Solvent Dynamical Control of Electron-Transfer Rates in Mixed-Valence Complexes Observed by Infrared Spectral Line Shape Coalescence

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The nuclear reorganization energy involved in electron transfer is typically separated into outer-sphere (solvent) and inner-sphere (molecular normal coordinate) terms.[1] That rates of electron transfer (ET) could be controlled by solvent dynamics was first suggested in 1980.[2] Since then, the relationship between electron transfer and solvent dynamics has been the subject of a substantial theoretical[3] and experimental effort.[4-7] Still, there are relatively few experimental systems where the relationship between ET and solvent dynamics has been demonstrated clearly.[3-7] All of these involve ultrafast laser excitation/probe methods. In the present communication, we report the determination of very fast rates of intramolecular ET by steady-state measurement of the infrared (IR) line shape of vibrational spectra of intervalence charge-transfer complexes. We show that rates of ET are controlled by solvent dynamics and that they scale clearly with solvent relaxation times determined by Maroncelli and co-workers.[7]

We previously reported the measurement of rates of ET in the complexes $[\{Ru_3O(OAc)_6(L)(CO)\}_2(\mu\text{-}pz)]^{1-}$ (where L = 4-(dimethylamino)pyridine, pyridine, 4-cyanopyridine; and pz = pyrazine), Figure 1, by coalescence of IR line shapes.[8,9]

To observe coalescence of vibrational bands in IR spectra, rates of chemical exchange must be on the time scale of ca. $10^{11}-10^{12}$ s^{-1}.[10,11] The dynamic exchange observed in the singly reduced intervalence charge-transfer complexes occurs between the two equivalent charge distributions related by ET from one trinuclear cluster to the other via the pyrazine bridge, Figure 2. Simulation of the extent of $\nu(CO)$ band coalescence can be used to estimate the ET rate constants.[8-10]

The IR spectra of the complexes $\mathbf{1-4}$[12] in their intervalence charge-transfer (-1) states in different organic solvents show that the extent of coalescence and the calculated ET rates are highly solvent-dependent. The -1 oxidation states were prepared in situ using a custom low-temperature reflectance IR spectroelectrochemical cell,[13] and all solutions contained 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.[14] Figure 3 shows examples of $\nu(CO)$ IR line shapes of $\mathbf{2}^-$ in tetrahydrofuran, methylene chloride, and acetonitrile. The differences are striking. The rate constants for ET in $\mathbf{1}^-$, $\mathbf{2}^-$, $\mathbf{3}^-$, and $\mathbf{4}^-$ were determined in seven solvents. Methods of calculating ET rate constants were reported previously.[8] The results are summarized in Table 1. The ET rate constants bear no relationship to static dielectric constants of the solvents studied. However, our data show a strong correlation with characteristic solvent relaxation times measured by Maroncelli and co-workers in time-resolved fluorescence experiments on Coumarin 153.[7] The best comparison is between our ET lifetimes (k_{ET}^{-1}) and the solvent relaxation time, t_{1e}, Figure 4. The time, t_{1e}, is that required for a time-dependent spectral response, $S_\nu(t)$, to
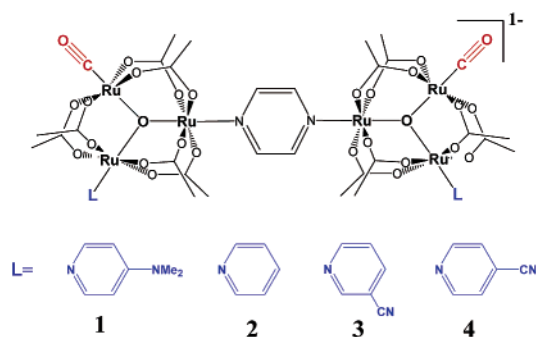

Figure 1. Pyrazine-bridged dimers of trinuclear ruthenium clusters. The singly reduced oxidation states are mixed-valence charge-transfer complexes.
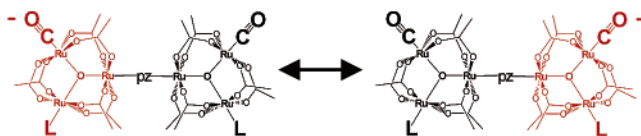

Figure 2. Electron transfer in the -1 state is a symmetric self-exchange between two isomers with the charge fluctuating from one side to the other.
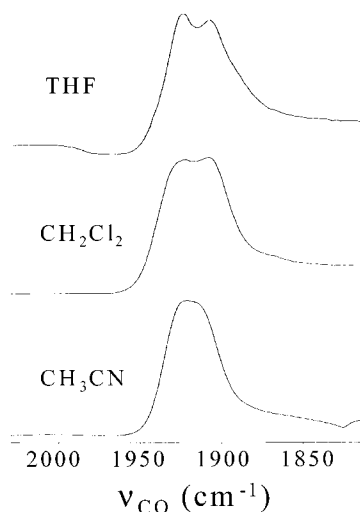

Figure 3. Solvent dependence of line shape coalescence in $\mathbf{2}^-$. In different solvents, a clear difference in the extent of line shape coalescence is observed.

