

# Inter-American Photochemical Society Newsletter



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**May 1998**

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President's Letter (typed in)

May 1, 1998

Dear Colleagues:

It hardly seems possible that this letter comes from me as the outgoing President of the Inter-American Photochemical Society. Despite the evidence to the contrary, I still regard myself as an impressionable young scientist, and in that spirit that I offer these few thoughts. One of the great things about our Society is the opportunity we have to meet people in other disciplines. A few personal experiences will illustrate the point.

Reading the literature convinced me that a fellow named Josef Michl was an insightful scientist, though he seemed to have too few vowels in his name. Articles on funnels and the absorption spectrum of azulene were especially good. By now, thanks to our Winter Conferences, I have had several chances to discuss concepts with him one on one, and each time was a treat. When I was a novice, Nick Turro was a long-distance mentor via his very cogent text. It has been a great pleasure to meet him and to watch him compose a manuscript while listening to a lecture at the same time. He is certainly wired, in parallel. Peter Wagner has been another find. When I was an Assistant Professor, he was and Associate Editor who gave me a break that I have yet to see repeated. One of our papers received some favorable reviews and one that was quite negative. Before I could even begin to argue, he said he had read the manuscript himself and would ignore that off-the-wall opinion. Now that was an editor! Years later, he pointed out that orbital overlap matters in associative reactions of excited states, and I have repeated that observation many times. Anecdotes about others like Harry Morrison, Srinivasan, Dick Caldwell, and Jack Saltiel also come to mind, but perhaps I have made the point.

In closing I would like to say a special thank you to my fellow Officers and the Board who have all been so cooperative these past couple of years. Good luck to Linda Johnston who assumed the job as President. To the members, I say: "This is a great society within society; let's keep it going."

Sincerely,

David R. McMillin

## Election Results — New Officers

The election results are in! Because the Candidates were all strong, many races were close. The new Officers are as follows:

### Vice President/President Elect

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The official terms begin on July 1, 1998. The Secretary serves a 2 year term, but the rest will be Officers for 4 years. (Fred Lewis is President for the second 2 yrs of his term.) The continuing members of the present Advisory Board are Lisa McElwee-White, Frank Quina and Richard Weiss. Finally, by a wide margin, the members ratified the proposed changes to the Constitution.

## **1999 I-APS Award in Photochemistry: Call for Nominations**

The Inter-American Photochemical Society Award was established in 1988 to recognize outstanding contributions by members of the Society to the advancement of the photochemical and photophysical sciences. The award recognizes achievements during the last ten years. The 1999 award will be presented at the Eleventh I-APS Winter Conference in January 2000.

Nominations should include a detailed justification that clearly outlines the nominee's scientific achievements during the last ten years, along with a curriculum vita and a publications list. Seconding letters from colleagues familiar with the nominee's work are also helpful to the committee. All documents should be forwarded to the Chair of the Awards Committee at the address below. The deadline for nominations is August 1, 1998.

## **I-APS Fellowship: Call for Nominations**

The Society established the honor of Fellowship in 1993. Fellowship recognizes outstanding lifetime scientific achievement in photochemistry or contributions to either the science of photochemistry as a discipline or the furtherance of the Society through service. Contributions made at any point during the nominee's career can be recognized. No more than two nominees can be elected in any year and the total number of Fellows must be less than four percent of the current Society membership. Fellowship includes a membership dues waiver and Fellows may be requested to make a short presentation at the next Winter Conference.

Nominations should include a statement describing the merit of the contribution to be recognized and should state clearly whether the award is for contributions in science or service. There is no requirement for seconding letters. The nominee must be a current member of the Society to be eligible, unless the nominator argues convincingly that there are exceptional circumstances. The deadline for nominations is August 1, 1998.

Please send nominations for either the I-APS Award or Fellowship to:

Dr. Linda J. Johnston  
Chair, I-APS Awards Committee  
Steacie Institute for Molecular Sciences  
National Research Council Canada  
Ottawa, Ontario K1A 0R6 Canada

## **Thanks to Kirk Schanze — Good Luck to William Jenks**

With this issue of the I-APS newsletter, its editorship moves from Kirk Schanze to William Jenks. The Society owes Kirk a debt of gratitude for his hard work over the last years and for maintaining the vibrant nature of this Newsletter. Kirk has also graciously assisted in the transition with this issue. Until further notice, all contributions for the Newsletter should be sent to William at [wsjenks@iastate.edu](mailto:wjenks@iastate.edu) or Department of Chemistry, Iowa State University, Ames, IA 50011-3111.

Ideas for research articles and other contributions are particularly welcome! If you will be attending a meeting of interest to the society, we would also be very happy to receive reports such as those published in this and previous issues.

## **I-APS Electronic Distribution Lists**

Electronic mail distribution lists have been created for general announcements to all I-APS members. The lists have been set up as one-way electronic mailings and are being maintained by Professor Mary Boyd at Loyola University of Chicago. If you have an announcement of interest to the general membership (e.g., postdoc openings, job postings, conference announcements), please send an e-mail message to [mboyd@luc.edu](mailto:mboyd@luc.edu) and the message will be sent to the membership.

If you have not been receiving these irregular mailings or have recently changed your email address, please forward your new address to Professor Boyd so that she may get you added to the list.

## Report on the Workshop on Recent Trends in Photochemical Sciences

January 7-9, 1998, Trivandrum, Kerala, India

Suresh Das

Photochemistry Research Unit, Regional Research Laboratory, Trivandrum, India  
and

C. V. Kumar

Department of Chemistry, University of Connecticut, Storrs CT 06269-3060

The Workshop held at Trivandrum, India was jointly organized by the Photochemistry Research Unit of the Regional Research Laboratory, Trivandrum, India and the Jawaharlal Nehru Center for Advanced Scientific Research, Bangalore, India. Trivandrum is the capital of Kerala; a state sandwiched between the Arabian Sea and the Western Ghats. This coastal city built on hills and liberally covered with green paddy fields and coconut groves provided an inspiring backdrop for the Workshop proceedings. The Scientific Program for the three-day workshop consisting of invited lectures (24) and posters (18) was chosen to provide a unique opportunity for the interaction of scientists working in different areas of photochemistry.





The first session consisted of two talks devoted to different aspects related to the design of artificial photosynthetic systems. Devens Gust (Arizona State University, USA) talked about efficient charge separation processes observed in novel fullerene diads and triads. Kurt Schaffner (Max-Planck-Institut fuer Strahlenchemie, Germany) described the light harvesting antenna systems of photosynthetic bacteria. Energy transfer studies with aggregates of bacteriochlorophyll-c as well as efforts to designing organized supramolecular assemblies capable of mimicking the natural photosynthetic antenna were also presented.

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Various aspects of photodynamic therapy were presented in the second session. Michel Chanon (Universite d'Aix-Marseille, France) discussed the mechanism of photodynamic activity of Victoria Blue. Type I mechanism was mainly involved leading to apoptosis of leukemic cells. Bhaskar Maiya (University of Hyderabad, India) described efforts in designing artificial nucleases based on porphyrins, metallo-polypyridyls and azoarenes. Benjamin Eherenberg (Bar Ilan University, Israel) talked about studies related to understanding the extent of sensitizer binding to cell membranes, estimation of singlet oxygen yields in biological samples and the photodynamic activity of several classical and "second generation" systems.

Use of zeolites to stabilize charge separated products was presented in the next session by Alexander Trifunac (Argonne National Laboratory, USA). The effect of the zeolite matrices on the structure, electronic properties as well as reactivities of the entrapped radical ions was described. Biman Bagchi (Indian Institute of Science, India) in his talk entitled "Effect of Ultrafast Solvation on Ionic Conductivity in Dipolar Solvents", described his newly developed theory which includes both the static two particle correlations among the ion and the dipolar solvent molecules and also the relevant dynamic response of the pure solvent. Richard Fessenden (Radiation laboratory and Department of Chemistry and Biochemistry of the University of Notre Dame, USA) spoke on the use of ESR and CIDEP to investigate the reaction mechanism of photochemical reactions, using several examples such as the formation of hydrated electrons, phenoxy radicals and radical adducts with fumarate. The use of time resolved ESR spectroscopy in the identification of the two photon ionization chemistry and ESR spectrum of the radical cation of a naphthalenetetracarboxylic acid was also described.

Recent progress in ultrafast spectroscopy in understanding of the dynamics of fast processes in organized media such as hydrophobic pockets of proteins, biomembranes, cyclodextrins, and on water surfaces was outlined by Kankan Bhattacharyya (Indian Association for the Cultivation of Science, India). The use of picosecond emission spectroscopy and surface second harmonic generation in the study of such organized assemblies was highlighted. The excited state reactions of triphenylpyrelium and triphenylthiopyrelium derivatives in the presence of various electron donors was presented, in the final talk of the day, by P. Ramamurthy (University of Madras, India). Radical yields, back electron transfer rate constants and indication of the "Marcus Inverted Region Effect" in some of these systems were discussed. In the evening a cultural program consisting of Indian classical dance was arranged for the entertainment of the participants.

The opening session on the second day started with a talk by V. Ramamurthy (Tulane University, USA) highlighting the role of zeolites as media to control product selectivities of organic phototransformations. The remarkable ability of zeolites to control regioselectivities in the oxidation of olefins, reduction of steroidal enones as

well as their ability to effect asymmetric induction were discussed. This was followed by a talk by S. Sankararaman (Indian Institute of Technology, Madras, India) on the metal ion complexation versus charge transfer complexation of bis(p-phenylene-34-crown-10). The formation of colored complexes of the crown derivatives with a variety of  $\pi$ -acceptors such as tetracyanoethylene, tropylium ion and methylviologen and the subsequent displacement of the acceptors by lithium ions were discussed. Challa V. Kumar (University of Connecticut, USA) discussed the site-specific cleavage of proteins and DNA using photoactivable chromophores covalently linked to specific recognition elements of biological significance. The site-specific cleavage of bovine serum albumin as well as the site specific photonuclease activity on DNA using these newly developed chemical photoproteases was also discussed. Ian Smith (University of Birmingham, UK) delineated the atmospheric photochemistry of hydrofluorocarbons (HFCs). The talk reviewed the present state of knowledge of atmospheric chemistry of HFCs and their acceptability as replacement compounds for the CFCs.

The intramolecular charge transfer (ICT) processes in 4-aminobenzonitriles and related compounds were discussed in the post-lunch session by K. A. Zachariasse (Max-Planck-Institut für Biophysikalische Chemie, Germany). Experiments were described which suggest that in the final charge-transfer state of this class of molecules, the amino group is strongly coupled with the rest of the molecule, and the energy gap  $D(S_1, S_2)$  plays an important role in the ICT mechanism. A. Samanta (University of Hyderabad, India) spoke on the photophysical behavior, and potential application of aminophthalimide derivatives. Studies on the development of fluorescent probes for the non-polar core region of micelles using this class of molecules was discussed.

The program for evening session of the second day consisted of three oral presentations of posters. Samita Basu (Saha Institute of Nuclear Physics, India) spoke on the identification of spin states in photoinduced electron transfer reactions by magnetic fields. V. Singh (Indian Institute of Technology, Bombay, India) spoke about the use of excited state chemistry as a versatile tool in organic synthesis and V. Jaythirtha Rao (Indian Institute of Chemical Technology, India) spoke on trans to cis quantum chain isomerization. The evening concluded with a dinner at Hotel Ashoka, an international beach resort at Kovalam.

