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Experimental Probes of the Electronic Matrix Element Contributions to Bimolecular Reactions: Metal-to-Ligand Charge-Transfer Perturbations of Electronic Transfer Rates[1]

Sir:

The relevance of purely electronic factors to electron-transfer reactivity patterns has been of growing interest.[2] We have been employing some very simple electron-transfer and energy-transfer systems to probe the kinetic manifestations of donor–acceptor electronic interactions.[3] In the course of this work, we have found that low-energy intermolecular charge-transfer (CT) excited states can decrease the degree of nonadiabaticity. The class of CT perturbations reported in earlier work[3] all involved anionic CT donors and trivalent metals as CT acceptors, so that they can be conveniently labeled as ligand-to-metal charge-transfer (LMCT) perturbations. These CT perturbations amount to second-order, or superexchange, effects, and they can in principle be either intramolecular or intermolecular.

In treating the qualitative similarities in the electronic perturbations found experimentally to alter electron-transfer and dipole forbidden energy-transfer reactions,[3] it is convenient to formulate the reactant–product surface coupling in terms of the electron exchange interaction.[3-5] The exchange integral (J) for an electron-transfer reaction of the type

$$\mathrm{A^{III}} + \mathrm{D^{II}} \rightleftarrows \mathrm{A^{II}} + \mathrm{D^{III}}$$

(where the superscripts have been assigned pertinent to the examples of formal oxidation states of II and III for the donors and acceptors, respectively, used in the present study) can be described as the interaction between the composite orbital charge densities of the oxidized (ψ^{III}) and the reduced (ψ^{II}) species;[4] i.e.

$$J = \int \psi^{\mathrm{III}}\left(\frac{e^2}{r}\right)\psi^{\mathrm{II}}\, \mathrm{d}\tau$$

where $\psi^{\mathrm{III}} = [\phi(\mathrm{A^{III}})][\phi(\mathrm{D^{III}})]$, $\psi^{\mathrm{II}} = [\phi(\mathrm{D^{II}})][\phi(\mathrm{A^{II}})]$, and the $\phi(\mathrm{X}^n)$ values are the respective redox orbital wave functions. The donor and acceptor designations are arbitrary with respect to J, and if LMCT perturbations can alter J, then metal-to-ligand charge-transfer (MLCT) perturbations should have a similar effect.

With a view to exploring the kinetic implications of the exchange coupling mechanism, we have sought electron-transfer systems in which the role of MLCT perturbations might be manifested. We have chosen the *cis*-$\mathrm{Co(en)_2(Am)Cl^{2+}}$ oxidants (Am = cyclohexylamine (cha), aniline ($\mathrm{C_6H_5NH_2}$), and *p*-nitroaniline (*p*-$\mathrm{NO_2C_6H_4NH_2}$)) for these studies since (1) there is a possibility that some of the variations in the "sensitivity" to the "nonbridging" ligand observed[6,7] with different reducing agents could result from variations in superexchange perturbations and (2) the large changes in bond length and spin multiplicity associated with these Co(III/II) couples could result in small values of the electronic transmission coefficient (κ_{el}) for these reactions.[8-12] We have used $\mathrm{Co(sep)^{2+}}$ (sep = (*S*)-1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) as the probe (for nonadiabatic effects) and $\mathrm{Ru(NH_3)_6{}^{2+}}$ as the relatively adiabatic reference reductant for reasons elaborated previously.[3c-f,12] Our observations (Table I) indicate that intermolecular (reductant-to-Am) MLCT interactions do affect the electronic matrix elements, with the electron-transfer reactions becoming more adiabatic as the acceptor orbitals of Am become lower in energy (or as the electron affinity energy (AE)[13] becomes less negative: note that we have adopted an energy convention for the sign of AE):

$$\kappa_{\mathrm{el}}(\mathrm{cha}) < \kappa_{\mathrm{el}}(\mathrm{C_6H_5NH_2}) < \kappa_{\mathrm{el}}(p\text{-}\mathrm{NO_2C_6H_4NH_2})$$

There are a number of points in our analysis that require elaboration. We have taken the ratio (R) of rates of the

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(2) For recent discussions see: (a) Taube, H. *Adv. Chem. Ser.* **1977**, *No. 162*, 127. (b) Sutin, N.; Brunschwig, B. S. *ACS Symp. Ser.* **1982**, *No. 198*, 105. (c) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (d) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640. (e) Potasek, M. J.; Hopfield, J. J. *Ibid.* **1977**, *74*, 229. (f) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746. (g) Chance, B., DeVault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds. "Tunneling in Biological Systems"; Academic Press: New York, 1979.

