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Deuterium NMR Kinetic Measurements of Solvent Effects on the Bimolecular Electron Transfer Self-Exchange Rates of Ruthenium Ammine Complexes. A Dominant Role for Solvent−Solute Hydrogen Bonding

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Abstract: Electron transfer self-exchange rate constants for a series of three ruthenium ammine complexes have been determined in a range of solvents using deuterium NMR line-broadening measurements. It is found for all three complexes that the observed rates slow dramatically in solvents of strong Lewis basicity as measured by the Gutman donor number. The rates do not correlate significantly with either the dielectric continuum-based Pekar factor, ($1/n^2 - 1/D_s$), or the solvent longitudinal relaxation time known to frequently characterize solvent dynamical effects on electron transfer rates. The nature of the self-exchange rate slow down is discussed within the context of Marcus−Hush theory and is attributed to redox-state-dependent rearrangements of hydrogen bonds between solvent and solute in the second coordination sphere. Quantitative comparisons between the observed donor-number effect on rate and relevant optical electron transfer data from chemically similar systems reveal evidence of an additional donor-number-dependent contribution to the work of reactant preassociation in the bimolecular process.

Studies in our lab over the past several years have concerned various aspects of specific solvent−solute interactions on the reorganizational barrier to optical electron transfer in ruthenium ammine complexes. Spectroscopic studies of optically-induced electron transfer show that if there is substantial hydrogen bonding between the solvent as a Lewis base and the ruthenium ammine complex as a Lewis acid (an H-bond donor by virtue of the ammine hydrogens), then the solvent-dependent portion of the Franck−Condon barrier to intervalence transfer in molecules such as **1** and **2** below will be dominated by the Lewis basicity of the solvent.[1,2]

$$\text{(bipy)}_2\text{ClRu}^{\text{II}}\text{(pyrazine)Ru}^{\text{III}}\text{(NH}_3)_4\text{py}^{4+} \xrightarrow{h\nu} \text{(bipy)}_2\text{ClRu}^{\text{III}}\text{(pyrazine)Ru}^{\text{II}}\text{(NH}_3)_4\text{py}^{4+}\,* \quad (1)$$

1

$$\textit{trans}\text{-py(NH}_3)_4\text{Ru}^{\text{II}}\text{(4-cyanopyridine)Ru}^{\text{III}}\text{(NH}_3)_4\text{py}^{5+} \xrightarrow{h\nu} \textit{trans}\text{-py(NH}_3)_4\text{Ru}^{\text{III}}\text{(4-cyanopyridine)Ru}^{\text{II}}\text{(NH}_3)_4\text{py}^{5+}\,* \quad (2)$$

2

A convenient index of the solvent Lewis basicity or electron donicity is the Gutmann donor number,[3] although related solvent parameters have been shown to work equally as well.[4] This dependence of the outer-sphere barrier on donor number presumably operates in addition to the more familiar dielectric-continuum-based solvent dependence predicted by Marcus−Hush theory,[5,6] which is now widely recognized as being of general importance in a wide range of different molecular systems.[7−10,11a] In a recent study in our lab we have been able to uncover the simultaneous existence of *both* the dielectric continuum-based and donor number-based solvent on optical electron transfer in properly chosen systems such as **3** below.[2]

$$\textit{trans}\text{-(bipy)(NH}_3)_3\text{Ru}^{\text{II}}\text{(pyrazine)Ru}^{\text{III}}\text{(NH}_3)_3\text{(bipy)}^{5+} \xrightarrow{h\nu} \textit{trans}\text{-(bipy)(NH}_3)_3\text{Ru}^{\text{III}}\text{(pyrazine)Ru}^{\text{II}}\text{(NH}_3)_3\text{(bipy)}^{5+}\,* \quad (3)$$

3

The accepted theoretical relationship between optical and thermal electron transfer predicts that high-donor-number solvents such as dimethyl sulfoxide, which lead to large outer-sphere barriers to optical electron transfer in species such as **1** and **2** above, should also give rise to large barriers to thermal electron transfer processes.[6,11] This idea has been discussed within the context of specific solvation effects on the shapes

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[7] In the absence of strong specific solvent−solute interactions, it has been demonstrated that the Franck−Condon barrier to optical, and in some cases thermal, electron transfer is well-correlated with the solvent's Pekar factor, ($1/n^2 - 1/D_s$), where n is the refractive index and D_s is the static dielectric constant.[8−10]

[8] For examples of dielectric continuum effects on optical et, see; (a) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289−1297. (b) Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 752−755.

