ELECTRON TRANSFER BETWEEN METAL COMPLEXES - RETROSPECTIVE

by
HENRY TAUBE

Department of Chemistry, Stanford University,
Stanford, CA 94305

This will be an account in historical perspective of the development of part of the field of chemistry that I have been active in for most of my professional life, the field that is loosely described by the phrase "electron transfer in chemical reactions". In the short time available to me for the preparation of this paper, I can't hope to provide anything significant in the way of original thought. But I can add some detail to the historical record, especially on just how some of the contributions which my co-workers and I have made came about. This kind of information may have some human interest and may even have scientific interest of a kind which cannot easily be gathered from the scientific journals. For publication there, the course of discovery as it actually took place may be rewritten to invest it with a logic that it did not fully acquire until after the event.

Simple electron transfer is realized only in systems such as $Ne + Ne^+$. The physics already becomes more complicated when we move to $N_2 + N_2^+$ for example, and with the metal ion complexes which I shall deal with, where a typical reagent is $Ru(NH_3)_6^{2+}$, and where charge trapping by the solvent, as well as within the molecule, must be taken into account, the complexity is much greater. Still, a great deal of progress has been made by a productive interplay of experiment, qualitative ideas, and more sophisticated theory, involving many workers. Because of space limitations, I will be unable to trace all the ramifications of the field today, and will emphasize the earlier history of the subject, when some of the ideas basic to the field were being formulated. This choice of emphasis is justified because, by an accident of history, I was a graduate student at the University of California, Berkeley, about the time the first natal stirrings of the subject of this article occurred, and at a place where these stirrings were most active. As a result, I may be in a unique position to deal knowledgeably and fairly with the early history of the subject. The emphasis on the early history is all the more justified because most of the topics touched on in this article, and also closely related topics, are brought up to date in a very recent volume of the series, Progress in Inorganic Chemistry (1).

Chemical reactions are commonly classified into two categories: substitution or oxidation-reduction. The latter can always be viewed as involving electron

transfer, though it is agreed that when we consider the mechanisms in solution, electron transfer is not as simple as it is in the Ne + Ne$^+$ case. Rearrangement of atoms always attend the changes in electron count at each center, and these must be allowed for. I will, however, simplify the subject by considering only processes of simple chemistry: those in which electron transfer leaves each of the reaction partners in a stable oxidation state. While substitution reactions can be discussed without concern for oxidation-reduction reactions, the reverse is not true. The changes that take place at each center when the electron count is changed is an essential part of the "electron transfer" process, and may be the dominating influence in fixing the rate of the reaction. Moreover, most of the early definitive experiments have depended on exploiting the substitution characteristics of the reactants, and of the products. Thus, the attention which will be devoted to the substitution properties of the metal ions is not a digression but is an integral part of the subject.

An appropriate place to begin this account is with the advent of artificial radioactivity. This enormously increased the scope of isotopic tracer methods applied to chemistry, and made it possible to measure the rates of a large number of oxidation reduction reactions such as:

$$*Fe^{2+}(aq) + Fe^{3+}(aq) = *Fe^{3+}(aq) + Fe^{2+}(aq) \tag{1}$$
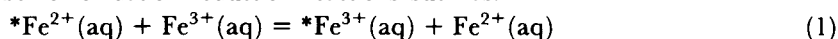
(The first demonstration of a redox electron exchange was made by von Hevesy and coworkers (2) who used naturally occurring isotopes to follow Pb(IV)/Pb(II) exchange in acetic acid.) Because chemists were there involved in the discovery of many of the new isotopes (3) an early interest in this kind of possibility developed in the chemistry community at the University of California, Berkeley, and was already evident when I was a graduate student there (1937-40). Mention is made in a review article by Seaborg (3) devoted to artificial radioactivity, of an attempt (4) to measure the rate of the $Fe^{3+/2+}$ exchange in aqueous chloride media, the result of this early attempt being that the exchange was found to be complete by the time the separation of Fe(III) from Fe (II) was made. It was appreciated by many that the separation procedure, in this case extraction of the Fe(III)-Cl$^-$ complex into ether, might have induced exchange. It was also appreciated that Cl$^-$ might have affected the reaction rate, possibly increasing it, and that quite different results might be obtained were the experiment done with Cl$^-$ being replaced by an indifferent anion.

There were several reasons for the interest, among many physical-inorganic chemists, in a reaction such as (1). That the interest in chemical applications of the new isotopes was keen in Berkeley may be traced in part to the involvement of much of the research body in teaching in the introductory chemistry course. We all had a background of qualitative observations on oxidation-reduction reactions of simple chemistry - as an example, on the reaction of Ce(IV)(aq) with Fe^{2+}(aq), - from experience in qualitative or quantitative analysis. Still, to my knowledge, at the time I was a graduate student, not a single measurement had been made of the rate of this kind of reaction. That a field of research, which has since grown enormously, was started by studying "self-exchange reactions" (5) such as (1), rather than net chemical changes (descriptor, "cross-reaction") (5), may reflect the intervention of a human factor. Measur-

ing the rate of a virtual process such as (1), today made commonplace for many systems by the introduction of new spectroscopic methods, seemed more glamorous than measuring the rate of oxidation of V^{2+}(aq) by Fe^{2+}(aq), for example. But I also recall from informal discussions that it was felt that driving force would affect the rate of reaction, and thus there would be special interest in determining the rates for reactions for which ΔG^0 (except for the entropic contributions to the driving force) is zero.

The interest in the measurement of the rates of self-exchange reactions which I witnessed as a graduate student, is not reflected in the literature of the years immediately following. Many of those who might have had plans to do the experiments were engaged in war related activities. Post war, at least live different studies on the rate of reaction (1), all carried out in non-complexing media, were reported, with conflicting results, some indicating a half-life for exchange on the order of days at concentration levels of 10^{-2}M. The discrepancies led to considerable controversy, and in informal discussions, strong opinions were expressed on just what the true rate of self-exchange might be. The basis for this kind of judgment, exercized in the absence of any body of quantitative measurements, is worth thinking about. I believe it reflected an intuitive feeling that there would be a relation between the rates of self-exchange and of the related cross-reactions, and of course each of us had at least some qualitative information on redox rates for the $Fe^{3+/2+}$ couple. The definitive measurements on the rate of reaction (1) in non-complexing media were made by Dodson (6). These measurements were soon extended (7) to reveal the effect of [H⁺] and of complexing anions on the rate and yielded rate functions such as $[Fe^{3+}]$ [X] $[Fe^{2+}]$ (because substitution is rapid compared to electron transfer, this is kinetically equivalent to $[FeX^{2+}][Fe^{2+}]$ and to $[Fe^{3+}][FeX^+]$), in addition to $[Fe^{3+}][Fe^{2+}]$, none specifying a unique structure for an activated complex. Particularly the terms involving the anions provided scope for speculation about mechanism. The coefficient for the simple second order function was found (7) to be 4 $M^{-1}s^{-1}$ at 25^0, μ=0.5, and those who had argued for "fast" exchange won out.

Another important experimental advance during the same period, important for several reasons, was the measurement (8) of the rate of self-exchange for $Coen_3^{3+/2+}$ ($k = 5.2 \times 10^{-5} M^{-1}s^{-1}$ at 25^0, μ = 0.98). This is, I believe, the first quantitative measurement of a rate for a self-exchange reaction and it may also be the first time that the oxidizing capability of a cobalt (III) ammine complex was deliberately exploited. In the article of ref. 8, the rate of the reaction of $Co(NH_3)_6^{3+}$ with $Coen_3^{2+}$ is also reported; this is, I believe, the first deliberate measurement of the rate of an electron transfer cross reaction. In contrast to the $Fe^{3+/2+}$ system, where both reactants are labile to substitution, $Coen_3^{3+}$ is very slow to undergo substitution and thus an important feature of the structure of the activated complex for the $Coen^{3+/2+}$ self exchange appeared to be settled. In considering the observations, the tacit assumption was made that the coordination sphere of $Coen_3^{3+}$ does not open up on the time scale of electron transfer, so that it was concluded that the activated complex for the reaction does not involve interpenetration of the coordination spheres of the two reac-

tants. We were thus obliged to think about a mechanism for electron transfer through two separate coordination spheres (descriptor "outer-sphere" mechanism) (9).

