclusions can be derived from the results. In common with other systems of this class (see below), the rate law has two terms (*92*) [the residue $Co(NH_3)_5$ (or $Cr(NH_3)_5$) will frequently be represented by Ro (or Rr)]:

$$k_1(RoOH_2^{+++})(Cr^{++}) + k_2' \frac{(RoOH_2^{+++})(Cr^{++})}{(H^+)}. \tag{6}$$

The kinetic data are summarized in Table IV. The specific rate k_2 which is the coefficient for the term $(RoOH^{++})(Cr^{++})$ is obviously equal to k_2'/K where K is the dissociation constant of $RoOH_2^{+++}$. The value of K has been determined (*16*) as 1.2×10^{-6} at 25° and $\mu = 1.00$; the associated value of ΔH is 10 kcal. The value of k_1 is a revision of that reported earlier (*92*), but the new value of k_2' agrees well with the earlier one.

The tracer work on oxygen atom transfer has already been referred to. Of equal significance are the experiments on the isotope fractionation effects for atoms bound to the oxidizing agent. There is a strong discrimination (*1.035*) in favor of the reaction of $O^{16}H$ compared to $O^{18}H$ in the bridging position. This result indicates that the bridging does not merely function to bond the metal ion centers but that stretching of the Co^{III}-OH^- bond is, in fact, part of the activation process. A significant discrimination (1.0035 for N^{14} compared to N^{15}) is also reported for the nitrogen in the bound ammonias so that stretching of Co^{III}-NH_3 bonds in the activation process in indicated. However, complete interpretation of this result is not possible, because it is not known whether the observed effect is distributed over the five nitrogen positions or whether it is localized in a single bond.

TABLE IV

KINETIC DATA (*143*) FOR THE REACTION $RoOH_2^{+++} + Cr^{++}$ ($\mu = 1.00$; AT 20°C)

	k_1 M^{-1} sec^{-1}	k_2' sec^{-1}	k_2 M^{-1} sec^{-1}	E_1 kcal	E_2 kcal	$\Delta S_1‡$ e.u.	$\Delta S_2‡$ e.u.
In H_2O	0.50	1.58	1.5×10^6	3.3	4.8	−48	−15
In D_2O	.13	0.40	—	—	—	—	—

The data on the effect of changing the solvent from H_2O to D_2O are incomplete, because the change in K with solvent in not known. It is unlikely, however, that the change in K will account completely for the decrease in k_2' by a factor of 3.8 which is observed when D_2O is used in place of H_2O [it should be noted that exchange of the aquo protons is rapid, so that in D_2O the reactant species is $(NH_3)_5CoOD_2^{+++}$], and a residual H_2O-D_2O effect is undoubtedly left. The origin of this effect may lie in this, that stretching of the O-H bond takes place in the activation process. This conclusion is also strongly indicated by the marked change in k_1 which occurs when the isotopic change in the solvent is made. However, the conclusion cannot be insisted on for the k_1 reaction, because the case for oxygen transfer in the reaction is not as strong as for the k_2' path. In the context of these results it should be mentioned that even for a system which does not involve a hydrogen-containing bridging group (and which certainly does not react by H-atom transfer), namely the reaction of $(NH_3)_5CrCl^{++}$ with Cr^{++}, a decrease in rate by approximately 30% is observed (*98*) in changing the solvent from H_2O to D_2O. Thus there is a noticeable solvent isotope effect even short of stretching H-O bonds in the bridging group or transferring H from the coordination sphere of reducing agent to oxidizing agent.

For a large number of reactions of Cr(III) complexes with Cr^{++}, a bridged activated complex is obviously also involved. Among these is a reaction of almost classical interest: the catalysis by Cr^{++} of the dissolution of anhydrous $CrCl_3$ (*1*). The product of the reaction has been shown to be $CrCl^{++}$ [rather than $Cr(OH_2)_6{}^{+++}$ as would be expected for ordinary dilute solutions if complete equilibrium were rapidly established], and the Cl^- retained has been proved not to have passed through the solution (*129*). The reaction can be formulated as

$$CrCl_3 + Cr^{*++} = Cr^{++} + 2Cl^- + Cr^*Cl^{++}. \qquad (7)$$

It is difficult to see an alternative formulation that accommodates the observations which have been cited. The rapid dissociation of $CrCl_2{}^+$ under the influence of Cr^{++} (*129*)—this also proceeds rapidly only to the $CrCl^{++}$ stage—can be understood in a similar manner:

$$CrCl_2{}^+ + Cr^{*++} \rightarrow Cr^{++} + Cl^- + Cr^*Cl^{++}. \qquad (8)$$

The next stage:

$$CrCl^{++} + Cr^{*++} \rightarrow Cr^{++} + Cr^*Cl^{++} \qquad (9)$$

does not lead to a net change, but through the use of isotopic tracers it has been shown (*128*) to be a rapid change also, and the similar reactions with F^-, NCS^-, and $N_3{}^-$ as bridging groups have also been studied (*11*).

A group of reactions which is analogous to those just mentioned, but in which the operation of the mechanism in question leads to net changes, is exemplified by

$$(NH_3)_5CrCl^{++} + 5H^+ = 5NH_4{}^+ + CrCl^{++}. \qquad (10)$$

The systems take this course only when Cr^{++} is present; in the ordinary aquotization process the products $(NH_3)_5CrOH_2{}^{+++} + X^-$ are formed. The rates of reaction are strictly first order in the Cr(III) complex and in the catalyst Cr^{++}, and are independent of acidity over a wide range of concentration. The mechanisms are obviously similar to those discussed in the previous paragraph. Kinetic data on the reactions of the Cr(III) complexes are summarized in Table V.

The data shown in Table V make possible comparison of the efficiency of various groups as electron mediators.[5] As shown by the quantitative data for Cr(III) complexes, and indicated also by qualitative observations with Co(III) complexes, the iodo complexes yield to reduction much more rapidly than the fluoro. This result indicates that the electron transfer does not occur by direct overlap (*76*) of the *d* orbitals of the metal ions but rather through the agency of the bridging groups (*142*). The order

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[5] Use of this term was suggested to us by Prof. John R. Platt, Department of Physics, University of Chicago.

TABLE V

THE RATES OF REACTION OF Cr^{++} WITH VARIOUS Cr(III) COMPLEXES

Oxidant	k (M^{-1} sec^{-1})	Temperature (°C)	$\Delta H\ddagger$ kcal	$\Delta S\ddagger$ e.u.	Reference
CrF^{++}	2.6×10^{-2}	27	13.7	-20	*11*
$CrCl^{++}$	$8.3 \pm 2, 9.1 \pm 1$	0	—	—	*128, 11*
$CrBr^{++}$	>60	0			*11*
$CrNCS^{++}$	1.8×10^{-4}	27	—	—	*11*
CrN_3^{++}	>1.2	0	—	—	*11*
$(NH_3)_5CrF^{++}$	2.7×10^{-4}	25	13.4	-30	*98*
$(NH_3)_5CrCl^{++}$	5.1×10^{-2}	25	11.1	-23	*98*
$(NH_3)_5CrBr^{++}$	3.2×10^{-1}	25	8.5	-33	*98*
$(NH_3)_5CrI^{++}$	5.5 ± 1.5	25	—	—	*98*
trans-$CrCl_2^+$ *(69)*	$\sim 23 \times 10^2$				*129*

of rates for the Cr(III) halide complexes is the same as is observed for attack of a series of organic halides by a free radical reagent such as Na. Although the observations cited thus far are accommodated by the simple statement that we are dealing with halogen atom removal by Cr^{++}, this is not an apt description for the entire field of phenomena. The circumstance that *d* electrons or orbitals are not used in the same way for binding as are the orbitals in question for a carbon atom center introduces features which are, as we shall see, absent in the carbon case.

The rate comparison for $RrNCS^{++}$, and RrN_3^{++}, which holds qualitatively also for the corresponding Co complexes, is especially interesting. Part of the reason for the greater rate for N_3^- may be that attack at the remote end in this case leads to a stable species, but with NCS^-, reaction at the remote site necessarily forms a system of higher energy. Ball and King (*11*) have pointed out that, if the reducing agent maintains octahedral coordination, attack at the atom bearing Co or Cr is impossible for steric reasons.

An important comparison is that of the rate of reaction of Cr^{++} with $(NH_3)_6Co^{+++}$ and with $(NH_3)_5CoOH_2^{+++}$. For the completely ammoniated species, the redox reaction is very slow, slower by at least a factor of 100 than for the aquo ion. The difference in rate can be ascribed to the availability of an electron pair when H_2O is coordinated to a central ion; all electron pairs are occupied for a coordinated NH_3. The mechanism by which the hexammino ion is reduced is not known; since the bridged activated complex has been made difficult of access, electron transfer may in fact take place through the coordination spheres of the two reactant ions. To arrive at a bridged activated complex in the case of coordinated NH_3 would require the dissociation of protons. Even with OH^- as the attacking base, this requires about 14 kcal (*7*) in the way of activation energy; when only water is available, the activation energy would be considerably greater.

Experiments with oxidizing agents of the pentamminecobalt(III) class and with complex organic molecules occupying the sixth coordination position have led to some new and interesting observations. In all of the systems referred to, only a single $(NH_3)_5Co$ is attached to each ligand; in every system, transfer of the organic ligand to chromium is observed on electron transfer, so that direct attack of Cr^{++} on the organic ligand can with confidence be accepted as a feature of the reaction mechanism. The data on these systems are summarized in Table VI.