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and displacements of the potential energy surfaces governing electron transfer in a previous paper from this laboratory.[1] Although the spectroscopic studies have necessarily been confined to ligand-bridged mixed-valence dimeric systems, the conclusion is a general one and should be equally valid for thermally activated bimolecular electron transfer reactions between mononuclear complexes of similar type. Hupp and Weaver have also predicted a dominant role for specific solvent−solute interactions.[12] In their work, the solvent rate effects on bimolecular (homogeneous) reactions are implied on the basis of a careful analysis of solvent effects on electrochemical (heterogeneous) electron transfer processes. Additionally, a detailed discussion of how specific solvent−solute interactions might be incorporated into the existing framework of the Marcus theory of thermal electron transfer rates has been presented by Lay.[13]

Despite the suggestive nature of the above-mentioned work, up to now, there has been no systematic investigation into the effects of specific solvent−solute interactions on bimolecular thermal electron transfer rates. In the current paper we present an NMR line-broadening kinetic study on the rates of bimolecular electron transfer self-exchange reactions for three different ruthenium ammine complexes in a range of solvents. Specific solvent−solute interactions are indeed found to be of primary importance in defining the solvent dependence of the thermal electron transfer rates, and the qualitative predictions based on the theoretical connection between optical and thermal electron transfer are born out. Furthermore, detailed comparison of the observed rate effects with known optical electron transfer effects in similar systems indicates that the rate variations in the bimolecular case probably stem from at least two different mechanistic origins: (1) donor number-dependent reorganizational energies of the hydrogen bonds in the second coordination spheres of the reacting species and (2) solvent effects on the work of association of the reactants to form the precursor complex.

Experimental Section

NMR Measurements. NMR line-broadening studies were done on a Bruker AF 200 MHz FTNMR instrument using a VT1000 temperature controller and monitor. Rates quoted in this work were all obtained at 22 ± 2 °C. Sample tubes (10 mm) were used throughout in a VSP broad-band multinuclear probe tuned to deuterium. Chemical shifts were measured relative to pure TMS in an internal standard 3 mm capillary tube or relative to the known positions of the sharp, natural-abundance deuterium peaks characteristic of the solvent. Self-exchange conditions were attained *via* stoichiometric oxidation of the pure Ru(II) species in the tube using 0.5 equiv of solid $\mathrm{Fe^{III}(bpy)_3(PF_6)_3}$ as oxidant (synthesized according to ref 1). After the spectrum of the Ru(II)/Ru(III) mixture was obtained, the solution was oxidized completely to Ru(III) using another $^1/_2$ equiv of oxidant and the corresponding Ru(III) spectrum was obtained. Resulting peak positions, line widths, and calculated self-exchange rate constants obtained for the three compounds studied as a function of solvent are listed in Table 1. In most cases, the line widths were readily measureable directly from the spectra, but in cases of significant overlap between the Ru(II) and Ru(III) peaks, deconvolution into component Lorentzians was performed using the Peakfit program from Jandel Scientific *(vide infra)*. The concentrations for most of the exchange rate measurements were in the range 3.5−5.0 mM. In a couple of cases solubility constraints required lower concentrations (noted in Table 1). Rates did not vary systematically with concentration over this range. Data collection for the NMR spectra typically required 40−50 min in order to obtain adequate signal-to-noise ratios. UV−vis spectroscopic measurements on dilute solutions (∼10^{-4}M) verify that the ruthenium ammine complexes used are indeed stable in solution over time periods of this duration as long as the samples are protected from light.

