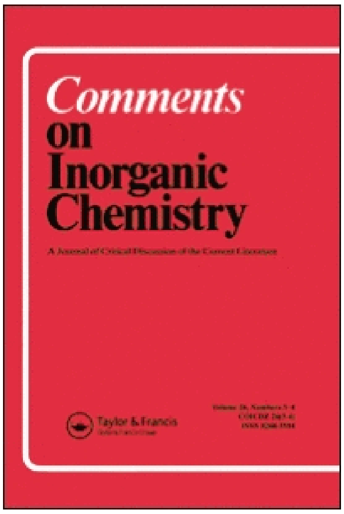

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Experimental Approaches to Measurement of Intramolecular Electron Transfer Rates

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To cite this Article Richardson, David E.(1985) 'Experimental Approaches to Measurement of Intramolecular Electron Transfer Rates', Comments on Inorganic Chemistry, 3: 6, 367 — 384

To link to this Article: DOI: 10.1080/02603598508079692

URL: http://dx.doi.org/10.1080/02603598508079692

Experimental Approaches to Measurement of Intramolecular Electron Transfer Rates

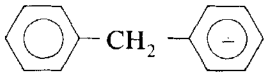
Various techniques used for the measurement of intramolecular electron-transfer rates in inorganic systems are considered, and recent applications are described. The methods include electron paramagnetic resonance, Mossbauer spectroscopy, nuclear magnetic resonance, vibrational spectroscopy, dielectric relaxation, pulse radiolysis, photochemistry, electrochemistry, and chemical approaches.

INTRODUCTION

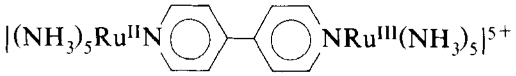
The study of oxidation-reduction reactions has in recent years entered a new phase where intramolecular electron-transfer (IET) processes are probed using increasingly sophisticated synthetic and experimental approaches. The majority of the effort expended has been directed toward a better understanding of the myriad of factors that control the rates of these fundamental redox phenomena. The purpose of this Comment is to provide an overview of the experimental techniques that have been used to study IET in inorganic (usually transition metal) systems. Reference will also be made to analogous experiments dealing with organic radical systems to point out the potentials and limitations of particular methods. A complete review is certainly not intended, but specific examples have been chosen to illustrate recent applications of the techniques. The interpretation of these experiments in light of modern electron-transfer theory will not be considered in any great detail, as excellent reviews are available elsewhere.[1-4]

Comments Inorg. Chem.
1985, Vol. 3, No. 6, pp. 367–384
0260-3594/85/0306-0367/$20.00/0

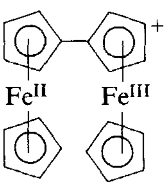
For organizational purposes, one can divide IET into two distinct chemical classes: symmetrical and asymmetrical. In the symmetrical cases, no net change occurs after the IET event and the ΔG° for the process is zero. A large number of examples exist for this class, and some are shown as **I–IV** below[5-8]:



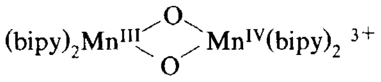
I



II



III

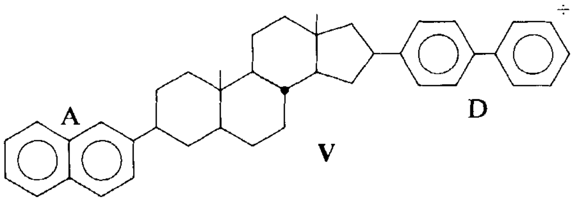


$$(\mathrm{bipy})_2\mathrm{Mn}^{\mathrm{III}}\begin{array}{c}\mathrm{O}\\ \mathrm{O}\end{array}\mathrm{Mn}^{\mathrm{IV}}(\mathrm{bipy})_2\ {}^{3+}$$

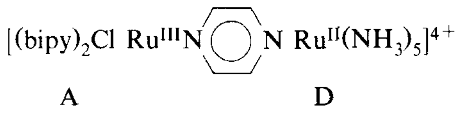
IV

Radical **I** is a prototype for organic systems in which the unpaired spin is localized on one acceptor site (usually aromatic). Using EPR, the rate at which the unpaired electron moves between the two available acceptor sites can be determined (*vide infra*).[5] Examples **II–IV** are symmetrical mixed-valence systems, which include both soluble, discrete dimers as shown and extended lattice compounds.[9-11] The lifetime of the extra electronic charge on an acceptor site will depend upon a number of factors, including the temperature, the solvent, the chemical nature of the acceptor, and the structure of the bridging group.[1,3]