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(5) It must be kept in mind that electron- and energy-transfer processes require different operators. For example, one- and two-electron exchange integrals, respectively, would have to be used in describing exchange coupling.

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Table I. Kinetic Parameters and Estimated Transmission Coefficients in Some Simple Electron-Transfer Reactions

oxidant	λ_{max},[a] nm (ϵ, M^{-1} cm^{-1})	k,[b] M^{-1} s^{-1} Co(sep)$^{2+}$	k,[b] M^{-1} s^{-1} $Ru(NH_3)_6^{2+}$	$R(X)_{obsd}$[c]	$\sim\kappa_{el}$[d]	AE,[e] eV
$Co(NH_3)_5Cl^{2+}$	525 (80)	58 ± 4	260 ± 20	0.22	0.03	
cis-$Co(en)_2(cha)Cl^{2+}$	525 (83)	0.82 ± 0.06	45 ± 4	0.018	0.0012	<<−1
cis-$Co(en)_2(C_6H_5NH_2)Cl^{2+}$	525 (83)	3.3 ± 0.3	56 ± 5	0.06	0.004	−1.13
cis-$Co(en)_2(p\text{-}NO_2C_6H_4NH_2)Cl^{2+}$	520 (85)	92 ± 6	81 ± 5	1.1	0.1	>0
$Co(NH_3)_5(C_6H_5NH_2)^{3+}$	480 (66)	0.60 ± 0.05	0.11 ± 0.01	5.5	0.1	
$Co(NH_3)_5(p\text{-}NO_2C_6H_4NH_2)^{3+}$	483 (59)	2.1 ± 0.2	0.14 ± 0.01	15	0.3	

[a] Lowest energy absorption maximum, $\sim(^1A_1 \rightarrow {}^1T_1)$. [b] Mean and mean deviation of four to six determinations (25 °C, 0.20 M $NaCF_3SO_3$). [c] $R(X)_{obsd} = k^{Co}/k^{Ru}$). [d] $\kappa_{el} = R(X)_{obsd}/R(X)_{ad}$; see text and ref 17. [e] Electron affinity energies for the reaction $Am + e^- \rightarrow Am^-$ based on ref 13.

Co(sep)$^{2+}$ to $Ru(NH_3)_6^{2+}$ reductions as a measure of the nonadiabaticity of the Co(III)–Co(sep)$^{2+}$ reactions since, on the basis of the Marcus square root relation,[14] first-order Franck–Condon contributions of the oxidant (X) cancel in the ratio; i.e.

$$R(X) = k^{Co}(X)/k^{Ru}(X) = [k_{exch}{}^{Co}K(Co,Ru)/k_{exch}{}^{Ru}]^{1/2}[f^{Co}(X)/f^{Ru}(X)]^{1/2}$$

where $k_{exch}{}^{Co}$ and $k_{exch}{}^{Ru}$ are the self-exchange rate constants for Co(sep)$^{3+,2+}$ and $Ru(NH_3)_6{}^{3+,2+}$ respectively, K(Co,Ru) is the Co(sep)$^{2+}$–$Ru(NH_3)_6{}^{3+}$ equilibrium constant, and log $f^i(X)$ = 2 log $[K(X,i)]/4$ log $(k_{exch}{}^{X}k_{exch}{}^{i}/A^2)$, with A = preexponential component of the rate constant expression[8c] and i = Co(sep)$^{2+}$ or $Ru(NH_3)_6{}^{2+}$. Even for adiabatic reactions $R(X)$ will vary from oxidant to oxidant through the second-order $f^i(X)$ terms; this variation is far more sensitive to differences in $K(X,i)$ than in k^X. To compensate for this, a small correction has been made for the oxidant contributions to observed values of $R(X)$. For $Co(en)_3{}^{3+}$ and $Co(NH_3)_6{}^{3+}$ the adiabatic value of $R(X)_{ad} \simeq 42$,[15] and this value has been used as a reference value for $\kappa_{el} \simeq R(X)_{obsd}/R(X)_{ad}$ of the $Co(NH_3)_5Am^{3+}$ oxidants in Table I. Substitution of an amine (or NH_3) by Cl^- renders the complex slightly more oxidizing,[16] and for the chloropentaammine complexes we have used $R(X)_{ad} = 15$.[17]