The talks on the final day covered various aspects of semiconductor photochemistry. K. Tennakone (Institute of Fundamental Studies, Sri Lanka) described the problems encountered in constructing efficient photo voltaic cells containing pigment molecules sandwiched between n- and p-type semiconductors. P. V. Kamat (Radiation Laboratory, USA) spoke on the photosensitization aspects of nanostructured semiconductor thin films. Several important issues related to the kinetics of SnO<sub>2</sub>, TiO<sub>2</sub> and ZnO thin films with ruthenium(II) complexes and other organic dyes were addressed during this talk. S. Yanagida (Osaka University Japan) described the studies on the elucidation of surface structures of II-VI semiconductor nanocrystallites in organic media. The use of these semiconductor systems as photocatalysts in the photoreduction of CO<sub>2</sub> was also discussed. K. Rajeshwar (University of Texas at Arlington, USA) spoke about the "Novel Approaches to Titanium Dioxide Assisted Photocatalysis". The electrocatalysis and photoelectrochemical behavior of a new class of TiO<sub>2</sub>/Ni nanocomposite films as well as a hybrid system incorporating a photocatalytic reactor and a ultra-filtration hollow fiber-membrane were described. In his talk, H. Yamashita (Osaka Prefecture University, Japan) highlighted the application of metal ion implantation methods for the design of unique TiO<sub>2</sub> photocatalysts capable of functioning with visible and solar light. A. Kumar (University of Roorkee, India) described mechanistic studies of colloidal CdS induced photochemical reactions of organic molecules, during the last talk of the workshop. Overall the international workshop was successful in highlighting the emerging trends in photochemical research. The informal and congenial atmosphere of the workshop also ensured lively discussions during the talks and poster sessions. Delicious spicy cuisine, warm beaches, and terrific hospitality enriched the workshop proceedings.

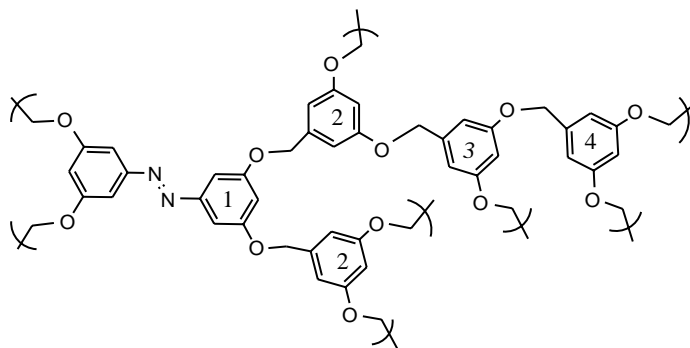
## Recent Noteworthy Articles in the Area of Photochemistry and Photophysics

Editor's note: It is our intention that in subsequent issues we will return to a more fully rounded coverage in this section. Because of some confusion during the editorial transition, only an "organic" contribution is available for this issue.

### Organic Photochemistry

Selected and abstracted by Dafni Amirsakis, University of California, Los Angeles

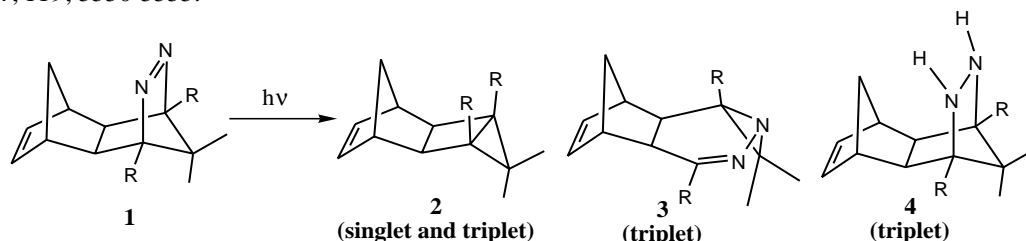
1. Jiang, D.-L.; Aida, T., "Photoisomerization in Dendrimers by Harvesting Low-Energy Photons" *Nature* **1997**, 388, 454-456.



Because of efficient and random dissipation through low frequency molecular vibrations, infrared energy is not useful in causing photochemical transformations. This interesting article by Jiang and Ida discusses how low energy irradiation may be used to trigger the infrared photoisomerization of an azobenzene chromophore located at the core of a highly branched aromatic dendrimer. Experiments were carried out with compounds ranging from a model 3,3',5,5'-tetrahydroxyazobenzene to dendrimers having up to four additional aromatic layers and as many as 62 aromatic units.

As expected, the thermally stable trans-azobenzenes isomerized to the cis-compounds on ultraviolet excitation, and the cis-isomers slowly converted back to the trans-compound upon standing in the dark. When exposed to infrared irradiation (75W, nichrome source), a remarkable rate acceleration was observed for cis-azobenzenes contained within dendrimers possessing four or five aromatic layers, but not in those containing three or less. Not only were there rate accelerations as high as 250-260 times faster than the thermal reaction, but a factor of 23 was detected as compared to that measured upon irradiation with visible light (440 nm, power not reported). Experiments carried out with monochromatic IR light at  $2500\text{ cm}^{-1}$  (no absorption),  $1597\text{ cm}^{-1}$  (aromatic stretch) and  $1155\text{ cm}^{-1}$  (C-O stretch) showed that vibrational excitation of the aromatic moieties was required for the reaction to occur. Finally, cis-to-trans rate acceleration was also observed in the higher dendrimers upon direct electronic excitation of the dialkoxybenzenes at 280 nm. Since this was only for the higher dendrimers, and since there was no changes in fluorescence quantum yields, the authors concluded that singlet deactivation by internal conversion can be channeled via vibrational relaxation to the azobenzene core. These experiments suggest that dendrimers can potentially be used as tunable traps of low energy photons.

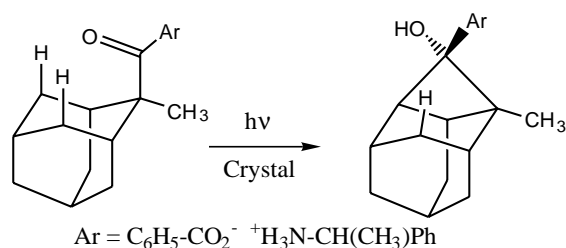
2. Adam, W.; Moorthy, J. N.; Nau, W. M.; Scaiano, J. C., "Solvent Effects on Product Distribution in Photochemical Pathways of  $\alpha$  C—N versus  $\beta$  C—C Cleavage of  $n,\pi^*$  Triplet-Excited Azoalkanes" *J. Am. Chem. Soc.*, **1997**, *119*, 5550-5555.



This paper is one of an interesting series by the groups of Adam and Scaiano dealing with the kaleidoscopic photochemistry of cyclic azoalkanes. With the photochromic cis-trans isomerization prevented by the rigid structure, several appealing analogies with carbonyl photochemistry greatly enrich the stepwise denitrogenation of the azo chromophore. In this paper, it was shown that housanes (2), aziranes (3) and hydrazones (4) can be obtained in from tetracyclic azoalkanes (1) in yields that depend on the solvent used in a fairly complex manner.

With a combination of product analysis, quenching studies, isotope effects and triplet lifetimes, the authors propose explanations that account well for all the trends observed. A very efficient single state denitrogenation to give the housane in compounds with aromatic R groups was found to account for the examples where no solvent effects were observed. In fact, it was suggested that solvent effects in the singlet do not affect the product distribution but simply reduce the quantum yields by a proton-assisted quenching mechanism that previously documented by the authors. Direct solvent effects on the product distribution were assigned to triplet photochemistry. Formation of hydrazines 4 was rarely observed because it requires good hydrogen donors such as isopropanol and cyclohexane. The competition between C—N and C—C cleavage to yield housanes (2) and aziranes (3) was found to correlate well with the proticity of the solvent and the absolute yields of azirane correlated well with solvent polarity. Rather than excited states with different electronic configurations, the authors suggests that  $\beta$ -cleavage may have a polar transition state, a suggestion that was supported by UHF calculations. Good mass balance, chemical and quantum yields are also reported.

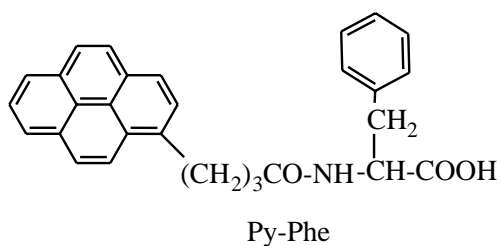
3. Leibovitch, M.; Olovsson, G.; Scheffer, J. R.; Trotter, J., "Determination of the Absolute Steric Course of an Enantioselective Single Crystal-to-Single Crystal Photorearrangement" *J. Am. Chem. Soc.* **1997**, *119*, 1462-1463.



In a remarkable example of solid state photochemistry, the dependable Yang cyclization and Scheffer's "ionic auxiliary concept" were showcased together in a remarkable single crystal-to-single crystal and enantioselective photoreaction. Although extremely rare, a unique aspect of the single crystal-to-single crystal reactions is that they

allow for X-ray structural elucidation of the reactant and the product as the reaction occurs and within a given specimen. These rare solid state reactions, also known as topotactic transformations, usually occur with high selectivities and high chemical yields and offer one of the greatest opportunities for detailed mechanistic analyses. The work described in this paper is particularly noteworthy because it represents one of the first examples where one such a reaction is obtained by a rational design. In Scheffer's strategy, the use of a carboxylic acid substrate and a chiral amine auxiliary are essential. The chirality of the environment is determined by the amine and helps insure an enantioselective reaction. The ionic contributions to crystal packing in the quaternary ammonium salt result in a high melting crystal (mp=210-213 °C) that is strong enough to withstand changes in composition. Chemical and optical yields greater than 85% were observed and the absolute steric course of the reaction was established.

4 Kumar, C.V.; Buranaprapukk, A., " Site-Specific Photocleavage of Proteins" *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2085-2087.



Although many photochemical nucleases have been developed for site-specific cleavage of DNA, until now, there has been no parallel developments in the case of photochemical proteases. In this noteworthy article by Kumar and Buranaprapukk, the site-specific photocleavage of proteins is achieved by use of a new and simple reagent generated by linking 4-(1-pyrenyl)butyric acid with L-phenylalanine. Spectral evidence shows that the hydrophobic pyrene moiety binds to the bovine serum albumin (BSA) protein. A decrease in the absorption of the pyrene chromophore and a change in its circular dichroism (CD) spectrum were noted when the concentration of BSA was increased. Also reflecting binding, the fluorescence lifetime of the probe increased from 106 ns for Py-Phe alone to 125 ns for the Py-Phe/BSA complex. Protein cleavage was accomplished by irradiation at 344 nm (direct excitation of the pyrene chromophore) in the presence of an electron acceptor ( $[\text{Co}(\text{NH}_3)_6]^{3+}$ ). Two new bands consisting of protein fragments of 41 and 28 kDa appeared on the gel after electrophoresis, thus demonstrating the specificity of the reagent. More work on identification of these fragments in addition to the cleavage mechanism is currently being pursued.

## Recent Advances in the Development of Metal Complexes as Artificial Photonucleases

Challa V. Kumar and Willy B. Tan

Department of Chemistry, University of Connecticut, Storrs, CT 06269

Studies leading to the design of artificial nucleases (molecules that cleave DNA) remains to be of much current interest because these molecules may be developed as probes for DNA structure and conformation, as DNA footprinting agents and as anti-tumor drugs. For purposes of footprinting, the ability of the designed molecule to produce reactive species such as hydroxyl radicals or singlet oxygen is enough to result in random cuts in the DNA. But for applications that require specificity of the cleavage such as in the development of drugs or structural probes, the reagents should have high binding affinity for the site of interest and cleave with high specificity.

Among the reagents studied over the past decade are numerous molecules that can be activated by photoirradiation. These DNA photonucleases are inactive in the dark but can be activated by irradiation at a particular wavelength - a property that gives specific advantages over other DNA cleaving agents. The DNA photocleaving agents developed so far may be classified as those that are based on derivatives of organic molecules and those that are based on metal complexes. Most of these molecules cause DNA strand-breaks through mechanisms that involve the formation of intermediates which participate in oxidation processes involving the base or the sugar of the DNA.

Several organic photochemical DNA-cleaving reagents such as anthraquinone derivatives<sup>1a-b</sup>, photocleaving amino-acids<sup>1c-e</sup>, riboflavin<sup>1f</sup> and naphthaldimides<sup>1g</sup> (all of which preferably cleave at the 5'-guanine (G) of a 5'-GG-3' sequence) are known. However, we would like to focus on progress reported in the last two years on metal complexes which are being developed as DNA photocleavers.