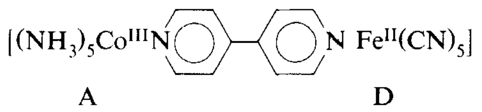
In the asymmetrical class, numerous examples of organic radicals (**V**)[12] and transition-metal systems (**VI**,[14] **VII**[15]) are known.



V



VI



VII

In each of the molecules **V**–**VII**, the oxidation states are shown in the thermodynamically *unstable* form with the odd electron on a donor site (D). Radical **V**, for example, decays to the more stable acceptor (A) naphthyl radical with $t\frac{1}{2} = 1$ μs.[12,13] Similarly, the metal complexes **VI** and **VII** will undergo IET to reduce the more strongly oxidizing centers ($(\text{bipy})_2\text{ClRu}^{\text{III}}$ and $(\text{NH}_3)_5\text{Co}^{\text{III}}$, respectively).[14,15]

The experimental techniques used to estimate or accurately determine IET rates in symmetrical systems are, with a few exceptions, different from those used for the asymmetrical cases. Put another way, some methods require a finite value of $\Delta G°$, while others are sensitive to the average time which one of two or more equivalent electronic states exists in a system with no net change.

DETERMINATION OF RATES IN SYMMETRICAL SYSTEMS

In the area of IET in symmetrical systems, very little is known about the absolute rates of electron exchange, and, in most cases, spectroscopic methods can provide only upper or lower limits on the value of k_{IET} by comparison to the timescale of the experiment (τ, given in s, see Table I). The rate may sometimes fall in a region accessible by line broadening techniques, and one can occasionally observe the transition from a localized ($k_{\text{IET}} << 1/\tau$) to delocalized ($k_{\text{IET}} >> 1/\tau$) behavior with measurements over a large temperature range.

Electron Paramagnetic Resonance

The earliest applications of EPR to IET involved organic radicals similar to I. Interest in this approach for radical systems has con-

TABLE I. Characteristic Timescales for Experimental Approaches to IET Rates

Method	τ,s
Electron paramagnetic resonance	
Organic radicals[a]	10^{-8}–10^{-5}
Transition metals[b]	10^{-9}–10^{-8}
Mossbauer spectroscopy[c]	10^{-9}–10^{-6}
Nuclear magnetic resonance[d]	$\sim 10^{-5}$
Vibrational spectroscopy	$\sim 10^{-13}$
Dielectric relaxation[e]	10^{-9}–$> 10^{-6}$
Pulse radiolysis[f]	$\gtrsim 10^{-9}$
Photochemical	$> 10^{-12}$
Electrochemical[g]	$\gtrsim 10^{-6}$
Chemical methods	[h]
Temperature jump	$> 10^{-8}$

[a] Timescale depends on the linewidths and hyperfine splittings of specific systems (see Ref. 69). Limits shown are typical for aromatic radicals (see Ref. 70).

[b] Given values are typical for normal Cu(II) with A $\simeq$ 40G (see Ref. 18).

[c] Timescale depends on linewidths and quadrapole splitting parameters. Limits given are typical for iron.

[d] Timescale depends on linewidths and spin coupling constants. Value given is typical for proton NMR.

[e] Limit on longer lifetimes not experimentally known at present.

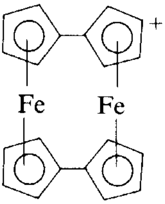
[f] Assuming the experiment outlined in equation 1 in the text, the rate constant for initial reduction is taken as 10^{10} $M^{-1}s^{-1}$ with the acceptor molecule at $\sim$1 M.

[g] Measurements at higher frequencies are complicated by inductive components of the circuits employed and, in some cases, distortions due to IR drop (M. Weaver, private communication).

