INTRAMOLECULAR ELECTRON TRANSFER

HENRY TAUBE

Department of Chemistry, Stanford University,
Stanford, California 94305, USA

ABSTRACT

In most of the oxidation–reduction reactions involving net electron transfer which have been studied, the experimental results yield only second order rates, and thus reflect the barrier to bringing reactants together as well as that for the electron transfer act itself. Recent advances in synthetic procedures make it possible to measure as ·an intramolecular or first order process, net electron transfer in complexes containing Co(III) and Ru(II) as oxidizing and reducing agents respectively for a wide variety of bridging groups. Systems in which the bridging groups mediate in electron transfer, as well as others, in which the bridging groups serve only to define the separation of the oxidizing agent and reducing centres become accessible to study. In a somewhat related class of reactions, a particular ligand in an oxidizing complex is converted by external means to a reducing agent, and the rate of reduction of the oxidizing metal ion by the damaged ligand is measured, as a first order process.

Closely related in principle to the work referred to are studies on mixed valence complexes such as

$$[(H_3N)_5Ru \, N \bigcirc N \, Ru(NH_3)_5]^{5+}$$

where electron transfer between a ruthenium (II) and a ruthenium (III) end can be considered. But the two classes differ dramatically because in the latter system there is no chemistry associated with electron transfer, in the sense that no bonds are broken or formed on electron transfer. The mixed valence complexes in fact require different experimental approaches for their study and feature elements of interest different from those exhibited by the Co(III)–Ru(II) class. The principles underlying the behaviour of the class of molecules will be outlined, and the results obtained in the study of their properties are described.

INTRODUCTION

Several lines of research, each guided by some specialized ideas and interests, have led to the current concern with intramolecular electron transfer. Only those subjects which have a chemical background will be dealt with here. It will be apparent, however, that at a basic level some of the issues which will be raised are identical to those which are important for understanding electronic phenomena in other fields, as for example, electronic conductance in solids. Thus, although in one sense the title subject represents a narrowing of focus in each of several fields, in the sense that it involves a confluence of ideas from these fields, it represents a broadening of the scientific horizon.

The subject will be dealt with under three headings: as it manifests itself (1) in traditional oxidation–reduction reactions, (2) in a special class of such reactions which has been denoted as 'induced' electron transfer, (3) in mixed valence complexes.

I. INNER SPHERE BIMOLECULAR OXIDATION REDUCTION

An interest in intramolecular transfer is a natural outgrowth of an interest in basic aspects of the mechanisms of oxidation–reduction reactions. The latter concern has motivated a great deal of research on oxidation–reduction reactions of simple chemistry during the past two decades. In an important class of the systems which have been studied a group is shared between the coordination spheres of the oxidizing and reducing centres and this bridging group plays a special role in the charge transfer process. In general terms, the bridging group can function by gathering the oxidizing and reducing centres together, but it can also function by mediating in the charge transfer process itself. When as is the case for the majority of reactions studied, the rate is second order, i.e. first order in the oxidizing agent and first order in the reducing agent, the two factors are difficult to separate, and in no case is the role of the bridging group fully understood.

The point at issue is illustrated by the reaction

$$(NH_3)_5CoCl^{2+} + Cr(H_2O)_6^{2+} \rightarrow Co^{2+} \text{ aq } + (H_2O)_5CrCl^{2+} + NH_4^+$$

which is governed by the rate law[1]

$$-d[Co(III)]/dt = (-d[Cr^{2+}]/dt) = k[Co(III)][Cr^{2+}]$$

and which takes place by transfer of chlorine from the oxidizing to the reducing complex[2]. When substitution in forming the inner-sphere activated complex is not rate determining—and this appears to be the case in the present system—the reaction sequence can be formulated as:

$$(NH_3)_5CoCl^{2+} + Cr(H_2O)_6^{2+} \overset{K_{eq}}{\rightleftarrows} [NH_3)_5CoClCr(H_2O)_5]^{4+} + H_2O$$

$$[(NH_3)_5CoClCr(H_2O)_5]^{4+} \overset{k_1}{\rightarrow} Co^{2+} \text{ aq } + [H_2O)_5CrCl]^{2+} + NH_4^+$$
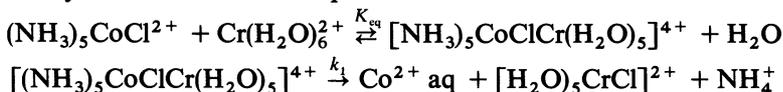
In this mechanism, a binuclear precursor complex is in equilibrium with the reactant (K_{eq}), and the slow step in the sequence is some rearrangement in the precursor complex resulting in net charge transfer (k_1). For a system such as this, the measured second order specific rate k is given by the product k_1K_{eq}; to obtain the values of k_1—these are more directly related to the charge transfer process itself than is k—the values of K_{eq} are needed.

Proposals have been made for measuring the values of K_{eq} by a relaxation technique[3], and it is likely that this method will be successful for a large number of systems. Such measurements would be particularly welcome for a class which has been intensively studied, especially by Gould[4] and coworkers, in which organic molecules are used as bridging groups, and these groups are then subjected to systematic variations in structure. This approach to the diagnosis of reaction mechanism is no less powerful in the systems under present consideration than it has proved to be in the field of physical

organic chemistry, but it is clear that to make the maximum use of the rate data, accurate experimental measurements of K_{eq} are needed, rather than the order of magnitude values that might be obtained by calculation.

First order specific rates, i.e. specific rates for intramolecular charge transfer, have in fact been reported for systems in which the precursor complex is stable enough with respect to dissociation so as to result in substantial or complete conversion to the precursor complex of the scarce reagent at high concentrations of the more abundant one. Under these conditions, the rate becomes independent of the concentration of the excess reagent at high concentration, and is governed by the first power of the concentration of the other.

An early report[5] of a study which features substantial conversion of the reactants to a precursor complex deals with the reduction of $(NH_3)_5Co^{III}O_2$-$CCH_2N(CH_2CO_2H)_2$ by Fe^{2+}. Though the heteroligand is attached to Co(III), at an appropriate pH it binds Fe^{2+} strongly, making it possible to determine K_{eq} (1.1×10^6 at 25°), and therefore also k_1($9.4 \times 10^{-2}\,s^{-1}$ at 25°). The kinetic effects in question have been described also for an outer sphere process. Substitution in $(NH_3)_5CoOH_2^{3+}$ by $Fe(CN)_6^{4-}$ is much slower than is the reduction by the latter complex[6]. Thus it is safe to conclude that reaction takes place by an outer sphere process. The association of the aquo ion with the cyanide complex is complete enough so that K_{eq} has been determined (1.5×10^3) and also k_1 ($0.19\,s^{-1}$ at 25°). The last system which will be mentioned has not been investigated in detail, but it clearly offers opportunities in the present context. When $(NH_3)_5Ru^{III}L$, where L bears an ethylenic link, is mixed with Cu^+, the reducing agent is bound strongly by the double bond and the resulting complex then decomposes by an internal charge transfer process[7].

