DYNAMIC STRUCTURAL EFFECTS AND ULTRAFAST
BIMOLECULAR KINETICS IN PHOTOINDUCED
CHARGE TRANSFER REACTIONS

Progress Report

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Abstract

During the first budget period significant progress was made in three areas:

1) assessment of dynamic structural effects accompanying charge transfer, 2) electrochemical assessment of site-to-site electronic coupling in simple inorganic systems, and 3) direct observation of intramolecular electron transfer kinetics in mixed-valence systems.

In area 1 the most significant finding was that Franck-Condon parameters for electron transfer (i.e. normal coordinate displacements, vibrational frequencies, and single-mode vibrational reorganizational energy components) could be obtained for weakly interacting (ion-paired) redox systems (J.Phys.Chem., 1991, 95, 10535). Studies in area 3 have yielded results in both the ultrafast (femtosecond/picosecond) time regime (J.Phys.Chem. 1991, 95, 5712) and the intermediate (microsecond/millisecond) time regime (J.Am.Chem.Soc., submitted).

DYNAMIC STRUCTURAL EFFECTS AND ULTRAFAST BIMOLECULAR KINETICS IN PHOTOINDUCED CHARGE-TRANSFER REACTIONS

(Joseph T. Hupp, Northwestern University)

Progress Report: 1990-91

During the first budget period significant progress was made in three areas: 1) assessment of dynamic structural effects accompanying charge transfer, 2) electrochemical assessment of site-to-site electronic coupling in simple inorganic systems, and 3) direct observation of intramolecular electron transfer kinetics in mixed-valence systems.

In area 1 the most significant finding was that Franck-Condon parameters for electron transfer (i.e. normal coordinate displacements, vibrational frequencies, and single-mode vibrational reorganizational energy components) could be obtained for weakly interacting (ion-paired) redox systems (*J.Phys.Chem.*, 1991, **95**, 10535). The system evaluated was 4-cyano-N-methylpyridinium/iodide:

Via implementation of a time-dependent Raman scattering technique, each of 13 separate reorganizational components was identified and quantified. These results are significant because they represent an experimental generalization of the time-dependent scattering methodology; previously we had applied the technique only to covalently linked donor-acceptor systems. (These most recent experiments, now successfully completed and published, were, by the way, deemed impossible by the one negative reviewer of our renewal proposal.)

In area 2 we have now extended our studies of orbital mixing and electronic coupling in metal-ligand systems (*Inorg.Chem.* in press) to metal-based mixed-valence systems, most notably $(\text{NC})_5\text{Fe}^{\text{II}}\text{-CN-Ru}^{\text{III}}(\text{NH}_3)_4\text{L}^+$ species. The pattern emerging from these studies is one in which electrochemical probes of electronic coupling lead to much higher estimates of donor-acceptor interaction energy than do simple oscillator strength (charge-transfer absorption) measurements. Furthermore, the electrochemical results seem to be corroborated by independent experimental measures of coupling. These findings, while of general importance and significance, also tie in very specifically to photo-induced electron transfer (ET) measurements described below.

Studies in area 3 have yielded results in both the ultrafast (femtosecond/picosecond) time regime (*J.Phys.Chem.* 1991, **95**, 5712) and the intermediate (microsecond/millisecond) time regime (*J.Am.Chem.Soc.*, submitted). The former were obtained in collaboration with Paul Barbara and co-workers. For the first time, thermal ET rate measurements were made for an intramolecular

reaction via direct intervalence pumping:

From these measurements, k_{ET} lies in the 10^{12} - $10^{13}s^{-1}$ range. These findings are particularly exciting because we have previously characterized (at Northwestern) both the Franck-Condon barrier aspects (via time-dependent scattering) and the extent of initial-state/final-state electronic coupling (electrochemical measurements, described above). The satisfactory completion of solvent reorganizational studies for reaction 2 will yield the first fully experimentally characterized (i.e. vibrational, solvational, thermodynamic, and electronic) intramolecular redox system displaying measurable charge-transfer kinetics.

Intramolecular ET rates over a much greater distance were obtained by a novel approach in which charge transfer is triggered by selective solvation:

Measurable kinetics ($k_{ET}=2 \times 10^4s^{-1}$) were obtained by employing a rapid (microsecond) mixing technique: pulsed-accelerated-flow spectrophotometry. Related studies (thermodynamic) have now shown us that redox isomerization can also be induced by highly selective macrocyclic ligand (crown ether) binding (*Inorg.Chem.* 1991, 30, 3856).

Plans for 1992-93

The 8 order-of-magnitude rate difference for directly measured intramolecular ET in eqs. 2 and 3 suggests several avenues for further exploration. For both systems (but for differing reasons) our efforts are turning towards temperature effects. Structural changes involving driving force effects and ET distance effects are also slated for investigation.

Studies of dynamic structural effects will be directed chiefly towards delocalized mixed-valence systems and towards systems which we have previously shown can be made to undergo localized $\rightarrow$ delocalized electronic isomerization. The primary experimental tool will be intervalence enhanced Raman scattering. In support of the Raman work, however, and also in support of solvent reorganization studies needed to complete the description of our ultrafast ET reactions (eq. 2), we are planning a new series of experiments based on intervalence Stark effect measurements. The planned studies should directly yield effective transition dipole lengths. These in turn can yield (with some interpretation) true charge-transfer distances, as well as amounts of charge actually transferred. We suspect that both quantities are highly significant variables in our systems. The necessary instrumentation for Stark spectroscopy is being acquired with award funding (Dreyfus Foundation); its use, however, will be largely for DOE-supported research (as described above).