[h] Highly dependent on natures of reducing center and acceptor, concentrations of reactants, free energy of initiation reaction, etc. (see Ref. 2).

tinued into this decade, and a large variety of related molecules have been studied.[16] When the radicals are generated in the presence of an excess of acceptor sites, the hyperfine interaction of the unpaired spin with the nuclear spins can be used to obtain the rates of electron exchange. If the radical is distributed equally over both acceptor sites (i.e., $k_{IET} >> 1/\tau$), the number of hyperfine lines observed will reflect interaction with all nuclear spins at both sites. In addition, the hyperfine coupling constant (A) will generally be half that observed in similar localized radicals or single acceptor site analogues (e.g., the toluene anion for I). Techniques for simulation of spectra in the intermediate region ($k_{IET} \simeq 1/\tau$) are available,[17] and the quality of the fits indicates that the deduced values of k_{IET} are reasonably reliable. However, interpretation of the rates requires caution, and accounting for such effects as ion pairing and intermolecular exchange can be difficult.

When the application of EPR to metal systems is considered, the situation becomes far more complex due to factors such as the potentially large g tensor anisotropy, unpredictable spin-lattice relaxation effects, and the typically broad resonances, to name a few. As a result, EPR has been used more qualitatively to estimate the limits on k_{IET} in metal systems. The application to symmetrical mixed-valence systems is nicely illustrated by the studies of Hendrickson and co-workers[18-22] and others[23,24] on numerous ferrocene–ferrocinium and cuprous–cupric dimers. The oxidized biferricenium ion **III** has an axial EPR spectrum found to be typical of localized valencies in this type of mixed-valence compound ($g_{\parallel} = 3.58$, $g_{\perp} = 1.72$ for the triodide salt at 12K). On the other hand, the biferricenylenium ion **VIII** has a rhombic EPR spectrum



VIII

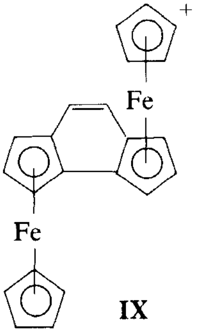
with a much reduced g-tensor anisotropy ($g_1 = 2.39$, $g_2 = 1.99$, $g_3 = 1.88$) and relatively narrow lines widths at 12K. This general type of spectrum in the oxidized biferrocenes is attributed to a delocalized ground state where the barrier to electron transfer is small or absent.

In some of the copper dimers studied,[18,23] it is possible to observe a temperature dependence in the solution EPR spectra that indicates a delocalized system at room temperature (seven lines due to the equivalent interaction with two $I = 3/2$ copper nuclei) and localization at low temperatures (a poorly resolved four-line pattern). From the "coalescence" temperature, it is possible to estimate the activation barriers to IET, but these values can only be considered very approximate. In principle, an improvement in the interpretations of the dynamics of these dimers would be possible with simulations, but variables such as temperature-dependent solvent viscosities and ion-pairing effects make this approach difficult to apply. However, Sanchez *et al.*[25] used peak-to-peak linewidths to estimate IET rates and associated thermal barriers of electron hopping in molybdenum polyanions.

Mossbauer Spectroscopy

The application of Mossbauer spectroscopy to measurement of IET rates is limited to only a few nuclei, with studies of iron mixed-valence compounds predominating. As in EPR, the rate of IET can be in principle accurately determined over a fairly broad timescale ($\sim 10^6$–$10^9\ s^{-1}$), but the more usually observed spectra indicate either localization or delocalization at all temperatures studied.

A few examples of strongly temperature dependent Mossbauer spectra are known for mixed-valence compounds. The studies by Berkooz *et al.* on Eu_3S_4 show a change from a delocalized spectrum at $T > 300$ K to a localized system with distinct Eu(III) and Eu(II) components at liquid nitrogen temperature.[26] Rates at various temperatures were estimated using a line shape model based on an activation barrier analysis for IET. The same model was used by Iijima *et al.*[27] to interpret the temperature-dependent Mossbauer spectra of **IX**,



IX

and values of k_{IET} at 100 K ($1.4 \times 10^7\ s^{-1}$) and 300 K ($2.0 \times 10^8\ s^{-1}$) were derived. Lupu *et al.*[28] and Brown and co-workers[29,30] studied the temperature-dependent spectra of $[Fe_2^{II}Fe_2^{III}O(CH_3COO)_6L_3] \cdot 5H_2O$ ($L = H_2O$ or pyridine), a trimeric mixed-valence iron acetate, and the latter authors attempted to derive rate constants from a intratrimer electronic relaxation model. Since solid samples are often used, temperature-dependent lattice effects must also be considered, but this variable has not generally been included in the spectral analyses.