In 1951, an important symposium on Electron Transfer Processes was held at the University of Notre Dame, and the proceedings are reported in J. Phys. Chem., Vol. 56, (1952). Though the meeting was organized mainly for the benefit of the chemists, the organizers had the perspicacity to include physicists in the program. Thus, the gamut of interests was covered, ranging from electron transfer in the gas phase in the simplest kind of systems, for example Ne + Ne$^+$, to the kind of system that the chemist ordinarily deals with. Much of the program was devoted to experimental work, the chemistry segment of which included reports on the rates of self-exchange reactions as well as of reactions involving net chemical change - but none on cross reactions. Two papers devoted to theory merit special mention: that by Holstein (10) whose contributions to the basic physics are now being applied in the chemistry community, and the paper by Libby, (11) in which he stressed the relevance of the Franck-Condon restriction (12) to the electron transfer process, and applied the principle in a qualitative way to some observations. It is clear from the discussion which several of the papers evoked that many of the participants had already appreciated the point which Libby made in this talk. Thus, in the course of the discussion, the slowness of the self-exchange in the cobaltammines was attributed (13) to the large change in the Co-N distances with change in oxidation state, then believed to be much larger than it actually is. During the meeting too) the distinction between outer- and inner-sphere activated complexes was drawn, and the suggestion was made that the role of Cl$^-$ in affecting the rate of the Fe$^{3+/2+}$ self-exchange might be that it bridges the two metal centers. (14) But of course, because of the lability of the high spin Fe(II) and Fe(III) complexes, no unique specification of the geometry of the activated complex can be made on the basis of the rate laws alone. During the discussion of Libby's paper, a third kind of mechanism was proposed (15), involving "hydrogen atom" transfer from reductant to oxidant.

PREPARATION

My own interest in basic aspects of electron transfer between metal complexes became active only after I came to the University of Chicago in 1946. During my time at Cornell University (1941 - 1946) I had been engaged in the study of oxidation-reduction reactions, and I was attempting to develop criteria to distinguish between 1e$^-$ and 2e$^-$ redox changes, and as an outgrowth of this interest, using 1e$^-$ reducing agents to generate atomic halogen, X, and studying the ensuing chain reactions of X$_2$ with organic molecules. My eventual involvement in research on electron transfer between metal complexes owes much to the fact that I knew many of the protagonists personally (A. C. Wahl, C. N. Rice, C. D. Coryell, C. S. Garner; the first two were fellow graduate students at Berkeley), and to the fact that I had W. F. Libby, with whom I had many provocative discussions, and J. Franck as well as F. H. Westheimer as col-

leagues at the University of Chicago. By the time of the meeting, at the University of Notre Dame, a meeting I did not participate in, I appreciated in a general way the special advantages which the $Cr^{3+/2+}$ couple offered in the investigation of the mechanism of electron transfer, and outlined my ideas to N. Davidson when he visited me en route to the meeting, but the experimental work which led to the first two papers (16, 17) was not done until 1953. In the interim, I had failed to interest any of my graduate students in the work, because, of course, no one foresaw what it might lead to, and because it seemed less exciting than other work in progress in my laboratories, much of it concerned with isotopic effects, tracer and kinetic. The bulk of the work reported in the two papers just cited was done by my own hands; I shall now outline the background for those early experiments.

My interest in coordination chemistry did not develop until I elected it as a topic for an advanced course given soon after coming to the University of Chicago. Instead of using the standard textbook material, I used as major source the relevant volume of the reference series by Gmelin in which the chemistry of the cobaltammines is described. At this time I already had a good background in the literature devoted to substitution at carbon and understood the issues raised in that context, and I soon became interested in raising the same issues for substitution at metal centers. Furthermore, it was evident that the complexes based on metal ions which undergo substitution slowly were readily amenable to experimental study. I became curious as well about the reasons underlying the enormous difference in rates of substitution for metal ions of the same charge and (approximately) the same radii. The ideas that resulted were presented in my course the next time it was given, but the extensive literature study that led to the paper published in February, 1952 (18) was not done until 1949 when I was on leave from the University of Chicago as a Guggenheim Fellow.

In this paper, a correlation with electronic structure was made of observations, mainly qualitative ("labile" complexes arbitrarily defined as those whose reactions appear to be complete on mixing and "inert" as those for which continuing reaction can be observed), for complexes of coordination no. 6. To make the correlation, it was necessary to break away from the practice which was common in the USA of classifying complexes as "ionic" and "covalent" according to electronic structure. Thus, for example, the comparison of the affinities of Cr(III) and Fe(III), the latter high spin and thus "ionic", convinced me that in the Fe(III) complexes, the bonds to the ligands might actually be somewhat more covalent than in the Cr(III) complexes. Furthermore, it appeared to me that in earlier discussions of relative rates of substitution, where attempts were made to understand the observations in terms of the existing classification, there was a failure to distinguish between thermodynamic stability, and inertia, the latter being understood as referring solely to rate. The affinity of Cl^- for Cr^{3+}(aq) is considerably less than it is for Fe^{3+}(aq), yet the aquation rate of $CrCl^{2+}$(aq) is much less than it is for $FeCl^{2+}$(aq). Rates, of course, cannot be accounted for by considering ground state properties alone, but the stability of the activated complex relative to the ground state must be

taken into account. When the effect of electronic structure on the relative stabilities is allowed for, a general correlation of rates with electronic structure emerges. (In the language of ligand field theory, for complexes of coordination number 6, substitution tends to be slow when the metal ions have each of the πd(non-bonding) orbitals, but none of the σd (anti-bonding) orbitals occupied. The specific rates of exchange of water between solvent and the hexaaquo ions of $V^{3+}(\pi d^2)$, $Cr^{3+}(\pi d^3)$ and $Fe^{3+}(\pi d^3 \sigma d^2)$ are $1 \times 10^3 s^{-1}$, $5 \times 10^{-6} s^{-1}$ and $1 \times 10^3 s^{-1}$ respectively (19)).
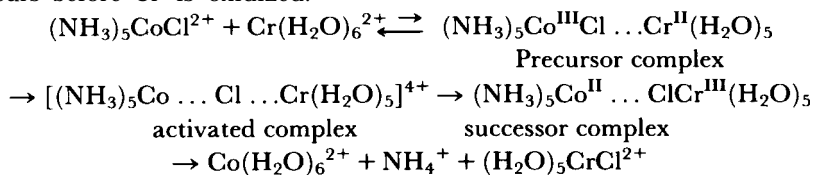
A shortcoming of this early effort is that such rationalizations of the correlation as were offered were given in the language of the valence bond approach to chemical binding, because, at the time I wrote the paper, I did not understand the principles of ligand field theory even in a qualitative way. The valence bond approach provides no simple rationale of the difference in rates of substitution for labile complexes, and these have been found to cover a very wide range, thanks to a pioneering study by Bjerrum and Poulsen (20), in which they used methanol as a solvent to make possible measurements at low temperature, and those of Eigen (21), in which he introduced relaxation methods to determine the rates of complex formation for labile systems.

Activated complexes have compositions and structures, and it is necessary to know what these are if rates are to be understood. It is hardly likely that these features can be established for the activated complexes if they are not even known for the reactants, and in 1950 we were not certain of the formula for any aquo cation in water. It seemed to me important, therefore, to try to determine the hydration numbers for aquo cations. Hydration number as I use it here does not mean the average number of water molecules affected by a metal ion as this is manifested in some property such as mobility, but has a structural connotation: how many water molecules occupy the first sphere of coordination? Because the rates of substitution for Cr^{3+}(aq) were known to be slow (22), J. P. Hunt and I undertook to determine the formula for Cr^{3+}(aq) in water (23), with some confidence that we would be successful even with the slow method we applied, isotopic dilution using ^{18}O enriched water. That the formula turned out to be $Cr(H_2O)_6^{3+}$ was no great surprise - although I must admit that at one point in our studies, before we had taken proper account of isotopic fractionation effects, $Cr(H_2O)_7^{3+}$ was indicated and, faced with the apparent necessity, I was quite prepared to give up my preconceived notions. It was also no great surprise that the exchange is slow ($t_{1/2}$ at $25°$, ca. 40 hr). Even so, the experiments were worth doing. They were the first of their kind, and they attracted the attention also of physical chemists, many of whom were astonished that aquo complexes could be as kinetically stable as our measurements indicated, and were impressed by the enormous difference in the residence time of a water molecule in contact with a cation, compared with water molecules just outside. That we dealt with hydration in terms of detailed structure rather than in terms of averaged effects may have encouraged the introduction into the field of other methods, such as nmr, to make the distinction between cation-bound and free water (19). As I will now detail, it also led directly to the experiments described in the papers of references 16 and 17.