Extensive studies in this area have been done mostly on ruthenium(II) complexes due to the ease with which these complexes containing mixed ligand systems can be synthesized.<sup>2a-c</sup> The absorption and emission properties of these complexes also provide a handle to study the interaction of the complex with DNA using simple spectroscopic methods. Much of the earlier studies were on ruthenium(II) complexes with 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (phen) ligands. Ru(phen)<sub>3</sub><sup>2+</sup>, Ru(bipy)<sub>3</sub><sup>2+</sup> and related Ru(II) complexes have been shown to bind to the DNA by partial insertion of one of the three ligands between DNA base pairs and photosensitize strand breakage in DNA.<sup>2d-2i</sup> While strand breakage has been attributed in large part due to the generation of singlet oxygen, the contribution from an oxygen-independent pathway has been noted. The facts that the photocleavage event occurs with low quantum yields and the mechanism of the reaction is still not well-explained, prompted several researchers to do modifications to the complexes by changing the ligands or the metal center of the complex.

Ruthenium complexes containing the ligands 1,4,5,8-tetraazaphenanthrene (TAP), 2,2'-bipyrazine (bpz) or 1,4,5,8,9,12-hexaazatriphenylene (HAT) were synthesized, characterized and studied for their activity for DNA cleavage.<sup>3</sup> Irradiation of Ru(bpy)<sub>n</sub>(TAP)<sub>3-n</sub><sup>2+</sup> or Ru(bpy)<sub>n</sub>(HAT)<sub>3-n</sub><sup>2+</sup> in the presence of DNA resulted in increased photocleavage as n decreased from 3 to 0. This was an observation related to the strength of the molecules as photooxidizers. Laser flash photolysis experiments supported an electron transfer mechanism for DNA cleavage, since both the reduced metal complex and oxidized nucleotide radical cation were observed. Dialysis of the a photolysed sample containing DNA and Ru(TAP)<sub>3</sub><sup>2+</sup> confirmed the formation of covalent adducts which was

shown to be due to a covalent bond formation between the C atom  $\beta$  to the coordinated N in the HAT ligand and the N2 of guanine in the mononucleotide guanosine-5'-monophosphate (GMP).

The use of  $\text{Ru}(\text{phen})_2(\text{pheat})^{2+}$  (pheat=1,10-phenanthroline[5,6-b]1,4,5,8,9,12-hexaazatriphenylene) where a phenanthroline is fused to an hexaazatriphenylene combines the properties of an intercalator and a photoreagent that has a highly oxidizing excited state.<sup>4</sup> Absorption and emission studies show that the complex binds to DNA by two binding modes. Laser flash photolysis experiments indicate the occurrence of electron transfer from the GMP to the excited state of the complex although at a poor efficiency. However, the detection of radical ion when the complex is reacted with calf thymus DNA (CT-DNA) instead of GMP was limited by the time scale for the detection.

The complexes  $\text{Ru}(\text{phen})_2(\text{DPPZ})^{2+}$ ,  $\text{Ru}(\text{bipy})_2(\text{DPPZ})^{2+}$  and  $\text{Ru}(\text{bpz})_2(\text{DPPZ})^{2+}$  (DPPZ=dipyrido[3,2-a:a',3'-c]phenazine) were shown to bind to DNA with improved affinity<sup>5</sup> compared to phen or bipy complexes of ruthenium. Based on results from viscometry,<sup>6a</sup> unwinding,<sup>6b</sup> linear dichroism<sup>6c</sup> and resonance raman studies,<sup>6d</sup> the binding mode of these complexes has been concluded to involve intercalation of the dppz ligand into the DNA. Intercalation occurs from the major groove with the dppz ligand in two orientations such that groove solvent is more accessible in one orientation. This would result in a shorter emission lifetime.<sup>5,7a-b</sup> Intercalation from the minor groove has also been suggested based on results from emission titration experiments using CT-DNA and T4-DNA (a phage DNA) and emission lifetime measurements using polynucleotides.<sup>7c</sup>

$\text{Ru}(\text{bpz})_2(\text{DPPZ})^{2+}$  was shown to be more efficient in inducing DNA strand breaks than  $\text{Ru}(\text{bipy})_2(\text{DPPZ})^{2+}$ .<sup>8</sup> This may be due to the increased redox potential when the ligand is changed from bipyridine to bipyrazine. The efficiencies of  $\text{Ru}(\text{bpz})_3^{2+}$ ,  $\text{Ru}(\text{bipy})_3^{2+}$  and  $\text{Ru}(\text{bpz})_2\text{Cl}_2$  in cleaving DNA were compared and the oxidizing property of the complex was found to determine its efficiency as a photosensitizer for DNA cleavage. This trend is consistent with those observed by others and suggests that for intercalators, the efficiency of DNA photocleavage due to electron transfer is greater than via the singlet oxygen pathway.

In a related study, the intercalative property of the dppz ligand was combined with a reactive oxoruthenium(IV) functionality to study the sequence and structure preference of the complex  $\text{Ru}(\text{tpy})(\text{dppz})\text{O}^{2+}$  complex (tpy= 2,2',2''-terpyridine) for single and double-stranded DNA and other nucleic acids.<sup>9</sup> This method, however, did not require activation by light but relied on the oxidizing ability of the oxoruthenium functionality. Almost all the cleavage occurred at G sites with some contributions from sugar oxidation.

While most of the metal complexes developed has ruthenium as the metal center, reports on the DNA interaction of non-ruthenium complexes had been only a few. Among them are complexes containing Co(II), Rh(III) and Cr(II) with phen or modified phen ligands.<sup>10a-c</sup> Those that contain DPPZ are  $\text{Os}(\text{phen})_2(\text{DPPZ})^{2+}$  and  $\text{Re}(\text{py})_2(\text{CO}_3)(\text{DPPZ})^+$  (py=pyridine).<sup>11a-b</sup> The synthesis, characterization, DNA-binding and photochemical DNA-cleavage characteristics of  $[\text{Co}(\text{phen})_2(\text{DPPZ})]^{3+}$  and  $[\text{Ni}(\text{phen})_2(\text{DPPZ})]^{2+}$  have been recently reported.<sup>12</sup> Only the complex containing cobalt photocleaved the supercoiled plasmid DNA irradiated at 350 nm. Irradiation of the sample that contained the Ni complex did not show any cleavage. The paramagnetic nature of the complex which may "inactivate" the excited state of the molecule has been suggested to be responsible for this observation.

The ability of various Vanadium(V)-peroxo complexes to photocleave DNA has also been reported recently.<sup>13</sup> The mechanism of DNA cleavage using  $[\text{VO}(\text{O}_2)_2(\text{bpy})]^-$  is proposed to be due to the formation of singlet oxygen but the sequence or site-specificity of the reaction and cleavage product analysis are yet to be done.

Attempts have been made to combine the advantages provided by these metal complexes with organic derivatives. This would improve the binding of the reagent to DNA.<sup>14a</sup> Research in our own laboratory utilized derivatives of anthracene (like 9-anthracene methyl ammonium chloride, AMAC) in combination with

hexaamincobalt(III) complex to cause DNA cleavage preferably at 5'-GGA-3' sites upon irradiation at 390 nm.<sup>14b</sup> Selectivity was suggested to be a result of longer lifetimes of the excited state of AMAC at AT sequences, coupled with the ease of oxidation of GG sites when AMAC\* is oxidized by the cobalt complex.

Much progress has been made in the field. A majority of the DNA photocleavage reactions with metal complexes achieved so far are either non-sequence specific or specific only for G sites. Increased understanding of the mechanism of DNA cleavage by these complexes would help in designing better reagents. Coupling with more selective and site-specific DNA binders as recognition elements may also improve the design. Such reports will no doubt be forthcoming.

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# Determination of Equilibrium Constants for Weakly Bound Charge Transfer Complexes<sup>1</sup>

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When asked if we would like to contribute to the newsletter the first question that came to mind was What could we submit that would be appropriate for such a forum? There are a few advantages to publishing here. You do not have to worry about the referee's pen. You get to ramble on in a more familiar way than you normally would. How do we get to use these advantages in a way that will be most effective? In keeping with the IAPS philosophy of being instructive toward novice photochemists we settled on a describing our attempts to measure equilibrium constants for the formation of charge transfer (CT) complexes. This has been a problem that has plagued our research group for quite a while and, apparently, many other groups as well. We were interested in obtaining the spectra of weakly bound CT complexes over the entire uv-visible range that were free from interference from unbound acceptor and donor absorbance. To do this we needed to accurately determine the equilibrium constants for complex formation ( $K_{CT}$ ). A quick glance at the literature leads one to Benesi-Hildebrand analysis (Bene-Hil). A second glance reveals a considerable variation in the measured values for equilibrium constants using this procedure, particularly for weakly bound complexes. In spite of what must be perceived as a problem with this type of analysis, reports using this, or similar methods, flood the literature. What is collected below is a description of the rationale behind our method of obtaining  $K_{CT}$  values and spectra of weakly bound charge transfer complexes.

We do not claim to be the first group to navigate the maze of pitfalls that await the would-be experimentalist nor is it likely that this is the best method to be used under all conditions. Strictly speaking only weakly bound complexes studied by uv-visible spectroscopy can be determined in this way. However, the ideas presented are readily adaptable to many types of complexes and measurement techniques which should make this discussion of general interest. It is hoped that the depth of this report is sufficient to serve as an introduction to this material for a senior undergraduate class and a literature review is not what we set out to do.<sup>2</sup> In light of the fact that there seem to be many variations in published values of  $K_{CT}$  for complexes of this type, a review may not even be a good idea until a rational explanation for the discrepancies can be found. What is hoped is that this report will foster a renewed interest in these measurements and lead to a critical examination of the available data.

In 1949 Benesi and Hildebrand published their seminal report on the determination of the equilibrium constant for the formation of an iodine/benzene charge transfer complex.<sup>3</sup> The determination was based on a simple one-to-one donor/acceptor complex being formed according to equation 1.



The equilibrium expression is:

$$K_{CT} = [AB]/[A][B] \quad (2)$$

Assuming the initial concentration of B,  $[B]_0$ , is present in vast excess of  $[A]_0$  and considering the mass balance expressions for A and B it can be shown that  $[B] \sim [B]_0$  under all conditions. This must be true since the complex concentration,  $[AB]$ , can never be greater than  $[A]_0$ . If we further assume that only the complex absorbs at the monitoring wavelength,  $OD = \epsilon_{CT} b[AB]$  and that  $\epsilon_{CT}$  does not change with changing concentration of B, we arrive at the Benesi-Hildebrand equation (Bene-Hil, equation 3).

$$1/OD = (1/bK\epsilon_{CT}[A]_0)1/[B]_0 + 1/b\epsilon_{CT}[A]_0 \quad (3)$$

A plot of  $1/OD$  versus  $1/[B]_0$  should be linear with a slope of  $1/bK\epsilon_{CT}[A]_0$  and y-intercept of  $1/b\epsilon_{CT}[A]_0$ . We will assume  $b = 1$  cm for the remainder of this report. The value of  $K_{CT}$  is determined by the ratio of the y-intercept to the slope or it can be obtained graphically from the  $-x$  intercept. The component to be held constant, A, must be lower in concentration than B and in practice the ratio  $[B]_0/[A]_0$  is at least 10-20. There are several alternative relationships that have been derived from equation 3, such the Scott equation<sup>4</sup> (equation 4), and the Foster-Hammick-Wardley (FHW) equation<sup>5</sup> (equation 5).

$$[A]_0[B]_0/OD = [B]_0/\epsilon_{CT} + 1/(K\epsilon_{CT}) \quad (4)$$

$$OD/[B]_0 = -K_{CT}(OD) + K\epsilon_{CT}[A]_0 \quad (5)$$

These relationships do not differ from (3) in substance and correctly weighted data will yield the same answer in each case. Using the Scott equation,  $[A]_0[B]_0/OD$  is plotted versus  $[B]_0$ . The value of  $1/K_{CT}$  is determined from the ratio of the y-intercept to the slope or it can be obtained graphically from the  $-x$  intercept. As with Bene-Hil analysis both the slope and intercept are required to determine  $K_{CT}$ . However, in this case, the plot extrapolates to infinite dilution, not infinite concentration as in Bene-Hil. As a result small deviations in baseline do not influence the Scott analysis as heavily. In the case of FHW analysis, the slope of the plot of  $OD/[B]_0$  versus  $OD$  gives  $-K_{CT}$  directly. If  $\epsilon_{CT}$  is required it can be obtained from the ratio of the y-intercept to the slope and again the extrapolation is to infinite dilution. Each of these equations require the use of large  $[B]_0/[A]_0$  ratios which may not always be convenient.