Nuclear Magnetic Resonance

The potential of NMR line broadening for the study of bimolecular self-exchange rates for transition metals has been appreciated for some time, and examples of its use have appeared.[31-34] However, the reported applications to IET are limited. One must often contend with the effect of paramagnetic shifts on the spectrum, and the time scale is rather slow compared to many IET processes ($\sim 10^5$ s^{-1} for proton NMR). For a system with appropriate nuclei and range of k_{IET}, the NMR technique would appear to have as much utility as the faster EPR and Mossbauer methods. Further work in this domain would be of great interest.

Vibrational Spectroscopy

Infrared and Raman spectroscopy can be used to estimate the timescale of IET when oxidation states have different characteristic vibrational frequencies. The timescale of the technique is about 10^{13} s^{-1}, and IR spectroscopy has been used to examine both valence delocalized and localized systems.[19-21,30,35,36] Unlike EPR, Mossbauer, and NMR, the potential for interference due to unrelated nearby transitions is substantial, but examples of "mode averaging" in delocalized species have been reported. The adherence to group theoretically derived selection rules in infrared and Raman experiments may provide evidence for the symmetry of the ground state. In principle, line-broadening techniques could be used to estimate rates, but this has not been reported for mixed-valence systems. In addition, it is recognized that the dynamics of mixed-valence compounds are closely tied to electron-vibrational coupling. This would appear to complicate interpretation in the intermediate ($k_{\mathrm{IET}} \simeq 1/\tau_{\mathrm{vib}}$) region, especially in complex systems where electronic motion is coupled to a number of vibrational modes.

Dielectric Relaxation and Conductivity

Drago and co-workers[37,38] have explored the usefulness of time domain reflectometry (TDR) in the measurement of k_{IET} in mixed-valence compounds. They have published details of experiments on mixed-valence europium sulfide, and, when combined with unpublished data,[39] their work indicates that TDR can find significant application in the study of IET.

The essence of the TDR method is the measurement of dielectric relaxation phenomena in samples mounted between two contacts in a capacitor-like arrangement. In an isotropic sample, the direction of the dipole moments will tend to follow an applied electric field.

When the field is stepped to a new value (within 40 ps in the work of Bunker et al.[37,38]), a number of relaxation events can occur in approach to a new equilibrium, and for mixed-valence materials one such process is IET. By comparison of observed traces to those of isovalent analogs, the presence of an IET relaxation process can be ascertained. The practical high frequency limit for TDR is $> 10^9$ s^{-1}, with the limit defined by instrumental risetime and inherent attenuation of signals by the coaxial cables employed. The low frequency limit is not known entirely, but values down to 10^6 s^{-1} are easily detected with current equipment.

For Eu_3S_4, the thermal barrier to electron-transfer was estimated as 0.177 eV by TDR,[38] which can be compared to the activation energy from conductance studies of 0.163 eV. The Mossbauer studies of Berkooz *et al.* result in a barrier of 0.277, but Bunker, Drago, and Kroeger[37] discuss limitations of the Mossbauer approach and suggest that the theory is not sufficient to derive meaningful activation parameters from the temperature-dependence in the case of Eu_3S_4. The relationship between rates of dielectric relaxation and conductivity has been examined by Rosseinsky *et al.*,[40] who studied the properties of mixed-valence potassium manganate–permanganate, $K_3(MnO_4)_2$, in the temperature range 200–400 K. They find an excellent correspondence between Arrhenius activation parameters derived from the two approaches. In addition, the barriers obtained for the solid were comparable to that observed in aqueous solution for the manganate–permanganate self-exchange reaction ($E_{aq} = 11 + 1$ kcal $mole^{-1}$, $E_{cond} = 11.0 \pm 0.25$ kcal $mole^{-1}$, $E_{diel} = 12.2 \pm 1.2$ kcal $mole^{-1}$). This latter result tends to support the contention of Drago and coworkers that the Mossbauer results on Eu_3S_4 are suspect, but the nonstoichiometric nature of their sample[38] may account in part for the difference in derived activation barriers.