## THE INNER SPHERE ACTIVATED COMPLEX

R. A. Plane undertook to measure the rate of self-exchange for $Cr(H_2O)_6^{3+}$-Cr^{2+}(aq) by using Cr^{2+}(aq) as a catalyst for the exchange of water between $Cr(H_2O)_6^{3+}$ and solvent. The expected catalysis was found, but owing to our inexperience in handling the air sensitive catalyst, the data were too irreproducible to lead to a value for the self-exchange rate. Catalysis on electron transfer was expected because the aquo complex of Cr^{2+}(aq) was known to be much more labile than $Cr(H_2O)_6^{3+}$- the lability is now known (24) to decrease by a factor of at least 10^{14} when Cr^{2+}(aq) is oxidized to $Cr(aq)^{3+}$ (note that Cr^{2+}, but not Cr^{3+}, has an anti-bonding electron). It occurred to me in the course of Plane's work that it would be worthwhile to test the potential of the Cr(III)/Cr(II) couple for diagnosis of mechanism using a non-metal oxidant. Following up on the idea, I did a simple test tube experiment, adding solid I_2 to a solution of Cr^{2+}(aq) which Plane had prepared for his own experiments. I observed that reaction occurs on mixing, that the product solution is green, and that the green color fades slowly, to produce a color characteristic of $Cr(H_2O)_6^{3+}$. The fading is important because it demonstrates that $(H_2O)_5CrI^{2+}$, which is responsible for the green color, is unstable with respect to $Cr(H_2O)_6^{3+}$ + I-, and thus we could conclude that the Cr(II)-I bond is established before Cr(II) is oxidized.

The principle having been demonstrated with a non-metal oxidant, I turned to the problem of finding a suitable metal complex as oxidant. What was needed was a reducible robust metal complex, having as ligand a potential bridging group, and the idea of using $(NH_3)_5CoCl^{2+}$ surfaced during a discussion of possibilities with another of my then graduate students, R. L. Rich. Because at that time virtually nothing was known about the rates of reduction of Co(III) ammines, and because they were not thought about as useful oxidants, I was by no means sanguine about the outcome of the first experiment, which again was done in a test tube. I was delighted by the outcome. Reaction was observed to be rapid (the specific rate has since been measured (25) as $6 \times 10^5 M^{-1}s^{-1}$ at 25°) and the green color of the product solution indicated that $(H_2O)_5CrCl^{2+}$ is formed. Further work (16,17) showed that this species is formed quantitatively, and that in being formed it picks up almost no radioactivity when labelled Cl- is present in the reaction solution, thus demonstrating that transfer is direct, i. e., Cl- bridges the two metal centers, and this occurs before Cr^{2+} is oxidized.

$$(NH_3)_5CoCl^{2+} + Cr(H_2O)_6^{2+} \rightleftharpoons (NH_3)_5Co^{III}Cl \ldots Cr^{II}(H_2O)_5$$
$$\text{Precursor complex}$$
$$\rightarrow [(NH_3)_5Co \ldots Cl \ldots Cr(H_2O)_5]^{4+} \rightarrow (NH_3)_5Co^{II} \ldots ClCr^{III}(H_2O)_5$$
$$\text{activated complex} \qquad \text{successor complex}$$
$$\rightarrow Co(H_2O)_6^{2+} + NH_4^+ + (H_2O)_5CrCl^{2+}$$

These early results were presented at a Gordon Conference on inorganic chemistry, which was held only a short time after they had been obtained, and they were received with much interest. E. L. King was present at the meeting,

and together we planned the experiment in which self-exchange by an "atom" transfer mechanism was first demonstrated (26).

$$(H_2O)_5{}^*CrCl^{2+} + Cr^{2+}(aq) = {}^*Cr^{2+}(aq) + (H_2O)_5CrCl^{2+} \qquad (2)$$
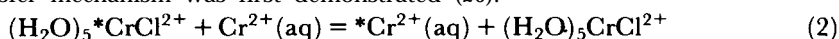
Note that in a process of this kind, the bridging group will remain bound to a Cr(III) center, but the auxiliary ligands about the original Cr(III) center will be exchanged or replaced because of the high lability of Cr(II).

(Several years later, King and co-workers (27) extended the self-exchange work to include other halides as bridging ligands, and still later (28) encountered the first example of "double bridging."

$$cis\text{-}[(H_2O)_4{}^*Cr(N_3)_2]^+ + Cr^{2+}(aq) \approx {}^*Cr^{2+}(aq) + cis\text{-}[(H_2O)_4Cr(N_3)_2]^+$$
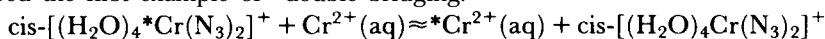
A good case can be made for this also being the first demonstration of "remote attack," that is, inner-sphere electron transfer where more than one atom separates the metal atoms in the activated complex.)

There is a brief hiatus in my work after the early experiments on inner-sphere mechanisms, caused by my taking leave from the University of Chicago in 1956. But before leaving, I hurriedly did some experiments (29), which, though semi-quantitative at best, showed that not only atoms but groups such as N_3^-, NCS^-, and carboxylates transfer to chromium when the corresponding pentaamminecobalt(III) complexes are reduced by $Cr(aq)^{2+}$, and that there are large differences in rate for different dicarboxylate complexes (maleate much more rapid than succinate). Moreover, it was shown that Cr(II) in being oxidized can incorporate other ligands such as $H_2P_2O_7^{2-}$ which are present in solution. In this paper the possibility of electron transfer through an extended bond system of a bridging group was raised, but was by no means demonstrated by the results. While I was away, Ogard (30) began his studies on the rates of aquation of $(NH_3)_5CrX^{2+}$ (X=Cl, Br, I) catalyzed by Cr^{2+}. By following the arguments made in connection with reaction (2), it can be seen that if an inner sphere mechanism operates, $(H_2O)_5CrX^{2+}$ and NH_4^+ (acid solution) will be products. The contrast with uncatalyzed aquation is worth noting, where $(NH_3)_5CrH_2O^{3+}$ and X^- are the products.

GENERAL PROGRESS

The hiatus referred to above provides me with a suitable opportunity to outline some of the advances that were being or were soon to be made on other fronts. An important one is that the rates of numerous self-exchange reactions were being measured. Here I want especially to acknowledge the contributions from the laboratories of A. C. Wahl and C. S. Garner. Some of the experiments by Wahl and co-workers made use of rapid mixing techniques - see for example, the measurement (31) of the rate of self-exchange for $MnO_4^{1-/2-}$. An important experimental contribution was also made by N. Sutin who introduced the rapid flow method (32), and later other rapid reaction techniques, into this field of study, and who helped others, including myself, to get started with the rapid flow technique. A spate of activity on the measurements of the rates of cross reactions followed, motivated in large part by the desire to test the validity of the cross reaction correlation (5).

At the quantitative theoretical level, attempts were being made to account for the barrier to reaction attending encounter and separation and that contributed by charge trapping within the metal complex and by the surrounding medium. The papers which most influenced the experimentalists, at least during the formative period in question, are those by Marcus (33) and Hush (34), dealing with adiabatic (35) electron transfer. Other theoretical approaches were being advanced during this period, and in some, attempts were made to account for non-adiabaticity, and the various theories are compared and evaluated in reference (33). (The current state of theory can be gathered from a recent article by Sutin (36)). Because this very important aspect of electron transfer reactions is not dealt with in this paper, it is essential to mention that the processes as they occur at electrodes were not being overlooked.

The correlation of the rates of cross reactions with the rates of the component self-exchange reactions (5), has been widely applied, especially to outer-sphere reactions. The limits of its validity were clearly set down by the author: allowance must be made for the work of bringing the reaction partners together and separating the products, electron delocalization must be great enough to ensure adiabatic behavior, but not so great as materially to reduce the activation energy. (The last condition, it should be noted, does not necessarily limit the applicability of the Marcus equation to outer sphere processes.) Hush's treatment (34) also leads to a correlation of rates of self-exchange and cross reactions. It also takes into account the contribution by driving force, and in fact the first calculation of the rate of a cross reaction, in this instance:

$$Pu^{3+}(aq) + PuO_2^{2+}(aq) = Pu^{4+}(aq) + PuO_2^{+}(aq)$$
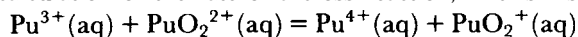
from those of the self exchange processes and the equilibrium constant appears in reference 34.