An alternative method<sup>6</sup> developed by Rose and Drago uses the relationship:

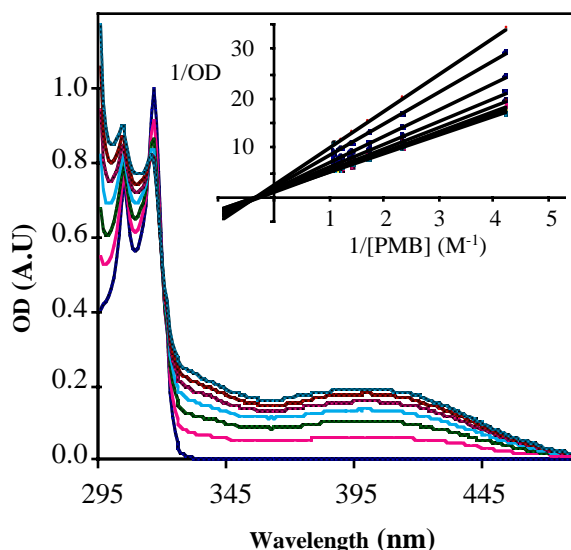
$$1/K_{CT} = OD/\epsilon_{CT} - [A]_0 - [B]_0 + ([A]_0[B]_0\epsilon_{CT})/OD \quad (6)$$

For this analysis the OD at one wavelength is measured for a solution of A and B and the calculated value of  $1/K_{CT}$  is plotted as a function of assumed values of  $\epsilon_{CT}$ . Subsequent measurements are taken for different concentrations of A and/or B and additional lines are plotted on the same graph. The intersection of all of the lines give the value of  $K_{CT}$  and  $\epsilon_{CT}$ . This method differs slightly from the other three in that no assumptions about the relative magnitudes of [A] and [B] are made. The accuracy of the determination depends on a judicious choice of the concentration of A and B used in the study.

With the increased access to computer power has come the ability to study entire sets of spectra simultaneously. These global analysis routines, using factor analysis,<sup>7</sup> have tremendous advantages over the single wavelength determinations described since they do not require assumptions as to the relative magnitudes of [A] and

[B] and, since a globally optimized parameter set is produced they have a signal averaging affect as well. Yet, as will be shown, all of these analyses share a common fault.

If the apparent  $K\epsilon_{CT}$  changes for each sample a single Bene-Hil plot may still be linear, but will give false results. To help detect this problem, data should be obtained at multiple wavelengths across the CT band. The series of spectra obtained for the formation of tetracyanobenzene/pentamethylbenzene (TCNB/PMB) CT complex is shown in Figure 1. Resulting Bene-Hil plots of  $1/OD$  versus  $1/[PMB]$  obtained these spectra are shown in the inset. The family of Bene-Hil plots was obtained by taking data at several wavelengths between 345 nm and 445 nm across the CT absorption band. If different x-intercepts were observed with changing wavelength, this would have been clear indicator that there is a problem with these data. Since the x-intercepts in this plot do not show a clear deviation with wavelength than the spread in values gives an idea of the precision of the determination (unfortunately not of the accuracy!). The Scott equation would also calculate a family of lines with the same x-intercept while the FHW relation yields parallel lines. In each case similar deviations can be observed. Since the family of lines shown in the inset of Figure 1 all intersect the x-axis at the same point  $K_{CT}$  and  $\epsilon_{CT}$  are accurately determined,  $K_{CT} = 0.31 M^{-1}$  and  $\epsilon_{CT} = 3540 cm^{-1}M^{-1}$  at 400 nm. Or are they?

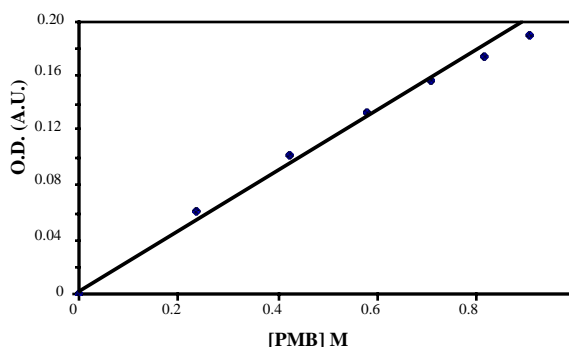


**Figure 1.** Spectra obtained by adding PMB (ca. 0.2 - 0.9 M) to a solution of TCNB ( $3.2 \times 10^{-4}$  M) in dichloroethane. Inset: Benesi-Hildebrand plots obtained using data at wavelengths between 350-445 nm. The value of the apparent  $K_{CT}$  obtained is  $0.31 M^{-1}$ .

A critical consideration in these measurements is the concentration range used. As a general rule, 20-80% of the complexation curve is required to accurately measure the equilibrium constant.<sup>8</sup> Here percent complexation is defined as  $C\% = [AB]/[A]_0$  where  $[A]_0$  is the concentration of the limiting reagent. Inherent in the assumption that B is present in large excess of A, and therefore that  $[B] \sim [B]_0$ , is that A is *not* in large excess with respect to AB. This usually requires high concentrations of either acceptor or donor (or both) to be present in solution. It is not possible to work at such high concentrations and avoid 2:1 or 1:2 complexes. This than is the conundrum with these analyses. At very low total concentration ( $C_t = [A]_0 + [B]_0$ ) it is (almost) as reasonable to assume  $[A] \sim [A]_0$  and as it is to assume  $[B] \sim [B]_0$ . Now equation 7 holds and only the product  $K\epsilon_{CT}$  can be obtained. The intercept is zero.

$$OD_i = K\epsilon_{CT} [A]_0[B]_0 \quad (7)$$

In this case a single parameter, the slope, is used to completely describe the data. Since this equation must hold at infinite dilution we call this the ideal optical density and experiments carried out such that equation 7 holds are the ideal conditions. Notice that ideal refers to “ideal solution behavior” and not to “ideal case scenario for determining  $K_{CT}$ ”. What we need to determine  $K_{CT}$  and  $\epsilon_{CT}$  separately is to require the data support the determination of two parameters. Fitting a plot of OD versus  $[B]_0$ , as shown in Figure 2, to a line with zero as the intercept and obtaining a correlation coefficient squared of ca.  $R^2 = 0.9903$  suggests there are very little “data” left to support the determination of a second parameter. What is required to accurately obtain both  $K_{CT}$  and  $\epsilon_{CT}$  is substantial curvature in a plot of OD versus  $[B]_0$ . Only then is it possible to determine  $K_{CT}$  and  $\epsilon_{CT}$  independently. It is not surprising that large discrepancies in  $K_{CT}$  and  $\epsilon_{CT}$  are found in the literature while the product,  $K\epsilon_{CT}$ , is quite consistent. In this case, to obtain even the small amount of curvature observed in Figure 2, very high concentrations of PMB are required. There is little doubt that under these conditions 2:1 complexes are also formed. Low total concentrations are required to avoid the formation of these higher order complexes.



**Figure 2.** Plot of OD versus the concentration of PMB for the data shown in Figure 1. Application of equation 7 gives the line shown with  $R^2 = 0.9903$ .

On the other hand, in order to accurately determine the product,  $K\epsilon_{CT}$ , what is required is *minimal* curvature in an  $OD_m$  versus  $[B]_0$  plot, a situation that is usually the case for weakly bound complexes. For these cases the *only* thing we can accurately determine is the product  $K\epsilon_{CT}$ . To do this we obtain the slope of the line connecting each point with the origin for all of the data available. Plotting these slopes versus  $[B]_0$  and extrapolating to infinite dilution gives us the best estimate of  $K\epsilon_{CT}$ . Analysis of all of our data, including data obtained with very low total concentrations, gives an average value of  $K\epsilon_{CT} = 1024 \text{ M}^{-2}$ .

Are Bene-Hil analyses done under the best conditions to obtain  $K_{CT}$  and  $\epsilon_{CT}$ ? To obtain the maximum curvature in an OD versus  $[B]_0$  plot we require the greatest relative deviation from ideal behavior. For initial concentrations of  $A = [A]_0$  and  $B = [B]_0$ , the equation of interest is:

$$K_{CT} = [AB] / \{([A]_0 - [AB]) ([B]_0 - [AB])\} \quad (8)$$

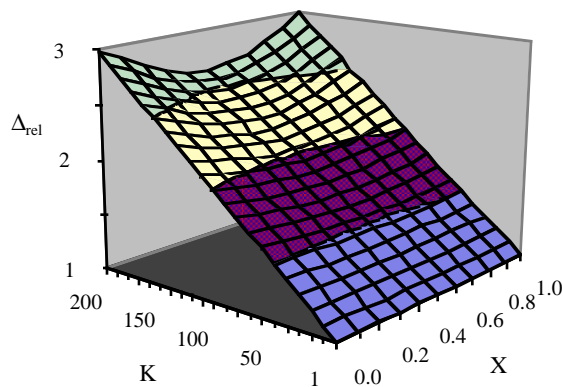
Substitution  $OD_m = \epsilon_{CT} [AB]$  and solving for  $OD_m$  in terms of  $[A]_0$  and  $[B]_0$  gives an exact solution:

$$OD_m = \epsilon_{CT} \left( ([A]_0 + [B]_0 + 1/K_{CT}) - \sqrt{([A]_0 + [B]_0 + 1/K_{CT})^2 - 4[A]_0[B]_0} \right) / 2 \quad (9)$$

To facilitate reasonable comparison we should compare data obtained at equal total concentration ( $C_t = [A]_0 + [B]_0$ ) but with different relative mole-fractions ( $X_{rel} = [A]_0 / C_t$ ). For simplicity we also require the product  $K\epsilon_{CT}$  to remain constant. We can then define the relative deviation from ideal behavior as being the ratio of the ideal optical density to the measured optical density,  $\Delta_{rel} = OD_i / OD_m$ .

$$\Delta_{rel} = 2K_{CT}[A]_0[B]_0 / \left( ([A]_0 + [B]_0 + 1/K_{CT}) - \sqrt{([A]_0 + [B]_0 + 1/K_{CT})^2 - 4[A]_0[B]_0} \right) \quad (10)$$

Figure 3 shows the relevant surface plot of  $\Delta_{rel}$  with the assumed conditions  $C_t = 0.01$  M and the product  $K\epsilon_{CT} = 100$  M<sup>-2</sup>. In this plot the ideal behavior corresponds to the bottom of the box. Examination of the  $\Delta_{rel}$  surface shows that the highest deviation from ideal behavior occurs for  $X$  close to 0 or 1. These correspond to the best conditions to obtain both  $K_{CT}$  and  $\epsilon_{CT}$  from a single set of data and are exactly the conditions used for collecting Benesi-Hildebrand data.



**Figure 3.** Surface plot showing the relative deviation from ideal behavior,  $\Delta_{rel}$ , under the assumed conditions  $C_t = 0.01$  M and  $K\epsilon_{CT} = 100$  M<sup>-2</sup>. (See Text)

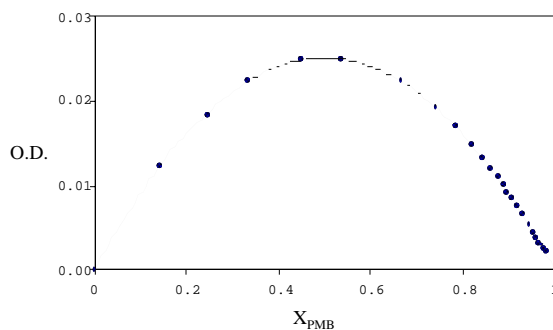
We are still faced with the problem How do we work in a reasonable concentration range, perhaps battling poor solubility, and have high percent complexation yet not allow 2:1 complexes to be formed competitively? We must work under conditions where the maximum deviation from ideal behavior can be observed under the constraints of low concentration. For weakly bound complexes what is required is the highest concentration of 1:1 complex at the lowest possible total concentration,  $C_t = [A]_0 + [B]_0$ . The important mass balance relationships are:

$$[A] = C_t(X) - [AB] \quad (11)$$

$$[B] = C_t(1-X) - [AB] \quad (12)$$

$$[AB] = K[A][B] \quad (13)$$

where  $X$  is the relative mole fraction of A given by  $X = [A]_0 / ([A]_0 + [B]_0) = [A]_0 / C_t$ . The condition that  $[AB]$  is a maximum requires that  $d[AB]/dX = 0$ . Combining equations 11, 12 and 13 and taking the derivative with respect to  $X$  shows that  $[AB]$  is a maximum when  $X = 0.5$ . This is the basis of continuous variations plots, or Job's analysis, for the determination of the compositions of complexes. A Job's plot for TCNB/PMB is shown in Figure 4 where  $C_t = 1.05 \times 10^{-2}$  M. The plot is symmetric about the maximum of  $X = 0.5$ . This is solid evidence that only 1:1 complexes are formed in this concentration range. It is also apparent that at any total concentration up to  $10^{-2}$  M the concentration of 1:1 complex will be the greatest when the concentrations of A and B are equal ( $X = 0.5$ ). In contrast, Bene-Hil plots are obtained when  $X$  is equal to 0.9 and greater (or 0.1 and smaller). This corresponds to the regions when the complex formation is at a minimum for the total concentration used. While Bene-Hil conditions are ideal for strongly bound complexes, weakly bound complexes can not be studied in this way.