Table 1. NMR Spectral Data, Calculated Rate Bimolecular Constants, and Selected Activational Parameters for the Compounds Studied as a Function of Solvent ([Ru(II)] = [Ru(III)] = 5 mM except where noted)

solvent	$\Delta\nu_{1/2}$ ($\mathrm{Ru^{III} + Ru^{II}}$)	$\Delta\nu_{1/2}$ $\mathrm{Ru^{III}}$ (pure)	ln k_{ex}
	$(\mathrm{py}\text{-}d_5)\mathrm{Ru(NH_3)_5}^{2+/3+}$		
NM	240	16	11.9
NB[a]	76	29	11.6
BN[b]	147	27	12.3
AN	64	14	10.3
PC	132	39	11.0
AC	92	12	10.8
DMF	35	20	9.2
	$(\mathrm{pic}\text{-}4\text{-}d_3)\mathrm{Ru(NH_3)_5}^{2+/3+}$		
NM[c]	129	10	11.6
NB[a]	27	8	10.7
AN	35	4	9.7
PC[d]	50	10	10.3
AC[d]	39	7	10.0
DMF[d]	12	6	8.5
	trans-$(\mathrm{pic}\text{-}4\text{-}d_3)\mathrm{Ru^{II}(NH_3)_4(3Fpy)}^{2+/3+}$		
NM	535	5	12.9
AN	147	4.5	11.4
PC	230	11	11.8
AC	202	3	11.7
DMF	39	9.5	9.9
MP	59	35	9.6

[a] 1.4 mM. [b] 1.75 mM. [c] 3.5 mM. [d] 4.4 mM.

Table 2. Solvents Used in This Study and Relevant Solvent Parameters

solvent	donor no.[a]	$(1/n^2 - 1/D_s)$[b]	τ_1(ps),[c] $\log_{10}\tau_1^{-1}$
(1) nitromethane (NM)	2.7	0.4978	0.2, 12.699
(2) nitrobenzene (NB)	4.4	0.3851	5.3, 11.276
(3) acetonitrile (AN)	14.1	0.5289	0.2, 12.699
(4) propylene carbonate (PC)	15.1	0.4811	1.7, 11.770
(5) acetone (AC)	17.0	0.4934	0.3, 12.523
(6) dimethylformamide (DMF)	26.6	0.4637	1.1, 11.959
(7) *N*-methylpyrrolidinone (NMP)	27.3[d]	0.4346	

[a] Donor numbers for solvent 1−7 were obtained from ref 3. [b] Pekar factors were calculated from the data compiled in: Koppel, I.; Palm, V. A. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum: London, 1972. Laurence, C.; Nicolet, P.; Dalati, M. T.; Abboud, J. M.; Notario, R. *J. Phys. Chem.* **1994**, *98*, 5807. [c] See ref 21 and: Fawcett, W. R.; Colby, A. F. *J. Electroanal. Chem.* **1989**, *270*, 103−118. [d] Taken from the extended list of donor number values compiled by Y. Marcus in ref 4.

Electrochemical measurements (differential pulse polarography) were carried out at a platinum disk electrode using an SCE reference on a Princeton Appled Research Versastat electrochemical analyzer. The supporting electrolyte was tetraethylammonium hexafluorophosphate (TEAH) synthesized according to the method described in ref 1. UV−vis spectra were obtained using an HP 8450A diode array spectrophotometer. Spectrophotometric or reagent grade solvents were purchased from either Aldrich or VWR and purified prior to use by passing them over a column of activated alumina. The solvents employed and relevant solvent parameters are listed in Table 2.

The complexes investigated in this study were synthesized according to the methods described in refs 1 and 14. The 3-fluoropyridine, pyridine-d_5, and picoline-4-d_3 ligands (picoline = methylpyridine) were

