Electron transfer at the class II/III borderline of mixed valency: dependence of rates on solvent dynamics and observation of a localized-to-delocalized transition in freezing solvents

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The dependence of the rates of intramolecular electron transfer (ET) of mixed-valence complexes of the type $\{[\text{Ru}_3\text{O}(\text{OAc})_6(\text{CO})(\text{L})]_2-\text{BL}\}$, where L is the pyridyl ligand and BL is the pyrazine on solvent type and temperature is described. Complexes were reduced chemically to obtain the mixed-valence anions in acetonitrile (CH$_3$CN) and methylene chloride (CH$_2$Cl$_2$). Rate constants for intramolecular ET were estimated by simulating the observed degree of $n$(CO) infrared (IR) bandshape coalescence in the mixed-valence state. In the strongly coupled mixed-valence states of these complexes, the electronic coupling, $H_{AB}$, approaches $\lambda/2$, where $\lambda$ is the total reorganization energy. The activation energy is thus nearly zero, and rate constants are in the ‘ultrafast’ regime where they depend on the pre-exponential terms within the frequency factor, $\nu_N$. The frequency factor contains both external (solvent dynamics) and internal (molecular vibrations) contributions. In general, external solvent motions are slower than internal vibrations, and therefore control ET rates in fluid solution. A profound increase in the degree of $n$(CO) IR bandshape coalescence is observed as the temperature approaches the freezing points of the solvents methylene chloride (f.p. -92°C) and acetonitrile (f.p. -44°C). Decoupling the slower solvent motions involved in the frequency factor $\nu_N$ for ET by freezing the solvent causes a transition from solvent dynamics to internal vibration-limited rates. The solvent phase transition causes a localized-to-delocalized transition in the mixed-valence ions that accelerates the rate of ET.

Keywords: mixed valence; electron transfer; dynamic infrared; solvent effects; solvent relaxation; non-Arrhenius behaviour

1. Introduction

Understanding the dynamics of electron transfer (ET) reactions has been of fundamental interest to chemists, physicists and biologists (Marcus 1956; Hush 1967). One widely studied class of chemical systems that undergoes
intramolecular ET is mixed-valence complexes. Nearly 40 years ago, Robin & Day (1967) introduced the systematic basis upon which all mixed-valence complexes are classified. In recent years, there has been particular interest in the sometimes vague boundary between weakly localized (class II) and fully delocalized (class III) systems. Meyer has discussed the localized-to-delocalized transition in mixed-valence chemistry, and has proposed the defining characteristics of a new class, class II–III, of mixed-valence complexes (Demadis et al. 2001). Briefly, class II, II–III and III systems are characterized in terms of how three types of motion, solvent, vibrational and electronic, behave in an exchanging system. In class II, the solvent and exchanging electron are localized. In class II–III, the solvent is averaged and the exchanging electron is localized. In class III, the solvent and vibrations are averaged and the exchanging electron is delocalized. Here we report our studies of solvent dynamical control of rates of ET in mixed-valence complexes as the solvent is frozen and the solvent dynamics arrested.

The complexes of interest in this study are dimers of trinuclear ruthenium clusters containing a pyrazine bridge (figure 1). Each triruthenium cluster contains a carbon monoxide ligand that has a distinct stretching absorption, \( \nu(\text{CO}) \), in the infrared (IR). Stretching frequencies of these ligands are sensitive to the electronic environment on each cluster; \( \nu(\text{CO}) \) bands will shift to lower frequencies in the presence of greater electron density and higher frequencies in regions of depleted electron density. In the singly reduced mixed-valence state, these complexes are highly electronically coupled and undergo groundstate ET on the picosecond time scale. IR spectroscopy in the \( \nu(\text{CO}) \) region has proven to be a useful method to determine rate constants in the range of \( 10^{11} \text{–} 10^{13} \text{s}^{-1} \) by
ν(CO) band coalescence (Ito et al. 1997). This range of measurable rates is also relevant to the time scale of solvent dipolar reorientation, which we will show here plays an important role in these ET reactions.