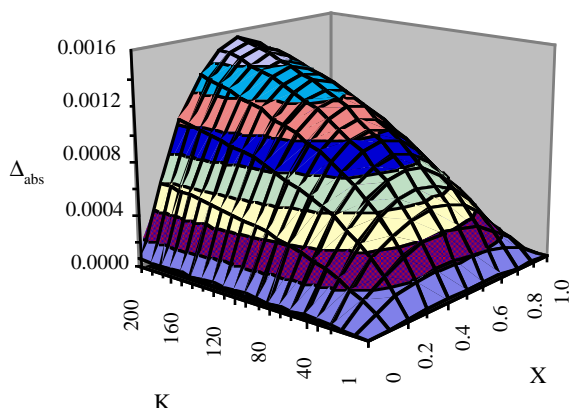


**Figure 4.** Plot of the optical density observed at 400 nm versus the relative mole fraction of PMB added (Job's plot). The total concentration used  $C_t = [\text{TCNB}]_0 + [\text{PMB}]_0 = 1.05 \times 10^{-2}$  M.

Instead we define the absolute deviation from ideal behavior as being the difference between the ideal optical density and the measured optical density,  $\Delta_{\text{abs}} = \text{OD}_i - \text{OD}_m$  where the following expression applies:

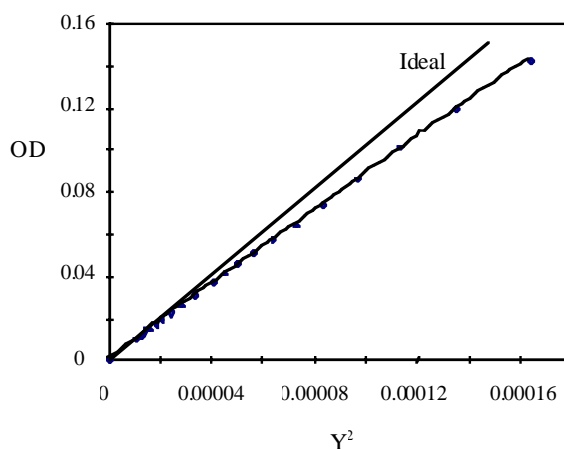
$$\Delta_{\text{abs}} = K\epsilon_{\text{CT}}[A]_0[B]_0 - \epsilon/2(( [A]_0 + [B]_0 + 1/K_{\text{CT}}) - \sqrt{(( [A]_0 + [B]_0 + 1/K_{\text{CT}})^2 - 4[A]_0[B]_0)}) \quad (14)$$

Figure 5 shows a plot of  $\Delta_{\text{abs}}$  under the same assumed conditions as Figure 3, namely  $C_t = 0.01$  M and the product  $K\epsilon_{\text{CT}} = 100$ . In contrast to Figure 3, now a maximum at equal concentration A and B is observed. Even at low  $K_{\text{CT}}$  values the  $\Delta_{\text{abs}}$  surface is sensitive to changes in  $X$ , particularly when compared to the  $\Delta_{\text{rel}}$  surface.



**Figure 5.** Surface plot showing the absolute deviation from ideal behavior,  $\Delta_{\text{abs}}$ , with the assumed conditions  $C_t = 0.01 \text{ M}$  and  $K\epsilon_{\text{CT}} = 100 \text{ M}^{-2}$ . (see text)

What is required is a series of spectra for samples with equal concentrations of A and B,  $[A]_0 = [B]_0 = Y$ , and plot the measured OD as a function of  $Y^2$ . Such a plot for TCNB/PMB solutions with the concentration varying between  $10^{-2} - 10^{-4} \text{ M}$ , at 400 nm, is shown in Figure 6. As was the case with the Bene-Hil plots, curvature in this plot is needed for the two parameters,  $K_{\text{CT}}$  and  $\epsilon_{\text{CT}}$ , to be determined independently. As can be seen, only the most careful of measurements will result in well defined curvature in these cases. These plots are usually straight, as was expected based on the analysis of the  $\Delta_{\text{rel}}$  surface. At first it might appear that we can not determine the desired quantities from this plot, and indeed from this plot alone we can not.



**Figure 6.** Plot of the observed optical density as a function of  $Y^2$  where  $Y = [\text{TCNB}]_0 = [\text{PMB}]_0$ . The line through the data is the best fit line obtained using equation 9 with  $K_{\text{CT}} = 6.8 \text{ M}^{-1}$  and  $\epsilon_{\text{CT}} = 150 \text{ cm}^{-1} \text{ M}^{-1}$ . The ideal line is calculated assuming ideal conditions (equation 7) with  $K\epsilon_{\text{CT}} = 1023 \text{ M}^{-2}$ . Both lines assume a  $1.0 \text{ cm}^{-1}$  cell (see text).



As outlined above, Bene-Hil type plots for weakly bound systems can be used to determine the product  $K\epsilon_{CT}$  quite accurately. This ideal behavior line is included on Figure 6. Since  $K_{CT}$  and  $\epsilon_{CT}$  are both constants, the product  $K\epsilon_{CT}$  must also be a constant for the system under study. We now require the data shown in Figure 6 to have the value  $K\epsilon_{CT} = 1024 \text{ M}^{-2}$ , as was determined from the average of our early data. We now fit the data, with this addition constraint, and accurately determine  $K_{CT}$ . Once  $K_{CT}$  is obtained  $\epsilon_{CT}$  is easily determined. Analysis of the data in Figure 6 leads to  $K_{CT} = 6.8 \text{ M}^{-1}$  and  $\epsilon_{CT} = 150 \text{ cm}^{-1}\text{M}^{-1}$  and the predicted line based on these values is shown. These values are a far cry from the Bene-Hil estimates<sup>10</sup> of  $K_{CT} = 0.32 \text{ M}^{-1}$  and  $\epsilon_{CT} = 3120 \text{ cm}^{-1}\text{M}^{-1}$ . If the Bene-Hil estimates are used to fit the data according to equation 9, a line very similar to that obtained for the ideal optical density is obtained, leaving no doubt they are in error.

Why are the Bene-Hil estimates so far off? This type of analysis, as well as Scott, FHW, Rose-Drago and global analysis, all require i) the largest possible relative deviation from ideal behavior and ii) the system under study must behave according to a model such as equation 1. In this case, and presumably many others, under the conditions needed to obtain high percent complexation, 2:1 complexes strongly influence the determination such that the model becomes invalid.

In conclusion, equilibrium constants of weakly bound complexes can be determined from data collected at moderately low percentage complexation but not by using Benesi-Hildebrand plots alone. Percent complexation is not the major consideration in these measurements but the maximum detectable deviation from ideal behavior is required, as described. Data obtained using Benesi-Hildebrand conditions in conjunction with data obtained at equal concentrations of A and B should be used to determine the independent values of  $K_{CT}$  and  $\epsilon_{CT}$ . These conditions combine to allow the most accurate determination of very small equilibrium constants.

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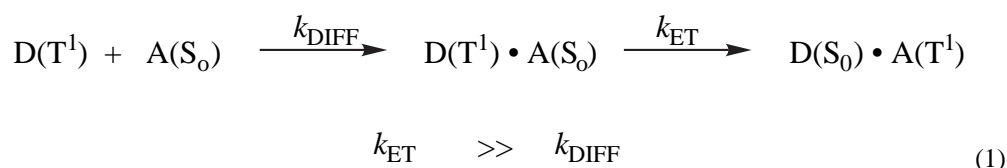
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- (10) These estimates are average values obtained from several sets of data similar to those shown in Figure 1. The product of these two values ( $K\varepsilon_{\text{BH}} = 998.4 \text{ M}^2$ ) is close to, but not exactly, the ideal conditions value obtained at infinite dilution ( $K\varepsilon_{\text{CT}} = 1024 \text{ M}^2$ ).

## The Close Relationship between Intermolecular Triplet Energy Transfer and Electron Transfer

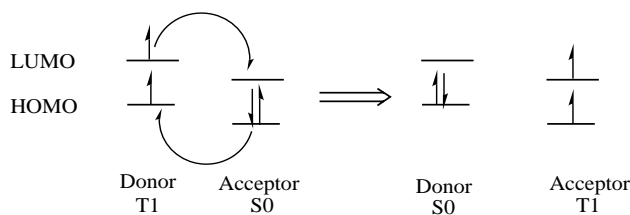
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A model for triplet energy transfer (TT) based on the Golden Rule formalism has emerged over the last several years that is both elegant and useful. We feel our results on intermolecular energy transfer are best understood using this treatment. Therefore, we would like to take this opportunity to discuss these results in the context of the work used to develop this interpretation.

Triplet energy transfer was originally observed in 1956 by Terenin and Ermolaev<sup>1</sup> who studied the quenching of the benzophenone phosphorescence by naphthalene at 77 K in a frozen matrix. The quenching of the benzophenone phosphorescence accompanied by a concomitant growth of naphthalene phosphorescence gave unambiguous evidence for triplet energy transfer. The diffusion limited rate constants typically observed in isotropic solution for exothermic triplet energy transfer has led to the proposal of a mechanism<sup>2</sup> in which the donor and acceptor molecules initially form a contact complex at the rate of diffusion ( $k_{\text{DIFF}}$ ), equation 1. Within the contact complex the donor decays to the ground state while the acceptor simultaneously moves into the triplet excited state in a process analogous to intersystem crossing within a unimolecular system. The rate of energy transfer within the complex is much greater than the rate of diffusion, so that diffusion is rate determining.



This phenomenon is congruous with the model attributed to Dexter<sup>3</sup> which describes TT as a nonradiative decay process that occurs by the simultaneous exchange of electrons between the donor and acceptor, Figure 1. Dexter describes the probability of TT in terms of both the magnitude of an exchange integral between the donor and acceptor as well as the Franck-Condon factors of the transition. This model serves as the foundation for research into the mechanism of exchange energy transfer.



**Figure 1.** FMO description of the Dexter exchange mechanism.

Because close contact is needed between the donor and acceptor is required for exchange energy transfer to occur efficiently a great deal of mechanistic information is buried by the rate of bimolecular transport. However,

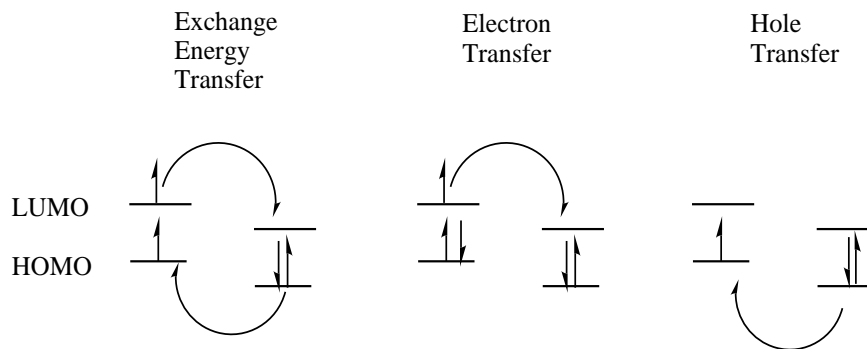
important clues about the mechanism of TT were obtained in isotropic solution. The observation that the rate constant for endothermic TT is greater than that predicted using the simple Boltzman distribution treatment of Sandros led to questions about the role of nuclear reorganization.<sup>4</sup> Another important observation was that although exothermic TT is generally so rapid at van der Waals separation distance as to preclude any steric effects, twisted  $\pi$ -systems minimize the electronic overlap so the rate constant falls below the diffusion limited value.<sup>5</sup> It became apparent that a more detailed description of triplet energy transfer was needed.