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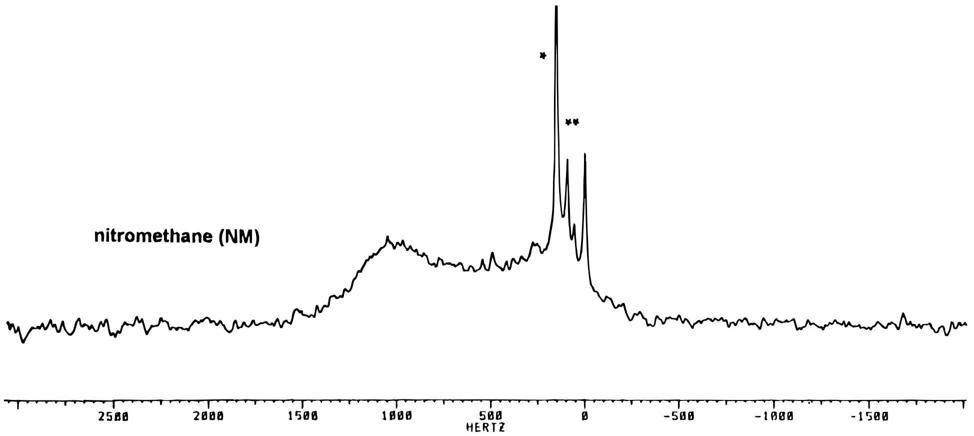

Figure 1. Example NMR spectrum illustrating self-exchange line broadening for the *trans*-(pic-*4*-d_3)Ru$(NH_3)_4$(3-Fpy)$^{2+/3+}$ reaction in NM. Concentration of Ru(II) = Ru(III) = 5.0 mM (unbroadened, pure Ru(II) and Ru(III) line widths listed in Table 1). The resonance arising from the Ru(II) resonance here (as in all cases) is partially obscured by overlapping solvent peaks due to naturally abundant deuterium in the solvents used (peaks marked with *). The reference at 0 Hz is TMS in an internal capillary tube.

Table 3. Visible (MLCT) Spectroscopic Data and Electrochemical Potentials in Nitromethane for the Three Compounds Studied

compd	λ_{max} (nm)	ϵ (cm^{-1} M^{-1})	$E_{1/2}$ (V)[a]
(py-d_5)Ru$(NH_3)_5^{2+}$	400	7640	0.129
(pic-d_3-*4*)Ru$(NH_3)_5^{2+}$	392	7520	0.091
trans-(pic-d_3-*4*)Ru$(NH_3)_4$(3F-py)$^{2+}$	420	17340	0.362

[a] Potentials *vs* ferrocene/ferrocenium (measured at a Pt disk electrode *via* differential pulse polarography).

purchased from Aldrich and used as received. Spectroscopic and electrochemical potential data for the ruthenium complexes are listed in Table 3.

(Pyridine-d_5)Ru^{II}$(NH_3)_5(PF_6)_2$. This complex was synthesized and purified according to the methods described in ref 14 until electrochemical and spectroscopic data agreed with previously reported[1,14] values (see Table 3). The picoline-*4*-d_3 complex was synthesized similarly. Microanalytical results (Oneida Research Services) for (picoline-*4*-d_3)Ru$(NH_3)_5(PF_6)_2\cdot H_2O$ were as follows: calcd (obsd): C, 12.21 (12.07); H, 4.61 (4.33); N, 14.24 (14.36); C/N, 0.857 (0.841).

***trans*-(Picoline-*4*-d_3)Ru$(NH_3)_4$(3-fluoropyridine)$(PF_6)_2$.** The *trans*-(picoline-*4*-d_3)Ru^{III}$(NH_3)_4(SO_4)$Cl starting material was synthesized and converted into the intermediate aquo compound *trans*-(picoline-*4*-d_3)-Ru^{II}$(NH_3)_4(OH_2)(PF_6)_2$ according to ref 1. This intermediate was then reacted with a 4-fold excess of the 3-fluoropyridine ligand in argon-degassed acetone at room temperature for at least 2 h. The product was isolated by filtering the reaction mixture into excess diethyl ether. Purification was accomplished by first reprecipitating the crude PF_6 salt from acetone using excess ether to force the PF_6^- salt out. Trace impurities (typically showing up as minor low-potential peaks in the differential pulse polarography of the product) could then be removed by dissolving 50−60 mg of the product in 15−20 mL of reagent grade acetone followed by slow addition of a few drops of 1/8-saturated tetraethylammonium chloride (TEACl) in a 70% acetone/30% methanol mixture. Addition was continued until a small amount of permanent precipitate just appeared. This precipitate was then excluded by filtration, and the rest of the product was isolated as the chloride by adding a larger amount of 1/4-saturated TEACl until almost all of the product had precipitated (the filtrate solution should still be slightly colored at this point so as to ensure that the precipitate will not be contaminated with excess TEACl). The product was then washed generously with acetone, briefly dried by air suction, and then dissolved in a near-minimum amount of water. The PF_6 salt was then precipitated via addition of solid NH_4PF_6 followed by dessication in vacuo and reprecipitation from acetone/ether. This procedure could be repeated as necessary until clean, single-peaked DP polarograms and constant UV−vis extinction coefficients were obtained (see Table 3). Microanalytical results for *trans*-(picoline-*4*-d_3)Ru$(NH_3)_4$(3F-py)$(PF_6)_2$ were as follows: calcd (obsd): C, 19.80 (20.11); H, 3.78 (4.12); N, 12.59 (12.86); C/N, 1.57 (1.56).