achieve 1/e of its original value. It is considered to represent an overall time scale for the decay of the solvent response.[7] The solvent response times τ_0 and $\langle\tau\rangle$ are also compared to our exchange times (k_{ET}^{-1}) in Table 1. They emphasize the short- and long-time behaviors of the solvent response, respectively.[7] It appears that the IR spectra of our mixed-valence complexes are a steady-state spectral probe of ultrafast, dynamic solvent relaxation processes

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Table 1.

| solvent	1 (k_{ET}^{-1}) (ps)	2 (k_{ET}^{-1}) (ps)	3 (k_{ET}^{-1}) (ps)	4 (k_{ET}^{-1}) (ps)	τ_0 (ps)[7]	t_{1e} (ps)[7]	$\langle\tau\rangle$ (ps)[7]	ϵ_0
acetonitrile	0.35(5)	0.38(5)	0.72(10)	0.91(12)	0.12	0.15	0.26	35.94
methylene chloride	0.50(5)	0.57(5)	0.72(12)	0.91(11)	0.25	0.38	0.56	8.93
dimethylformamide	0.67(12)	0.77(15)	0.91(10)	1.0(2)	0.38	0.67	0.92	36.71
tetrahydrofuran	0.83(15)	0.95(15)	1.0(1)	1.0(1)	0.43	0.7	0.94	7.58
dimethyl sulfoxide	0.77(10)	0.87(14)		1.1(1)	0.40	0.9	1.79	46.45
chloroform	1.5(2)	1.8(2)	1.9(1)	2.0(1)	0.71	2.3	2.8	4.81
hexamethylphosphoramide	1.5(2)	2.2(2)	2.5(2)	3.3(3)	0.70	5.9	9.9	29.30
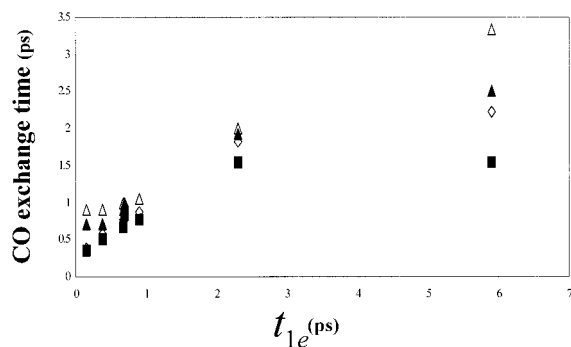
Figure 4. Exchange time (k_{ET}^{-1}) from infrared line shape coalescence simulation versus solvent inertial relaxation time, t_{1e}.[7] (■) Data for **1**. (◇) Data for **2**. (▲) Data for **3**. (△) Data for **4**.

which are otherwise only accessible using laser-pumped, ultrafast time-resolved measurements.

The comparison between our ET lifetimes in different solvents and solvent relaxation times determined by ultrafast emission red-shifts for dyes is remarkable given the differences in both spectroscopic chromophore and experimental conditions. Since our complexes are strongly coupled mixed-valence compounds, the charge transferred is probably not that of a full electron, while in Coumarin 153 excitation results in transfer of virtually an entire electronic charge. Our experiments are performed in the presence of supporting electrolyte under electrochemical conditions, and the chromophore is a ground-state monoanion, not a charge-separated excited state.

Given these differences, we expect some differences in overall solvent relaxation times due to potential ion-pairing and electrolyte-induced dielectric effects. Although there is a virtually linear dependence of our ET lifetimes (k_{ET}^{-1}) on t_{1e}, the intercept of the linear relationship is not zero, and the relative donor strength of the ancillary pyridine ligand (L = 4-(dimethylamino)pyridine, pyridine, 3-cyanopyridine, and 4-cyanopyridine) clearly affects the rate. Thus, while there is a large degree of solvent control of the ET rate, solvent dipolar response is not the only rate-determining factor (although it is clearly the most important here). Indeed, for

the complex with the slowest ET rates (**4**), the rate does not appear to be solvent-dependent in the solvents with the shortest relaxation times. This may be an indication of a transition from solvent control to inner-sphere control of ET rate, and further studies are underway to elucidate this point.

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(12) Complexes **1**, **2**, and **4** were prepared as described previously.[9] Complex **3** was prepared in a manner identical to that used for the preparation of **4**, but substituting 3-cyanopyridine for 4-cyanopyridine, with final purity achieved by size-exclusion chromatography over Bio-Beads SX-3 in chloroform. For **3**: Anal. Calcd for $Ru_6C_{42}H_{48}O_{28}N_6$: C 29.6, H 4.96, N 2.83. Found: C 29.7, H 4.83, N 2.92. ^{1}H NMR (300 MHz, $CDCl_3$): 9.12 (4H, pz), 8.99 (s, 2H, 3-cpy), 8.91 (d, 2H, 3-cpy), 8.36 (d, 2H, 3-cpy), 8.18 (t, 2H, 3-cpy), 2.27 (12H, acetate CH_3), 2.18 (12H, acetate CH_3), 2.05 (12H, acetate CH_3).
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(14) Infrared spectra were recorded at −30 °C in methylene chloride, tetrafydrofuran, acetonitrile, and chloroform to prolong stability of the −1 oxidation states. Spectra were recorded at 20 °C in dimethyl sulfoxide, dimethylformamide and hexamethylphosphoramide since low-*T* spectra were not possible in these solvents. All spectra have no observable temperature dependence in the range permitted by the experimental apparatus.

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