Theory of another kind has profoundly influenced the development of the field, even though it is qualitative. It responds to the question of how the choice of mechanism, and relative rates, are to be understood in terms of the electronic structures of the reactants. As is true also of rates of substitution, the observations are so sensitive to electronic structure that even qualitative ideas are useful in correlating observations, and in pointing the way to new experiments. Orgel (37) early applied qualitative ligand field theory in discussing the inner-sphere mechanisms for the reduction of Cr(III) and low spin Co(III) complexes. When electron transfer takes place through a bridging group, it is important to distinguish a chemical or "hopping" mechanism - here a low lying orbital of the ligand is populated by the reductant, or a hole is generated by the oxidant in an occupied orbital - from resonance transfer, that is, electron tunneling through the barrier separating the two metal centers. This distinction was drawn rather early by George and Griffith (38) who moreover proposed alternative mechanisms for resonance transfer. Shortly thereafter, Halpern and Orgel (39) gave a more formal treatment of resonance transfer through bridging ligands. Concerns about the relation between electronic structure and the observations on electron transfer strongly influenced my own work, but before tracing this theme, I want to report on the progress made, mainly by others, in extending the descriptive chemistry of electron transfer reactions.

    The unambiguous demonstration of an inner sphere mechanism in a sense
introduced a second dimension to the field of electron transfer mechanisms.
That in certain systems reaction perforce took place by an outer sphere mecha-
nism had long been known, but until the experiments of references 16 and 17
were done, the inner sphere mechanism was only conjecture, and, as frequently
happens in research in chemistry, only after conjecture, however reasonable, is
upgraded by proof, is it accepted as a base for further development. That the
distinction between the two reaction classes is meaningful, not only in terms of
chemistry but also in rates, will be illustrated by a single comparison: the
specific rates of reaction of $Cr^{2+}(aq)$ with $(NH_3)_5CoCl^{2+}$ is ca. 10^8 greater than
it is with $CO(NH_3)_6^{3+}$ (40) (the latter can only react by an outer sphere
mechanism). The classification of reaction paths as inner sphere or outer
sphere, on the basis of rate comparisons, involving effects (such as those
exerted by non-bridging ligands) established with reactions of known mecha-
nism, became the focus of experiment and discussion when direct proof based
on product or intermediate identification was lacking.

    Early in the 1960s new metal centers were added to the roster of those
proven to react by inner sphere mechanisms. For $Co(CN)_5^{3-}$ as reducing agent
(41), the demonstration of an inner sphere path again depended on the charac-
terization of product complexes by orthodox means. Sutin and co-workers have
been particularly resourceful in using flow techniques to provide direct proof of
mechanism for oxidizing centers ordinarily considered as labile to substitution:
thus   note   the proof of inner   sphere   mechanism   for $FeCl^{2+}(aq)$
$+ Cr^{2+}(aq)(42), CoCl^{2+}(aq) + Fe^{2+}(aq)$ (43), even the much studied $Fe^{3+/2+}$
exchange (44). It was early appreciated (17) that atom or group transfer is not
a necessary concomitant of an inner sphere process. Whether the bridging
group transfers to reductant, remains with the oxidant, or transfers from
reductant to oxidant depends on the substitution labilities of reactants and
products. Early qualitative observations (17) on the $Cr^{2+}(aq) + IrCl_6^{2-}$ system
had apparently exposed an example of reaction by an inner sphere mechanism,
but leading to no net transfer of the bridging atom. Here $(H_2O)_5CrClIrCl_5$ is
formed as an intermediate, but this then aquates to $Cr(H_2O)_6^{3+} + IrCl_6^{3-}$
(later work (45) has shown the inner sphere path to be minor compared to the
outer sphere, and that $Cr(H_2O)_6^{3+}$ is the lesser product of the former path).
Experiments (46, 47) with $V(H_2O)_6^{2+}$ as reducing agent provided numerous
examples of systems in which substitution on the reducing complex is rate
determining for the net redox process (note that $V(H_2O)_6^{2+}$ because of its
electronic structure (πd^3) is expected (18) to undergo substitution relatively
slowly). Unstable forms of linkage isomers were prepared by taking advantage
of the chemistry of the inner sphere mechanism: $(H_2O)_5CrSCN^{2+}(48)$ by the
reaction of $Cr^{2+}(aq)$ with $FeNCS^{2+}$;(49) $(H_2O)_5CrNC^{2+}(50)$ by the reaction of
$Cr^{2+}(aq)$ with $(NH_3)_5CoCN^{2+}$. Oxygen atom transfer was shown to be com-
plete (51) in the reaction of $(NH_3)_5CoOH_2^{3+}$ with $Cr^{2+}(aq)$. (The path involv-
ing direct attack on the aquo complex was later (52) shown to be unobservable
compared to attack on the hydroxo. Bridging by H_2O has to date not been
demonstrated.) The inner sphere path was demonstrated (53) also for net 2e⁻

processes in an elegant series of studies involving the reactions of Pt(IV) complexes with those of Pt(II). In an important departure, Anet (54) showed that the "capture" property of Cr^{2+}(aq) in being oxidized can be exploited to produce complexes in which an organic radical is ligated to Cr(III). An entire chapter of the volume of reference 1 is devoted to the chemistry of similar organochromium complexes(55).

ELECTRONIC STRUCTURE AND MECHANISM

A major theme in my own research, on returning from leave, was to try to understand the large differences in rate, noted qualitatively in my early work (29), and later made more quantitative, for the reactions Cr^{2+}(aq) with carboxylate complexes of $(NH_3)_5$Co(III). Many of the ligands were dicarboxylic acids, and to explain the observation that when a conjugated bond system connects the two carboxylates, reaction is usually more rapid than it is for the saturated analog, it seemed reasonable then to assume that in the case of conjugated ligands, the reducing agent attacks the exo carboxyl (remote attack), the conjugated bond system serving as a "conduit" for electron transfer. In adopting this view the tacit assumption was made that the reactions are non-adiabatic so that the extent of electronic coupling would be reflected in the rate. In retrospect, this assumption is naive, because the effect of conjugation would be exerted even if the reducing agent attacked at the endo carboxyl.

A false start was made in demonstrating remote attack defined as above. Activation effects accompanying electron transfer were reported (56), which if true, would have constituted proof of remote attack for these systems. These effects could not be reproduced (57) in later work (I had by now moved from University of Chicago to Stanford University). Remote attack for the large organic ligands was finally demonstrated (58) in the reaction of

$$\left[(NH_3)_5CoN\underset{NH_2}{\bigcirc}\!\!-\!\!C = O\right]^{3+} \text{ with } Cr^{2+}(aq).$$ This work, which also yielded

a measurement of the rate of reaction of Cr^{2+}(aq) with the analogous Cr(III) species, provided the clue to understanding, at least in a qualitative way, the rate differences observed for different conjugated ligands. The astonishing result was that the rate of reduction of the Co(III) complex is only about 10-fold greater than that of the Cr(III) complex. When the bridging group is a non-reducible species such as acetate, the ratio is $> 10^4$. The insensitivity of rate to the nature of the oxidant suggested that the electron does not transfer directly from Cr(II) to the oxidizing center but that the mechanism rather involves the le⁻reduction (59) of the ligand by the strong reducing agent Cr^{2+}, followed by reduction of the oxidizing center by the organic radical - i.e., a "hopping" mechanism obtains. This view provided satisfactory rationalizations of most of the observations of rates made with organic ligands. For example, the fact that the rate is considerably greater for $HO_2C\text{-}CH\text{=}CH\text{-}CO_2^-$ (fumarate) than for $CH_3CO_2^-$ as ligand on Co(III), may have little to do with the opportunity that Cr(II) has to attack the remote carboxyl in the

former case, and only reflects the fact that fumarate can be reduced by Cr^{2+}(aq). Moreover, the otherwise puzzling observation that the rate for the fumarate complex is increased (60) by H⁻ is now easily understood; positive charge added to the ligand makes it easier to reduce. That many reactions of the class under consideration proceed by a stepwise mechanism has been convincingly demonstrated and amply illustrated in subsequent work, most of it done by Gould and co-workers (61).