The normal rate expression for a symmetric mixed-valence complex (Sutin 1983; Brunschwig et al. 2002) with no driving force depends on the transition probability, \( k \); effective nuclear frequency, \( \nu_N \); electronic coupling, \( H_{AB} \); and thermal activation energy barrier, \( \Delta G^*_{\lambda} \)

\[
k_{et} = \kappa \nu_N \exp[-(\Delta G^*_{\lambda} - H_{AB} + H^2_{AB}/4\Delta G^*_{\lambda})/RT]. \tag{1.1}
\]

The transition probability gives the fraction of systems which attain the transition state and will transfer from the reactant potential energy surface to the product surface. In the adiabatic limit, \( \kappa = 1 \) for ET reactions. The frequency factor, \( \nu_N \), is often described in ET reactions as the frequency at which inner and outer sphere modes are in configurations required by conservation of energy for an electron to transfer from reactants to products. The thermal activation barrier depends on the vertical reorganization energy, \( \lambda \), and the electronic coupling, \( H_{AB} \), (equation (1.2); Sutin 1983)

\[
\Delta G^*_{\lambda} = (\lambda - 2H_{AB})^2/4\lambda. \tag{1.2}
\]

In diabatic ET reactions, where there is no electronic coupling, \( H_{AB} = 0 \) and the thermal activation barrier is equal to \( \lambda/4 \). In the limit that the electron is totally delocalized, \( H_{AB} = \lambda/2 \) and the barrier for ET, \( \Delta G^*_{\lambda} \), equals zero. The reorganization energy is a sum of inner sphere and outer sphere contributions (Sutin 1983)

\[
\lambda = \lambda_0 + \lambda_i. \tag{1.3}
\]

\( \lambda_i \) depends on molecular vibrations, the amount of energy required for the nuclear coordinates to rearrange prior to ET. \( \lambda_0 \) is the outer sphere reorganization energy and naturally includes the properties of the solvent. \( \lambda_0 \) is determined by the optical and static dielectric constants of the solvent, \( \varepsilon_{op} \) and \( \varepsilon_s \) in the Marcus dielectric continuum model (Sutin 1983). For localized systems, \( \lambda_0 \) will vary as a function of \((1/\varepsilon_{op} - 1/\varepsilon_s)\). When mixed-valence complexes approach complete delocalization (Robin–Day class III), the solvent dependence on total reorganization energy disappears due to averaging of solvent environments.

The rate of ET depends also on \( \nu_N \), the pre-exponential ‘frequency factor’, which is a weighted average of nuclear frequencies for all modes that contribute to the ET reorganization energy. For intramolecular ET reactions in solution, these modes include solvent frequencies and intramolecular vibrations that promote ET (Weaver 1992)

\[
\nu_N = \left[ \frac{\sum_i \nu_i^2 E_i}{\sum_i E_i} \right]^{1/2}. \tag{1.4}
\]

For class II mixed-valence ions, the exponential terms govern the rate expression (equation (1.1)). These exponential terms, \( \lambda \) and \( H_{AB} \), are generally considered to be time independent. As \( H_{AB} \) assumes values approaching \( \lambda/2 \), the exponential term in equation (1.1) moves towards unity and the time-dependent pre-exponential terms are expected to govern the rate.

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The importance of solvent dipolar reorientation times on $k_{et}$ has been shown in a previous study (Londergan et al. 2002), where it was demonstrated that $k_{et}$'s scale linearly with $t_{1e}$'s determined by Maroncelli and co-workers and not with normal (time independent) solvent reorganization (Horng et al. 1995). This group measured the time-resolved multiexponential Stokes shift in the fluorescence of Coumarin 153 in a wide range of solvents. $t_{1e}$ is the time required for the solvent response function to reach $1/e$ of its initial value. This parameter may be thought of as encompassing the total evolution of solvent dynamic response to changes in local electronic environment, of which solvent rotational motion were attributed to the fastest response times. The dependence of the ET rate on $t_{1e}$ is easily seen in the $\nu$(CO) bandshape of $2^-$ in various solvents. Figure 2 shows this bandshape in acetonitrile ($t_{1e}=0.15$), methylene chloride ($t_{1e}=0.38$) and tetrahydrofuran ($t_{1e}=0.7$). $\nu$(CO) is most coalesced (fastest $k_{et}$) in acetonitrile (shortest $t_{1e}$) and least coalesced (slowest $k_{et}$) in tetrahydrofuran (longest $t_{1e}$). This suggests that the dynamics of the solvent contribute significantly to the rate of ET. These dimers are known to have very large electronic coupling ($H_{AB}$ approaching $\lambda/2$) and so pre-exponential control of $k_{et}$ is unusual, but not surprising.

Of all the modes that contribute to $\nu_N$, the solvent dynamics are expected to be the major contributors in fluid solution. However, the solvent dynamics are expected to be much slower than the internal vibrational modes of the molecule that contribute to ET. For comparison, it is known that the $\nu_{8a}$ mode of the bridging pyrazine is strongly coupled to the ET event in these complexes (Londergan et al. 2003) and, therefore, should be figured into the pre-exponential term. The frequency of this vibration is $4.8 \times 10^{13}$ s$^{-1}$ while the relaxation 'frequency' of even the fastest solvent we have used (acetonitrile) is $6.7 \times 10^{12}$ s$^{-1}$ (using $t_{1e}$). Clearly, the relaxation of the solvent is a process that limits the ET rate of the complexes. Thus, if it were possible to decouple the solvent dynamics from the ET event, we would remove the 'solvent friction' from the system, and this should in principle accelerate the ET rate.