Results and Discussion

In most of the cases investigated, the downfield peak corresponding to the Ru(III) species is well-resolved, while the upfield Ru(II) peak tends to be somewhat obscured by overlapping solvent peaks. For this reason we chose to make our rate measurements using the Ru(III) peak line widths. Deuterium NMR offers the advantage that line widths are relatively unaffected by paramagnetic broadening, thus signals from paramagnetic species such as Ru(III) complexes are readily observable and exclusion of oxygen as a trace paramagnetic contaminant is unnecessary.[16]

For the two pentaammine complexes, the Ru(II) and Ru(III) deuterium resonances in the redox-state mixtures were in all cases well-separated and the systems clearly fell into the slow-exchange region of NMR rate processes.[17] For the *trans*-tetraammine species, however, rates were faster, and in three solvents (nitromethane, acetone, and methylpyrrolidinone), the combination of line broadening and frequency shift with oxidation state were such that significant overlap occurred. Figure 1 shows the deuterium NMR spectrum obtained for a 1:1 mixture of Ru(II) and Ru(III) *trans*-(picoline-*4*-d_3)Ru$(NH_3)_4$-(3F-py)$^{2+/3+}$ in nitromethane.

Most of the electron transfer self-exchange rates were calculated using standard NMR slow-exchange limit expressions:

$$1/\tau = \pi(\Delta\nu'_{1/2} - \Delta\nu_{1/2})$$

$$k_{ex} = \pi(\Delta\nu'_{1/2} - \Delta\nu_{1/2})/[\mathrm{Ru(II)}] \tag{4}$$

where in this case $\Delta\nu'_{1/2}$ refers to the Ru(III) peak line width in the presence of exchange and $\Delta\nu_{1/2}$ is the reference, nonbroadened width obtained with pure Ru(III).[17] Table 1 summarizes the NMR peak positions, line widths, and calculated self-exchange rate constants for each of the compounds studied as a function of solvent. We note that in one case, the (picoline-*4*-d_3)Ru$(NH_3)_5^{2+/3+}$ reaction in nitromethane, our measurements agree with a recent set of NMR measurements reported by Nielson et al. using ammine protons as the probe nuclei.[18] Their

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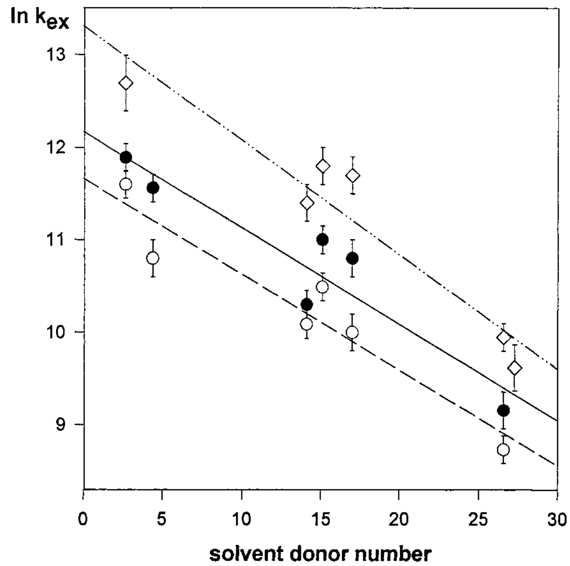

Figure 2. Calculated self-exchange rate constant vs solvent donor number at 292 ± 2 K: open diamonds, *trans*-(pic-*4*-d_3)Ru(NH_3)$_4$(3-Fpy)$^{2+/3+}$; closed circles, (py-d_5)Ru(NH_3)$_5$$^{2+/3+}$; open circles, (pic-*4*-d_3)Ru(NH_3)$_5$$^{2+/3+}$.