DETERMINATION OF RATES IN ASYMMETRIC SYSTEMS

The techniques discussed above for symmetrical IET are ground state methods where no higher energy electronic state is involved. (An exception would be resonance Raman spectroscopy, where information on excited electronic states can be obtained via excitation profiles.) The inclusion of asymmetry in related systems will tend to localize the ground state with the population of higher energy states being determined by the Boltzmann distribution. Unless the value of ΔG° is $\leq kT$, the spectroscopic approaches outlined above are of no practical value in measuring IET rates in asymmetric systems with weak electronic coupling between acceptor sites, since the ground state is effectively localized. If a strong electronic interaction between acceptor sites is present, delocalization can be retained in asymmetric systems.

In the case of anionic organic radicals, the unpaired spin would reside primarily on the acceptor site with the higher electron affinity. In localized, asymmetric mixed-valence compounds and related heteronuclear complexes, the thermodynamically stable form is determined by the reduction potentials of the metal centers. Rates of IET for numerous types of asymmetric compounds have been measured using techniques such as pulse radiolysis, photochemistry, electrochemistry, and chemical synthesis. All of these approaches rely on generation of a thermodynamically unstable form of the system which then decays to the ground state (ostensibly via IET, although this point is not always clear!). While providing for ease of distinguishing initial and final states, the presence of an excited state(s) also can complicate interpretation of the results. Perhaps of greatest concern in some experiments is identification of the "transient" state from which the measured decay to the ground state occurs. This is usually accomplished by determining the spectral properties of the intermediate followed by comparison to known electronic and structural analogs.

Pulse Radiolysis

Radiolysis represents one of the more versatile and adaptable methods for generating transient redox states.[41,42] The hydrated electron, e_{aq}^-, is a strong reducing agent ($E^\circ = -2.8$V), and other less powerful reductants can be generated rapidly with addition of appropriate acceptors (e.g., CO_2, alcohols). Solutions saturated with N_2O are used to produce the strong oxidant OH ($E^\circ \simeq 2$V). In addition, a vast amount of data is available on radiolysis of organic and metal species to aid in planning experiments.[42,43]

The pulse width used in radiolysis can be on the order of picoseconds, with values up to > 10 ns being employed when appropriate. The second-order rate constants for reduction of acceptor molecules by e_{aq}^- cover a large range, but for reasonably oxidizing metal centers (e.g., Co^{III}, Cr^{III}, Ru^{III}) they are in the range of 10^{10}–10^{11} M^{-1} s^{-1}.[42] When two acceptor sites are in the same molecule, indiscriminate reduction of the sites may occur yielding a thermodynamically unstable state in some fraction of the reduced forms

$$\begin{tikzcd}
{[D - A]} \arrow[r, "\text{pulse}", "e_{aq}^{-},\ R^{\dot{-}},\ \text{etc.}"'] & {[D - A^{-}]} & {+} & {[D^{-} - A]} \arrow[ll, bend left, "\text{IET}"]
\end{tikzcd} \qquad (1)$$

The decay of the unstable $[D^{-} - A]$ form is then followed to determine the value of k_{IET}. Typically, the change in optical absorbance during the process is followed with sensitive photomultiplier detectors.

The recent work of Miller, Closs, and co-workers[12,13,44] using organic radicals nicely illustrates the potential of the technique in the measurement of IET rates. They have synthesized asymmetric biacceptor molecules with a rigid steroidal bridging group. The two acceptor sites (e.g., D = biphenyl, A = naphthyl, V) are separated by ~15Å, and the pulse rapidly generates a portion of unstable $[D^{-} - A]$ molecules. When the $\Delta G°$ for the decay to ground state is varied by changes in the nature of A, the k_{IET} is observed to vary from 10^6 s^{-1} to > 10^9 s^{-1}. Using this approach, Miller *et al.*[12] provided strong evidence for the existence of the "inverted" region theoretically predicted many years ago for strongly exothermic redox reactions.