2. Synthesis and characterization

Complexes used in this study were of the type $[\text{Ru}_3\text{O(OAc)}_6(\text{CO})\text{L}]_2\mu$-pz, where pz is the pyrazine with ancillary ligands $1=4$-dimethylaminopyridine, $2=pyridine$ and $3=4$-cyanopyridine (figure 1). Complexes 1–3 were prepared as described previously (Kido et al. 1996). Solvents for this study were chosen.
such that the mixed-valence state of the complex is soluble and is stable over a wide range of temperatures. For the optical cryostat studies, acetonitrile and methylene chloride were dried over basic alumina with a custom dry solvent system. Solutions (10 mM) of each dimer were chemically reduced to the mixed-valence state with 1.1 molar equivalents of cobaltocene \((E^{\circ} = -1.33 \text{ V versus Fc/Fc}^+; \text{Connelly & Geiger 1996})\) in an inert atmosphere. Spectra of mixed-valence dimers were recorded on a Bruker Equinox 55 Fourier transform infrared spectrometer in a flow-through optical cryostat (Specac, model number 21 525). The sample cell, consisting of CaF₂ windows with path length of 0.1 mm, is contained in a vacuum-jacketed housing. Addition of liquid nitrogen to the cooling compartment followed by heating to the desired temperature with a computer-controlled thermocouple/heating coil regulates temperature in the sample cell. Simulation of IR spectra to estimate ET rate constants was performed with VibexGL, a program for the simulation of IR spectra of exchanging systems (McClung).

3. Decoupling of solvent modes from rates of ET

It has been predicted that the decoupling of the solvent modes from the ET rate may be achieved by freezing the solvent in which the ET is occurring (Chen & Meyer 1996). The main effect of this decoupling is that solvent dipolar reorientation will no longer play a dynamic role in the reorganization of the system and \(v_N\) will consist only of a weighted average of intramolecular vibrations. When solvent friction is removed, the pre-exponential is expected to increase from \(10^{12}\) to \(10^{13} \text{ s}^{-1}\). The interesting and counter-intuitive result that must follow from this is that the rate of ET is expected to increase as the solvent temperature decreases. However, this increase in rate should only occur at the freezing point of each solvent and then change no further (i.e. solvent modes decouple once frozen and remain uncoupled.) Using \(1^- 3^-\) in methylene chloride (m.p. = 181 K), and \(2^- 3^-\) in acetonitrile (m.p. = 229 K), Fourier transform infrared spectra were collected from 298 K to the freezing point of each solvent. In all cases, as the temperature of the system was decreased from 298 K to just above the freezing point of the solvent, non-Arrhenius behaviour of the ET rate was observed (a slight increase in estimated rate constants occurred at lower temperatures). This is consistent with very low barriers to ET. As the freezing point of the solvent was approached, a dramatic increase in the \(v(\text{CO})\) bandshape occurred. Lowering the temperature past the freezing point of the solvent resulted in no further coalescence or change in the IR spectra. Figures 3 and 4 show \(3^-\) in acetonitrile and methylene chloride. It is clear that as the solvent freezes, the \(v(\text{CO})\) bandshape coalesces. Complex \(3^-\) which has the slowest exchange rate of \(1^- 3^-\) shows the most dramatic change in coalescence. Complexes \(1^-\) and \(2^-\) which show more coalesced \(v(\text{CO})\) spectra at 298 K compared with \(3^-\) do not show as striking an increase in the bandshape coalescence. Tables 1 and 2 summarize simulated ET rates as a function of temperature.

The mixed-valence complexes \(1^- 3^-\) show slower \(k_{ets}\) in ‘slower’ solvents, i.e. those with longer \(t_{1e}\). How then does freezing the solvent produce faster \(k_{ets}\)? Freezing the solvent causes the dynamic solvent modes to decouple from very fast ET. The dependence on solvent dipole reorientation is then lifted, faster
internal modes dominate and we expect the $\nu$(CO) bandshapes to reflect the fully delocalized electronic structures. However, note that the frozen bandshape for $3^-$ in methylene chloride is not as coalesced as that for $3^-$ in acetonitrile. At first, this may seem troubling. Once the solvent modes are decoupled from the ET event, all that remains in the pre-exponential is the internal modes of the complex. Because the time scale of freezing solvent molecules is much slower
than ET, the mixed-valence ions must exist in ‘averaged’ solvent environments upon freezing. This is how valence trapping is avoided at low temperatures. Thus, following the freezing of the solvent, the frequency of internal vibrational modes of a particular dimer should be independent of the solvent. Perhaps, more subtle solvent dynamic effects still exist even as the solvent becomes rigid, giving rise to the slight differences between the IR spectra in different frozen solvents.