The rationalization offered for the operation of the stepwise mechanism in the Co(III)-Cr(II) systems is that the carrier orbital on the ligand has π symmetry, while the donor and acceptor orbitals have σ symmetry. This renders as highly improbable an event in which the four conditions: Franck-Condon restrictions at each center, and the symmetry restrictions at each center, are simultaneously met. Whether or not this is the correct explanation, it led me to search for an oxidizing center of the ammine class in which the acceptor orbital has π symmetry.

When the important condition that the complexes undergo substitution slowly was added, only one couple within the entire periodic table, $Ru^{3+/2+}$ ($\pi d^5/\pi d^6$) then qualified (62). In principle, the $Os^{3+/2+}$ couple is also a candidate, but unless some strong π acid ligands are present, the couple is too strongly reducing to be useful. The ruthenium species had the added advantage that much more in the way of preparative work was known (63), and further that the redox potentials are close to those of the much studied cobalt couples. Since the π orbital on Ru(III) can overlap with the π∗ orbital on the ligand, we expected that the "hopping" mechanism would no longer obtain. Reaction with Cr^{2+}(aq) is in fact much more rapid (2×10^4) than it is in the case of the Co(III) isonicotinamide complex, and moreover, the rates are now quite sensitive to changes in the redox potential of the oxidizing center (64). The chemistry also differs in an interesting way from the Co(III)-Cr(II) case. The bond between Ru and the ligand is not severed when Ru(III) is reduced to Ru(II), and a kinetically stable binuclear intermediate is formed, as is expected (18) from the electronic structures of the products, πd^6 for Ru(II) and πd^3 for Cr(III).

Though the main intent of this paper is to provide historical background rather than the develop the subject itself in detail, because the reaction proper-ties are so sensitive to electronic structure, it may be appropriate in concluding this section to illustrate the connection with a few examples. Effects arising from differences in electronic structure are manifested in several different ways: by affecting the rates of substitution, they can affect the choice of mechanism, and, for an inner sphere reaction path, can determine whether binuclear intermediates are easily observable, and whether there is net transfer of a group from one center to another; even after the precursor complex is assembled, orbital symmetry can affect the mechanism itself, as in the example offered in an earlier paragraph, and can profoundly affect the rate of conversion of the precursor to the successor complex.

The Cr(III)/Cr(II) ($\pi d^3/\pi d^3 \sigma d^1$) and Ru(III)/Ru(II) ($\pi d^5/\pi d^6$) couples offer perhaps the greatest contrasts in behavior. It should be noted that the σ

electron in Cr(II) is antibonding, thus accounting for the tetragonal distortion in Cr(II) complexes, and their enormous lability compared to those of Cr(III). By contrast, the complexes of both oxidation states of ruthenium undergo substitution slowly, with the useful exception of water as a ligand, where the residence time on Ru(II) is a fraction of a second.

The reducing agent Cr(II) shows preference for an inner sphere mechanism, and this is especially marked if the acceptor orbital has σ symmetry. There is a great economy of motion for electron transfer by an inner sphere path for the σ donor - σ acceptor cases which arises from the reciprocity, at the two centers, of the events which are required in overcoming the inner sphere Franck-Condon barrier. This point is illustrated for the $(H_2O)_5{}^*CrCl^{2+} + Cr(H_2O)_6{}^{2+}$ self exchange reaction in Fig. 1 where the electronic levels are shown for the precursor complex, for the activated complex, and for the successor complex. Motion of the bridging Cl⁻ from Cr(III) to Cr(II) lowers the energy of a acceptor orbital on Cr(III), and at the same time raises that of the donor orbital on Cr(II), and although other nuclear motions are also required, there is some correlation of the events required for activation to electron transfer, a correlation which is absent in the case of an outer sphere mechanism. The high substitution lability of Cr(II) of course means that the precursor complex can be formed rapidly.

The comparison of the rates of self exchange for $Cr(H_2O)_6{}^{3+}/Cr(H_2O)_6{}^{2+}$ vs. $(NH_3)_5RuH_2O^{3+}/(NH_3)_5RuH_2O^{2+}$ and how these respond when the higher oxidation state for each couple is converted to the hydroxo complex is quite instructive. The upper limit for the specific rate of self-exchange for the Cr(III)/Cr(II) couple is $2 \times 10^{-5}M^{-1}s^{-1}$ (65, 55); although it has not been directly measured for the ruthenium couple, the specific rate can reasonably be taken to be close to that (67) for $Ru(NH_3)_6{}^{3+/2+}$, namely ~

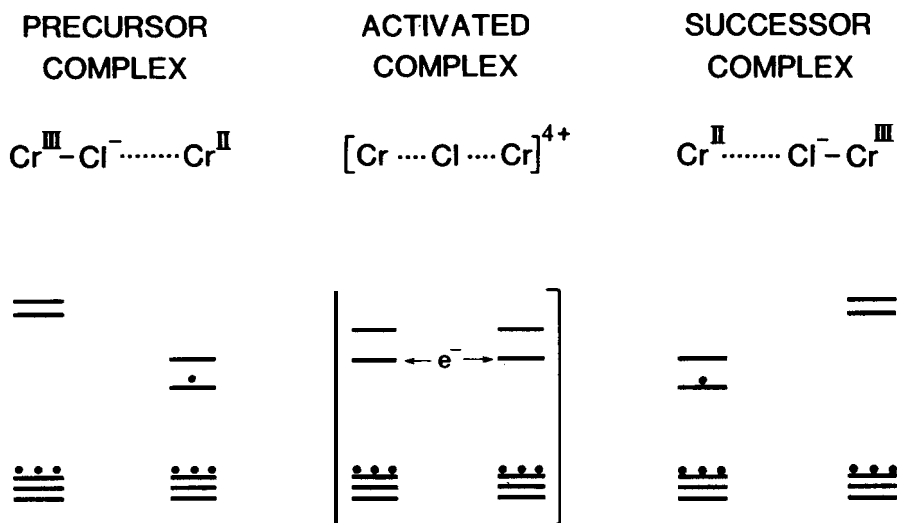**PRECURSOR COMPLEX** **ACTIVATED COMPLEX** **SUCCESSOR COMPLEX**

$Cr^{III}-Cl^- \cdots\cdots Cr^{II}$ $[Cr \cdots Cl \cdots Cr]^{4+}$ $Cr^{II} \cdots\cdots Cl^- - Cr^{III}$

Fig. 1. Electronic structure and "atom" transfer in the self-exchange reaction: $(H_2O)_5CrCl^{2+} + Cr(H_2O)_6{}^{2+}$.

$1 \times 10^3 M^{-1}s^{-1}$. Because the redox change for the ruthenium couple involves a π electron, it causes only a small change in the dimensions of the complex (68). Thus the Franck-Condon barrier to electron transfer arising from inner sphere reorganization is small, and facile transfer by an outer sphere mechanism is observed. By contrast, because Cr(III) has no anti-bonding electrons, and the electron added on reduction is anti-bonding, there is a large change in dimensions and shape attending the reduction, and the slowness of the selfexchange can be attributed in part at least to the inner sphere barrier (69). Why the water molecule, which as a ligand on the oxidizing agent still has available an electron pair for sharing with the reducing agent, is such a poor bridging group, remains to be understood.

On deprotonation of a water molecule in each oxidant, the inner sphere path for the Cr(III)/Cr(II) system opens up, and a marked increase in rate is observed (65) (k=0.66 $M^{-1}s^{-1}$ at 25º) - the increase may be as large as a factor (66) of 10^9. The self-exchange rate for $(NH_3)_5RuOH^{2+} + (NH_3)_5$-$RuOH_2^{2+}$ has not been measured, but it can be asserted with confidence that the rate by either an inner sphere path or an orthodox outer sphere path will be much less than it is for the aquo couple. The rate by the inner sphere path will be limited by the rate of bridge formation, and thus will be no greater than $1 \times 10^2 M^{-1}s^{-1}$ (neutral ligands in substituting on $(NH_3)_5RuOH_2^{2+}$ show specific rates (70) of the order of 0.1 $M^{-1}s^{-1}$). The orthodox outer sphere path now has a composition barrier, as well as a Franck-Condon barrier to overcome (K_{eq} for the production of $(NH_3)_5RuOH^+$ and $(NH_3)_5RuOH_2^{3+}$ from $(NH_3)_5RuOH^{2+}$ and $(NH_3)_5R\sim OHz^{2+}$ is ca. 10^9). Reaction by "hydrogen atom" transfer (15) is a reasonable possibility, that is, electron transfer concomitant with proton transfer from the Ru(II) complex to the Ru(III), and some evidence in support of this kind of mechanism has been advanced to explain observations (71) made in the oxidation by Fe^{3+} and $FeOH^{2+}$ of $(NH_3)_5RuOH_2^{2+}$. Reaction by such a path might be quite facile and a specific rate in excess of 1 $M^{-1}s^{-1}$ would be strong evidence in its favor.