In the reaction of the acetato and butyrato complexes, attack can be only at the carbonyl group, and following the argument of Ball and King, it is likely that it takes place on the oxygen which does not have the Co(III) residue. In view of the similarity of the rate of reaction of the acid succinate complex to that of the acetato or butyrato, it is reasonable to conclude that for the acid succinate the attack is also at the carbonyl adjacent to the Co(III) center; this conclusion is supported by the fact that the methylsuccinate complex also reacts at about the same rate. The acceleration noted in proceeding to the succinate ion can be attributed to the influence of negative charge and/or of chelation of Cr^{++} in the activated complex.

Fumarate and succinate appear to afford a clear cut intercomparison; the more rapid rate for fumarate, in spite of the circumstance that there is no possibility of benefit from chelation in the activated complex, suggests that, for this ion, attack is not restricted to the carbonyl adjacent to the Co(III) but takes place at the remote end. The conjugated bond system provides a mechanism for electron transport, and there is made available to the system the benefit of avoiding close approach of the positive charges of the cations. The comparisons including the phthalate complexes support the conclusion reached. For the meta and ortho complexes, the conducting systems of bonds are lacking, in the first case because of the relative positions on the benzene ring, and in the second because the close approach of the carboxyls prevents them from assuming a coplanar configuration. In the *p*-phthalate complex, the conjugated bond system can be achieved, and the rate of reaction is correspondingly more rapid.

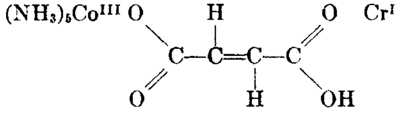
An important new effect of acid does not fit the form adopted for reporting the data in Table VI. Examples of the usual behavior, that the reaction with a bridging anion is more rapid than with the acid in the bridging position, are shown there. With fumarate as the bridging group,

TABLE VI

CARBOXYLIC ACIDS AS ELECTRON MEDIATORS, $\mu = 1.00$

Ligand	Temperature (°C)	k (M^{-1} sec^{-1})	E (kcal)	$\Delta S\ddagger$ e.u.	Reference
Acetate	25	0.15			*125*
Butyrate	25	0.08			*125*
Crotonate	25	0.18			*125*
Succinic acid	25	0.19			*114a*
Succinate ion	25	$\sim$1.0			*114a*
Me-succinate ester	25	0.22			*114a*
Oxalic acid	5	>20			*125*
Maleic acid	5	>20			*125*
Fumaric acid	5	0.5	7.5	33	*114a*
Fumarate ion	5	$\sim$2			*114a*
o-Phthalic acid	25	0.057	5.1	47	*114a*
o-Phthalate ion	25	$\sim$10			*114a*
m-Phthalic acid	25	0.10	2.6	56	*114a*
p-Phthalic acid	25	$\sim$40			*114a*

these features are also present, but there is an added term in the rate law of the form $k(\text{RoFH}^{++})(\text{H}^{+})(\text{Cr}^{++})$. The acceleration by acid is so marked that in 1 M $HClO_4$, 80% of the reaction proceeds by the acid accelerated path. This effect, which is marked also for the *p*-phthalate complexes, presumably arises from this: In a complex constituted as follows,



(11)

conjugation between the metal ion centers is incomplete. Placing a proton on the carbonyl oxygen adjacent to the Co(III) causes a redistribution of the carbonyl electrons and improves the conjugation through the molecule. As is required by this interpretation, there is no hint of acceleration by acid when bifunctional ligands which are unconjugated (succinate, *o*- and *m*-phthalates) are the bridging groups.

The very rapid rates of reaction observed for the oxalate and maleate complexes are not accommodated by any of the factors which have been discussed thus far. The experiments with the succinate complexes show the chelation effect to be small. Chelation implies attack by Cr^{++} at the carbonyl adjacent to the Co(III), and if this is the case the benefit from having a conjugated structure is not required; in fact, if there is chelation with maleate, the coplanar arrangement of the carboxyls required for effective conjugation is impossible. In explanation of the difference between maleate and fumarate, it is suggested that two different mechanisms of electron transfer by the bridging groups must be discussed. In one of these mechanisms, exemplified by fumarate, as electron density is removed at one end of the conjugated π system, it is replaced at the other; in the second, there is net transfer of an electron from the reducing agent to the bridging group. Such a mechanism does not require the same configuration of atoms as does the one discussed for the fumarate ion and will come into question for systems which have unoccupied low-lying orbitals. The fact that, of all the bridging groups discussed, oxalate (*88*) and maleate are the most easily reduced, fits in with the suggestion made about the mechanism of electron transport for these groups as electron mediator. The suggestion also explains the difference between maleate and *o*-phthalate, which have similar geometry about the carboxyls, but differ in reducibility. It should be mentioned that with neither fumarate nor maleate is there a change in configuration of the bridging group on electron transfer. Isomerization of the maleate is not required by the mechanism proposed because the Cr^{++}, in attacking maleate, may impose restrictions on its geometry.

Thus far the only ligand effects which have been discussed are those concerned with their role as electron mediators in bridging positions. This takes account of only one of the eleven coordination positions which need to be considered for a bridged activated complex between two reactants of normal coordination number six. It is to be expected that changing groups in nonbridging positions will also influence rates, and such effects can easily and unambiguously be demonstrated. Taking $(NH_3)_5CoOH_2^{+++}$ as oxidizing agent ana Cr^{++} as reducing agent, it is observed (*125*) that there is a marked acceleration of the reaction by $SO_4^{=}$, and particularly by pyrophosphate, and both of these ions are incorporated into the product Cr(III) complex. That a group other than these ligands is involved as a bridging group is demonstrated by using $(NH_3)_5CoCl^{++}$ as oxidizing agent; when pyrophosphate is present, both Cl^- and pyrophosphate are incorporated in the product Cr(III) complex. Groups differ enormously in their capacity to accelerate the rate of electron transfer by simple ligand intervention. Thus, in the system now under discussion, pyrophosphate is very effective, $SO_4^{=}$ less so, and an effect of Cl^- at 0.1 *M* level is not discernible (*92*). It seems likely that there will be a parallelism between the ability of the ligand to stabilize Cr(III) over Cr(II) and its ability to accelerate the rate of oxidation by simple attachment to Cr^{++} in the activated complex (the relationship would presumably hold in the reverse way also). The ligand effect of Cl^-, though slight, must exist to explain catalysis by Cr^{++} of the $CrCl^{++}$-Cl^- exchange (*128*); or, looking at it in the reverse direction, to explain why $CrCl_2^+$ reacts so much more rapidly with Cr^{++} than does $CrCl^{++}$ (see Table V).

Cis and trans positions can be distinguished in the bridged activated complexes under present discussion, and in considering the influence of nonbridging ligands, it is of interest to differentiate the effects at the two positions. Orgel (*99*) has suggested that for Co(III) and Cr(III) complexes the incoming electron is accepted in the $d_z{}^2$ orbital, the energy of this orbital being lowered to the necessary extent by moving groups trans to each other from the metal ion center. The stretching of the Co(III)-OH^- bond, when OH is the bridging group, has been demonstrated (*92*); Orgel's suggestion that the group trans to the bridging group also moves out helps explain some recent observations which have been made. It is found (*127*) that *trans*-$Cl_2en_2Co^{+++}$ is reduced more rapidly by Cr^{++} (and other reducing agents) than is the cis form. The result is surprising, at least in the context of a philosophy that omits consideration of the individuality of different central ions. Thus, attention (*144*) has been directed to the advantages of double bridges for electron transfer, and it does seem reasonable, if account is taken only of forces external to the ions, to use both negative ions in reducing the energy of interaction between ions of the same charge. On Orgel's interpretation the trans effect operates in this way: stretching of a H_3N-Co(III) bond trans to the bridging group is necessary to lower the $d_z{}^2$ orbital to the same extent as is necessary for a *trans*-Cl^-. In a similar way, the relative rates for $(NH_3)_5CrCl^{++}$, $(H_2O)_5CrCl^{++}$, and *trans*-$Cl(H_2O)_4CrCl^{++}$ (see Table V) can be understood. But there is a disturbing feature in the comparison of $(NH_3)_5CrCl^{++}$ with $(H_2O)_5CrCl^{++}$, for the difference in rate appears to be in the entropies rather than in the energies of activation (Table V).

Some general observations on the energies and entropies of activation of redox reactions which proceed by bridged activated complexes are in order. These quantities, even for the few systems for which they have been determined, cover the range 4 to 14 kcal and −20 to −45 e.u. respectively. The ranges overlap with those for the outer-sphere activated complexes and, except possibly in extreme cases, it is not safe to use the magnitude of these quantities as diagnostic of mechanism. The comparison of $\Delta S^\ddagger$ for the process

$$(NH_3)_5CrBr^{++} + Cr^{++} \rightarrow; \quad \Delta S = -33 \text{ at } \mu = 1.0 \ (98) \tag{12}$$

and

$$(NH_3)_5CoBr^{++} + Hg^{++} \rightarrow; \quad \Delta S = -16 \text{ at } \mu = 0 \ (23) \tag{13}$$

is instructive. In both systems the activated complexes presumably have the same general geometry and are of the same charge type, so that the entropy effects caused by concentration of charge in the dielectric should be much the same. The disparity in the values of $\Delta S^\ddagger$ is very great, however, and would probably be even greater if the entropies were compared at the same ionic strength (*4*). The differences in $\Delta S^\ddagger$ are in part attributable to this, that much more in the way of simultaneous bond readjustment may be required in the electron transfer than in the substitution reaction. There is evidence that, in the latter case, a true intermediate of coordination number 5 is formed from the ammine complex (*106*), and thus the principal bond dislocations may be only the motion of Br^- from Co(III) to Hg^{++}. In the electron transfer case under discussion, simultaneous with the movement of Br^- from Co(III) to Cr(II), motion of a group trans to the bridging Br^- away from the Co, and again trans to the Br^-, toward the Cr may be necessary. In addition, a change in the bond angle from something which at equilibrium may be less than 180°, to 180°, may be required, for in the colinear arrangement, there will be the most efficient overlap of the $d_z{}^2$ orbitals of the metal ion with a $p\sigma$ orbital in the Br^- (*142*).