When, as in all the cases which were introduced for illustration, the association to form the binuclear complex is labile, a serious ambiguity is left in the interpretation of the results. Thus, in the last example, even though the dominant form of the complex has Cu^+ bound to the unsaturated linkage, in the activated complex for electron transfer, the reducing agent may be attached to an oxygen, or for that matter, it may act by an outer sphere process. To emphasize the point at issue, we draw attention to the CoEDTA–$Fe(CN)_6^{4-}$ system. Here a relatively stable inner sphere complex between the two reactants is formed[8, 9]. Recent work has shown[10], however, that in forming the products, the 'precursor' complex first dissociates and the redox reaction takes place by an outer sphere mechanism. Of those mentioned earlier, only for the Co^{III}–Cl^-–Cr^{2+} reaction is the precursor complex necessarily closely related in geometry to the activated complex. The connection here follows because it is known from the chemistry that in the activated complex, Cr^{2+} is situated on the chloride ion and it is highly likely, though admittedly not proved, that this is also the preferred site for Cr^{2+} in the precursor complex.

We have sought to reduce the ambiguity under discussion by turning to systems in which both the oxidizing and the reducing agents make substitution-inert bonds to the bridging ligand. For this purpose, we have combined experience on the stabilities and labilities of Co(III) complexes with the same considerations for those of ruthenium(II) and (III). A typical example

of the kind of system under present study is the following

$$\left[(NH_3)_5Co^{III}-O-\underset{\underset{O}{\|}}{C}-\text{⟨C_6H_4⟩}-N\big\backslash Ru^{II}(NH_3)_4H_2O \right]^{4+} \qquad \textbf{I}$$
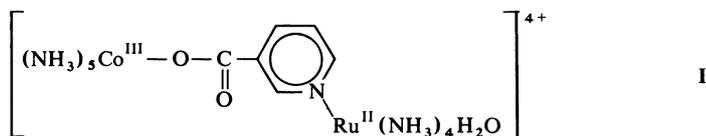
Replacement of Co(III) from the carboxyl and Ru(II) from the unsaturated nitrogen is on the time scale of days or longer while, as will be shown presently, intramolecular electron transfer in the systems thus far studied takes place in a very much shorter time. Though by no means all the structural features of the activated complex are fixed in a system such as this, at least the connexity of the bond system is known with some degree of certainty.

The experiments referred to, though straightforward in conception, have proved to be quite difficult in execution. The direct approach of forming a complex such as I by the reaction of the cobalt complex with $(NH_3)_5RuOH_2^{2+}$ fails because substitution on Ru(II) to form the inner-sphere binuclear complex is slower than is outer-sphere reduction of the Co(III) complex by Ru(II)[11]. The strategy which proved successful was to produce the Co(III)–Ru(III) binuclear complex, then to take advantage of the facile reducibility of Ru(III) compared to Co(III). It should be emphasized that in the present systems, there is no doubt of the success of the reduction step. The Ru(II)–N heterocyclic combination is characterized by a strong absorption band in the visible, and this band was in fact used to follow the rate of the internal redox process. All of a large number of direct approaches to forming the Ru(III) analogue of I, for example, failed, but the indirect method to be outlined, with suitable modifications for individual cases, seems to be a rather general one.

The complex $\left[Co^{III}O_2C-\text{⟨C_6H_4⟩}-N\big\backslash Ru^{II}(NH_3)_4SO_3 \right]^{2+}$
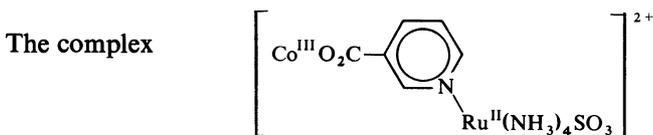
is first produced by the reaction of the cobalt complex with $t\text{-}(H_2O)(SO_3)\text{-}(NH_3)_4Ru(II)$. The sulphite ligand moderates Ru(II) sufficiently as a reducing agent to make decomposition by internal electron transfer slow enough for present purposes, and at the same time labilizes the *trans* water molecule. On oxidizing the complex with Br_2 or H_2O_2, the ruthenium moiety is converted to $Ru^{III}(NH_3)_4SO_4$. When the resulting binuclear complex is reduced by $Ru(NH_3)_6^{2+}$ or Eu_{aq}^{2+}, Ru(II) is produced and unless intramolecular electron transfer is very rapid, SO_4^{2-} is replaced by H_2O before the internal redox change takes place.

The results obtained thus far are summarized in *Table 1.*

Of interest in the data is the wide disparity in rate between the 4-carboxy and 3-carboxy systems (it seems likely that having SO_4^{2-} in place of H_2O on Ru in the former case accounts for only a small part of the rate difference), the fact that internal electron transfer is quite rapid even with a saturated

Table 1. Intramolecular electron transfer in Co(III)–Ru(II) binuclear complexes[a]

Bridging ligand[b]	Medium	$k_1 \text{ s}^{-1}$
O_2C—⟨benzene ring⟩—N	0.1 M CF_3SO_3H	$\sim 1 \times 10^2$
O_2C—CH_2—⟨benzene ring⟩—N	1 M NaTos	13×10^{-3}
	1 M HTos	16×10^{-3}
O_2C—⟨pyridine ring⟩	0.4 M NaTos, 0.05 M HTos	1.7×10^{-3}
	1 M HTos	1.6×10^{-3}
O_2C—CH_2—⟨pyridine ring⟩	1 M NaTos	0.86×10^{-3}
	1 M HTos	5.5×10^{-3}
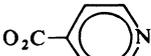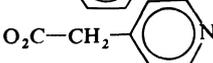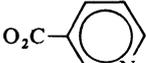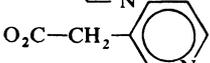
[a] At 25°. [b] $(NH_3)_5Co^{III}$ on the carboxylate and $H_2O(NH_3)_4Ru^{II}$ on the nitrogen except in the first case where electron transfer is rapid compared to replacement of SO_4^{2-} by H_2O from Ru(II).

link inserted into the bond system, and finally the fact that for the meta isomer, insertion of a CH_2 causes the rate to become sensitive to the concentration of hydrogen ion, with the result that the rate can actually become greater when $^-O_2CCH_2$-3-pyridine is the bridging ligand than when nicotinate is.

Each of these comparisons raises interesting questions but only the last one will be commented on here. Molecular models show that Ru(II) approaches Co(III) more closely when $^-O_2CCH_2$-3-pyridine rather than nicotinate is the bridging group. It seems likely that, whereas nicotinate serves to mediate in electron transfer, the homologue serves only to fix the relation of Ru(II) to Co(III), electron transfer then being directly between the metal ions. The variation of rate with concentration of H^+ supports the view that though an inner-sphere complex is reacting, the mechanism of electron transfer is of the outer-sphere type. The reduction of carboxylate complexes at a mercury cathode has been shown[13] to be first order in $[H^+]$, and Gould[14] reports similar behaviour for some homogeneous reducing agents which can reasonably be construed to be reacting by outer sphere paths. The system seems well suited to the study of outer sphere processes, where by judicious choice of the bridging ligand, the separation between the oxidizing and reducing centres can be selected. Moreover, by resorting to chelating functions on the bridging group, the orientation of the centres can be fixed, and the response in reaction rate to substitution in the coordination spheres of the metal ions can be studied systematically.