APPLICATIONS OF THE RU(III)/RU(II) COUPLE

Some unexpected benefits have accrued from introducing Ru(III)-Ru(II) ammine couples into this field of research. Ruthenium(II) engages in back bonding interactions to a degree unprecedented among the dipositive ions of the first transition series. A discovery (72) which forcefully brought this message home, is that $(NH3)_5RuN_2^{2+}$ is formed in aqueous solution by the direct reaction of $(NH_3)_3RuOH_2^{2+}$ with N_2. When the heteroligand in $(NH_3)_5RuL^{2+}$ is pyridine or a derivative, the complexes of both oxidation states are slow to undergo substitution, and by changing the number of π acid ligands, a versatile series of outer-sphere redox couples is made available, spanning a range in redox potential of over 1 volt. When derivatives of the Os(III)-Os(II) ammines are included, the useful range in aqueous solution is extended by approximately 0.5 V. These reagents are finding wide application in research on redox processes.

1. Intramolecular Electron Transfer

It has occurred to many that in trying to arrive at a basic understanding of electron transfer processes, it would be a great advantage if the reactions could be studied in an intramolecular mode rather than, as is commonly done, in the bimolecular or (intermolecular) mode, particularly if the geometrical relation between the two metal centers were unambiguosly defined. Such systems had been encountered in studies of "induced" electron transfer: (73) when a powerful

$1 e^-$ oxidant acts on $\left[(NH_3)_5CoN\!\!\left\langle\bigcirc\right\rangle\!\!-\underset{\underset{H}{|}}{C}=O\right]^{3+}$ for example, the result-

ing coordinated organic radical can undergo intramolecular electron transfer, the oxidation of the ligand to the carboxylic acid being completed by Co(III). In some cases, intramolecular electron transfer can be intercepted by reaction of the radical with the external oxidant, but at best, only relative rates were obtained for these systems. In an elaboration of this kind of approach, in which pulse radiolysis is used to convert the organic ligand to a radical - usually by reduction - intramolecular transfer rates can be measured (74). These results are important in their own right, but they do not substitute for experiments in which metal-to-metal transfer is studied.

A strategy for dealing with the metal-to-metal case was devised (75a), which depends on the special properties of the Co(III)/Co(II) and Ru(III)/Ru(II) couples. The principle is the following: when a molecule (76) such as

$$(NH_3)_5Co^{III}N\!\!\left\langle\bigcirc\right\rangle\!\!\left\langle\bigcirc\right\rangle\!\!NRu^{III}(NH_3)_5$$
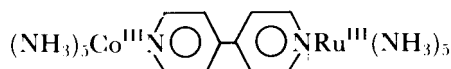
which has both metal centers in the oxidized state, is treated with an external reducing agent, Ru(III) is reduced more rapidly than Co(III). This is a direct result of the differences in electronic structure, πd^6 and πd^5 for Co(III) and Ru(III) respectively, the former requiring much more in the way of reorganization energy because the incoming electron is anti-bonding. In a subsequent step, Ru(II) reduces Co(II) by an intramolecular process, at least if the solution of the binuclear complex is sufficiently dilute.

The first method (75a) devised to produce the [III,III] molecule is rather ingenious, but it involves many steps, and it has the disadvantage that SO_4^{2-} rather than NH_3 is trans to the pyridine on Ru(III). Schiffer (77) has greatly simplified the preparative procedure by taking advantage of chemistry developed by Sargeson and co-workers (78) and has studied intramolecular electron

transfer for $(NH_3)_5Co^{III}NC\!\!\left\langle\bigcirc\right\rangle\!\!-CNRu^{II}(NH_3)_5$ and for the related mole-

cules with the ortho and meta isomers as the bridging ligands. Quite independently of our work, Haim et al. (79) have done experiments similar to those described, but with $Fe(CN)_5H_2O^{3-}$ as the reducing agent. Substitution on $Fe(CN)_5H_2O^{3-}$ takes place readily so that the simple mixing procedure attempted by Roberts (75b) often can be used with this particular kind of reducing agent.

A point of interest in all of these studies is to learn how the rate of reaction responds to changes in the structure of the bridging group. In the bipyridine case, the coupling between the pyridine rings has been variously modified (76); since the immediate environment about each metal is left unaltered, the driving force for the reaction is but little affected, and changes in rate can then be attributed to changes in electronic coupling. The results obtained in studies of this kind are outlined in a recent review article by Haim (80). Here I will only mention an extension of this kind of strategy to a system of biochemical interest. Gray et al (81) and Isied et al (82) have succeeded in placing $(NH_3)_5Ru$ on cytochrome C at a position remote from the porphyrin (Ru(III)-Fe(III) separation 15Å). Different pulse methods were used by the two groups to reduce Ru(III) preferentially over Fe(III), and though the results of the two studies differ somewhat ($k = 20 \pm 5s^{-1}, 82 \pm 20s^{-1}$ respectively), it is clear that the general strategy is effective.

2. Robust Mixed Valence Molecules

The resurgence of interest (83) in the properties of mixed valence compounds can be traced to review articles (84, 85, 86) which appeared in 1967, and to the first deliberate synthesis of a robust mixed valence molecule, the species shown below, which is commonly referred to as the Creutz-Taube (87) ion

$$\left[(NH_3)_5RuN \bigcirc NRu(NH_3)_5 \right]^{5+} I$$
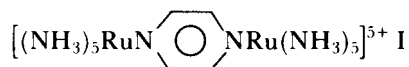
(Quite independently of our work, Cowan and Kaufman (88) prepared a molecule based on the ferricinium/ferrocene couple.) Peter Ford and I first produced the Creutz-Taube ion in 1967. In undertaking its preparation, we were motivated by simple curiosity rather than by questions which might arise from a deep understanding of the issues raised by the properties of the mixed valence compounds. The fully reduced ([II,II]) state is readily prepared by direct substitution using pyrazine and $(NH_3)_5RuOH_2^{2+}$, and in undertaking the project, we were taking advantage of our knowledge of affinities and rates of substitution for both oxidation states of ruthenium. Complexes with Ru(II) attached to heterocyclic nitrogen show very strong absorption in the visible region of the spectrum ($\pi^* \leftarrow \pi d$) (89) and on observing that the quality of the color was not significantly altered when the [II,II] species is half oxidized, we did not pursue the matter further. Fortunately Carol Creutz took up the subject again. The electrochemical results which she obtained about June 1968 showed that the mixed valence state is very stable relative to the isovalent, and this suggested to us that electronic coupling in the mixed valence species is strong. By now, the review papers by Hush (85) and Robin & Day (86) had appeared, and taking their content to heart, we felt certain that an intervalence band must exist, which Carol Creutz then located in the near infra red region (λ_{max} = 1570 nm) where it does not affect the color (heretofore this region of the spectrum had been little investigated by chemists). Intervalence absorption corresponds to using the energy of a photon to transfer an electron from the reduced to the oxidized metal center, subject to the Franck-Condon restriction. Intervalence

absorption confers on Prussian Blue its characteristic blue color. The interva-
lence absorption is at longer wave length for species I than for Prussian Blue
because the two iron sites in the latter are not substitutionally equivalent. This
leads to a ground state energy difference which is then added to that associated
with the Franck-Condon barrier when the process is induced by a quantum of
light.