Table 4. Regression Parameters Arising from the Rate−Donor Number Correlations Shown in Figure 2

reaction	slope (ln *k*/DN)	intercept	r^2
(NH_3)$_5$Ru(pic-d_3-*4*)$^{2+/3+}$	−0.1085	11.78	0.899
(NH_3)$_5$Ru(py-d_5)$^{2+/3+}$	−0.1041	12.17	0.881
trans-(3-fluoropyridine)-Ru-(NH_3)$_4$(pic-d_3-*4*)$^{2+/3+}$	−0.1028	12.86	0.807

results of ln k_{ex} = 11.9, $\Delta H^{\ddagger} = +20.1$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -79.5$ J mol^{-1} K^{-1} are in reasonable agreement with the values we observe; ln k_{ex} = 11.6 ± 0.3, 18.2 ± 0.8 kJ mol^{-1}, and −85 ± 5 J mol^{-1} K^{-1}, respectively (temperature range 235−305 K).

For cases with significant overlap such as the one shown in Figure 1, we found that deconvolution of the spectrum into two Lorentzians and subsequent treatment of those peaks in the slow-exchange limit gave rates within error of those obtained using the more rigorous intermediate-range rate equation of Takeda and Stejskai[19] (as described more recently by Sandstrom[20]).

Figure 2 shows that the bimolecular self-exchange rates are well-correlated with the solvent donor number. Regression parameters are listed in Table 4. The differences in the slopes for all three compounds appear to be insignificant within error even though the *trans*-3-fluoropyridine−picoline-*4*-d_3 complex bears one less ammine ligand than the other two. This is somewhat surprising given observations from optical experiments showing that donor-number effects scale fairly sensitively with the number of ammine ligands on a given complex.[14] The differences in the intercepts are currently thought to represent ligand-dependent variations in the efficiency of the operative electron-exchange pathway in bimolecular reactions such as these and will be discussed in a subsequent publication.[21]

The observed role of solvent donicity, and by implication specific solvent−solute H-bonding interactions, in defining the solvent dependences of these reaction rates agrees well with what one would qualitatively predict on the basis of studies of optical electron transfer in related mixed-valence dimers such the one shown in eq 2[1,2] and the established theoretical relationship between optical and thermal electron transfer.[5,6,11] Plots of measured rate against various other solvent parameters show that the solvent donor-number effect completely overwhelms any residual solvent effects due to dielectric continuum or solvent dynamical effects. This is evident from the fact that the observed rates do not correlate significantly either with the Pekar factor, $(1/n^2 - 1/D_s)$, which is known to characterize dielectric polarizability effects,[5,6,8−11] or with the log of the inverse solvent longitudinal relaxation time τ^{-1}, which has been shown to characterize solvent dynamical effects on rates in at least some cases where specfic solvent−solute interactions are small.[22−24] Importantly, we also find that the *residuals* from our donor number plots are uncorrelated with either of these two solvent parameters. Thus there is no evidence for the simultaneous operation of two forms of solvent barrier within the precision of these data (in contrast to what has been observed for optical electron transfer in related systems[2]).

Another possible contribution to the solvent dependence of the bimolecular rate constant might result if ion-pairing or ion-atmosphere effects were significant and if they varied from solvent to solvent.[25−29] We find that the residuals from our donor-number plots show no correlation either with $1/D_s$ (D_s is the static dielectric constant) or with solvent acceptor number.[3] The former parameter is expected to be important in current models of ion-pairing/ion-atmosphere effects,[28−31] and the latter parameter has been shown to dominate the solvent dependence of salt effects on optical electron transfer in ruthenium ammine mixed-valence dimeric complexes chemically similar to the ones reported on here.[25] The noncorrelation of our measured rates or their residuals with either $1/D_s$ or acceptor number indicates that any ion-pairing/ion-atmosphere effects are small or at least not contributing significantly to the observed solvent dependences of the rates.