It is important to consider whether the bridged complexes which have been discussed are merely activated complexes or whether binuclear species of similar geometry must be invoked as intermediates. In the cases encountered thus far, the concentration of such intermediates appears to be so small that direct detection is difficult, if not impossible, yet there are powerful arguments which support such a formulation of the mechanism.

When an activation energy as small as 4 kcal is in question for the bridged activated complex, we face the difficulty that the activation energy for substitution on the Cr^{++} probably exceeds this value. A mechanism in which the reaction occurs in a single step,

$$(NH_3)_5CoOH_2{}^{+++} + Cr^{++} \rightarrow, \tag{14}$$

would require activation energy at least as great as the activation energy for substitution in the more labile partner (here Cr^{++}), and considerable additional contributions from other sources can be expected as well. The situation would not be materially improved by adopting the formulation (we assume Cr^{++}aq. is a hexa-aquo ion):

$$Cr(OH_2)_6{}^{++} \rightleftarrows Cr(OH_2)_5{}^{++} + H_2O \tag{15}$$

$$Cr(OH_2)_5{}^{++} + (NH_3)_5CoOH_2{}^{+++} \rightarrow \text{products} \tag{16}$$

$\Delta H^\ddagger$ over-all would necessarily exceed ΔH for process (15), and 4 kcal appears to be a conservative lower limit for ΔH, even taking into consideration the probable tetragonal symmetry of $Cr(OH_2)_6{}^{++}$. The high cost in energy for substitution can be avoided if we formulate the substitution process giving rise to the binuclear intermediate species as an equilibrium. In this situation, the reaction can be represented as:

$$\mathrm{Ro}X^{++} + \mathrm{Cr(OH_2)_6}^{++} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [\mathrm{Ro}X\mathrm{Cr(H_2O)_5}]^{++} + \mathrm{H_2O} \qquad (17)$$

$$[\mathrm{Ro}X\mathrm{Cr}]^{++} \underset{k_2}{\rightarrow} \text{products.} \qquad (18)$$

Then the rate of reaction will be given by

$$\frac{k_1k_2}{(k_{-1} + k_2)} (\mathrm{Cr}^{++})(\mathrm{Ro}X^{++}). \qquad (19)$$

If $k_{-1} >> k_2$, $\Delta H^\ddagger$ over-all $= \Delta H_1 + \Delta H_2{}^\ddagger$. The value of ΔH_1 can be considerably less than $\Delta H^\ddagger$ for substitution, because energy is paid back in the new Cr^{++}-X bond formed, and there may also be a gain from energy of interaction of the *d* electrons of the metal ion centers. But we must now consider why k_{-1} can be larger than k_2, even though the corresponding activation energy is probably larger. The compensating factor is necessarily in the entropies of activation. The entropies of activation for substitution are usually small in simple cases, and in a situation such as the present, involving separation of positive charges, may well be positive; for a reaction such as (18), as we have already seen, the entropies of activation have large negative values.

This analysis suggests, particularly for systems with low values of $\Delta H^\ddagger$ total, fairly strong interactions of *d* electrons of the metal ion centers. This interaction leads to a lowering of ΔH_1 (and in certain cases may be so low as to make it possible to detect the binuclear intermediates), but it benefits the reaction path in process (18), also. In the case of strong overlap, as is postulated, the energy required to compress the Cr-ligand bonds and to stretch the Co-ligand bonds is reduced, if the electron in question is to some extent distributed over both centers. In the absence of effects such as these, it is difficult to understand how a reaction between a dipositive and a tripositive center can take place by such intimate approach as obtains in a bridged activated complex with an activation energy as low as 4, or even as low as 10, kcal. The most instructive way to compare various groups as electron mediators would be to refer to the coefficients for the rates expressed in terms of the concentration of the binuclear intermediates, but so little is known of the relative stabilities of such species that an analysis of this kind must be put aside for the present.

The electronic interpretations of the observations for the particular systems which have been discussed will form an important part, and perhaps the basis, of generalizations which include other cases, but they cannot be adopted without careful scrutiny and possible modification for systems of different electron structure. We have been dealing in every instance with a situation in which the oxidizing agent has $d\epsilon$ orbitals only occupied and cannot readily accept additional electrons, and the reducing agent, in every case Cr^{++}, has a $d\gamma$ electron outside a stable half-filled subshell of the $d\epsilon$ electrons. In fact, even the feature characteristic of the systems so far discussed, that group transfer from oxidizing agent to reducing agent accompanies the electron transfer, does not necessarily apply to other systems in which a bridge activated complex nevertheless provides the path for reaction. For example, a binuclear complex is undoubtedly formed in the reaction of $IrCl_6^{=}$ with Cr^{++}, Cr and Ir sharing the bridging group, yet the net reaction, after the short time needed to permit dissociation of the binuclear product complex has elapsed, is to form $IrCl_6^{\equiv}$ and $Cr(OH_2)_6^{+++}$. In this system, the $IrCl_6$ group, having a vacancy in the $d\epsilon$ set of orbitals, can absorb an electron without a major readjustment of distances; the Cr-Cl distance does decrease when the electron is lost to the Ir; the product complex, however, more readily undergoes substitution at the Cr(III) than at the Ir(III) center when it is aquotized to form the separate (*129*) ions. In the inorganic systems, the case can readily be imagined that electron transfer is accompanied by the movement of an electronegative group from reducing agent to oxidizing agent—it is for this reason if for no other that it is inappropriate to discuss these reactions as atom transfers in analogy to the case of free radical attack at carbon. A system which would undoubtedly show such "reverse" transfer is that of a Cr(IV) complex reacting with Cr(III). Cr(IV) complexes are almost certainly substitution labile (*97, 126*), so that when $Cr^{*}X^{++}$ and Cr(IV) react to form $Cr^{*}(III)XCr(IV)$, the ion in the *lower* oxidation state brings the bridging group into the activated complex; on electron transfer $Cr^{*}(III)$ becomes $Cr^{*}(IV)$; when the product binuclear complex dissociates, it separates into $Cr^{*}(IV)$ and CrX^{++}. Attempts (*97*) to demonstrate this reaction have thus far failed, not necessarily because the chemistry outlined is faulty, but probably because Cr(IV), being unstable, is a rather intractable species.

To summarize this section: the evidence for a bridged binuclear complex as an activated complex and an intermediate has been outlined, the efficiency of various groups as bridging group compared, the particular role of the bridging groups discussed, as well as the role of groups in the activated complexes in nonbridging positions, and the rationalization of these observations in terms of the electronic structures of the central atoms and ligands attempted. Notably lacking is the extension of the conclusions to systems other than Co(III) and Cr(III) as oxidizing agents and Cr^{++} as reducing agent. This does not imply that the particular mechanism applies only to these reactants, but the examples have purposely been limited to those in which the conclusions about mechanism are unambiguous. In the next section, some of these results are applied to an analysis of observation for the more labile systems, in which direct conclusions about mechanism are more difficult to derive.

VII. Reactions Proceeding by Mechanisms of Uncertain Classification

The characteristics which have made possible the conclusions about mechanism for the systems considered thus far are (a) both oxidizing agent and reducing agent undergo substitution much more slowly than electron transfer or (b) the oxidizing agent and the oxidized product complex undergo substitution much less rapidly than the electron transfer takes place, but the reducing agent is substitution labile. The majority of the systems do not meet these sets of conditions, and for them the conclusions about mechanism are more limited in scope. The reactions are, nevertheless, as interesting and important, and it is a challenge to devise new experiments in the hope of differentiating between the possible mechanisms. The models for the activated complexes which have been proposed to explain the electron transfer in a typical case, such as $Fe^{++} - Fe^{+++}$, are the two which have been discussed thus far, together with a modification of the outer-sphere activated complex in which a specific role is assigned to protons in carrying the electrons from the reducing agent to the oxidizing agent. Because the greatest effort has been expended on the $Fe^{++} - Fe^{+++}$ reaction, with respect to both experimentation and theorizing, this system will be considered first, and such conclusions about mechanism as seem justified drawn. The problems of mechanism for other systems are similar, but usually some new element is featured, so that most of the systems for which rates have been measured, and which have come to the attention of the author, are referred to.

The early lore on the rate of $Fe^{++} - Fe^{+++}$ electron exchange is confused by paradoxes (*19, 68, 79, 132, 136*). Partly because of this, the problem challenged a large number of skillful experimenters, and a general growth of activity in the entire field ensued. The first definitive experiments were done by Dodson (*32*); his results are consistent with those of Linnenbom and Wahl (*79*) and with those of Betts *et al.* (*19*), but not with those of van Alten and Rice (*132*), or those of Kierstead (*68*).