   One of my main interests in the field of mixed valence molecules has been to
explore and to try to understand the energetics of the systems. I will illustrate
by a single example the kind of conclusion which we have reached in pursuing
these interests and where we have relied on theory introduced into the field by
Hush (85), by Mulliken (90), and for the correlation of extent of electron
delocalization with electronic structure, Mayoh and Day (91), and choose for
illustration the localized mixed valence molecule (92)

$$[(NH_3)_5RuN\underset{}{\bigcirc}\underset{}{\bigcirc}NRu(NH_3)_5]^{5+}$$
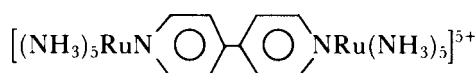
The stability conferred on the ground state of the molecule by charge delocali-
zation is only of the order of 50 cal, far below the upper limit of 5×10^2 cal set by
the electrochemical results, which measure the total stabilization of the mixed
valent compared to the isovalent state. When the nuclear coordinates about
each center are adjusted so that the Franck-Condon condition is met, the
energy separating the bonding and anti-bonding states which arise from elec-
tron delocalization is calculated as 2.2 kcal (93). This is taken to be sufficient to
ensure adiabatic transfer (94) in agreement with the conclusion reached in the
course of studying intramolecular electron transfer in Co(III)-Ru(II) systems
with 4,4'-bipyridine and related molecules as bridging ligands (76). If electron
transfer is assumed to be adiabatic, the specific rate for intramolecular electron
transfer is calculated as $3 \times 10^8 s^{-1}$, in reasonable agreement with an estimate
$(1.6 \times 10^8 s^{-1})$ reached from measurements of intermolecular electron transfer
rates for pyrinedinepentaammineruthenium species (95).

   Mixed valence molecules have been prepared (96) which are delocalized
even though the bridging group is so large that direct metal-to-metal orbital
overlap cannot be responsible for the delocalization. These have remarkably
interesting properties in their own right, and are the subject of current studies
(97).

CONCLUDING REMARKS

In this paper I have focussed rather narrowly on electron transfer reactions
between metal complexes. The separation of this subclass from other possible
ones which can be assembled from the reactant categories: metal complexes,
organic molecules (98) molecules derived from other non-metallic elements,
any of the above in excited states (99, 100), electrodes, is not totally arbitrary as
it might be were it dictated solely by limitations of space. Admittedly, all the
possible electron transfer processes are governed by the same principles, at
least when these are stated in a general enough way. But as these principles

manifest themselves in the different subclasses, the descriptive chemistry can be quite different, and these differences are the fabric of chemistry. The subclass which has been treated has perhaps been the most thoroughly studied, yet, as the article by Sutin shows (36), our understanding at a basic level is far from complete. Even for the much studied Fe^{3+}/Fe^{2+} self exchange reaction, which served to introduce this subject, the important question of whether the reaction is adiabatic or not has not been settled to everyone's satisfaction. Still a great deal of progress has been made. The descriptive matter has increased enormously since 1940, and our understanding of it, both in scope and depth, has more than kept pace with observations. A great deal of progress has also been made in many of the other subclasses - for example in the study of electrode processes, and in "atom transfer" reactions (as a specific case the use of transition metal species to carry the oxidizing capacity of O_2 to a substrate such as an organic molecule).

Both are of the greatest importance in industrial applications, and the latter also in reaching an understanding of the chemistry of living cells. Because the subclasses are interrelated, progress in one leads to progress in another.

REFERENCES

(1) Progress in Inorganic Chemistry, Vol. 30. (Editor, S. J. Lippard), Wiley & Sons, N. Y., 1983.

(2) von Hevesy, G.; Zechmeister, L., Ber. (1920) 53, 410.

(3) Seaborg, G. T. Chem. Rev. (1940) 27, 199.

(4) Kennedy, J.; Ruben S.; Seaborg, G. T.: see Ref. 3, p 256.

(5) This descriptor and that following were introduced by R. A. Marcus (Faraday Society Discussions (1960) 29, 21. J. Phys. Chem. (1963) 67, 853) in proposing an equation which correlates the specific rate for a "cross reaction" such as
$$Fe^{3+} + V^{2+} \rightleftharpoons Fe^{2+} + V^{3+}$$
with the specific rates of the component "self exchange" reactions $Fe^{3+/2+}$ and $V^{3+/2+}$. Allowance is made in the equation for the effect of driving force on the rate.

(6) Dodson, R. W., J. Am Chem. Soc. (1950) 72, 3315.

(7) Silverman, J.; Dodson, R. W., J. Phys, Chem. (1952) 56, 846.

(8) Lewis, W. B.; Coryell, C. D.; Irvine, S. W., Jr. J. Chem. Soc. (1949) S386.

(9) The descriptor "inner sphere" is used for a reaction in which oxidant and reductant metal centers are linked through primary bonds to a bridging group. In the early work it was assumed that the bridging group would play a special role in the electron transfer reaction. In more recent work on intramolecular transfer (vida infra) examples have been found of systems in which the bridging group seems to serve only to hold the two partners together. "Inner sphere" or "outer sphere"?

(10) Holstein, T., J. Phys, Chem. (1956) 56, 832.

(11) Libby, W. F., J. Phys. Chem. (1956) 56, 863.

(12) As a historical note, I wish to add that James Franck was very much interested in electron transfer in chemical reactions and fully appreciated the importance of keeping the Franck-Condon restriction in mind in trying to understand the observations

(13) Brown, H. C., discussion of the paper of ref. 11, p 868.

(14) Libby, W. F., discussion following the paper of ref. 11, p 866. See also Brown, H. C., discussion following paper of ref. 7, p 852.

(15) Dodson, R. W.; Davidson, N., discussion following the paper of ref. 11, p 866.

(16) Taube, H.; Myers, H.; Rich, R. L., J. Am. Chem. Soc. (1953) 7.5, 4118.

(17) Taube, H.; Myers, H., J. Am. Chem. Soc. (1954) 26, 2103.

(18) Taube, H., Chem. Rev. (1952) 50, 69.

(19) The subject of ionic hydration is brought up to date in an article by J. P. Hunt and H. L. Friedman, p 359, ref 1.

(20) Bjerrum, J.; Paulsen, K., Nature (1952) 169, 463.

(21) Eigen, M., Faraday Soc. Discussions, (1954) No. 17, p 1.

(22) Bjerrum, J., Z. Physik. Chem. (1907) 59, 336, 581; Z. Anorg. Allgem. Chem. (1921) 119, 179.

(23) Hunt, J. P.; Taube, H., J. Chem, Phys. (1950) 18, 757; ibid (1951) 19, 602.

(24) Meredith, C. W., U. S. Atomic Energy Rept. UCRL-11704 (1965) Berkeley. Work done under supervision of R. E. Connick.

(25) Candlin, J. P.; Halpern, J., Inorg. Chem. (1965) 4, 766

(26) Taube, H.; King, E. L., J. Am. Chem. Soc. (1954) 76, 4053.

(27) Ball, D. L.; King E. L., J. Am. Chem. Soc. (1958) 80, 1091.

(28) Snellgrove, R.; King, E. L., J. Am. Chem. Soc. (1962) 84; 8609

(29) Taube, H., J. Am. Soc. (1955) 77, 4481.

(30) Ogard, A. E.; Taube, H. J., Am. Chem. Soc. (1958) 80, 1084.

(31) Gjertsen, L.; Wahl, A. C., J. Am. Chem. Soc. (1959) 81, 1572; Sheppard, J. C.; Wahl, A. C., J, Am. Chem. Soc. (1957) 79, 1020.

(32) Sutin, N.; Gordon, B. M., J. Am. Chem. Soc. (1961) 83, 70.

(33) Marcus, R. A., Ann. Rev. Phys. Chem. (1964), 15, 155; also earlier papers.

(34) Hush, N. S., Trans. Faraday Soc. (1961) 57, 557.

(35) Consider the process: $A \cdot B^- \rightarrow [A \cdot B]^- \rightarrow A^- \cdot B$
            I   II

State I is the precursor complex; in state II the energy is independent of whether the electron is on atom A or B, i. e., the Franck-Condon condition has been met. In adiabatic transfer, electron delocalozation is great enough so that whenever state II is reached, electron transfer can take place, and the rate of the chemical reaction is determined solely by the rate at which state II is reached. In non adiabatic transfer, the system passes through state II a number of times before electron transfer occurs, and both the Franck-Condon barrier, and the rate of electron transfer in state II are rate determining.

(36) Sutin, N., p 441 of ref. 1.