Other metal ion centres can be used[15] and lead-in groups in variety are suitable for each of the metal ion centres[12]. A number of important issues can be studied for inner sphere reactions, many of which have already been recognized in the course of the studies of the bimolecular processes which have been made. Two will be considered briefly.

It is obvious that in the reactions described the rate of electron transfer between Ru(II) and Co(III) is not being measured, but rather the rate at which an electron originating on Ru(II) is irreversibly trapped on Co(III). Since the electron being lost from Ru(II) is in an orbital that matches a π^*

29

orbital of the ligand, the electron is to some extent delocalized to the ligand. The rate-determining step probably involves largely dislocation on the Co(III) complex. Even though the rate of electron transfer is not being measured, the rates for a series of reactions in which the lead-in group to Co(III) is kept the same will probably be found to bear a close relation to the electron density contributed by the Ru(II) to, say, the carbon bearing the carboxyl group [if carboxyl is the lead-in group for Co(III)]. Related to the point being considered is the question of the effect on the rate of making the bridging group a stronger π-acid, but keeping other parameters as much as possible the same. Making the bridging group a stronger π-acid will weaken Ru(II) as a reducing agent and this is ordinarily expected to diminish the rate of reduction by Ru(II). However, the present situation has an unusual feature, and it is not unlikely, in accord with an earlier surmise, that the rate of reduction will actually increase as more electron density is extracted from Ru(II) into the bridging group.

II. INDUCED ELECTRON TRANSFER

In the systems discussed in the previous section, the electron source is external to the bridging ligands. In those about to be described, a ligand attached to an oxidizing centre is acted upon so as to convert it to a reducing agent, and the damaged ligand in turn reduces the oxidizing metal centre. For present purposes those systems are the most interesting in which the reducing electron originates at some distance from the oxidizing metal ion.

Two kinds of reactions for converting a ligand to a reducing agent will be described. Of these only the first can strictly be described as featuring induced electron transfer. When complex **II** is acted upon by the 1e⁻ oxidizing agent Ce(IV), not only the external oxidizing agent but also the complexed Co(III) participates in oxidizing the ligand[16,17] The general

$$[(NH_3)_5CoN\!\!\left<\!\!\bigcirc\!\!\right>\!\!-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}OH]^{3+} \qquad \qquad \textbf{II}$$
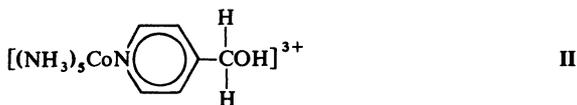
features of the process are quite straightforward and are reasonably well understood. The 1e⁻ oxidizing agent converts the organic ligand to a radical and the radical, in a subsequent step, reduces the internal oxidizing metal ion. The reduction of the Co(III) is by no means instantaneous and the internal electron transfer process can be interfered with by the external oxidizing agent. The general reaction scheme is:

$$(NH_3)_5CoN\!\!\left<\!\!\bigcirc\!\!\right>\!\!-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}OH^{3+} + Ce(IV) \longrightarrow (NH_3)_5CoN\!\!\left<\!\!\bigcirc\!\!\right>\!\!-\overset{\overset{\displaystyle H}{|}}{\underset{\displaystyle \cdot}{C}}OH^{3+} + Ce^{3+} + H^+ \qquad (1)$$

30

$$(NH_3)_5CoN\langle\bigcirc\rangle - \overset{\overset{H}{|}}{\underset{\cdot}{C}} - OH^{3+} \longrightarrow Co^{2+} aq + [HN\langle\bigcirc\rangle - \overset{\overset{H}{|}}{C} = O]^+ + NH_4^+$$

$$(2)$$

$$(NH_3)_5CoN\langle\bigcirc\rangle - \overset{\overset{H}{|}}{\underset{\cdot}{C}} - OH^{3+} + Ce(IV) \longrightarrow (NH_3)_5CoN\langle\bigcirc\rangle - \overset{\overset{H}{|}}{C} = O^{3+} + Ce^{3+}$$

$$(3)$$
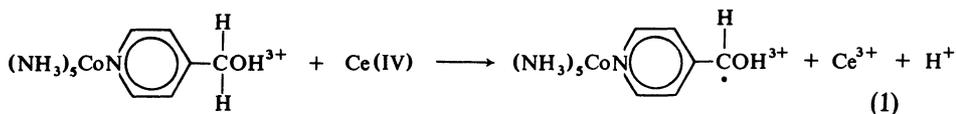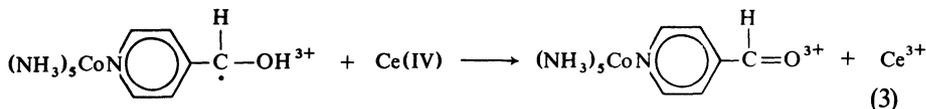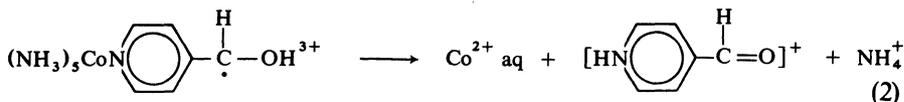
Other $1e^-$ oxidizing agents can be used in place of Ce(IV) as the external reagent and other oxidants to compete against internal electron transfer. If the assumption is made that for a series of radical intermediates the reactions of the type of (3) have the same specific rate, by measuring the competition between reactions (2) and (3) for a series of compounds, the relative rates of internal electron transfer can be estimated. Analysis of the data for the pentaammine(4-pyridinemethanol) and pentaammine(3-pyridinemethanol) reactions suggests that internal electron transfer is more than 50 times faster for the radical derived from the former complex than it is for the latter[16]. Absolute rates of internal electron transfer may of course also be determined if the value of k_3 for some external oxidant is known, but this has not been the case for any system thus far studied.

The most important application of the effect described has been in the diagnosis of mechanism of ligand oxidation. By examining products, a clear distinction can be made between external oxidizing agents which act upon the ligand by $2e^-$ changes (yielding as the only product the oxidized ligand coordinated to cobaltammine) and those which act by $1e^-$ changes (the products now are Co^{2+} accompanied by an equimolar amount of free ligand, as well as the product observed with $2e^-$ oxidants). In fact, in the particular system used for illustration, some unexpected complexities were indicated by the results, namely that for both isomers of pyridinemethanol, two different intermediates are produced by the external oxidizing agent[16].