Many IET systems initiated by pulse radiolysis and involving metal centers have been reported. A number of studies concerning intramolecular reduction of Co^{III} by a bound ligand radical have demonstrated the function of "lead-in" groups in the redox reactions of metal ions.[45-47] The initial reduction produces a radical species identifiable by its optical absorption spectrum or EPR (Eq. 2). Following IET (Eq. 3), the molecule rapidly aquates (Eq. 4):

$$Co^{III} - L + e_{aq}^{-} \rightarrow Co^{III} - L^{\dot{-}} \qquad (2)$$

$$Co^{III} - L^{\dot{-}} \xrightarrow{\text{IET}} Co^{II} - L \qquad (3)$$

$$Co^{II} - L \xrightarrow{\text{irrev}} Co^{II} + L. \qquad (4)$$

Lead-in groups studied in this way include nitrophenyls,[45] imidazole,[46] and pyrazines,[47] and the importance of the ligand structure on the rates of IET is clearly seen. If the Co^{III} center is separated from the radical by methylene spacers, a reduction in k_{IET} occurs. Additionally, the substitution pattern on aromatic rings is important, and this has been explained by the variation in unpaired spin density in the ring system.

There are few examples using pulse radiolysis where both acceptors are metal centers. The elegant studies of Isied and co-workers[48] on ruthenium modified cytochrome c point to the potential of this approach for measurement of IET rates in binuclear metal complexes. In Isied's experiment, histidine(33) of horse-heart cytochrome c was bound to pentaammineruthenium(III) with the heme iron in the ferric state. The radiolytic pulse generated a mixture of $[Fe^{II}\ Ru^{III}]$ and $[Fe^{III}\ Ru^{II}]$, the latter being unstable. The rather slow IET was followed at 550 nm and k_{IET} was found to be $< 100\ s^{-1}$ at 25°C. Especially noteworthy was the variation in the initial concentration of the $[Fe^{III}\ Ru^{II}]$ form with reducing agent, with the fraction produced ranging from 35% (2-propanol radical) to > 95% (pentaerythritol radical). The selectivity in these experiments is probably associated with the complexity of reduction kinetics for the metalloprotein, but clever synthesis may produce molecular dimers where similar effects could be seen.

Photochemical Methods

With the advent of picosecond pulsed laser technology, the photophysics of metal complexes opened a new approach to measurement of rapid IET rates. One strategy has been to prepare a dimeric system where one metal center is photosensitive to a laser line. The excited state created may be either a stronger oxidant and/or reductant depending on the specifics of the complex. For example, Norton and Hurst[49] studied long range electron transfer in Co(III)–Cu(I) binuclear ions using a pulsed laser in the visible and near UV. The Cu(I) center was π-bonded to an alkenyl bridging ligand (e.g., 4-vinylpyridine), and excitation of the Cu(I) $\rightarrow \pi^*$ MLCT band creates a strongly reducing center. IET to form Co(II) was observed to occur with a $t½ < 10$ ns, which was said to be more rapid than conformational rearrangements of the flexible bridging ligands.

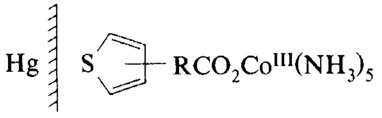
On the other hand, Reagor *et al.*[50] studied the picosecond photochemistry of $(NC)_5Fe^{II}$–CN–$Co^{III}L$, where a light pulse was used to form a more strongly oxidizing Co^{III} center. Excitation into the Co(III) ${}^1T_{1g} \leftarrow {}^1A_{1g}$ band led to rapid reduction of the Co^{III} to $Co^{II}({}^2E)$ by the Fe(II) center ($t½ < 1$ ps).

Creutz *et al.*[51] used flash photolysis (pulse width ~8 ps) to study the IET rate in asymmetric mixed-valence complex $[(NH_3)_5Ru^{II}$ (μ-pyrazine) $Ru^{III}(EDTA)]^+$. Excitation into a $(NH_3)Ru^{II} \rightarrow$ pyrazine charge transfer band in the visible region apparently is followed by decay to the transient unstable form $[(NH_3)_5Ru^{III}$ N  N $Ru^{II}(EDTA)]^+$ rather than to the ground state directly. Decay to the intermediate state was thought to be favored by energy gap considerations, which applies for "imbedded" potential surfaces. The value of k_{IET} was estimated as $0.8 \times 10^{11}\ s^{-1}$, which is comparable to the value calculated from the optical intervalence transfer band (*vide infra*), $5 \times 10^{11}\ s^{-1}$. This particular work is notable in that it is one of a few cases[25,30] where optical and thermal intervalence transfer are compared in a solvated binuclear molecule.