A lucid application of the Dexter model was presented by Balzani, Bolletta and Scandola in which the rate constant of TT was described to be a product of both electronic overlap and nuclear reorganization factors.<sup>6</sup> A compelling argument was made that the apparent anomalies observed in energy transfer rate constants could be explained using a theoretical treatment in which differences in nuclear reorganization that accompany the  $S_0 \rightarrow T_1$  transition affect both the intrinsic barrier to TT as well as the energetics of the transition. The authors also pointed out that the orbital overlap criterion is very stringent since favorable and simultaneous overlap of four orbitals is required (HOMO-HOMO and LUMO-LUMO). This description of exchange energy transfer argues that weakly coupled systems can be described by the Golden Rule formalism, equation 2:

$$k = (4\pi/\hbar)|V|^2 \text{FCWDS} \quad (2)$$

where  $V$  is the electronic coupling matrix element, and FCWDS is the Franck-Condon Weighted Density of States containing the nuclear reorganization terms for both the reactants and the solvent. In principal the Golden Rule is applicable to any nonadiabatic radiationless transtion, where  $V \ll k_B T$ , and therefore should describe both long range electron and exchange energy transfer. It was mentioned in the Balzani discussion of the Dexter mechanism that the theories developed for describing electron transfer should also be applicable to exchange energy transfer.<sup>6</sup> This statement would prove prophetic.

The relationship between the electron and energy transfer in intramolecular systems was firmly established experimentally by Closs et. al. in 1988.<sup>7</sup> The investigators studied systems in which the donor and acceptor pair were attached to an interconnecting rigid spacer. This technique circumvented the kinetic complications inherent in bimolecular energy transfer, and had been used previously in qualitative studies.<sup>8</sup> In this series of elegant experiments, the Dexter description of TT was confirmed by correlating quantitatively the rates of exchange energy transfer within a number of related molecules. Varying interchromophoric distances, and orientations, provided rates of charge transfer involving both electron and hole transfer in the same molecular system.



**Figure 2.** Comparison of exchange energy transfer, electron transfer and hole transfer.

If the depiction shown in Figure 2 is correct, the probability of exchange energy transfer should be proportional to the product of the probability of electron and hole transfer. A satisfactory correlation was obtained when corrections were made for variations in the solvent reorganization energy. The authors found that because exchange energy transfer produces a nonpolar triplet state, solvent reorganization is not influenced by changes in the intervening distance between donor and acceptor. In addition, since the solvent reorganization energy is modest for energy transfer, the rate constant is more sensitive to contributions from the electronic coupling and internal reorganization terms (Franck-Condon factors) than in the analogous charge transfer reactions. In summary, the results of Closs comprise a convincing argument that the Golden Rule formalism is a useful foundation from which to base investigations of exchange energy transfer.

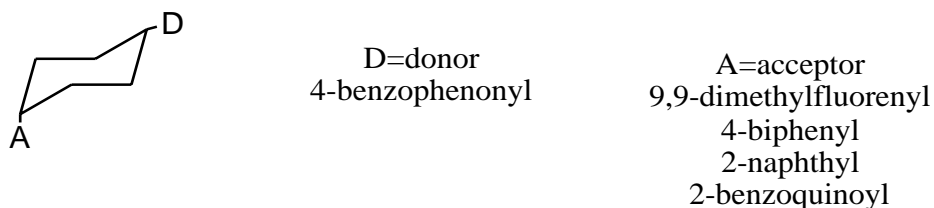
The correlation of energy transfer with electron transfer implies that the experimentally confirmed proposal of Marcus<sup>9-10</sup> concerning the dependence of electron transfer rate on driving force in weakly coupled systems should also apply to exchange energy transfer. The semiclassical Marcus equation follows where  $\lambda$  is the overall reorganization energy,  $-\Delta G$  is the driving force for the reaction, and the other parameters have the standard meaning.

$$k = \sqrt{\frac{\pi}{h\lambda k_B T}} |V|^2 \exp \left\{ - \left[ \frac{(\lambda - (-\Delta G))^2}{4\lambda k_B T} \right] \right\} \quad (3)$$

The distinctive feature of the Marcus model is that it predicts that the rate of exchange energy transfer will depend on reaction free energy so that the electron transfer rates initially increase with increased driving force (normal region), but once the driving force becomes greater than the nuclear reorganization terms the rate decreases with additional driving force (inverted region).

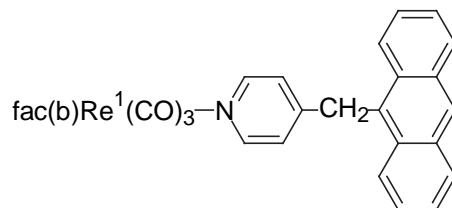
Because solvent reorganization is a minor component of the overall reorganization energy, it is necessary to divide the Frank-Condon factors into a high energy component representing the internal reorganization of the donor and acceptor, and a low energy component representing solvent reorganization. Accordingly, analysis of experimental results rely upon the Marcus-Jortner treatment<sup>11</sup> which explicitly divides the FCWDS into low energy ( $h\nu < k_B T$ ) modes for solvent reorganization and high energy modes ( $h\nu \gg k_B T$ ) for the internal reorganization of the donor and acceptor, in terms of a single frequency  $\nu$ . This approach makes it possible to treat the different vibrational modes explicitly, which is critical for a quantitative treatment of exchange energy transfer data.

The inverted region was observed for energy transfer using intramolecular systems by the Closs<sup>12</sup> and Schanze<sup>13</sup> groups. These results illustrate the significant effect of internal reorganization energy upon exchange energy transfer. Closs chose a 1,4-cyclohexanediyl spacer to separate 4-benzophenone and different organic acceptors within the same molecule in order to vary the driving force for energy transfer while keeping the other variables constant, Figure 3.



**Figure 3:** Closs's system for investigating the rate dependence on driving force for exchange energy transfer.

Although the inverted region was observed, the data obtained with this combination of donor and acceptors did not give a very good fit to a theoretical model based on an expanded Marcus-Jortner treatment. One possible problem is that in this series it was not feasible to fit the data to a single set of Franck-Condon factors due to the variations in the internal reorganization energy within the series.<sup>12</sup> In contrast Schanze et. al were able to successfully correlate the energy transfer rates from the  $d\pi(\text{Re}) \rightarrow \pi^*$  (diimine) MLCT chromophore to anthracene, Figure 4, with the Marcus-Jortner expression.<sup>13</sup>

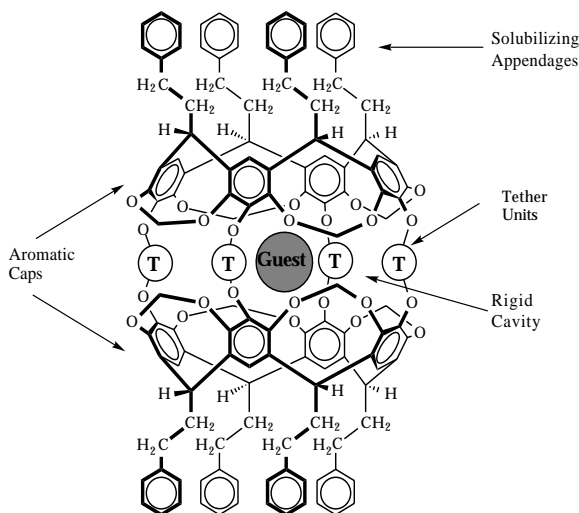


**Figure 4.** Schanze's system for investigating the rate dependence on driving force for exchange energy transfer.

The changes in the fac ligand used to vary reaction driving force do not appear to significantly affect the modest internal reorganization energy of 3.8 kcal/mol, and therefore a good correlation was observed. The nonpolar nature of the  $S_0 \rightarrow T_1$  transition was evidenced in the low solvent reorganization energy of 3.5 kcal/mol so that exchange energy transfer moves into the inverted region at a driving force of 7.3 Kcal/mol. As predicted,<sup>7</sup> this value is much lower than the driving force needed to move electron transfer into the inverted region.<sup>14</sup> Most importantly, the clearly observed inverted region removes any question about the close relationship between electron and exchange energy transfer.

Results of special interest to us were obtained with an intermolecular system by the Meyer group.<sup>15</sup> The rate constants for bimolecular energy transfer reactions between 2,3-benzanthracene and several  $[\text{Os}(\text{bpy})_3]^{+2}$  complexes fall below the diffusion limited value and follow a Marcus dependence on driving force. We set out to see if this situation could be reproduced using supramolecular systems.

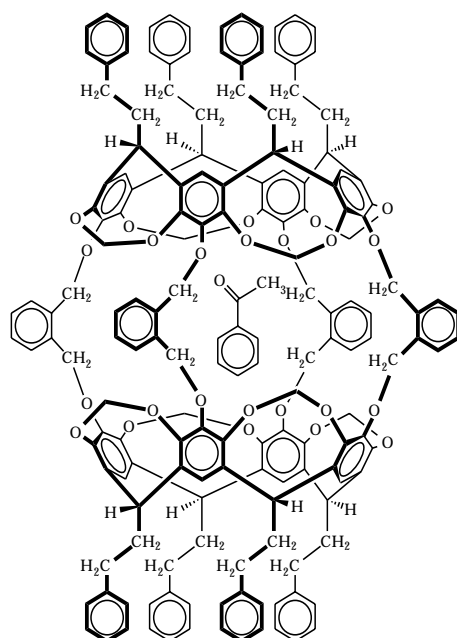
The systems employed in our study were originally developed in the group of Prof. Donald J. Cram at UCLA and are defined by two aromatic caps joined together by four tether molecules.<sup>16</sup> The top and bottom of the cage have surface appendages that provide solubility in organic solvents, Figure 5.



**Figure 5.** Typical Hemicarcerand Structure.

This approach is attractive because: **1.** The donor and acceptor are prevented from coming into direct contact with each other. **2.** No bonds connect donor and acceptor, so the through bond mechanism as it is commonly defined will not be operative. For example, molecular incarceration has been used to generate cyclobutadiene<sup>17</sup> and benzyne.<sup>18</sup> If cyclobutadiene were to come into contact with oxygen or another cyclobutadiene immediate reaction would occur, and benzyne would not be observed if contact with other molecules was not rigorously excluded. The remarkable stability of incarcerated molecules demonstrate that species deeply buried within the host have no "bond-forming" contact with the external milieu.

Our first experiment was the determination of the rate of energy transfer from a triplet sensitizer encapsulated within a hemicarcerand to acceptors in the same solutions but outside of the hemicarcerand.<sup>19</sup> Modeling studies predicted that acetophenone would fit tightly within hemicarcerand **1** constructed using *o*-xylyl tether units to give **1**•acetophenone (**1**•Ac), Figure 6.

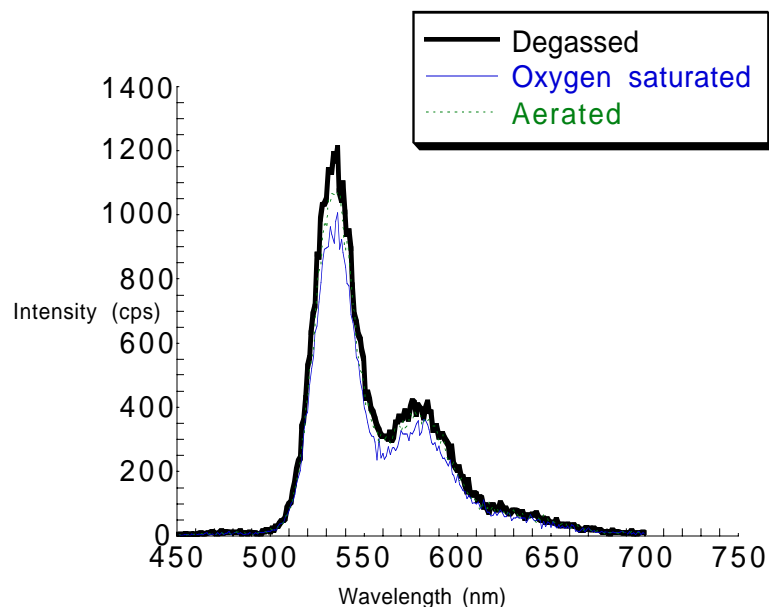


**Figure 6.** Structure of **1·acetophenone**.

Both the acetophenone and **1·Ac** transfer triplet energy to *cis*-piperylene at, or very near, diffusion controlled rates. At least part of the observed small difference could be attributed to the fact that **1·Ac**, being much more massive than acetophenone, will have a smaller diffusion rate. While the results established that atom-to-atom contact between donor and acceptor is not required for exchange energy transfer it does not give any information about the relative rates of excitation transfer within the contact complexes. We only know that transfer is concluded within the lifetime of the contact complex.