In Table VII is a summary of the data which have been obtained on the $Fe^{++} - Fe^{+++}$ reaction. The observation that the values of E are so nearly the same for a variety of paths has inclined some authors (*112*) to the view that a common process, assumed to be H-atom transfer between the hydration spheres, is taking place for all the systems. This view has been strengthened by the observation made by Hudis and Dodson (*62*) that the specific rate coefficients for the terms

$$(Fe^{++})(Fe^{+++}) \quad \text{and} \quad \frac{(Fe^{++})(Fe^{+++})}{(H^+)}$$

TABLE VII

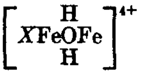
SUMMARY OF KINETIC DATA ON $Fe^{++} - Fe^{+++}$ EXCHANGE
(TEMPERATURE 25°, $\mu = 0.5$)

	k_0 (M^{-1} sec^{-1})	E	$\Delta S\ddagger$	Reference
Fe^{+++}	0.87	9.9	−25	*117*
$FeOH^{++}$	1010.	7.4	−20	*117*
$FeNCS^{++}$	41.5	7.5	−28	*74*
FeF^{++}	9.7	9.1	−21	*63*
$FeCl^{++}$	9.7	8.8	−24	*117*
FeF_2^+	2.5	9.5	−22	*63*
$FeCl_2^+$	~15			*117*
FeF_3	~0.5			*63*

each decrease by a factor of approximately 2 in changing to D_2O as the solvent. Neither argument is convincing. The $H_2O - D_2O$ experiments with $(NH_3)_5CoOH_2^{+++}$ as oxidizing agents show that isotope effects even larger than those reported by Hudis and Dodson are observed when transfer of hydrogen atoms does not take place—although substantial weakening of an O-H bond must be inferred. Comparisons of the energies and entropies of activation can be made with systems which are known to react by bridged activated complexes and can equally well be taken to indicate that the $Fe^{++} - Fe(III)$ reactions are similar in mechanism.

Since the Fe(III) complexes in question are substitution labile, the composition of the activated complex does not establish its geometry, nor can the form of the rate law $(FeX^{++})(Fe^{++})$, for example, even be taken to mean that Fe(III) brings the group X^- into the activated complex. Thus, for the rate term $(FeX^{++})(Fe^{++})$, all of the following formulations will satisfy equally the kinetic requirements:

(a) Fe^{+++} aq. X^- Fe^{++} aq. (no X^--Fe bonds)
(b) (XFe^{++}) aq. Fe^{++} aq.
(c) Fe^{+++} aq. FeX^+ aq.
(d) $[FeXFe]^{4+}$
(e)



$$\left[XFe\overset{H}{\underset{H}{O}}Fe\right]^{4+}$$

Observations made by Lewis *et al.* (*75*), Anderson and Bonner (*6*), and others (*92*), for systems of the charge type +2, +3, show that when substitution in the first sphere of coordination of the oxidizing agent is excluded, Cl^- does not exert its usual catalytic effect. Thus it seems likely that, in the $Fe^{++} - Fe^{+++}$ systems, activated complexes (a) and (c) can be excluded. It is admitted that this conclusion is based on reasoning by analogy, but there appears to be no basis for concluding that such reasoning will fail here. The argument is strengthened when it is noted that, when Cl^- is placed in the first coordination sphere of Co(III) and Cr(III), the usual large acceleration of rate by Cl^- is observed. The fact that the reaction of Cr^{++}, in catalyzing the dissociation of $CrCl^{++}$ [for this purpose an activated complex such as either (b) or (e) would serve], is very slow compared to electron transfer accompanied by atom transfer [activated complex (d)], taken with the previous arguments, suggests that in the present system the activated complex (d) also serves as the reaction path.

The comparison (*129*) of the relative rates at which a series of Fe(III) complexes react with Cr^{++}, with the relative rates at which the same complexes react with Fe^{++}, suggests that similar mechanisms operate in the two series. The argument that the Cr^{++} – Fe(III) reactions, at least with catalytic groups other than OH^- in the activated complex, proceed by a bridged activated complex, is this. When Cr^{++} reacts with Fe^{+++} in the presence of X^-, catalysis by X^- is observed and CrX^{++} is formed quantitatively by this path (*129*). When $Cr(OH_2)_6{}^{+++}$ is oxidizing agent, catalysis by Cl^- has not been observed[6] (*6*, *92*), and $CrCl^{++}$ is not formed. The formation of $CrCl^{++}$ in the reaction of Fe(III) with Cr^{++}, in the presence of Cl^-, proves that a Cr-Cl bond is joined in the activated complex. The comparison of the sensitivity to Cl^- catalysis of Fe(III), which is substitution labile, to that of Cr(III) or Co(III), which are not, shows that substitution in the first coordination sphere is a condition for marked catalysis by Cl^-. Hence, the conclusion that Cl^- makes a bond not only to Cr^{++} but also to Fe^{+++} in the activated complex is strongly indicated if not, in fact, proven. This line of argument, therefore, also supports the bridged activated complex for the reaction of Fe^{++} with Fe^{+++}.

At best, the kind of argument used here can indicate that a major part of the reaction takes place by a particular reaction path. Based as it is on gross comparisons of rate, it does not make possible an assessment of the contribution to the total reaction of rival, but minor, paths. And yet, only such a complete description can be regarded as satisfactory. To take a particular example, we are perhaps prepared to accept the conclusion that with $X = F$ a part of the reaction takes place by the bridged activated

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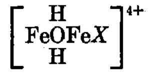
[6] Plane and Taube report marked catalysis by Cl^- of the $Cr^{++} - Cr^{+++}$ reaction, but the data of Anderson and Bonner allow at most a slight effect. It is quite likely that the conclusion of the former authors is wrong. They observed erratic and unexplained catalysis in several of their experiments and were probably misled by such accidental catalysis appearing in the experiment on the effect of Cl^-.

complex. But in this case it is not unlikely that an activated complex such as



$$\left[\mathrm{Fe}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{O}}}\mathrm{Fe}X\right]^{4+}$$

also accommodates a good fraction of the reaction. It obviously would be of some interest to discover how the reaction divides between the two routes for the series of the halides.

Very little that is definite can be said about paths involving more than one nonsolvent ligand in the activated complex. When a single anionic ligand is present, it is reasonable, in view of the rather general behavior that anions are better electron mediators than neutral molecules, that this ligand be used in the bridging position. The most reasonable disposition of a second anionic ligand is much more difficult to choose; further work on effects for nonbridging ligands using substitution-inert oxidizing agents is required to illuminate this subject. As before, it is likely that only configurations in which the ligands are directly attached to either Fe^{++} or Fe^{+++} would appear to come into consideration. But even granting this, the second X^- may be in association with the oxidant, with the reductant, or with both simultaneously as in a system in which a double bridge is involved. The trans effect noted in the reactions of Co(III) complexes with Cr^{++} does not necessarily hold for oxidizing agents of differing electron structure. Thus when Fe^{+++} is being reduced the dislocations required to cause this center to accept the incoming electrons are probably more symmetrical than those sufficient for Cr(III) or Co(III) as the oxidizing agent.

A number of other electron exchange reactions of the +2, +3 charge type have been studied, those of Cr, Co, V, and Eu. Anderson and Bonner (*6*) observed for the $Cr^{++} - Cr^{+++}$ exchange the rate law

$$k_1(\mathrm{Cr}^{++})(\mathrm{Cr}^{+++}) + \frac{k_2'(\mathrm{Cr}^{++})(\mathrm{Cr}^{+++})}{(\mathrm{H}^+)}. \tag{20}$$

Even in strongly acidic solution the acid inverse path is the dominant one, and a good value of k_1 was not obtained. They report $18 \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$ as an upper limit for k_1 at 25°C and $\mu = 1.0$ and k_2' under the same conditions as $1.0 \times 10^{-4}\ \mathrm{sec}^{-1}$. From the data of Plane and Taube (*103*) on the catalysis by Cr^{++} of the $Cr(OH_2)_6^{+++} - H_2O$ exchange, and using Anderson and Bonner's conclusion that the acid inverse path is dominant, k_2' is calculated as $1.6 \times 10^{-4}\ \mathrm{sec}^{-1}$ at 25°C and $\mu = 6.0$, in satisfactory agreement with the more direct measurement of Anderson and Bonner. Using the known value (*107*) of K for $Cr(OH_2)_6^{+++}$ at $\mu = 0.068$, and assuming the same variation of K with μ as for $Fe^{+++}aq.$ (*89*), k_2, the coefficient for the term $(Cr^{++})(CrOH^{++})$ is calculated as

1.4 M^{-1} sec^{-1}. Finally, using the reported temperature coefficient for k_2' and 9.4 kcal as the value of ΔH_D for $Cr(OH_2)_6^{+++}$ (*107*), E_2 is found to be 12.6 ± 2, and $\Delta S^\ddagger$ is calculated as −16 ± 7 eu. There is no proof that the reaction of Cr^{++} with $Cr(OH_2)_6^{+++}$ involves a bridged activated complex, but in view of the known behavior of other Cr(III) complexes with Cr^{++}, there is every likelihood that this is indeed the case. Such proof could be obtained by comparing the specific rate for the $Cr^{++} - Cr(OH_2)_6^{+++}$ exchange measured using radioactive Cr with the value obtained by the method of Plane and Taube; in calculating the rate of electron transfer from data on the rate of water exchange catalysed by Cr^{++}, an assumption is made as to the number of H_2O molecules which exchange per electron transfer. The value reported was calculated assuming 6; if a bridged activated complex is involved, then only 5 will be exchanged, and the value of k calculated should be only 5/6 of that reported. Careful measurements would be required to expose the 20% difference in rate, and the present data are by no means accurate enough to settle the question.