The observed magnitude of the effect of solvent donor strength on bimolecular rate can be quantitatively compared with what one would predict on the basis of known IT solvatochromic effects in mixed-valence dimers. From previous IT spectroscopic data for the *trans*-tetraammine species **2** and its pentaammine analogue $(NH_3)_5Ru^{II}$(4-cyanopyridine)$Ru^{III}(NH_3)_5{}^{5+}$ over the donor-number range from 0 to 30, we find an average additive contribution of 0.128 eV to the Franck−Condon barrier to electron transfer which can be ascribed to specific solvent−solute interactions.[2] If the simple one-fourth relationship from Marcus−Hush theory holds such that the added increment in activation energy $\Delta\Delta G^*$ for the thermal reaction can be calculated to be $(^1/_4)\Delta E_{IT}$, then we would predict an additional contribution of 0.032 eV or 3.1 kJ mol^{-1} to the thermal

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activation energy due to donicity-dependent effects over this solvent range.

A modified transition-state theory expression frequently used for the bimolecular self-exchange rate constant is

$$k_{\mathrm{ex}} = K_{\mathrm{A}}\kappa_{\mathrm{el}}\nu_{\mathrm{n}} \exp(-\Delta G^{*}/RT) \qquad (5)$$

where K_A is the preequilibrium association constant to form the precursor complex, κ_{el} is the electronic transmission coefficient, ν_n is a nuclear vibrational frequency which characterizes motion along the reaction coordinate, and ΔG^* is the free energy of activation for the electron transfer within the associated pair.[11b,22,23] If we consider how the natural log of the rate constant would be expected to change with donor number (DN) (treated as a continuous variable), we obtain the following expression:

$$\partial(\ln k_{\mathrm{ex}})/\partial DN = \partial[\ln(K_{\mathrm{A}}\kappa_{\mathrm{el}}\nu_{\mathrm{n}})]/\partial DN + \partial(-\Delta G^{*}/RT)/\partial DN \qquad (6)$$

From the regression lines in Figure 2 (see also Table 4) we calculate an average decrease in ln k_{ex} for bimolecular exchange of 3.15 over the range of 0−30 in donor number. This would imply an average increase in the activation barrier $\Delta\Delta G^*$ of 7.7 kJ mol^{-1} if only the second term on the right-hand side of eq 6 were significant. Clearly this value is not in good agreement with the $\Delta\Delta G^*$ estimate of 3.1 kJ mol^{-1} based on optical electron transfer data. The additional decrease in rate with increasing solvent−solute H-bonding must necessarily come from the $\partial[\ln(K_A\kappa_{el}\nu_n)]/\partial$DN term in eq 6.[32]

Which of the three variables in this term dominates is impossible to say with certainty at this time. The value of ν_n would probably go up to some degree with increased H-bonding between solute and solvent in stronger donor solvents.[36] Any change in ν_n, however, would probably not significantly affect the rate due to the predicted constancy of the $\kappa_{el}\nu_n$ product upon variations in ν_n for nonadiabatic or only partially adiabatic reactions (*vide infra*).[22−24] Thus the additional decrease in rate probably comes from some donor-number dependence in K_A. An attractively simple explanation for the additional slow down is evident if we consider one of the established expressions for K_A:[22,23]

$$K_{\mathrm{A}} = \frac{4\pi N r_{\mathrm{m}}2\ \delta r}{1000} \exp\left[-\frac{w(r_{\mathrm{m}})}{RT}\right] \qquad (7)$$

where N is Avogadro's number, r_m is the value of the separation distance corresponding to the maximum rate, δr is the range of distances over which the rate is significant, and $w(r_m)$ is the work necessary in order to associate the reactants to this distance. The $w(r_m)$ term is usually calculated using a purely electrostatic model.[11,23,24,29−31] If, however, desolvation of reactants in the form of disruption of favorable second-coordination-sphere interactions between solvent and solute is required in order to bring the separated reactants to r_m, then there may be an additional donor-number-dependent contribution to $w(r_m)$. The possibility of some kind of solvent structure-related, non-Coulombic contribution to the work of association of reactants was noted early on in the development of electron transfer theory by Marcus.[37] There is also a brief discussion of this possibility in the context of specific solvation effects in ref 13.