It is fairly safe to conclude that diagnoses which apply to the ligand associated with Co(III), apply also to the free protonated ligands. This follows because the rate of oxidation of the ligand by the external oxidizing agent is very nearly the same in the two situations. This is an expected result when both the proton and the Co(III) are far enough removed from the site of ligand oxidation so that electrostatic and inductive effects are attenuated. Co(III) is an indifferent oxidizing agent for present purposes because there are no low-lying vacant πd orbitals to interact with π orbitals on the ligand. But it seems a reasonable possibility that when Co(III) is replaced by Ru(III) which has a low-spin πd^5 configuration, situations will be encountered in which the Ru(III) cooperates in the oxidation by an external $1e^-$ oxidant.

A second way of converting the ligand to a reducing agent is to deposit an electron on it. Studies of this kind have been done[18] subjecting the isomeric nitrobenzoate ions coordinated to pentaammine cobalt(III) to attack by reducing agents. By suitable choice of reducing agent, the reduction of the nitro group in place of the reduction of Co(III) can be arranged. In the systems under discussion, a number of steps are involved in the net reduction of the nitro group to an amine, and at each stage, there is the possibility of

31

reduction of Co(III) by intramolecular electron transfer in competition with further reduction or reaction of the ligand radical itself. The studies have proved to be instructive, but, as is the case with those involving attack on the ligand by an oxidizing agent, they do not readily yield rates of internal electron transfer.

The approach of depositing an electron on the ligand by pulse radiolysis is, however, admirably suited to measuring rates of intramolecular electron transfer. A small number of studies of this kind has been done, enough to make it clear that they are very worthwhile continuing and extending. When p-nitrobenzoatopentaamminecobalt(III) absorbs an electron a species is produced showing strong absorption at 330 nm[19]. This species decays by a first order process ($k = 2.6 \times 10^3 \, s^{-1}$ at 25°) to produce Co^{2+}. It is reasonable to suppose that the electron is first trapped by the nitro group and that the process being measured is transfer from the trapped site to the metal ion centre, producing the final product. For the meta and ortho derivatives[20] the first order decay rates are $1.5 \times 10^2 \, s^{-1}$ and $4.0 \times 10^5 \, s^{-1}$ respectively. The relative order of the specific rates for the three isomers is as expected, but in view of other experience with meta and para isomers, the rate disparity between the two seems surprisingly small.

Pulse radiolysis is also adaptable to providing a source of the strongly oxidizing radical, HO. When benzoatopentaamminecobalt(III) is attacked by HO, no reduction of Co(III) by internal electron transfer is observed ($k < 10^2 \, s^{-1}$) and other reactions of the radical produced when HO adds to the aromatic ring take precedence over intramolecular electron transfer[21].

The rather slow reduction of Co(III) by electron transfer through the ligand, which characterizes the studies outlined, is expected on the basis of other experience. It is ascribable in part to the need for a severe dislocation at Co(III) before the reducing electron is trapped there and in part also to the fact that there is a mismatch in symmetry between the carrier orbital on the ligand (π) and the acceptor orbital on the metal ion (σ). Quite different results would be expected, at least in respect to absolute rates, with a low spin d^5 acceptor centre such as Ru(III) in place of Co(III). Definitive studies with Ru(III) might be difficult, however, because of the facile reduction of the metal ion by an outer sphere mechanism, and for that matter, direct oxidation of Ru(III) by hydroxyl radical is probably a very rapid reaction also.

The advantage of the pulse radiolysis method over chemical methods of damaging a ligand has been acknowledged but the use of orthodox redox reagents has an advantage in that a greater selectivity in site and mechanism of attack is possible. The two approaches should be considered to be complementary, and as more studies are done, results from one will help understanding of observations made using the other.

III. MIXED VALENCE COMPLEXES

As the brief historical account to follow will show, this subject is by no means new but interest in it has recently been revived. Several developments are responsible for this. Important among them are the articles by Allen and Hush[22], by Hush[23], and by Robin and Day[24], which not only provided a

good review of the subject but also a means to understand many of the observations. Another development was experimental: whereas in the past mixed valence complexes were for the most part encountered in solids, where the compositions are determined by whatever caprice governs crystal stability, or as very labile species in solution, more recently an effort has been made to synthesize compositions and structures of choice, taking advantage of the substitution-inertia of certain metal centres. This approach was taken independently by two laboratories, one describing the synthesis of the ion[25]

$$[(NH_3)_5RuN\bigcirc NRu(NH_3)_5]^{5+} \qquad\qquad \text{III}$$
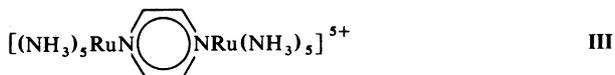
and another of the biferrocenyl ion[26]

IV
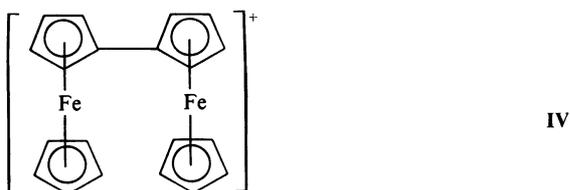
Both species retain their integrity in the [2, 2], [2, 3] and [3, 3] oxidation states, the reduced forms of electronic structure πd^6 and the oxidized forms πd^5 both being substitution-inert at least with selected ligands. In contrast to the systems discussed in the previous two sections where one centre at least suffers a severe bond dislocation accompanying irreversible electron transfer, in the systems which will be considered now, bond connexity is retained through the three oxidation states. Though for these systems the rates of intramolecular electron transfer remain of paramount importance, as will be seen, there is no general method of measuring them.

A rapid growth of interest in the rates and mechanisms of redox reaction took place several decades ago when artifically radioactive isotopes became available. Soon after, the possible connection between the much older subject, mixed valence chemistry, and the new observations on rates of exchange reactions was suggested. Of particular interest was the phenomenon of 'interaction absorption', namely the appearance of a new absorption band in some mixtures containing an element in two different oxidation states. Examples of systems showing interaction absorption are Fe(II)–Fe(III)[27], Ti(III)–Ti(IV), Cu(I)–Cu(II)[27], Sb(III)–Sb(V), in the presence of one of the more polarizable halides, as well as some non-metal systems, $ClO_2^- - ClO_2$ for example[28].

It was often assumed that the complexes responsible for the new absorption band were, to borrow parlance introduced more recently, precursor complexes for electron transfer. A number of studies of the mixed valence systems were initiated using the characteristic absorption band as a measure of the concentration of the mixed valence species. For a number of such systems, it

33

was found that the interaction absorption was proportional to the concentration of each of the two oxidation states in the mixture[27, 28]. While this result serves to demonstrate that the mixed valence species contains one molecular unit of each of the two oxidation states, it also demonstrates that the mutual affinity of the two species is very small.