One possible complication of estimating electron exchange rate constants by simulating IR bandshapes is the intrinsic temperature dependence of the contributing bandshapes. It is well known that IR bandshapes change with temperature. It is important to determine the contributions of IR bandshapes, independent of electron exchange. In order to rule out effects stemming from changes in temperature, reference spectra of $3^-$ were taken in the neutral state in methylene chloride from 298 to 183 K. The full-width-at-half-height, peak position and absorbance values were measured for $\nu$(CO) bands and are summarized in table 3. As the solvent temperature decreases a slight narrowing, approximately 2 cm$^{-1}$, of the $\nu$(CO) band is observed, accompanied by an increase in intensity of 25%. We also see a shift in peak position of approximately 5 cm$^{-1}$, which is consistent with the data collected for mixed-valence systems. This result confirms that CO-stretching bands do not broaden upon freezing of the solvent, and that the increase in coalescence we have observed in mixed-valence ruthenium dimers is due to an increase in the rate of dynamic electron exchange, not the intrinsic temperature dependence of IR bandshapes.

4. Conclusions

IR spectral analysis has been used to probe the effects of solvent upon the rates of ET in mixed-valence systems which are at the class II–III borderline. Previously,

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Table 1. $k_{et}^a$ for complexes 1, 2 and 3 in CH$_2$Cl$_2$.

<table>
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<tr>
<th>Temperature (°C)</th>
<th>25</th>
<th>-40</th>
<th>-60</th>
<th>-80</th>
<th>-90</th>
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<td>2.00</td>
<td>2.30</td>
<td>2.30</td>
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<td>1.79</td>
<td>2.10</td>
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</tr>
<tr>
<td>3</td>
<td>1.05</td>
<td>1.10</td>
<td>1.15</td>
<td>1.40</td>
<td>1.46</td>
</tr>
</tbody>
</table>

$^a$The values of $k_{et}$ are given in units of ps$^{-1}$.

Table 2. $k_{et}^a$ for complexes 2 and 3 in CH$_3$CN.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
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<th>-20</th>
<th>-30</th>
<th>-40</th>
<th>-50</th>
</tr>
</thead>
<tbody>
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<td>1.66</td>
<td>1.80</td>
<td>1.90</td>
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</tr>
<tr>
<td>3</td>
<td>0.83</td>
<td>0.90</td>
<td>1.09</td>
<td>1.80</td>
<td>1.80</td>
</tr>
</tbody>
</table>

$^a$The values of $k_{et}$ are given in units of ps$^{-1}$.
we have demonstrated that exchange rates for intramolecular transfer reactions in 1–3 show strong dependence on solvent dynamics. Building upon this knowledge, we have also shown that the solvent dynamics may be decoupled from the ET event in mixed-valence systems through freezing of the solvent. This decoupling effectively removes the solvent dynamical term from the frequency factor, \( N \), from equation (1.1). Removal of the solvent dynamic contributions leaves only the faster internal modes of the molecule. As such, the ET rate increases, observable as an increase in the coalescence of the \( \nu (\text{CO}) \) bands. This behaviour further supports the theoretical model that the dynamics of the solvent are controlling the ET rate of the dimers reported in this study.

In light of the results described in this study, we believe a refinement of the defining characteristics of borderline class II–III mixed-valence systems is in order. It is currently accepted that in class II–III systems solvent dynamics are averaged with respect to their contribution to ET. This is not what is observed in the systems described here (1–3), which are generally accepted as being on the class II–III borderline (Crutchley 2005). Were the solvent dynamics averaged when the solvent is in the fluid state, we would not expect to observe such dramatic changes in the ET rate upon freezing. The fact that we do observe a rate increase upon freezing indicates that ET is strongly influenced by the dynamics of the solvent. We conclude that it is time to reconsider the definition of class II–III systems to capture the solvent dependence of this class of mixed-valence compounds. Future work in our group will explicitly address the dynamic and thermodynamic influences of the solvent on ET reactions.

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### References


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McClung, R. E. D. *VIBEXGL: program for the simulation of IR spectra of exchanging systems.* Program made available by Professor R. E. D. McClung, University of Alberta, Edmonton, Alberta, Canada.