In an attempt to achieve more discrimination we switched to a system that uses biacetyl (2,3-butanedione), which has a lower triplet excitation energy than acetophenone, as a donor.<sup>20</sup> In addition to having the desired lower triplet excitation energy, the biacetyl system is attractive since triplet lifetime can be conveniently measured by determination of the phosphorescence intensity.<sup>20</sup> Phosphorescence of acetophenone is too weak to allow its quenching to be monitored easily with equipment available to us. The **1·biacetyl** complex was prepared, and solutions of the complex were found to be stable for weeks at room temperature.<sup>21</sup> The rates of quenching of naked biacetyl for exoergic energy transfer is near or at the diffusion controlled limit ( $>10^9 \text{ M}^{-1}\text{s}^{-1}$ ). However, the rates of quenching are much slower for **1·biacetyl**, and vary systematically with different acceptors. The change in rate constant for the quenching of **1·biacetyl** by oxygen is demonstrated by the persistent phosphorescence of **1·biacetyl** in the presence of oxygen, Figure 7.

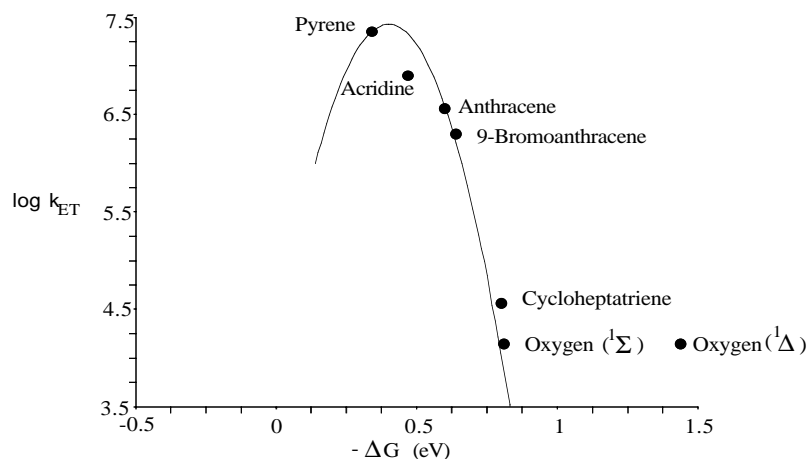




**Figure 7:** The effect of adding oxygen on the phosphorescence intensity of the 1-biacetyl complex.

Since all of the rates with 1-biacetyl are well below the diffusion limited value they can be interpreted as reflecting differences in the rates of energy transfer. The result is especially dramatic with oxygen, which does quench 1-biacetyl, but at a rate three orders of magnitude lower than that for pyrene, Figure 8. In fact, when observed in the absence of other data, the slow oxygen quenching of 1-biacetyl was interpreted by the Balzani group as indicating that no quenching occurred and was extrapolated to the conclusion that energy transfer through the walls of a hemicarceplex cage could not occur.<sup>22</sup> The decrease in the observed rate constant is attributed in a reduction in the electronic coupling due to the increase in intervening distance imposed by the hemicarceplex skeleton so that  $V \ll k_B T$ , and TT through the hemicarceplex is a nonadiabatic process.

If the low TT rate constants are due to the nonadiabatic nature of the transitions the observed data should correlate with a curve generated using equation 3. Indeed a plot of  $\log k_{TT}$  vs.  $(-\Delta G)$  gives good qualitative agreement with a normalized theoretical curve, Figure 8, indicating we are observing a nonadiabatic energy transfer that moves into the inverted region at approximately 9 Kcal/mol driving force.



**Figure 8:** A plot of  $\log k_{ET}$  vs.  $(-\Delta G^\circ)$  for the triplet energy transfer involving 1-biacetyl and a curve generated using eq. 3 where  $\lambda$  equal 0.40 eV (9 Kcal/mol).

The domination of the Franck-Condon factors by vibrational modes within the donor and acceptor suggests the comparatively slow rate of energy transfer to oxygen is due to two factors: **1.** The huge electronic energy gap, and **2.** the scarcity of vibrational modes in  $O_2$ ,<sup>23</sup> and is not an anomaly due to the unique structure of the 1-biacetyl complex. At present we can not say whether the  $^1\Sigma$  or  $^1\Delta$  singlet state of oxygen is involved in the energy transfer reaction. However, since the driving force is smaller for transfer to the  $^1\Sigma$  state, and transfer to this state has been shown to be kinetically favorable in isotropic solution<sup>23b</sup> we believe that we are predominantly forming the  $^1\Sigma$  state

The qualitative model was developed to reconcile the discrepancies between our original views and those of the Balzani group. Important questions about how variations in internal reorganization energy influence the energy transfer rate constants were not addressed. This omission was corrected by Balzani et. al. with an attempt to fit acceptors of different structural classes to a single Marcus curve.<sup>23</sup> It was found that no one set of parameters correlated well with all the data points. This is not surprising since the internal reorganization will vary greatly between ketones, aromatic and alkene acceptors, and molecular oxygen will certainly have distinctly different Franck-Condon factors. This analysis suggests in order to obtain information about electronic coupling it is necessary to keep the internal reorganization energy constant within the series being investigated. We are currently analyzing data from different acceptors classes, and the preliminary results are consistent with the proposal that different structural classes have distinctly different Franck-Condon factors.<sup>25</sup>

In conclusion, exchange energy and electron transfer have been postulated to involve similar manipulations of electronic structure, and once the rate of energy transfer is decoupled from the rate of bimolecular transport, a picture emerges that shows these two processes share many basic features.

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# Photoinduced Intramolecular Electron Transfer in Metal-Organic Systems

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## I. Metal-to-Ligand Charge Transfer Excited States in $d^6$ Polypyridine Complexes

Transition metal complexes have played a key role in the development of an understanding of the factors that control photoinduced ET reactions.<sup>1-8</sup> Although photoinduced ET has been examined in a wide variety of transition metal-organic systems, most experimental work has been carried out with polypyridine complexes of the  $d^6$  transition metal ions Ru(II), Os(II) and Re(I). These complexes feature long-lived excited states based on a metal-to-ligand charge transfer (MLCT) transition.<sup>9</sup>

In a one-electron approximation, the MLCT state arises by promotion of an electron from a metal-based  $d$  orbital into a  $\pi^*$  orbital of the polypyridine ligand. For example, in  $\text{Ru}(\text{bpy})_3^{3+}$  (bpy = 2,2'-bipyridine) the MLCT state can be described as illustrated in eq 1, where light absorption promotes an electron from Ru to bpy.



Note that MLCT excitation simultaneously produces a strongly oxidizing metal center and a strongly reducing organic anion radical (i.e., in the above example  $\text{Ru}^{\text{III}}$  and  $\text{bpy}^{\cdot-}$ , respectively). Consequently, MLCT states are simultaneously strong oxidants and strong reductants, a feature which accounts (in part) for their widespread use in photoinduced ET schemes. MLCT excited states are also comparatively long-lived and luminescent, which are also desirable features for kinetic studies of ET processes.

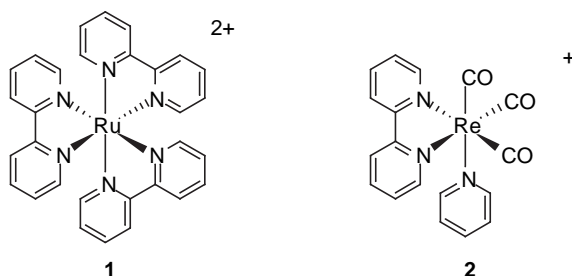


Figure 1. Chemical formulas of  $d^6$  polypyridine metal complexes.

The preponderance of work on photoinduced electron transfer in metal-organic systems has been carried out using two transition metal chromophores,  $\text{Ru}^{\text{II}}(\text{bpy})_3^{2+}$  and  $(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3(\text{py})^{1+}$  (**1** and **2**, Figure 1). Both of these complexes feature a  $d^6$  metal ion and a lowest excited state based on  $d\pi(\text{M}) \rightarrow \pi^*(\text{bpy})$  MLCT. The properties of these chromophores have been discussed in separate reviews,<sup>10,11</sup> but Table 1 briefly summarizes the important photophysical parameters of the two complexes. Note that in both complexes the  $d\pi(\text{M}) \rightarrow \pi^*(\text{bpy})$  MLCT state is moderately long-lived and luminescent. The long lifetime arises because, despite the presence of strong spin-orbit coupling, the lowest MLCT state has a substantial degree (i.e., > 85%) of triplet spin character.<sup>12-15</sup> Interestingly,

the excited state oxidation and reduction potentials of **1** ( $E_{1/2}(*/+)$  and  $E_{1/2}(*/-)$ , respectively) are symmetrically positioned with respect to the SCE reference, which indicates that the excited complex is an equally strong oxidant and reductant. By contrast, excited state **2** is a more powerful oxidant, but less powerful reductant than excited state **1**. Finally, an important feature that is shared by both the Ru(II) and Re(I) chromophores is that it is possible to systematically vary or “tune” the excited state redox potentials by changing substituents on the diimine ligands.<sup>10,11</sup> Examples of the application of this technique to study the driving force dependence of photoinduced ET are provided below.

**Table 1. Photophysical Properties of Ru(II) and Re(I) MLCT Chromophores**<sup>a</sup>

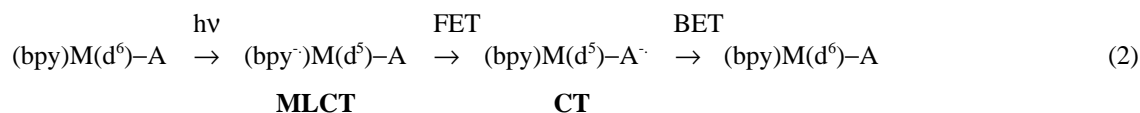
Complex	$\lambda_{\max}^{\text{abs}}$ nm	$\lambda_{\max}^{\text{em}}$ nm	$\Phi_{\text{em}}$	$\tau_{\text{em}}$ ns	$E_{1/2}(*/-)^{\text{b}}$ V	$E_{1/2}(*/+)^{\text{c}}$ V	ref
<b>1</b>	450	600	0.06	860	+0.74	-0.77	10
<b>2</b>	360	592	0.055	235	+1.22	-0.58	11

<sup>a</sup> Data for CH<sub>3</sub>CN solutions. <sup>b</sup> Potential for reduction of the excited state complex. <sup>c</sup> Potential for oxidation of the excited state complex

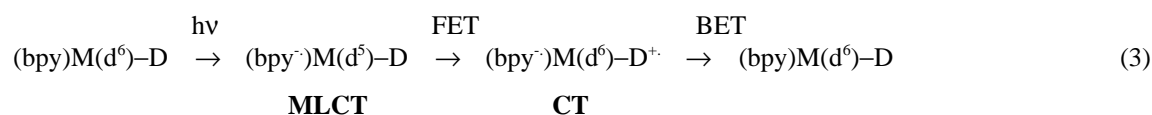
## II. Forward and Back ET in Metal-Organic Dyads: Consequences of the MLCT Excited State

A large number of studies have been carried out that examined photoinduced ET in assemblies consisting of a single transition metal chromophore covalently linked to one or more organic electron donors and/or acceptors.<sup>16-25</sup> However, owing to the limited scope of this article it is possible only to provide illustrative examples drawn from the large body of work that has been done. In this article we will focus mainly on *metal-organic dyads* (i.e., a metal complex covalently linked to a single organic donor or acceptor).