More recently mixed valence species have been described which are stable enough in either the kinetic or thermodynamic sense—or both—to exist at significant concentration. A mixed valence species is formed in mixtures of V(II) and V(IV), or by hydrolysis of V(III), which is stable enough so that ε_{max} can be measured ($6800\ M^{-1}\ cm^{-1}$ at $23.2 \times 10^3\ cm^{-1}$)[29]. This is true also of the binuclear mixed valence complex of Cu(I) and Cu(II) acetate in methanol solution described by Sigwart et al.[30]. Consideration of the structure of Cu(II) carboxylate complexes raises the question of direct metal–metal interaction in the species. There is, in fact, a gradation from species such as III or IV in which direct metal interaction is presumably weak, and the bridging group provides a means of electron coupling between the metal–metal centres, to odd valence 'cluster' compounds where the principal interaction is directly metal to metal, and the odd electron plays a minor role in coupling. In the well characterized[31] solution species $(NH_3)_3RuCl_3$-$Ru(NH_3)_3^{2+}$ there is probably strong direct metal–metal interaction as there is known to be in the species $Ru_2(O_2CC_3H_7)_4^{+}$[32] and $Mo_2Cl_8^{3-}$[33] where structure determinations of solids containing the ions have been done.

In putting the current work on mixed valence species into historical perspective, its relation to studies made on purely organic systems remains to be acknowledged, and, as will become evident, the issues raised in the inorganic or organometal systems and in the fully organic ones have much

Table 2. Conproportionation equilibrium constants K_c and rates of intramolecular electron transfer for bis(p-nitrophenyl) radicals[a]

Radical anion of	K_c	$k_1\ s^{-1}$
O_2N—⟨ring⟩—⟨ring⟩—NO_2	9	$\geqslant 10^8$
O_2N—⟨ring⟩—CH_2—CH_2—⟨ring⟩—NO_2	15	2×10^6
O_2N—⟨ring⟩—$\overset{H}{\underset{H}{C}}$—⟨ring⟩—$NO_2$	36	$\geqslant 10^8$
O_2N—⟨ring⟩—O—⟨ring⟩—NO_2	210	3×10^6
O_2N—⟨ring⟩—S—⟨ring⟩—$NO_2^{(b)}$	1.1×10^3	9×10^6
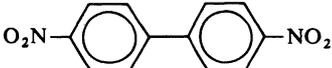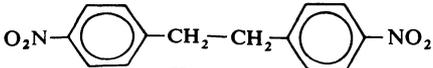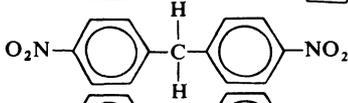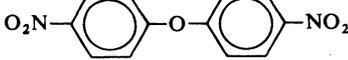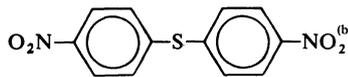
[a] 25° in DMSO.
[b] For reaction $S + S^{2-} = 2S^-$.

34

in common. By using e.p.r. methods, estimates have been made of the rate of intramolecular electron transfer in half-reduced paracyclophanes[34], in diphenylalkanes[35], and in bis(p-nitrophenyl)s[36]. The studies on the nitrophenyls were broadest in scope and detailed reference will be made only to them. A summary of the observations reported by Harriman and Maki is shown in *Table 2*.

Two questions, which will reappear in some of the inorganic systems to be discussed presently, are immediately raised by the data shown: (1) What is the nature of the interaction that leads to the marked changes in stability of the radical ions with respect to disproportionation? (2) What is the mechanism of charge trapping for the systems showing measurable rates of exchange? As to the first, the increase in stability noted in *Table 2* for the series may be directly related to separation of the aromatic rings and thus to the repulsion between charges on the dinegative ions. These are strongly, but presumably not completely, shielded by the cations. As to the second, the authors conclude that trapping of charge is largely a matter of solvent polarization and that fluctuations in the solvent determine the rate of electron transfer.

Additional issues are raised by the inorganic systems to be described, justifying the current interest in them even in the face of the persuasive analyses which have been made of some analogous organic ones. Hush's treatment[23] of the mixed valence systems is an excellent framework for organizing and discussing the observations and it is convenient to begin with a normal system, that is, one that behaves in major respects in conformity with expectations based on Hush's theories.

When

$$(NH_3)_5RuN \overbrace{\bigcirc} - \overbrace{\bigcirc} NRu(NH_3)_5^{4+}$$
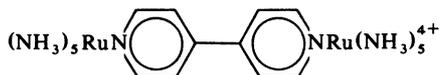
is oxidized the [2, 3] and [3, 3] species are formed reversibly in a stepwise manner[37]. The oxidation potentials for the two steps are close and an accurate value of the equilibrium constant is difficult to obtain. Whatever the exact value, it is clear from what follows that the [2, 3] state is produced, and indications are that K_c for the conproportionation reaction is close to, perhaps slightly in excess of, the statistical value of 4. The [2, 2] ion in the visible shows only the expected[38] πd–π^* absorption (λ_{max} 521 nm), and no absorption in the near infra-red. When the [2, 2] ion is oxidized, the absorption maximum at 521 nm changes only in intensity but a new band develops in the n.i.r. with a maximum in D_2O as solvent at 980 nm. This band reaches a maximum at 1 equiv. of oxidant per mole of the [2, 2] ion, and at 2 equiv. per mole it, as well as the band in the visible, disappears.

Following Hush[23], we assign the n.i.r. band to intervalence absorption in the mixed oxidation state species. In agreement with Hush's treatment, the energy of the n.i.r. band varies with $(1/n^2 - 1/D)$ for the solvent (cf. *Figures 1* and *2*)—though it must be admitted that the variation shown on *Figure 2* is not a sensitive test of the theory. The band shape (see *Figure 3*) suggests that the band is not composite; the halfwidth is somewhat greater (a factor