As a general caveat, we must recognize that the form of the prefactor in eq 5 is derived on the assumption of spherical symmetry for both reacting species in the associated precursor complex.[11b,23,24,29−31] Recent stopped-flow and NMR studies from our lab[21] support the conclusion arrived at by Haim and co-workers[38] that ruthenium pyridyl ammine complexes can behave in an anisotropic manner with regards to electron transfer reactivity; they have a "conductive patch" on their surfaces corresponding to the pyridyl ligand. Geometry-dependent variations in κ_{el} would require a more complex treatment of the prefactor in eq 5, including the incorporation of some kind of angularly-dependent steric factor.[22,39] It may be that the structure of the second coordination sphere is involved in dictating the degree of angular orientation necessary to obtain the transition state. If so, there may be interesting clues in the solvent dependences of the activation parameters to electron transfer in these systems. Such studies are currently underway.[40]

Conclusions

The self-exchange kinetic studies described here show that the dominant solvent influence on the rate of bimolecular electron transfer in simple ruthenium ammine complexes arises through solvent donor-number-dependent specific solvent−solute interactions. While these interactions fall outside of the realm of the dielectric continuum approximation usually employed in theoretical treatments of electron transfer,[5,6,11] the observed qualitative correlation between the herein-reported

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[32] A reviewer has made the point that this same discrepancy might arise if the bimolecular process went via a stepwise or square scheme rather than via a concerted process in which both the inner-sphere and outer-sphere barriers are surmounted simultaneously. Evidence for square scheme behavior has been found now in bimolecular and heterogeneous electron transfer reactions where large conformational changes impose dynamical constraints along the reaction coordinate.[18,33] Although we cannot rigorously rule this possibility out, we conclude that it is unlikely given recent studies we have conducted on electrochemical electron transfer rates as a function of solvent using some of the same complexes as described in the current paper. In the heterogeneous electron transfer case, rapid scan cyclic voltammetric studies show that the electron transfer rate correlates with solvent longitudinal relaxation time, τ_l, and not with DN at all.[34] This is the same qualitative solvent dependence as that which is observed by Weaver and co-workers for the heterogeneous rates of nonspecifically solvated redox couples such as cobaltocene and ferrocene.[35] Although the reason for our observed shift in qualitative solvent dependence upon going from bimolecular to heterogeneous electron transfer remains to be explained, the result indicates that H-bond rearrangements are certainly not slow enough to cause gated or stepwise behavior in electrochemical electron transfer. Presumably the same is also true for bimolecular electron transfer since slowness of conformational changes on the electrochemical time scale appears to coincide with the onset of conformational gating in the bimolecular cases studied so far.[18,33]

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(36) The nuclear frequency factor is generally given as

$$\nu_{\mathrm{n}} = \left[\frac{\nu^{2}_{\mathrm{in}}\lambda_{\mathrm{in}} + \nu^{2}_{\mathrm{out}}\lambda_{\mathrm{out}}}{(\lambda_{\mathrm{in}} + \lambda_{\mathrm{out}})}\right]^{1/2}$$

where ν^2_{in} and ν^2_{out} are the inner and outer sphere vibrational frequencies and λ_{in} and λ_{out} are the corresponding reorganizational barriers (see refs 22−24). Application of the bond length variation rules described by Gutmann implies an increase in ν_n with increased solvent−solute H-bonding (see refs 1 and 3). Sanchez−Burgos[24] has made the point that solvent can affect both the inner- and outer-sphere terms since they can and do interact (see also ref 13); this interplay would probably be especially strong in the cases under consideration here.

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thermal rate effects and previously-measured optical effects in related systems[1,2] strongly supports the predicted theoretical relationship between optical and thermal electron transfer. The larger than predicted rate decrease with increasing donor strength points toward a probable role for specific solvent–solute interactions in defining the energetics of reactant pair association and perhaps transition state structure as well.

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