There is a clear and dramatic increase in efficiency of Co(sep)$^{2+}$ reductions of $Co(en)_2(Am)Cl^{2+}$ complexes when Am is varied from a saturated amine (cyclohexylamine = cha) to *p*-nitroaniline, with $R(X)_{obsd}$ (or κ_{el}) increasing by about 10^2. The very different rates of reduction, as well as the smaller than adiabatic rate ratios, found for reductions of *cis*-$Co(en)_2(p\text{-}NO_2C_6H_4NH_2)Cl^{2+}$ and $Co(NH_3)_5(p\text{-}NO_2C_6H_4NH_2)^{3+}$ rule out intervention of direct reduction of the ligand.

We have elsewhere noted[3c,d,12,16b] for related reactions that, in the absence of CT perturbations, the more similar the electronic structures of reactants and products, the more nearly adiabatic are the experimentally observed electron-transfer rates. Thus, Co(sep)$^{2+}$ reductions of $Co^{III}(Am)_6$ complexes tend to approach the adiabatic limit while the *cis*-$Co(en)_2(cha)Cl^{2+}$–Co(sep)$^{2+}$ reaction is the least adiabatic reaction of this class that we have found.[16b] This behavior can be mostly ascribed to an increase in the effective value of ψ^{III}, and therefore in J, as the oxidized reactant and product species become more similar in electronic structure (one expects a related, but probably smaller, contribution from ψ^{II}). For J sufficiently large, $\kappa_{el} \rightarrow 1$, and CT perturbations no longer contribute much to the reactivity patterns.[3d,16d] Thus, we find only a small difference in the electron-transfer behavior of $Co(NH_3)_5(C_6H_5NH_2)^{3+}$ and $Co(NH_3)_5(p\text{-}NO_2C_6H_4NH_2)^{3+}$, in contrast to relatively large differences in the electron-transfer behavior of *cis*-$Co(en)_2(C_6H_5NH_2)Cl^{2+}$ and *cis*-$Co(en)_2(p\text{-}NO_2C_6H_4NH_2)Cl^{2+}$ (see Table I). We can now add MLCT to LMCT perturbations as the kinds of environmental factors that enhance electronic coupling between spatially separated donors and acceptors.

We find that the concept of electron exchange coupling of reactant and product potential energy surfaces is very useful in the design of experiments that explore the nonadiabatic behavior of simple electron-transfer reactions and also in the interpretation of this behavior. The exchange[4] and tunneling[2d,e] formulations provide somewhat different approaches to the description of the electronic matrix element. Insofar as each of these approaches provides a reasonable approximation to the physical situation, each will provide a means for interpreting the variations in adiabaticity of electron-transfer reactions. At a very primitive, intuitive level, the tunneling formalism focuses on the properties of the donor while the exchange formalism gives equal weight to donor and acceptor. Thus, the observation that both LMCT and MLCT perturbations can alter the extent of donor–acceptor coupling seems superficially more readily accommodated in the context of the exchange formalism. Nevertheless, the induced dipole moments of the LMCT and MLCT perturbations that we have examined do have a similar directional sense with respect to the donor–acceptor axis, and it is probably possible to adjust the tunneling parameters to accommodate these observations.

Registry No. Co(sep)$^{2+}$, 63218-22-4; $Ru(NH_3)_6{}^{2+}$, 19052-44-9; *cis*-$Co(en)_2(cha)Cl^{2+}$, 28121-20-2; *cis*-$Co(en)_2(C_6H_5NH_2)Cl^{2+}$, 46753-03-1; *cis*-$Co(en)_2(p\text{-}NO_2C_6H_4NH_2)Cl^{2+}$, 91312-06-0; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5(PhNH_2)^{3+}$, 91312-07-1; $Co(NH_3)_5(p\text{-}NO_2C_6H_4NH_2)^{3+}$, 91312-08-2.

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X-ray Structure and Physical Properties of the Mixed-Valence Compound 1,12-Dimethyl[1.1]ferrocenophanium Triiodide

Sir:

The study of electron transfer in mixed-valence complexes leads to insight about electron transfer in oxidation–reduction, electrochemical, and biological processes.[1] Bridged ferrocenes