35
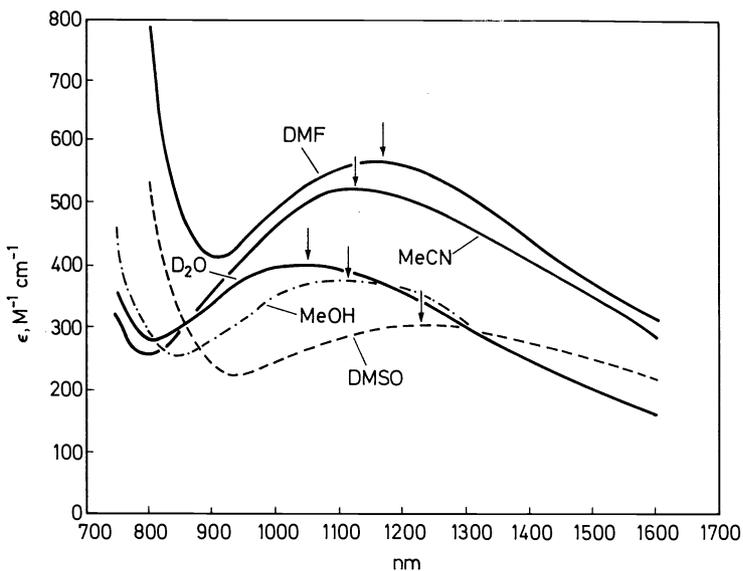
Figure 1. The n.i.r. band for the [2,3] state derived from μ-(4,4'-bipyridine) bis-pentaammineruthenium in a variety of solvents.
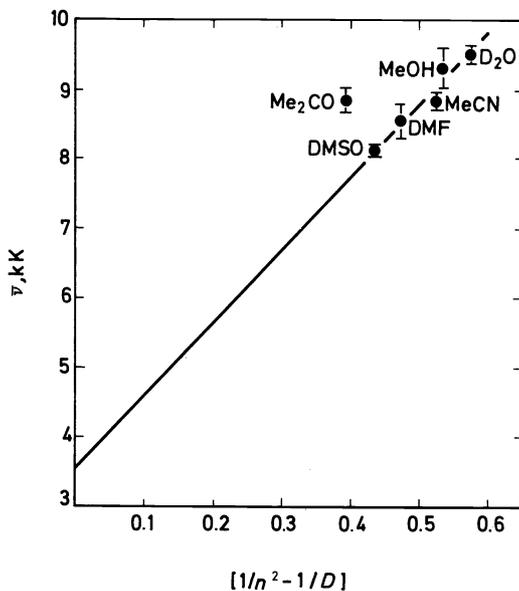

$$[1/n^2 - 1/D]$$

Figure 2. The variation of the energy of the n.i.r. band for the mixed valence 4,4'-bipyridine bridged species as a function of $(1/n^2 - 1/D)$ where n^2 is the optical and D the static dielectric constant. The deviation of the point for acetone may be attributable to the fact that it is difficult to remove traces of water from this solvent.

of 1.6) than is predicted by theory, but this may have the simple explanation that a number of molecular configurations give rise to the absorption.
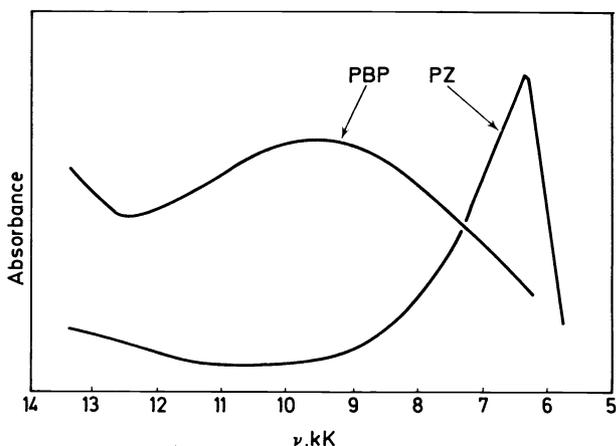

Figure 3. Band shapes for the mixed valence 4,4'-bipyridine (PBP) and pyrazine (PZ) bridged bis-rutheniumpentaammine species. Arbitrary zero for the vertical scale.

Unfortunately the n.i.r. absorption is so close to that arising from the $\pi d-\pi^*$ transition that a sensitive test of the energy of the n.i.r. band as a function of molecular asymmetry is not possible. Qualitatively, it can be concluded that the band moves to shorter wavelengths when NH_3 on one Ru is substituted by isonicotinamide. Symmetrical substitution by isonicotinamide, whether *cis* or *trans*, alters neither the band intensity nor band position significantly.

Table 3. Summary of data on mixed valence complexes based on Ru(II)–Ru(III) ammines

Bridging ligand[a]	Band max, nm		$\Delta_{\frac{1}{2}}$, n.i.r., kK		α[e]	K_c^f
	$\pi d-\pi^*$	n.i.r.[b]	exp.	calc.		
N⬡N	565	1570	1.5	3.8	0.10	$\sim 10^6$
N≡C—C≡N	360[c]	1475	1.7	4.0	0.03	$> 10^5$
N⬡—⬡N	521	980	7.3	4.7	0.04	~ 4
N⬡⬡⬡N	525	1000[d]	7.8	4.7	0.04	~ 4

[a] Work on the pyrazine system, refs. 25 and 42; on 4,4'-bipyridine, ref. 37; on 2,7-diazapyrene, ref. 39; on cyanogen, ref. 39a.
[b] In D_2O.
[c] For the [2,2] species.
[d] Actual measurements in D_2O–DCl. Shift in changing to D_2O assumed to be that measured for the 4,4'-bipyridine.
[e] α^2 measures electron delocalization. Calculated using equation given by Hush[23].
[f] For the conproportionation reaction at 25°.

37

As seen from the summary shown in *Table 3*, when the azapyrene shown below
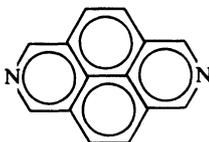
replaces 4,4'-bipyridine in the mixed valence complex, none of the observations are significantly altered[39]. This result was at first astonishing but became less so when the πd–π^* transition proved to be at almost the same wavelength as it is for 4,4'-bipyridine as bridging group. Calculations by R. Jacobs and B. Hudson[40] show that although the lowest unoccupied orbital for the azapyrene is lower than for 4,4'-bipyridine, this orbital has nodes at nitrogen in the former case. The next higher orbital of suitable symmetry has an energy about the same as the lowest unoccupied for the bipyridine when the rings are tilted about 60°.

There is little doubt that in the two systems described, the valence states are deeply trapped, and except for the n.i.r. band, the properties are those expected for a Ru(II)–Ru(III) mixture. The rate of intramolecular electron transfer is not known. If the energy of the n.i.r. band is used to estimate the standard free energy of activation, k is calculated at $\sim 10^7\,\mathrm{s}^{-1}$ and there is no reason to believe that it is much faster than this.

Some singly bridged binuclear systems in which the coupling is so strong that the complexes probably belong to Robin and Day Class (III) have been prepared based on Os(II)–Os(III) with dinitrogen as the bridging group. The properties differ from those of the systems just described in major respects. In the first place, the equilibrium constant for the conproportionation reaction is very much higher—note[41] that for $[(NH_3)_4(H_2O)OsN_2Os(NH_3)_5]^{4+,5+,6+}$ it exceeds 10^{17}. Secondly, the n.i.r. region is rich in transitions, the spectra being very sensitive to molecular symmetry. Thirdly, the N≡N stretch is inactive in the substitutionally symmetrical species $[Cl(NH_3)_5OsN]_2^{3+}$ (it does appear in the Raman spectrum). Because even the slight asymmetry present in $[Cl(NH_3)_4OsNNOs(NH_3)_5]^{4+}$ causes the N≡N stretch to appear in the infra-red, it can be concluded that the lifetime of a specific Os(III)–Os(II) state is very short—of the order of $2 \times 10^{-14}\,\mathrm{s}$ or less[41a]. Finally, the chemical properties, specifically the substitution labilities, do not seem to be characteristic of either Os(II) or Os(III). All in all, the observations suggest that the species cannot be usefully regarded as containing Os(II) + Os(III). Rather, interaction between the osmium atoms is so strong that the atoms are equivalent. The mechanism of the interaction between the metal atoms is not understood. It is possible, in view of the large radial extension to be expected for the valence d orbital of osmium, that there is direct overlap between them.