The specific rate for the exchange between Co^{++}aq. and Co^{+++}aq. has been measured as 0.77 M^{-1} sec^{-1} at 0° and 1 M $HClO_4$ (*20a*). No data have been published on the variation of rate with acidity. The comparison of the rate of this reaction with that of $Co(NH_3)_6^{+++} - Co(NH_3)_6^{++}$ is interesting. Part of the difference is probably attributable to the circumstance that the bridged activated complex is readily accessible for the aquo ion but not for the ammonated one; an additional factor likely is this, that with NH_3 as ligand, a greater distortion of the coordination sphere is required to make the energy of the electron to be transferred match at the two sites. The exchange between CoY^{-2} and CoY^{-1} (Y represents the ethylenediaminetetraacetate) has been shown (*3*) to be very slow. The specific rate at 85° is 2.1×10^{-4} M^{-1} sec^{-1}, and E is 22 kcal. The nature of the activated complex in this system is not known—electron transfer may be through the intact coordination shells or may require some dislocation on the substitution—labile Co(II) complex. Adamson and Vorres (*3*) have discussed the relation of crystal field stabilization of electronic states to rates of electron transfer in Co(II) − Co(III) systems.

The exchange of Mn^{++} with Mn^{+++} appears to be measureable. The experiments by Adamson (*2*) indicate that k at $\mu = 3.2$ and 25°C is about 100 M^{-1} sec^{-1}. The exchange reaction V^{++}aq. − V^{+++} aq. would provide an interesting comparison with the systems already described in this section because, for the pair, only electrons in the $d\epsilon$ levels come into question. In the only work published on this reaction (*70*), complete exchange in 1 min at a concentration level of 0.1 M is reported, and no conclusions as to the rate of electron transfer can be drawn. The issue of relation of rate and mechanism to electronic structure is also raised in comparing the kinetic behavior of Eu^{++}aq. – Eu^{+++}aq. (*85*) with the systems already discussed. The rate of exchange is very slow, and no contribution by an aquo or even hydroxo path could be detected (the reduction of water by Eu^{++} limits the time during which exchange can be measured). Exchange in the presence of Cl^- was observed, and this reaction path is described by:

$$\text{Rate } (M\ \text{sec}^{-1}) = 6.5 \times 10^{11} e^{-20{,}800/RT}(\text{Eu}^{++})(\text{Eu}^{+++})(\text{Cl}^-), \qquad \text{at } \mu = 2.0.$$

This rate law can be cast into the same form as those for the Fe^{+++} – Fe^{++} exchange, but the data on the stability of $EuCl^{++}$ are lacking, and a meaningful and dependable comparison cannot be made. It seems likely, however, that even when expressed in the form $(Eu^{++})(EuCl^{++})$, the corresponding activation energy will be as large as 15 kcal.

The rate of electron exchange between Cu(I) and Cu(II) in 12 F HCl has been measured (*80*) by a nuclear resonance technique. The specific rate is reported as $5 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. In the context of this result, the observation by Gordon and Wahl (*45*) that the bimolecular reaction between Ag(I) and Ag(II) leading to exchange is less than $10\ M^{-1}\ \text{sec}^{-1}$ is all the more surprising. The environment is different, 5.9 M $HClO_4$ in place of 12 M HCl, and perhaps the rate comparison reflects the difference, which Cl^- in place of ClO_4^- or H_2O, exerts on the rate of electron transfer for these ions. The reaction which carries the exchange in the case of the Ag(I) – Ag(II) reaction is 2 Ag(II)→. The specific rate at 0° is 1020 ± 40 F^{-1} sec^{-1} and E is 12.5 ± 1.2 kcal (45). For the exchange of oxidation state between $AuCl_4^-$ and Au(II) (the latter as a chloride complex of unknown formula), a specific rate at 0° in excess of $10^7\ M^{-1}\ \text{sec}^{-1}$ has been estimated (*110*) and, for the disproportionation of Au(II), a specific rate in excess of $10^8\ M^{-1}\ \text{sec}^{-1}$. The comparison of the latter value with the corresponding one measured for the disproportionation of Ag(II) again may be taken to illustrate the great sensitivity of the electron exchange reactions of ions of this group to chloride ions. The disproportionation reaction of Ag(II) does not take place between ions of charge +2, but extensive loss of protons takes place in forming the activated complex (*45*).

Considerable work on electron exchange reactions of cations of oxidation state +3, +4 has been done. In only one of the systems of this class studied are the ions involved (reactants and products) actually of charge +3 and +4. Keenan (*66*) reports the rate of electron exchange between Pu^{+++} and Pu^{4+} to be given by:

$$\begin{aligned}\text{Rate } (M\ \text{sec}^{-1}) &= 3 \times 10^8(\text{Pu}^{+++})(\text{Pu}^{4+})e^{-7{,}700/RT}\\ &\quad + 2.2 \times 10^6(\text{Pu}^{+++})(\text{PuOH}^{+++})e^{-2{,}800/RT}, \qquad \text{at } \mu = 2.0. \qquad (21)\end{aligned}$$

We encounter again an extremely low activation energy, as in the Cr^{++} – $(NH_3)_5CoOH^{++}$ reaction, and perhaps again the formation of a binuclear complex in the system is indicated.

The kinetic interpretation of reactions in which Ce(IV) is a reactant is complicated because Ce(IV) is apparently considerably hydrolyzed even in acidic solution (*116*) and furthermore may condense to polynuclear species (*54*). The pioneer work of Gryder and Dodson (*47*) was checked by the later work of Duke and Parchen (*35*) in most of the essential features, except in this: Gryder and Dodson reported a path for the reaction in which the rate is independent of the concentration of Ce(IV), but no evidence for this remarkable feature is found in the later work. The dependence of rate on acidity is complex, and Duke and Parchen interpret the data as indicating activated complexes of composition $(Ce^{+++})(Ce(OH)_2^{++})$, $(Ce^{+++})(Ce(OH)_3^{+})$, $(Ce^{+++})(CeOCeOH^{5+})$. The reaction is subject to strong catalysis by F^- (*60*), $SO_4^=$ and $H_2PO_4^-$ (*8*), but the effect of Cl^- is very slight (*8, 60*).

The strong influence of acid is noted in other systems, in which extensive changes in degree of hydrolysis for one or both metal ion centers accompany reaction. Thus Furman and Garner (*42*) report the rate law for the V(III)-V(IV) exchange as

$$\text{Rate } (M \text{ sec}^{-1}) = 4.5 \times 10^{12} e^{-20{,}700/RT} \frac{(V(III))(V(IV))}{(H^+)}. \tag{22}$$

V(IV) is presumably present as VO^{++}, thus loss of H^+ from the V(III) center must take place to convert it to V(IV). Inverse acid dependence is reported for the reaction of Co^{+++} with Ce^{+3}; the conclusion that the activated complex for this reaction also contains ClO_4^- is somewhat questionable (*123*).

The redox reactions of the ions of U, Np, Pu, and Am provide a fertile field for exploring the influence of (H^+) on the rates of reactions which involve a change in the state of hydrolysis of the metal ion center. A singular feature of the chemistry is that, whereas species of oxidation state +3 and +4 can exist as ions of the same respective charge, those of +5 and +6 in water exist as ions of the type TuO_2^+ and TuO_2^{++}. With the exception of Am^{4+}, ions corresponding to each of the oxidation states +3 to +6 exist for each element, and a large number of reactions between members of this class, as well as with other reagents, are possible.

A complete review of the reactions of these interesting ions is not attempted, and the reader is directed to papers by Newton (*95*) and Hindman (*55*) for a more complete discussion. A few of the reactions are referred to in order to develop some of the features of the chemistry. Among the reactions in which the extent of hydrolysis is increased are:

$$Np^{4+} + Fe^{+++} + 2H_2O = NpO_2^{+} + Fe^{++} + 4H^{+} \qquad (23)$$

$$U^{4+} + 2Fe^{+++} + 2H_2O = UO_2^{++} + 2Fe^{++} + 4H^{+} \qquad (24)$$

$$U^{4+} + 2Ce(IV) + 2H_2O = UO_2^{+} + Ce^{+++} + 4H^{+}. \qquad (25)$$

The rate laws are, respectively,

$$k(Np^{4+})(Fe^{+++})(H^{+})^{-3} \quad (\mathit{81}) \qquad (26)$$

$$(U^{4+})(Fe^{+++})[k(H^{+})^{-1} + k'(H^{+})^{-2})] \quad (\mathit{18}) \qquad (27)$$

$$(U^{4+})[Ce(IV])[k(H^{+})^{-2} + k'(H^{+})^{-3}] \quad (\mathit{9}) \qquad (28)$$

In the reactions of U^{4+}, the primary products of the bimolecular steps are presumably formed by $1e^{-}$ transfer. In the three reactions the loss of proton is needed, not only to provide a proper bridging group (if indeed the mechanism is of this type), but also as a pure ligand effect. Direct loss of an electron from an ion such as U^{4+} or Np^{4+} may require an oxidizing agent of exceptional electron affinity. Prior proton loss, so that the state of hydrolysis of the reducing agent approaches that of the product, does give an opportunity for energy matching with oxidizing agents of ordinary potential. It is not at all clear, however, why the differences in the compositions of the activated complexes appear; indeed, it would be expected that Ce(IV) in reacting with U(IV) could get by with a weaker inverse dependence on (H^{+}) than is the case for Fe^{+++}, contrary to the case actually observed.