Electrochemical Methods

Electrochemical methods have typically not been considered as an approach to the study of IET by those concerned with solvated molecules or solid state phenomena. This may in part be due to the notion that a heterogenous system with a solid/solution interface is difficult to characterize and understand in comparison to homogeneous processes. Considering a conducting metal electrode such as mercury or platinum, it is well known that the valence electrons are incorporated into a partially filled band to yield a continuum of states. This would seem at first glance to make the application of traditional ET theory suspect in the sense that the orbital-to-orbital picture usually envisioned for bimolecular reactions cannot apply. However, as Marcus has pointed out,[52] transfer to and from the electrode surface will involve only states near the Fermi level of the metal (within about kT). Therefore, the theoretical basis for heterogeneous and homogeneous ET processes are very much alike, and an electrode can be considered to be one-half of a redox pair.

With the above concepts established, one can also speak of inner-sphere and outer-sphere ET at electrodes, and a few studies demonstrating the usefulness of electrochemistry in determination of bridge-assisted IET rates have appeared. In the method of Weaver and co-workers,[53–56] pentaamminecobalt(III) complexes with a potentially bridging ligand were reduced at platinum or gold electrodes. For halide complexes, the inner-sphere contribution to the overall rate was found to exceed that of the outer sphere. In a series of experiments using thiophenecarboxylates as the bridging ligand to a mercury electrode (X), the inner-sphere rates were found to be lower when saturated linkages separated the thiophene and carboxylate groups



X

The selection of thiophene was based on its affinity for the mercury electrode, and a prequilibrium model was used to extract estimated values of k_{IET} from the apparent rate constants. The estimated values from this model agreed with the directly determined values of k_{IET}, demonstrating the similarity between electron-transfer at surfaces and bimolecular redox reactions in solution. Hupp *et al.*[57] have considered the application of contemporary theories to electrochemical reactivities, and the comparisons with experiment are encouraging. Some discrepancies are noted, and explanations specific to the nature of the electrode surface are offered.

Finally, it is clear that the fundamental studies being carried out by Weaver and others will have significant implications for the design of catalytically modified electrodes, where ET and IET rates to attached or adsorbed species are of paramount importance.

Chemical Methods

In the chemical initiation of IET, two major approaches have been taken. In the first, the reductant and oxidant are mixed to form a precursor complex of some stability, and electron-transfer proceeds via an electron-hopping or transient radical ("chemical") mechanism.

This classical inner-sphere method has been investigated for many years, and excellent reviews are available.[2,4,58]

In a second method, a binuclear complex containing the oxidized forms of both centers is assembled. A chemical reducing agent (e.g., Cr^{2+}, Eu^{2+}, $Ru(NH_3)_6^{2+}$) is then used to prepare the unstable redox pair which then decays via IET before significant decomposition occurs. The experiment hinges on having a rapid reducing agent which has a kinetic preference for the less strongly oxidizing metal center. This approach has also been adequately reviewed elsewhere,[2] so specific examples will not be offered here.

COMMENTS AND THE FUTURE

It is clear that a wide variety of techniques can be applied to the measurement of IET rates, and no single method is applicable to all or even most systems. To exploit the potential of every method, the emphasis must now be on the *synthesis* of molecules or materials that have the right combination of properties. In choosing one of the ground state techniques for application to symmetrical systems (EPR, Mossbauer, NMR, vibrational spectroscopy, dielectric relaxation), the factor of greatest importance is the absolute rate of IET. Only if this rate falls in the range of the experimental timescale can true rate constants be obtained. Otherwise, one is left to state only whether the value of k_{IET} is substantially greater or less than the experimental timescale. The number of cases in symmetrical systems where a value for k_{IET} has been deduced is quite small, and further work in this area will no doubt appear in the wake of synthetic advances.