Having considered a normal case, in the sense that it conforms to Hush's theories, and the other extreme, a system where the interaction is very strong and the theory is not expected to be applicable, we turn to an intermediate case which, as we will see, introduces some conceptual problems. Species **III**

shows an absorption at 565 nm, shifted *ca.* 18 nm to longer wavelengths compared to that shown by the corresponding [2, 2] species and of diminished intensity. Another band appears at 1 570 nm, which has been interpreted[25, 42] as an intervalence transition. This assignment is supported by the fact that on the scale of time resolution of an ESCA experiment[43], the mixed valence species shows two different kinds of ruthenium to be present, by the fact that unsymmetrical substitution shifts the n.i.r. band to higher energies by amounts at least approximately equal to the stabilization of the ground state and by the fact that the n.i.r. band appears at a reasonable position for an intervalence transition. But this interpretation is faced by some serious difficulties. The band position proves to be rather insensitive to the dielectric properties of the solvent[25]. The band has an abnormal shape and the plot shown in *Figure 3* suggests that it is a composite. But even treating the band as arising from a single transition, it is much narrower than is calculated from theory[23]. Assigning the band to an intervalence transition makes it hard to understand why a corresponding band is not observed when the pentaammine ligands are replaced by $(bipy)_2 + Cl^-$—note that replacement of NH_3 by isonicotinamide in the bipyridine bridged species causes no noticeable change in intensity and only a small change in the band position.[44] Finally, the point needs to be mentioned that measurements of infra-red frequencies[42] on a compound containing species **III** show that these appear at the average of those expected for a 2^+ and a 3^+ ion. Taking into account the frequency difference and the fact of averaging, the i.r. observations set a lower limit of about $10^{12} s^{-1}$ in the rate of intramolecular electron transfer.

Many of these difficulties are featured also by the species[39a]

$$[(NH_3)_5RuN\equiv C\text{---}C\equiv NRu(NH_3)_5]^{5+} \qquad (V)$$
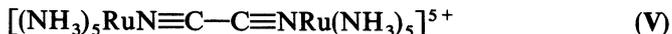
As recorded in *Table 3* here again the band is too narrow for an intervalence transition. The band shape is very much like that observed for **III**, and the band position again is insensitive to the nature of the solvent. In the cyanogen system an even higher lower-limit on the rate of intramolecular electron transfer can be set than is the case for **III**. The $C\equiv N$ stretch in nitriles co-ordinated to Ru(II) or to Ru(III) differs by *ca.* $200 cm^{-1}$. In species **V** a single i.r. band corresponding to the $C\equiv N$ stretch is observed at a position intermediate between those expected for Ru(II) and Ru(III). Thus, k for intramolecular transfer must be rapid compared to the frequency shift, or, greater than $6 \times 10^{12} s^{-1}$. If it is more rapid than molecular vibration, how then is the electron or electron hole trapped?

It is clear that these intermediate cases, which appear to be on the borderline between the trapped case and the case where electron transfer is so rapid that it constitutes chemical binding, pose some challenging theoretical problems. Further research is clearly necessary to round out the evidence on systems which have already been studied partially, as well as to discover new systems. Much work is in progress in this area and some of that published recently will be considered in the light of the issues which have been raised.

The bisfulvalenediiron system[45, 46] features at least some of the problems which were encountered in the study of **III**. In the bisfulvalenediiron species

the n.i.r. band is definitely composite and can be decomposed into two with maxima at 1140 and 1550 nm. Each band, however, has about the width expected on the basis of Hush's treatment[23] of the intervalence transition. A n.i.r. band is reported[47] for (tfd)$_2$Co–L–L–Co(tfd)$_2^-$ [where tfd represents the dithiolene (CF$_3$)$_2$C$_2$S$_2$ and L–L is *trans*-1,2-bis(diphenylphosphino)-ethylene] with a maximum at 1360 nm. This band is again 'too narrow' by a factor of about 2, but in this case there is no reason to believe that it is composite. For (CN)$_5$FeCNFe(CN)$_5^{6-}$ a n.i.r. band is reported[48] at 1300 nm. In this species electron transfer is definitely rather slow, at least as compared to the cyanogen-bridged Ru(II)–Ru(III) species. Two distinct C≡N vibrations are observed; we can conclude therefore that the rate is slow compared to the frequency difference, which is about 4×10^{12} s^{-1}. Observations on the solvent dependence of the n.i.r. band for the Prussian blue fragment have not been reported, nor information on the shape of the n.i.r. band. It seems likely that when the species is more completely investigated it will be found to be normal.

If the current proportion of the systems showing the abnormalities which **III** exhibits is maintained as more are investigated, they will constitute a significant subclass of the Robin and Day classification. A feature which they may have in common is strong interaction as reflected in values of K_c, the equilibrium constant for conproportionation, far above the statistical value of 4.

There are observations which bear on the question of the stability of **IV** with respect to disproportionation. The values of E^0 governing the steps in the reduction of [3, 3] are

$$[3, 3] \xrightarrow{\ 0.76\ } [2, 3] \xrightarrow{\ 0.37\ } [2, 2]$$

The value of E^0 for the 1e$^-$ reduction of $[(NH_3)_5RuN\bigcirc NRh(NH_3)_5]^{6+}$ has been measured as 0.71. It is apparent that the fact that Ru(III) is πd^5 while Rh(III) is πd^6 makes only a small difference in the ease of reduction of the other Ru(III) in the binuclear ion, and thus the inherent excess stability of the [2, 3] state amounts to only 0.05 V. Arguing then that Ru(III) is affected by Ru(III) acting through the ligand in much the same way as Ru(III) is affected by Rh(III), the stability of the intermediate oxidation state becomes largely—though not completely—a matter of the instability of the [2, 2] state. Such instability can arise from the interaction of the two Ru(II) centres with a common π^* orbital on the ligand. Population of the orbital by the πd electrons of one Ru(II) diminishes the tendency for back-donation in the other. It is interesting to note (cf. *Table 3*) that there is no correlation of K_c nor of abnormal behaviour with the values of α. But if in fact the n.i.r. bands for **III** and the cyanogen-bridged species are not intervalence transitions, then of course the values of α lose the significance which has been assigned to them.