In another group of reactions, the extent of hydrolysis of some metal ion centers is diminished on electron transfer. It will suffice to cite the rate laws for the four disproportionation reactions:

$$2TuO_2^{+} + 4H^{+} = TuO_2^{++} + Tu^{4+} + 2H_2O. \qquad (29)$$

They are

$k(UO_2^{+})^2(H^{+})$ (*53, 67*), $(NpO_2^{+})^2[k(H^{+}) + k'(H^{+})^2]$ (*56*), (*121a*),

$k(PuO_2^{+})^2(H^{+})$ (*109*), $k(AmO_2^{+})(H^{+})^4$ (*121*).

The necessity for the increase in rate with acidity can qualitatively be understood by following the arguments given earlier. It is difficult to understand, however, why such apparently similar substances show such variety in the rate laws for similar reactions. Particularly striking is the extreme behavior of AmO_2^{+}.

An important result which is significant for all the reactions which have been considered was obtained by Newton (*96*) in a study of the reaction

$$2PuO_2^{++} + U^{4+} + 2H_2O = UO_2^{++} + 2PuO_2^{+} + 4H^{+}. \qquad (30)$$

The form of the rate law suggests that U^{4+} and PuO_2^{++} react to form an intermediate containing both U and Pu; all three reactions, formation of intermediate, intermediate to reactants, and intermediate to products, are rate determining. It is difficult to formulate an intermediate which behaves in this manner without invoking a species with definite linkages between U and Pu, and thus the observation indicates a bridged activated complex for this reaction as well.

The exchange reaction $NpO_2^+ - NpO_2^{++}$ has been studied thoroughly by Cohen *et al.* (*27*). The interesting feature of this system is that part of the coordination sphere remains intact on electron transfer. However, since substitution in girdle positions can take place readily, it is by no means certain that the activated complex is of the outer-sphere type, and in fact the authors incline to the view that a bridged activated complex is involved in some paths. The reaction is first order in each of the redox species and is independent of (H^+) over a considerable range; k at 0°C, $\mu = 1$, is 29 M^{-1} sec^{-1}, $E = 8.3$ kcal M^{-1} and $\Delta S^\ddagger = -24$ e.u. Cl^- increases the rate of reaction (*28*). The observations can be interpreted as follows: Exchange for $NpO_2^+ - NpO_2Cl^+$ is more rapid than for $NpO_2^+ - NpO_2^{++}$ or $NpO_2^+ - NpO_2Cl_2$. An important result (*29*) is the demonstration that the rate of reaction is independent of the ethylene glycol or sucrose content over a range wide enough so that the dielectric constant is reduced to 68; this result is in striking variance with the requirements of the quantitative theory proposed by Marcus *et al.* (*84*). A reduction in rate by 40% in changing H_2O to D_2O was noted (*122*). As has already been indicated, this kind of observation at the present level of understanding these systems is not a particularly searching diagnostic tool.

In the reactions considered thus far, ions having charges of the same sign have been involved. For these, particularly, there can be serious question whether the intimate contact obtaining in a bridged activated complex is allowed. However, it has been shown that, even in such cases, a reaction path of this kind provides a means for electron transfer. When the reactants are oppositely charged, and at least one is substitution labile, it seems likely that in the usual case there will be intimate contact between reductant and oxidant. It is highly unlikely that in the reaction of Fe^{+++} with hydroquinone (*14, 15*) reaction takes place by electron transfer through the intact coordination shell of Fe^{+++} (as suggested by Marcus, *83*), when substitution on Fe^{+++} can so easily occur. In the reaction of Cr^{++} with quinone, chromium-oxygen bonds are established (*127*); by analogy, therefore, a similar mechanism can be expected in the Fe^{+++} reaction. Not many reactions of this kind, of simple chemistry, have been studied. An interesting reaction recently studied (*13*) is that of Fe^{++} with $Co(C_2O_4)_3^{\equiv}$. The reaction is quite rapid: k at 20.3°C, $\mu = 0$, is 11 ×

$10^3\ M^{-1}\ \mathrm{sec}^{-1}$, $E = 12.6$ kcal/mole^{-1} and $\Delta S^\ddagger \simeq 0$. Because the reaction can be studied at low concentration, it proves useful in testing theories of the influence of inert ions on the rates of ionic reactions.

No claim can be made that a complete review has been made of the reactions which qualify for discussion in this section. An attempt was made, however, to present enough of the observations so that the different aspects of behavior which seem significant are outlined. Much interesting work readily suggests itself; it is much more difficult, however, to devise experiments for these labile systems which will lead to definite answers to the important question: how are the various groups known to be in the activated complex arranged with respect to each other?

VIII. Systems in Which a Net Two Electron Change Is Involved

The systems which are treated here are those in which a net $2e^-$ change takes place for both partners on reaction. In some instances, the reaction may proceed by a series of two $1e^-$ steps; in others, it is almost certain that the reaction proceeds directly by a $2e^-$ change.

A feature which distinguishes the $2e^-$ processes as a class from the $1e^-$ class is this, that with few exceptions, serious dislocations in the coordination sphere accompany reaction. Thus in the changes Cl(VII) → Cl(V) → Cl(III) → Cl(I), there is a progressive reduction in coordination number as the oxidation state decreases by $2e^-$ steps. The reason for this is quite obviously that the incoming electrons, occupying as they do *s* and *p* orbitals, interfere with the ligand electrons. The ions for which coordination number may be preserved on a $2e^-$ change are those which have *d* orbitals available for occupancy, for example, Mn(VII) → Mn(V), $\mathrm{Cr(dip)_3}^{+++} \rightarrow \mathrm{Cr(dip)_3}^{+}$. But even in these cases, considerable changes in geometry may accompany the change in oxidation state.

In certain cases, clear-cut evidence that the redox process is accompanied by atom transfer has been obtained. Thus when $\mathrm{SO_3}^{=}$ brings about the changes $\mathrm{ClO_3}^- \rightarrow \mathrm{ClO_2}^-$, $\mathrm{ClO_2}^- \rightarrow \mathrm{ClO}^-$, $\mathrm{BrO_3}^- \rightarrow \mathrm{BrO}^-$, essentially complete transfer of an atom of oxygen for each $2e^-$ stage of oxidation occurs (*49*). The reaction can be formulated (using $\mathrm{ClO_3}^-$ as an example of an oxidizing agent), as involving as an intermediate

$$(\mathrm{O_2SOClO_2})^-.$$

The reaction is completed by decomposition into $\mathrm{SO_3}$ and $\mathrm{ClO_2}^-$ (or, if a base such as $\mathrm{H_2O}$ is required, into $\mathrm{SO_4}^{=} + 2\mathrm{H}^+ + \mathrm{ClO_2}^-$). Since Cl(V) undergoes substitution less readily than S(IV), the bridging oxygen is derived from $\mathrm{ClO_3}^-$ rather than $\mathrm{SO_3}^{=}$, and net transfer is therefore observed. This kind of mechanism apparently operates also when $\mathrm{MnO_2}$ is the oxidizing agent; when $SO_4^{=}$ is formed, one atom of oxygen is derived from the oxidizing agent (*49*)

The kind of mechanism in which atom transfer occurs can perhaps be reasonably expected for these systems in which a state of changed electron population but unchanged coordination would presumably be at a very high energy. A mechanism in which changes in the coordination sphere of each reactant accompanies electron transfer over a distance, even if favorable energetically, is excluded on probability grounds. The accident that independent changes, involving large dislocations at the two sites, would take place to match the energies while the sites are close enough for electron transfer to occur is likely rare indeed. By adopting a more intimate association, the changes at one site influence those at the other. This arrangement is particularly happy when, as in the case of $ClO_3^- - SO_3^{=}$, the oxidizing agent needs to lose one oxygen atom, and the reducing agent to gain one, in completing the net change.

It seems likely that in a system such as Tl(I) − Tl(III), similar ideas may be applicable. The difference between these reagents and Cl(V) − S(IV) is one of degree rather than kind. The arrangement of water molecules about Tl is undoubtedly strongly disturbed by the pair of *s* electrons that constitute the electronic difference between the two states of oxidation. However, there is no basis for a definite pronouncement about the mechanism in this or other of the metal ion systems which will be referred to. The treatment of these systems will feature mainly a review of the experimental observations.

In their study of the Tl(I) − Tl(III) exchange, Prestwood and Wahl (*108*) used acidic nitrate media, and Harbottle and Dodson (*50*) used perchlorate media; except for differences attributable to difference in the media, the two sets of experiments agree. Evidence is obtained for the separate paths: $(Tl^+)(Tl^{+++})$, $(Tl^+)(TlOH^{++})$, and $(Tl^+)(TlNO_3^{++})$ (*108*). For the path $(Tl^+)(TlOH^{++})$, k at $\mu = 6.0$ and at 25°C is reported (*108*) as 2.6×10^{-5} M^{-1} sec^{-1}; E is 14.7 kcal mole^{-1} and $\Delta S^{\ddagger}$ is −32.