(37) Orgel, L. E., Rept X°Conseil Inst. Intern, Chem. Solvay (1956) 289.

(38) George, P.; Griffith, J., Enzymes (1959) 1, 347.

(39) Halpern, J.; Orgel, L. E., Discussions Faraday Soc. (1960) 29, 32.

(40) Zwickel, A. M.; Taube. H., J. Am. Chem. Soc. (1959) 81, 2915.

(41) Halpern, J.; Nakamura, S., J. Am. Chem. Soc. (1965) 87, 3002.

(42) Dulz, G.; Sutin, N., J. Am. Chem. Soc. (1964) 86, 829.

(43) Connochioli T. J.; Nancolles, G. H.; Sutin, N., J. Am. Chem. Soc. (1969) 86, 1453.

(44) Connochioli T. J.; Nancolles, G. H.; Sutin, N., J. Am. Chem. Soc. (1964) 86, 459.

(45) Sykes, A. G.; Thorneley, R. N. V., J. Chem. Soc. (1970) A232.

(46) Espenson, J. H., J. Am. Chem. Soc. (1967) 89, 1276.

(47) Price, H. J.; Taube, H., Inorg. Chem. (1968) 7, 1

(48) Haim, A.; Sutin, N., J. Am. Chem. Soc. (1965) 87, 4210.

(49) Fronaeus, S.; Larsson, R., Acta Chem. Scand. (1962) 16, 1447.

(50) Espenson, J. H.; Birk. J. P., J. Am. Chem. Soc. (1965) 87, 3280; ibid, (1968) 90, 1153.

(51) Kruse, W.; Taube, H., J. Am. Chem. Soc. (1960) 82, 526

(52) Toppen, D. L.; Linck, R. G., Inorg. Chem. (1971) 10, 2635.

(53) Basolo, F.; Morris, M. L.; Pearson, R. G., Disc. Faraday Soc. (1960) 29, 80.

(54) Anet, F. A. L.; Leblanc, E., J. Am. Chem. Soc. (1957) 79, 2649.

(55) Espenson, J. H.; p. 189 of the volume of ref. 1.

(56) Last in the series. Fraser, R. T. M. and Taube, H., J. Am. Chem. Soc. (1961) 83, 2239

(57) I owe my associates during my first years at Stanford an enormous debt of gratitude for helping to set the record straight. Special thanks are due to E. S. Gould, who first uncovered discrepancies, and to J. K. Hurst who repeated much of the dubious earlier work.

(58) Nordmeyer, F. R.; Taube, H., J. Am. Chem. Soc. (1966) 88,4295; ibid (1968) 90, 1162.

(59) The relation between reducibility of the ligands, and their effectiveness in mediating electron transfer was developed in an earlier paper. Gould, E. S.; Taube, H., J. Am. Chem. Soc. (1964) 86, 1318.

(60) Sebera, D. K.; Taube, H., J. Am. Chem. Soc. (1961) 83, 1785.

(61) See, for example: Gould E. S., J. Am. Chem. Soc. (1972) 94, 4360.

(62) Endicott, J. F.; Taube, H., J. Am. Chem. Soc. (1962) 84, 4989; ibid (1964) 86, 1686; Inorg. Chem. (1965) 4, 437.

(63) Gleu, K.; Breuel, K., Z. Anorg. Allg. Chem. (1938) 237, 335.

(64) Gaunder, R.; Taube, H., Inorg. Chem. (1970) 9, 2627.

(65) Anderson, A.; Bonner, N. A., J. Am. Chem. Soc. (1954) 76, 3826.

(66) Indirect evidence, which is quite convincing, suggests the outer sphere self exchange rate for $Cr(H_2O)_6^{3+}/Cr(H_2O)_6^{2+}$ to be $\sim 5 \times 10^{-10} M^{-1} s^{-1}$. Melvin, W. S.; Haim. A., Inorg. Chem. (1977) 16, 2016.

(67) Meyer, T. J.; Taube, H., Inorg. Chem. (1968) 7, 2369.

(68) Stynes, H. D.; Ibers, J. A., inorg. Chem. (1971) 10, 2304.

(69) Calculations of the barrier associated with inner sphere electron reorganization leave room for a non-adiabaticity factor of a few orders of magnitude. See Endicott, J. F.; Krishan, K.; Ramasami, T; Rotzinger, F. P., p 141 of ref. 1.

(70) Isied, S. S.; Taube, H., Inorg. Chem. (1976) 15, 3070.

(71) Meyer, T. J.; Taube, H., Inorg. Chem. (1968) 7, 2361.

(72) Harrison, D. E.; Taube, H., J. Am. Chem. Soc. (1967) 89, 5706.

(73) Robson, R.; Taube, H., J. Am. Chem. Soc. (1967) 89,6487; French, J.; Taube, H., J. Am. Chem. Soc. (1969) 91, 6951, earliest example: Saffir, P., J. Am. Chem. Soc. (1960) 82, 13.

(74) Hoffman, M. Z.; Simic, M., J. Am. Chem. Soc. (1972) 94, 1957.

(75) (a) Isied, S. S., J. Am. Chem. Soc. (1973) 95, 8198.
    (b) In an earlier effort, Kirk Roberts tried the simple procedure of mixing the Co(III) complex with $(NH_3)_5RuOH_2^{2+,2+}$ Substitution is too slow relative to intramolecular transfer for the method to work in these systems.

(76) Fischer, H.; Tom, G. M.; Taube, H., J. Am. Chem. Soc. (1976) 98, 5512.

(77) Schäffer, L. - work in progress.

(78) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M., Inorg. Chem. (1983) 22, 846.

(79) Gaswick, D. G.; Haim. A., J. Am. Chem. Soc. (1974) 96, 7845.

(80) Haim, A. see p 273 of ref. 1.

(81) Winkler, J. R.; Nocera, D. G.; Yocom, K. M.; Bordignon, E.; Gray, H. B., J. Am. Chem. Soc. (1982) 104, 5798.

(82) Isied, S. S.; Worosila, G.; Atherton, S. J., J. Am. Chem. Soc. (1982) 104, 7659.

(83) The level of current activity in the field can be gauged by the recent review of the subject of mixed valence molecules based on $\pi d^5/\pi d^6$ couples by C. Creutz: see ref. 1, p 1.

(84) Allen, G. C.; Hush, N. S., Prog. Inorg. Chem. (1967) 8, 357.

(85) Hush, N. S., Prog. Inorg. Chem. (1967) 8, 391.

(86) Robin, M. B.; Day, P., Ad. Inorg. Chem. Radiochem (1967) 10, 247.

(87) Creutz, C.; Taube, H., J. Am. Chem. Soc. (1969) 91, 3988; ibid (1973) 95, 1086.

(88) Cowan, D. 0.; Kaufman, F., J. Am. Chem. Soc. (1970) 92, 219.

(89) Ford, P.; Rudd, de F. P.; Gander, R.; Taube, H., J. Am. Chem. Soc. (1968) 90, 1187.

(90) Mulliken, R. S.; Person, W. B., Molecular Complexes; Wiley, New York (1969) Chapter 2.

(91) Mayoh, B.; Day, P., J. Am. Chem. Soc. (1972) 94, 2885; Inorg. Chem. (1974) 13, 2273.

(92) Tom, G. M.; Creutz, C.; Taube, H., J. Am. Chem. Soc. (1974) 96, 7828.

(93) Sutton, J, E.; Sutton, P. M.; Taube, H., Inorg. Chem. (1979) 18, 1017. Sutton, J. E.; Taube, H., Inorg. Chem. (1981) 20, 3125.

(94) Sutin, N., Inorganic Diochemistry, Vol. 2, G. L. Eichhorn, Ed., American Elsevier, N. Y. (1973), p611.

(95) Brown, G. M.; Krentzien, H. J.: Abe, M.; Taube, H., Inorg. Chem. (1979) 18, 3374.

(96) Lay, P. A.; Magnuson, R. H.; Taube, H., J. Am. Chem. Soc. (1983) 105, 2507.

(97) Spectroscopic studies by J. Ferguson and co-workers (Australia National University) are in progress.

(98) Sheldon, R. A.; Kochi. J., Metal Catalyzed Oxidations of Organic Compounds. Academic Press, New York, 1981.

(99) Ford, P.; Wink, D.; Dibenedetto, J., p 213 ofref. 1.

(100) Meyer, T. J., p 389 of ref. 1.