Opportunities for extending and developing each of the three areas which have been dealt with are abundant. Some obvious ones have been mentioned and others readily come to mind. In concluding, a few additional remarks

will be made on the problems and opportunities in the field of mixed valence complexes. A major goal of such research is to understand the coupling between the metal ions through the solvent and through saturated bridging groups if this proves to be significant—this subject is currently being investigated[49]—and also through conjugated bond systems. Interest is by no means limited to binuclear combinations and in fact some trinuclear and tetranuclear species have already been described[44]. Another goal is, by a systematic increase in molecular size, to bridge the gap between electron transfer in the bimolecular case, and electron transfer as it plays a role in electronic conduction in solids. Such research, though easy enough to formulate, will be extremely difficult to do, whether the task is preparation or characterization. For example, in an extended chain when several electron holes have been generated, what method can be used to determine their relation to each other, or the speed at which they move from one centre to another? The extension of the work to biologically important molecules such as proteins also presents interesting challenges. Much progress is being made in the study of natural metal-containing enzymes, but there is reason also to study synthetic systems in which metal ions are attached to specific sites on proteins and electron transfer rates are studied. An experiment can be visualized in which one Ru(III) is located in the body of the protein molecule and another at the surface. By using a pulse method, the surface ion can be reduced first, and intramolecular electron transfer to the interior site observed. By judicious choice of the ligands on ruthenium, there need be no ambiguity about the site of attack by the external transient reducing agent.

REFERENCES

[1] J. P. Candlin, J. Halpern and D. L. Trimm, *J. Amer. Chem. Soc.* **86**, 1019 (1964).

[2] H. Taube and H. Myers, *J. Amer. Chem. Soc.* **76**, 2103 (1954).

[3] J. K. Hurst, private communication.

[4] E. S. Gould, *J. Amer. Chem. Soc.* **95**, 5539 (1973). Paper XIV in a series.

[5] R. D. Cannon and J. Gardiner, *J. Amer. Chem. Soc.* **92**, 3800 (1970).

[6] D. Gaswick and A. Haim, *J. Amer. Chem. Soc.* **93**, 7347 (1971).

[7] J. K. Hurst and R. H. Lane, *J. Amer. Chem. Soc.* **95**, 1703 (1973).

[8] A. W. Adamson and E. Gonick, *Inorg. Chem.* **2**, 129 (1963).

[9] D. Huchital and R. G. Wilkins, *Inorg. Chem.* **6**, 1022 (1967).

[10] L. Rosenheim, D. Speiser and A. Haim, *Inorg. Chem.* **13**, 1571 (1974).

[11] E. Kirk Roberts Jr, unpublished observations.

[12] S. Isied and H. Taube, *J. Amer. Chem. Soc.* **95**, 8198 (1973).

[13] A. Vlček, in *Advances in the Chemistry of Coordination Compounds*, p 560. S. Kirschner (Ed.), McMillan: New York (1961).

[14] E. S. Gould, personal communication.

[15] E. Toma and J. Malin have used $Fe(CN)_5^{3-}$ in place of Ru(II). For the particular cases they studied, internal electron transfer was slow compared to dissociation of the complex, but the research was by no means exhaustive.

[16] J. E. French and H. Taube, *J. Amer. Chem. Soc.* **91**, 6951 (1969). Similar effects have been observed[17] for 4-hydroxymethylbenzoatopentaamminecobalt(III) but have not been so exhaustively studied for this system.

[17] R. Robson and H. Taube, *J. Amer. Chem. Soc.* **89**, 6487 (1967).

[18] E. S. Gould, unpublished observations.

[19] M. Z. Hoffman and M. Simic, *J. Amer. Chem. Soc.* **94**, 1757 (1972).

[20] M. Simic, private communication.

[21] H. Cohen and D. Meyerstein, *J. Amer. Chem. Soc.* **93**, 4179 (1971).

[22] G. C. Allen and N. S. Hush, *Progr. Inorg. Chem.* **8**, 357 (1967).

[23] N. S. Hush, *Progr. Inorg. Chem.* **8**, 391 (1967).

[24] M. B. Robin and P. Day, *Advanc. Inorg. Chem., Radiochem.* **10**, 247 (1967).

[25] C. Creutz and H. Taube, *J. Amer. Chem. Soc.* **91**, 3988 (1969).

[26] D. O. Cowan and F. Kaufman, *J. Amer. Chem. Soc.* **92**, 219 (1970).

[27] Sb(III)—Sb(V)—Cl⁻ : N. R. Davidson, *J. Amer. Chem. Soc.* **73**, 2361 (1951); Cu(I)—Cu(II)—Cl⁻ : H. McConnell and N. R. Davidson, *J. Amer. Chem. Soc.* **72**, 3168 (1950).

[28] ClO_2—ClO_2^- : H. Taube, unpublished observations.

[29] T. W. Newton and F. B. Baker, *Inorg. Chem.* **3**, 569 (1964).

[30] C. Sigwart, P. Hemmerich and J. T. Spence, *Inorg. Chem.* **7**, 2545 (1968).

[31] E. E. Mercer and L. W. Gray, *J. Amer. Chem. Soc.* **94**, 6726 (1972).

[32] M. J. Bennett, K. G. Caulton and F. A. Cotton, *Inorg. Chem.* **8**, 1 (1969).

[33] M. J. Bennett, J. V. Brencic and F. A. Cotton, *Inorg. Chem.* **8**, 1060 (1969).

[34] S. I. Weissman, *J. Amer. Chem. Soc.* **80**, 6462 (1959).

[35] V. V. Voevodskii, S. P. Solodovnikov and V. M. Chibrikin, *Dokl. Akad. Nauk SSSR*, **129**, 1082 (1959).

[36] J. E. Harriman and A. H. Maki, *J. Chem. Phys.* **39**, 778 (1963).

[37] G. Tom, C. Creutz and H. Taube, submitted for publication.

[38] P. C. Ford, DeF. P. Rudd, R. Gaunder and H. Taube, *J. Amer. Chem. Soc.* **90**, 1187 (1968).

[39] G. Tom and H. Fischer, research in progress.

[39] (a) G. Tom, research in progress.

[40] R. Jacobs and B. Hudson, personal communication.

[41] R. H. Magnuson, *Ph. D. Thesis*, Stanford University (1973).

[41] (a) R. H. Magnuson and H. Taube, *J. Amer. Chem. Soc.* **94**, 7213 (1972).

[42] C. Creutz and H. Taube, *J. Amer. Chem. Soc.* **95**, 1086 (1973).

[43] P. H. Citrin, *J. Amer. Chem. Soc.* **95**, 6972 (1973).

[44] S. A. Adeyemi, J. N. Braddock, G. M. Brown, J. A. Ferguson, F. M. Miller and T. J. Meyer, *J. Amer. Chem. Soc.* **94**, 300 (1972).

[45] D. O. Cowan and C. LeVanda, *J. Amer. Chem. Soc.* **94**, 9271 (1971).

[46] U. T. Mueller-Westerhoff and P. Eilbracht, *J. Amer. Chem. Soc.* **94**, 9274 (1972).

[47] G. R. Eaton and R. H. Holm, *Inorg. Chem.* **10**, 805 (1971).

[48] R. Glauser, U. Hauser, F. Herren, A. Ludi, P. Roder, E. Schmidt, H. Siegenthaler and F. Wenk, *J. Amer. Chem. Soc.* **95**, 8457 (1973).

[49] H. Krentzien, research in progress.