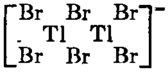
Cl^- exerts a marked effect (*50*), acting at low concentration to diminish the rate and at higher concentration to increase it. Complex formation must be invoked to explain the decrease in rate and is supported by other evidence. The interesting problem is to explain why the specific rate for the term $(TlCl^{++})(Tl^+)$ is so much less than for $(Tl^+)(Tl^{+++})$ and why, with an increase in the degree of complex formation, the rates increase. The similar system with Br^- added has been thoroughly worked out (*26*). It shows the interesting behavior that the exchange rate first decreases, then rises to a maximum at about 10^{-2} M Br^-, falls to a minimum between 10^{-2} and 10^{-1} M Br^- and then rises again. These data have been quantitatively accounted for by the rate law:

$$k_1(\mathrm{Tl^+})(\mathrm{Tl^{+++}}) + k_2(\mathrm{TlBr_2^+}) + k_3(\mathrm{TlBr_3}) + k_4(\mathrm{TlBr_2^-})(\mathrm{TlBr_4^-}).$$

The second and third terms presumably correspond to the establishment of the redox equilibrium with Tl^+ and Br_2, the first and fourth to direct exchange. The coefficients at 25°, $\mu = 0.5\ M$ H^+ are $1.2 \times 10^{-4}\ M^{-1}\ \mathrm{sec}^{-1}$, $6.2 \times 10^{-7}\ \mathrm{sec}^{-1}$, $2.7 \times 10^{-7}\ \mathrm{sec}^{-1}$, and $7.4 \times 10^{-1}\ M^{-1}\ \mathrm{sec}^{-1}$.

With CN^-, a diminution in rate at low CN^- is observed, and the increase sets in after approximately enough CN^- has been added to form $Tl(CN)_4^-$ (*101*). Brubaker and Michael (*25*) require, to explain their observations on the effect of $SO_4^=$, complexes which in addition to Tl^+ and Tl^{+++} contain respectively, zero, one, and three sulfate ions.

It is impossible at the present level of knowledge of this subject to find a unique explanation of the interesting ligand effects which have been observed. Carpenter and Dodson (*26*) propose for the activated complex of composition $(TlBr_2^-)$ $(TlBr_4^-)$ the structure



$$\left[\begin{array}{ccccc} \mathrm{Br} & & \mathrm{Br} & & \mathrm{Br} \\ & \mathrm{Tl} & & \mathrm{Tl} & \\ \mathrm{Br} & & \mathrm{Br} & & \mathrm{Br} \end{array}\right]^-$$

and this is certainly reasonable. It is not clear, however, why a double bridge should be required in these systems, nor why the activated complex $(Tl^+)(Tl^{+++})(Br^-)^2$ is not also an effective pathway to products. Further, it is difficult to see why $(TlCl^{++})(Tl^+)$ is actually less effective than $(Tl^+)(Tl^{+++})$, or why $SO_4^=$ is more effective than Br^- or Cl^- in promoting the electron transfer.

The exchange between Sn(II) and Sn(IV) in strong HCl has been studied (*24*). The solutions show strong interaction absorption, and it is of interest to inquire into the relation between the species causing the absorption and the activated complexes. That they are not precisely the same is true by definition, but it is possible that a small dislocation of binuclear species causing the interaction absorption suffices to form the activated complex. The observations on the Sn(II) – Sn(IV) exchange are summarized by the equation

$$\text{Rate } (M\ \mathrm{sec}^{-1}) = (\mathrm{Sn(II)})\ (\mathrm{Sn(IV)})\ 7.5 \times 10^5 e^{-10{,}500/RT}; \qquad \Delta S\ddagger = -50 \text{ e.u.} \qquad (31)$$

Unfortunately, the formulae of the species Sn(II) and Sn(IV) are not known, nor is the composition of the activated complex defined with respect to Cl^- (or H_2O) content.

Some attention (*20*, *94*) has been paid to the exchange of Sb(III) and Sb(V) in strong HCl. A considerable advance in understanding these reactions was made by Neumann and Brown (*94*). Realizing that $SbCl_6^-$

reaches dissociation equilibrium only slowly, they studied the exchange between Sb(III) and $SbCl_6^-$ in HCl solution. There is a diminution in rate at high Cl^-, suggesting the conclusion that the optimum composition for the activated complex is $Sb^{+++} \cdot 3Cl^- \cdot SbCl_6^-$. A reasonable structure for an activated complex of this formula is two condensed octahedra sharing one face.

Thus, evidence for multiple halide bridges in bringing about exchanges comes up also in the Sb(III) – Sb(V) case, and in fact finds support also from work in nonaqueous media.

For the cases considered thus far, it suffices to construct a relatively simple bridged activated complex, and no evidence for complicated chemistry involving intermediate oxidation states is obtained. Not all systems of the present class are this simple. Thus Rona (*113*) finds for the exchange $U^{4+} - UO_2^{++}$ the rate law

$$\frac{k(U^{4+})(UO_2^{++})^2}{(H^+)^2}$$

and this and other similar observations add a new dimension to the field: Why in some cases, but not in others, can the transfer of oxidation states be brought about simply by transfer of one or more groups?

IX. Reactions in Nonaqueous Solvents

There are certain experiments done in hydrogen-labile solvents which could economically have been discussed in relation to the corresponding experiments in water. However, work in solvents as little different from H_2O as CH_3OH promises such new and striking results, that it seemed preferable to emphasize the importance of the work by collecting the relevant data in one section.

Experiments on the $Fe^{++} - Fe^{+++}$ exchange in various alcohols have been done by Horne and Dodson (*59*). It is remarkable that the rate of exchange decreases to very low values at zero content of water, so low that within the precision of the experiments no exchange is detected. As H_2O is added, the specific rate first increases linearly, then at a diminishing rate. At comparable concentrations of water, say 1 *M*, the rate in isopropanol is much less (perhaps by a factor of 10^{-5}) than it is in ethanol. If a bridged activated complex is indeed involved, the results indicate that an alcohol is much less effective than is water, a result that seems qualitatively reasonable on the basis of such a formulation of mechanism; for if substantial separation of the groups in the bridge must be achieved in the activated complex, this is more difficult for alcohol than for H_2O. The large difference between ethanol and water does not seem explicable on the basis of a simple barrier penetration mechanism. But left unexplained still is the tremendous difference in rate between isopropanol and ethanol as solvents. Is there perhaps a change in coordination number for Fe(III) between ethanol and isopropanol as solvents? The large bulk of isopropanol would favor a lower coordination number. To complete the hypothesis, it would be necessary to assume that the coordination number of Fe^{++} remains at 6. From this brief essay into the changes produced by the substitution of alcohols for H_2O, it is evident that extension of this work is very worthwhile. An added attractive feature is that the CH_3OH remains liquid down to $-98°$. At this temperature other ions may behave like Cr^{++} does in water at room temperature and definite evidence about mechanism may be obtainable simply from product analysis.

Experiments in NH_3 would also appear to have special significance in view of the fact that the bridged activated complex, at least in acid solution, is not readily accessible for an ammoniated ion. A beginning in this field has been made by Grossman and Garner (*46*) who studied the Co(II)-Co(III) exchange. The exchange rates were observed to be much the same as in water; the authors attach significance to the circumstance that the rates are comparable to those for the $Co(NH_3)_6^{+++} - NH_3$ exchange (*140*), and the comparison does in fact suggest that more than electron penetration of the coordination spheres is involved.

The experiments of Ward and Weissman (*135*) have already been referred to. They represent the only work on redox reactions of highly polar substances in solvents of low dielectric constant and are to be regarded as the beginning of a field of work which can be expected to develop considerably. An interesting feature of the results is not only the magnitude of the specific rates they were able to measure but also the dependence of rate on the nature of the cation. Table VIII contains a summary of their data.

TABLE VIII

THE EXCHANGE OF ALKALI NAPHTHALENIDES WITH NAPHTHALENE

Cation	Solvent	k (M^{-1} sec^{-1})
K^+	Tetrahydrofurane	$5.7 \pm 1 \times 10^7$
Na^+	Tetrahydrofurane	$\sim 10^7$
Li^+	Tetrahydrofurane	$4.6 \pm 3 \times 10^8$
K^+	1,2-Dimethoxyethane	$7.6 \pm 3 \times 10^7$
Na^+	1,2-Dimethoxyethane	$\sim 10^9$

Interesting differences in the kinetics of the Sn(II) − Sn(IV) and Sb(III) − Sb(IV) reactions are produced by changing from water to media in which the species exist as discrete molecules. For the conditions under which the reactions are studied in water, the system can make up from the supply of Cl^-, or deliver to the surrounding medium, whatever is needed to meet the demands of the activated complex. But for the conditions under which the following experiments were run, the systems must make do with solvent molecules or with reactant molecules. When CCl_4 is solvent, little help can be expected from it for any influences in the first coordination sphere of each reactant which might be required.