While the timescale limitations of approaches for asymmetric systems are not so severe, the dependence of this area on synthesis is also apparent. Interpretation of data from those experiments producing transient, unstable species is complicated by the excited electronic state nature of the intermediate. There is a strong relationship between the theories for IET and those for radiationless decay of excited states, as discussed recently by Meyer.[59] The distinction depends intimately on the relationship between the ground state and excited-state potential surfaces. The participation of a number of intermediate states may be important, and a thorough knowledge of the various available excited states in the system of interest is crucial.

The *optical* counterpart of IET is the intervalence transfer (IT) transition, where radiation induces the transfer of an electron to the other acceptor site. These transitions have been studied extensively in mixed-valence systems, and the bandshapes and energies can be related theoretically to the thermal IET rates.[60] This theoretical approach to estimation of k_{IET} has been used repeatedly in the literature, but few cases exist[25,30,51] where both optical IT and thermal ET have been measured accurately in the same system. Until such extensive comparisons become available, the quality of the derived rate constants can usually be demonstrated only indirectly (by estimates based on bimolecular reactions, for example).

Among the excited state techniques, photoelectron spectroscopy was once viewed as the fastest probe of the localized versus delocalized question in symmetrical mixed-valence systems. If a mixed-valence complex displayed two different binding energies for core electrons, then it was assumed to be localized on the photoelectron time scale $(> 10^{16}\ \mathrm{s}^{\ 1})$. This incorrect supposition is a classic example of the danger in using excited electronic state techniques to answer questions concerning the ground state. The substantial perturbation of ionizing a core electron at one center may localize the *excited state* giving rise to two apparent binding energies despite delocalization in the ground state.[61,62] Similarly, care must be used in interpretation of other experiments involving excited states such as UV-visible spectroscopy.

One technique which was not mentioned above is the temperature-jump relaxation experiment.[63] The author is not aware of any experiments in IET where this technique was used successfully, but it seems to be an approach worth investigating. A pulsed laser with Q-switching and wavelength shifting has produced a temperature rise of a few degrees in 20–25 ns for aqueous solutions by irradiation into near-infrared absorption of water.[64] In the less complicated Joule heating cable capacitor apparatus, a similar rise can be induced within 10 ns.[65] An ideal dimeric redox system for study by T jump would have a substantial value of ΔH° offset by ΔS° to yield an equilibrium constant K near unity at room emperature.

$$\mathrm{M_A^{II}\text{–}BL\text{–}M_B^{III}} \overset{\mathrm{K}}{\rightleftarrows} \mathrm{M_A^{III}\text{–}BL\text{–}M_B^{II}} \tag{5}$$

The individual redox couples for $\mathrm{M_A}$ and $\mathrm{M_B}$ would have to be quite different in their ΔH° and ΔS° values, suggesting that a mixed-metal dimer would be appropriate. For example, the ruthenium ammines ($Ru^{2+/3+}$) and ferrocenes ($Fe^{2+/3+}$) have similar E° values but much different ΔS° values,[66,67] and a $(Cp)_2Fe$–Ru dimer[68] might, therefore, be a good choice.

The need for accurate activation parameters for IET reactions cannot be overemphasized. It is this information which provides the first clues about the detailed mechanism of the reaction, and when compared for an extended series of systems they become all the more informative. For example, large negative values of $\Delta S^{\neq}$ may be indicative of either nonadiabaticity (transfer coefficient < 1) or conformational ordering in the transition state. Data for a series of cases involving rigid and non-rigid bridging groups can help to distinguish these possibilities.

CONCLUSION

The physical chemist accustomed to the study of gas phase kinetics may shake his head in wonder at the complications inorganic chemists introduce into the study of electron-transfer processes. Not only are polynuclear species usually studied, but the situation is further muddled by the presence of a solvent or crystalline lattice. However, it is a simple truth that most of the redox reactions occurring in nature involve such complexities, and intramolecular electron-transfer is a fundamental part of many of these reactions. Substantial progress has been made toward understanding inorganic redox chemistry, and the application of the physical techniques described here coupled with instrumental and synthetic advances will no doubt answer many questions now being posed.

Acknowledgments

The author thanks Dr. Carol Creutz, Dr. Thomas Meyer, Dr. David Hendrickson, Dr. Paul Schatz, and Dr. Michael Weaver for helpful discussions.

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