DOE SUPPORTED PUBLICATIONS

"Resonance Enhanced Raman Scattering in the Near Infrared. Preliminary Studies of Charge Transfer in the Symmetric Dimers $(2,2'bpy)_2ClRu-4,4'bpy-RuCl(2,2'bpy)_2^{4+/3+/2+}$, $(H_3N)_5Ru-4,4'bpy-Ru(NH_3)_5^{6+/5+/4+}$, and $(NC)_5Fe-4,4'bpy-Fe(CN)_5^{4-/5-/6-}$ ", S. K. Doorn, J. T. Hupp, D. R. Porterfield, A. Campion, and D. B. Chase, J. Am. Chem. Soc., **1990**, *112*, 4999-5002.

"Does Marcus-Hush Theory Really Work? Optical Studies of Intervalence Transfer In Acetylene-Bridged Biferrocene Monocation at Infinite Dilution and at Finite Ionic Strengths" R. L. Blackburn and J. T. Hupp, J. Phys. Chem., **1990**, *94*, 1788-1793.

"Solvent Induced and Crown-Ligand Induced Redox Isomerization within an Asymmetrically Coordinated Mixed-Valence Ion: *trans*-(pyridine)(NH_3) $_4Ru(4$ -cyanopyridine) $Ru(2,2'bpy)_2Cl^{4+}$ ", J.C. Curtis, Y. Dong, M. Massum, C.S. Johnson, J. A. Roberts, R. L. Blackburn, J. C. Curtis, and J. T. Hupp, Inorg. Chem., **1991**, *30*, 3856-3860.

"Experimental Assessment of Dynamic Structural Parameters for Homogeneous and Interfacial Charge-Transfer Reactions: Case Studies Based on Time-Dependent Raman Scattering Methods", S. K. Doorn, R. L. Blackburn, C. S. Johnson and J. T. Hupp, Electrochimica Acta, **1991**, *36*, 1775-1785 (invited paper, Asilomar Conference Proceedings issue).

"Electrochemical and Spectral Probes of Metal/Ligand Orbital Mixing in $Ru(NH_3)_4(2,2'bpy)^{2+}$ and $Ru(NH_3)_4(phenanthroline)^{2+}$ ", G. A. Mines, J. A. Roberts and J. T. Hupp, Inorg. Chem., in press.

"Ultrafast Measurements on Direct Photoinduced Electron Transfer in a Mixed Valence Complex", G. C. Walker, P. F. Barbara, S. K. Doorn, Y. Dong, and J. T. Hupp, J. Phys. Chem., **1991**, *95*, 5712-5715.

"A Complete Experimental Assessment of Franck-Condon Structural Effects for an Irreversible Outer-Sphere Electron Transfer Reaction: Applications of Time-Dependent Raman Scattering Theory to the One-electron Reduction of 4-Cyano-N-methylpyridinium", R.L. Blackburn, C.S. Johnson, J.T. Hupp, M.A. Bryant, R.L. Sobocinski, J.E. Pemberton, J. Phys. Chem., **1991**, *95*, 10535-10537.

"An Electrochemical Variational Study of Donor/Acceptor Orbital Mixing and Electronic Coupling in Cyanide-Bridged Mixed-Valence Complexes", Y. Dong and J. T. Hupp, Inorg. Chem., submitted.

"Solvent-Triggered Intramolecular Electron Transfer: Time Resolution via Pulsed Accelerated Flow Spectroscopy", J. A. Roberts, J. C. Bebel, M. P. Absi and J. T. Hupp, J. Am. Chem. Soc., submitted.

INVITED TALKS ON DOE RESEARCH

"Optical Electron Transfer Reactions", Analytical Seminar, Penn State University, University Park, Pennsylvania, October, 1990.

"Optical Electron Transfer Reactions", Departmental Seminar, University of Wyoming, Laramie, Wyoming, November, 1990.

"Dynamic Structural Studies of Optical Electron Transfer Reactions", Analytical Seminar, Department of Chemistry, Texas A&M University, November, 1990.

"Dynamic Structural Studies of Optical Electron Transfer Reactions", Analytical Seminar, Department of Chemistry, University of Houston, Texas, November 1990.

"Optical Electron Transfer Reactions", Departmental Seminar, University of Ottawa, Canada, December 1990.

"Optical Electron Transfer Reactions", Departmental Seminar, Indiana University - Purdue University at Indianapolis, February, 1990.

"Dynamic Structural Effects in Optical Electron Transfer Reactions", Analytical Seminar, University of Wisconsin, Madison, February, 1990.

"Optical Electron Transfer Reactions", Cornell University, April, 1990.

"New Kinetic and Structural Approaches to Intramolecular and Interfacial Electron Transfer", Gordon Research Conference on Electrochemistry, Ventura, CA, January, 1992

"Light Driven Redox Reactions", Departmental Seminar, North Carolina State University, Raleigh, February, 1992.

"Optical Electron Transfer Reactions", State-of-the-Art Symposium on Electron Transfer, American Chemical Society National Meeting, San Francisco, April, 1992.

Ph.D. Dissertations (D.O.E. research)

Robert L. Blackburn "Ionic Strength Effects on Electron Transfer Energetics and Resonance Raman Studies of Vibrational Reorganization Energetics", March, 1991.

Jody A. Roberts "The Mechanism and Rate of Intramolecular Electron Transfer in Mixed-Valence Systems", October, 1991.

Award: Henry and Camille Dreyfus Teacher-Scholar Award, 1991-96

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