The exchange reaction of $SnCl_2$ with $SnCl_4$ in C_2H_5OH (*86*) takes place by the rate law

$$\text{Rate } (M \text{ sec}^{-1}) = 1.4 \times 10^{13}\, e^{-23{,}700/RT}\, (\text{SnCl}_2)(\text{SnCl}_4); \qquad (32)$$

$\Delta S^\ddagger$ is calculated as -0.4 e.u. The activation energy for the reaction is much higher than that in concentrated HCl; presumably, some use is made in the latter case of the large fund of additional Cl^- available. When CH_3OH is the solvent (*87*) the rate is given by

$$5.5 \times 10^{10}\, e^{-20{,}900/RT}\, (\text{SnCl}_2)(\text{SnCl}_4). \qquad (33)$$

The rate law for the exchange reaction of $SbCl_3$ with $SbCl_5$ in CCl_4 is:

$$\text{Rate } (M \text{ sec}^{-1}) = 10^{6}\, e^{-19{,}000/RT}\, (\text{SbCl}_5) + 4 \times 10^{6}\, e^{-15{,}000/RT}\, (\text{SbCl}_3)(\text{SbCl}_5)^2. \qquad (34)$$

The first term presumably corresponds to operation of the equilibrium to form Cl_2 and $SbCl_3$; the second demands a remarkable activated complex which Barker and Kahn (*12*) have succeeded in formulating in a plausible way. For the analogous exchange of PCl_3 with PCl_5 (*17*) only the decomposition term is observed. For this path,

$$\text{Rate } (M \text{ sec}^{-1}) = 1.2 \times 10^{6}\, e^{-15{,}900/RT}\, (\text{PCl}_5). \qquad (35)$$

These kinds of reactions, extended to include systems in which there is a net change, and emphasizing solvents such as CCl_4, deserve much more attention. There appears to be a better opportunity to define the activated complex than is the case when water is a solvent, in part because the specific influence of this solvent is probably much reduced, and in part because the substitution lability of the molecules has been much reduced. Thus, in the $SbCl_5 - SbCl_3$ case, it may be possible to study Cl exchange between the two forms, and a comparison of these data with those on Sb exchange may illuminate the mechanism further.

X. Conclusion

Much of the work reported has taken place in the last few years. During this time interest has continued in questions of specific chemistry, but research has also penetrated to the more general questions with which we have been concerned. The resulting investigations have brought about advances not only in the direction of the general goals, but also have brought out new facts of chemistry. Further developments can be expected as research workers turn to new systems to seek answers to the general questions.

Some of the areas in which further work is called for have been outlined in the individual sections, and there too some of the problems pertaining to each area have been acknowledged. In this section, a few additional points will be raised which bring the various sections into closer context.

An aspect of this subject which merits systematic and intensive exploration is the variation of rate and mechanism with electronic structure. To be considered is the influence of the distribution of electrons between the $d\epsilon$ and $d\gamma$ levels, the comparison of d electrons with f electrons, and the comparisons for states of differing principal quantum number. It is significant that the rate of electron exchange for the $Eu^{++} - Eu^{+++}$ system is lower, but not much lower, than for systems of this charge type in which d electrons are involved in the redox reaction. There is a large difference in the radial extension of an electron in the $4f$ orbital of a rare earth ion, as compared to a d orbital for a transition metal ion so that if an outer-sphere activated complex is involved a much lower rate of electron transfer for $Eu^{++} - Eu^{+++}$ would be expected. The fact that the rate for the rare earth system is only slightly less suggests that the system finds a path in which the factor of barrier penetration is less rate determining, as may well be the case in the bridged activated complex. The higher activation energy for $Eu^{++} - Eu^{+++}$ as compared to $Fe^{++} - Fe^{+++}$ may reflect the smaller contribution of f electrons in the binding of the binuclear complex. Experiments in which a variety of reducing agents presenting different features of electronic structure—for example, Ti^{++}, V^{++}, Cr^{++}, Fe^{++}, Eu^{++}—are used in reaction with a group of substitution-inert oxidizing agents, such as a series of Co^{+++} complexes, should be particularly instructive.

The different sensitivities of different reactions to the influence of ligands is not understood and has, in fact, been little commented on. In Table IX are collected some data illustrating the point.

The advantage of OH^- over H_2O as electron mediator decreases in order from Co(III) to Cr(III) to Fe(III). This is also the order of increasing acidity of the corresponding aquo ions and the correlation suggests that Fe^{+++}, because of its greater capacity for polarizing the ligand, benefits less from the substitution of OH^- for H_2O. The decreased sensitivity of the Fe^{+++}aq. reaction compared to that of $(NH_3)_5CoOH_2^{+++}$ to the substitution of D_2O for H_2O fits in with this suggestion—far less in the way of stretching the OH bond is necessary to make the electrons

TABLE IX

COMPARISON OF LIGAND EFFECTS FOR SYSTEMS OF COMMON CHARGE TYPE (COMPARISONS FOR $M(III)L + M^{++}$)

	Relative k for		
	H_2O	HO^-	Cl^-
$Fe^{+++} - Fe^{++}$	1	1160	11
$Fe^{+++} - Cr^{++}$	1	2800	18
$(H_2O)_5Cr^{+++} - Cr^{++}$	1	$>8 \times 10^4$	$>2 \times 10^6$
$(NH_3)_5Co^{+++} - Cr^{++}$	1	3×10^6	>50
$Eu^{+++} - Eu^{++}$	1		>100[a]

[a] Calculated assuming K_{ass} for $EuCl^{++}$ is <1 (*85*), and this is probably a generous upper limit.

available in the case of Fe^{+++}, as compared to Co(III). A remarkable result exposed in Table IX is the enormous change in the relative efficiencies of Cl^- and OH^- even for cases of the same charge type. This again may be a consequence of the differing capacities of the ions to cause dissociation of the proton in the activated complex. A comparison which avoids this complicating factor, as for example of the halide ions, would be very worthwhile.

The relative efficiencies of ligands in promoting electron transfer appear also to be a strong function of charge type. Thus Cl^- is almost ineffective in promoting electron transfer between Ce^{+++} – Ce(IV), although it is quite effective in systems of the charge type +2, +3 in which the inner-sphere activated complex is accessible and even more effective for Cu(I) – Cu(II). The evidence (*97*) for the reaction of $CrCl^{++}$ with Mn^{+++} is that Mn^{+++} chooses a path involving OH^- as bridging group in preference to Cl^-, even when the acidity is large. It may be fairly general that when ions of large positive charge are involved the hydroxy path prevails. As has already been pointed out, the analysis of these effects is difficult and complex. The efficiency of the bridging group in making the binuclear complex must be considered, the rate of decomposition of the binuclear complex to products, and for the labile systems there is also the question of whether the catalytic group is involved in a bridging or simple ligand position, or both.

The study of binuclear intermediates is strongly called for. Thus far such species have not been detected in a direct measurement, but it seems likely that with properly chosen cations, ligands, and conditions, appreciable concentrations can be built up. This subject has been a matter of concern in investigations of "interaction absorption," but in most of the systems studied the halides were used as ligands, and these ions are not particularly effective in making stable bridged species. Groups such as OH^-, OAc^-, and perhaps ions with conjugated bond systems, may be more effective. Another type of intermediate that merits investigation is the one formed as the immediate product of the reduction of Co(III) or Cr(III) complexes. No evidence for a Cr^{++} species different from Cr^{++}aq. was found in the experiments done by Ogard and Taube (*98*), but the techniques used were not particularly searching. The Co(III) system has the additional interesting feature that the primary product of reduction of a Co(III) complex may be in a different electronic state from Co^{++}aq. The transition involves a change in spin, and the state of high energy may persist sufficiently long to be detected. The anomalous dependence (*75*) of the rate of the exchange between $Co(en)_3^{+++} - Co(en)_3^{++}$ on the concentration of $Co(en)_3^{+++}$ can be interpreted qualitatively on the assumption that the process

$$Co(en)_3^{++} \text{ (quartet state)} \rightarrow Co(en)_3^{++} \text{ (doublet state)}$$

is to some extent rate determining.

A recent observation which may lead to an advance in understanding the operation of the bridged *versus* outer-sphere activated complex is this: $Cr(dip)_3^{++}$ (*143*) has been shown to react very rapidly with Co(III) complexes, including $Co(NH_3)_6^{+++}$; V $(dip)_3^{++}$ reacts much less rapidly with the same Co(III) complexes. In these reactions we are almost certainly concerned with outer-sphere activated complexes. It will thus be possible to compare rates for the two types of mechanisms for a common group of oxidizing agents which can be formed in great variety.

An area which has been little touched on is the influence of cations in promoting redox reactions between anions. There is of course the obvious effect of inducing reactions by generating intermediates in a redox process, and such effects have been the subject of considerable study. But there should also be effects which arise from including both reactants in a complex with the metal ions. In such a case the intermediates would not necessarily be formed as discrete entities. The question at issue is this: Do cations act as electron mediators for reactions of anions in the same way that anions serve for cations? There is no reason why this should not be the case and, in fact, the work of Ward and Weissman (*135*) on cation influence on the rate of electron transfer between naphthalene and naphthalenide salts is a beginning in this field.

Much can be learned from studies in nonaqueous solvents. Some of the special features to be expected from work in NH_3 and CH_3OH have been pointed out. In addition, NH_3 offers the interesting possibility of studying reactions of solvated electrons, and some new kinetic features can be expected when reducing agents are used which approach the alkali metals in reducing potential but perhaps do not yield an appreciable equilibrium concentration of solvated electrons.

A vigorous development in these areas, in others which have not been touched on, and in some not anticipated by the author, can be expected.

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