In metal-organic dyads, the MLCT basis for the reactive excited state has interesting consequences with respect to the orbitals involved in photoinduced forward and back ET (FET and BET, respectively). In order to illustrate this feature two categories of dyads will be defined: (1) *acceptor dyads* contain an electron acceptor covalently attached to the d<sup>6</sup> metal chromophore; (2) *donor dyads* contain an electron donor covalently attached to the d<sup>6</sup> metal chromophore. In the acceptor dyads, forward ET involves transfer of an electron from a  $\pi^*$  orbital localized on a bpy ligand to a  $\pi^*$  orbital on the organic acceptor (A), whereas back ET involves transfer of an electron from a  $\pi^*$  orbital of A to the d $\pi$  level of the transition metal center:



By contrast, in the donor dyads, forward ET involves transfer of an electron from a  $\pi$  orbital on the organic donor, D, into the hole in the d $\pi$  level of the excited metal, whereas back ET involves transfer of an electron from a  $\pi^*$  orbital localized on the bpy ligand to a  $\pi$  orbital localized on D:



The significant point is that in the donor dyads FET involves donor to metal ET, while BET is essentially a charge recombination reaction between an organic radical anion ( $\text{bpy}^{\cdot-}$ ) and an organic radical cation ( $\text{D}^{\cdot+}$ )—orbitals localized on the transition metal center are not involved! The impact that this difference has on the rates of back ET in the donor and acceptor dyads will become apparent below.

### III. Driving Force Dependence of Intramolecular ET in Metal-Organic Dyads

Several systematic studies of the driving force dependence of the rate of forward and back ET in acceptor dyads were carried out during the past decade. The acceptor dyads used in those investigations consist of covalently linked assemblies of polypyridine Ru(II) complexes linked to pyridinium acceptors such as paraquat and diquat (quaternized 4,4'- and 2,2'-bipyridines, respectively).

The first detailed study of the driving force dependence for photoinduced ET was reported by Elliott and co-workers.<sup>26</sup> The dyads used in Elliott's work consist of  $\text{Ru}(\text{bpy})_3^{2+}$  covalently linked to a series of diquat electron acceptors (**3** in Figure 2,  $n = 1, 2$  or  $3$ ). The driving force dependence of ET in this series is varied by changing the length of the  $-(\text{CH}_2)_n-$  bridge in the diquat acceptor. The driving force for forward ET ( $\Delta G_{\text{FET}}$ ) in **3** varies from  $-0.24$  to  $-0.57$  eV and rates of forward ET, determined by monitoring the  $\text{Ru} \rightarrow \text{bpy}$  MLCT emission decay, increase with driving force and vary from  $0.16 - 4.0 \times 10^9 \text{ s}^{-1}$ . Analysis of the rate-free energy correlation for **3** with Marcus semi-classical theory<sup>27</sup> suggests that  $k^0 \approx 1.4 \times 10^{11} \text{ s}^{-1}$  and  $\lambda \approx 0.85 \text{ eV}$  ( $H_{\text{AB}} \approx 22 \text{ cm}^{-1}$ ). Picosecond transient absorption spectroscopy was applied to **3** in order to detect the charge separated state that is produced by forward ET (CT in eq 2); however, the only transient observed was the MLCT state, and it was concluded that back ET is significantly faster than forward ET (i.e.,  $k_{\text{BET}} \gg k_{\text{FET}} \approx 10^9 \text{ s}^{-1}$ ).

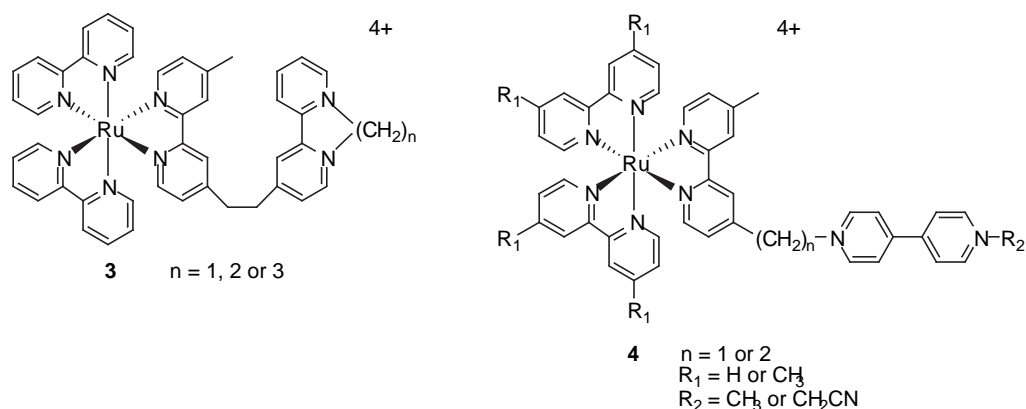


Figure 2. Formulas of Ru-acceptor dyads

More recently, Mallouk and co-workers examined the driving force dependence of photoinduced ET in another series of acceptor dyads that feature the  $\text{Ru}(\text{bpy})_3^{2+}$  chromophore covalently linked to a series of paraquat derivatives (**4** in Figure 2).<sup>28</sup> In this series the driving force for forward and back ET is varied by changing (1) the substituents on the diimine ligands, and (2) the N-alkyl substituent on the paraquat acceptor. The mean separation distance between  $\text{Ru}(\text{bpy})_3^{2+}$  and paraquat is also varied by using one or two methylene groups in the linker chain. The dynamics of photoinduced ET in series **4** was studied by using picosecond transient absorption spectroscopy and analysis of the time-resolved absorption data affords estimates of  $k_{\text{FET}}$  and  $k_{\text{BET}}$ . The driving force for forward ET in **4** varies from  $-0.42$  to  $-0.62$  eV and the rates of forward ET range from  $7.9 \times 10^9$  to  $1.6 \times 10^{11} \text{ s}^{-1}$ . Overall, the rate increases with increasing driving force, and for a given driving force, forward ET is 4 to 5 times faster in the

complexes with a single methylene spacer. Figure 3 compares the experimental forward ET rate data for series **4** with rates computed using the semi-classical expression. The theoretical fit of the experimental data shown in this figure implies that for the series with a single methylene spacer,  $k^0 \approx 2.0 \times 10^{11} \text{ s}^{-1}$  and  $\lambda \approx 0.7 \text{ eV}$  ( $H_{AB} \approx 25 \text{ cm}^{-1}$ ), whereas for the series with two methylene spacers,  $k^0 \approx 1.5 \times 10^{11} \text{ s}^{-1}$  and  $\lambda \approx 1.0 \text{ eV}$  ( $H_{AB} \approx 24 \text{ cm}^{-1}$ ).<sup>27</sup> In other words, the analysis suggests that the generally faster rates observed for the complexes with the shorter methylene spacer are primarily due to a smaller reorganization energy-- electronic coupling is very similar in the two systems.

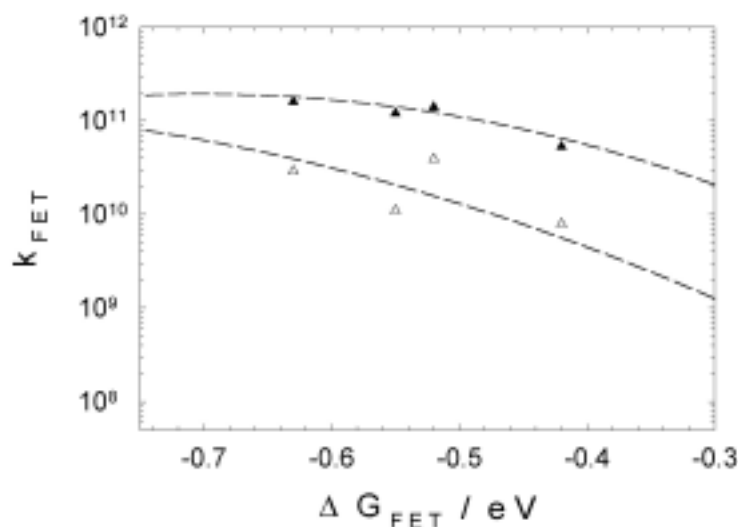


Figure 3. Forward ET in acceptor dyad series **4**. Filled triangles data for  $n = 2$  and open triangles data for  $n = 1$  (see Figure 2 for structures).

Rates of back ET in **4** vary from  $1.6 \times 10^{10}$  to  $1.2 \times 10^{11} \text{ s}^{-1}$  for driving forces ranging from  $-1.42$  to  $-1.65 \text{ eV}$  (Marcus inverted region). The back ET rates increase with *decreasing* driving force, as expected given the large driving force for the reactions. A significant aspect of this investigation is that **4** remains as the only metal-organic *acceptor* dyad system in which it has been possible to determine the rates for back ET. In general, it has been found that in the acceptor dyads  $k_{BET} > k_{FET}$ , and therefore it is not possible to detect the charge separated state that is produced by forward ET. The significance of this point will be noted below.

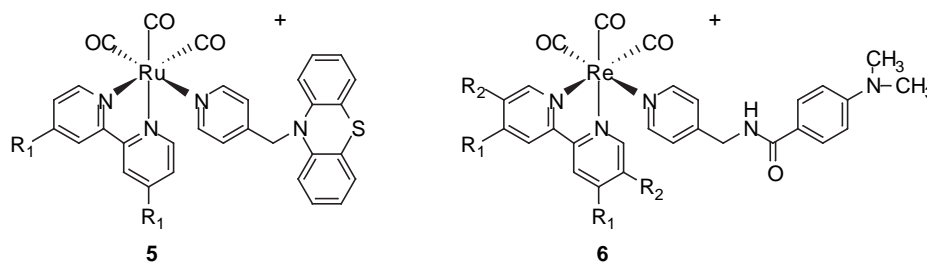


Figure 4. Chemical formulas of Re-donor dyads

Most donor dyads consist of the (diimine)Re<sup>I</sup>(CO)<sub>3</sub>(py)<sup>+</sup> chromophore (**2**, Figure 1) covalently attached to an organic electron donor. This is because the excited state Re(I) complex is a stronger oxidant compared to Ru(bpy)<sub>3</sub><sup>2+</sup>. Thus, Meyer and co-workers carried out an investigation on series **5** which consist of the Re(I) chromophore covalently linked to a phenothiazine (PTZ) electron donor (Figure 4).<sup>29-33</sup> In this series, the driving force for back ET was varied from -1.4 to -2.2 eV by changing the substituents (i.e., R<sub>1</sub> and R<sub>2</sub>) on the diimine ligand. Rates of back ET in **5**, determined by using flash photolysis, vary from 10<sup>7</sup> to 10<sup>8</sup> s<sup>-1</sup>. Interestingly, the rate data clearly reveals Marcus inverted region behavior, in that k<sub>BET</sub> increases as the driving force decreases. However, an unusual feature is that the back ET rate only varies by one order of magnitude despite a 0.8 eV range of driving force. This rather weak driving force dependence is irregular compared to other systems in which inverted region behavior is observed. Unfortunately, the rates of forward ET were not determined for the series **5**.

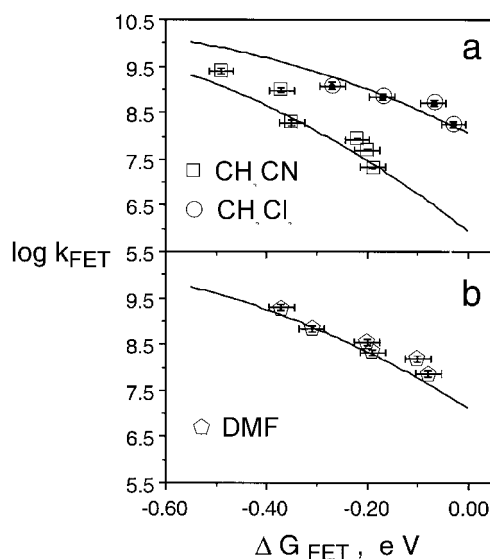


Figure 5. Solvent and driving force dependence of forward ET in donor dyads **6**

MacQueen and Schanze reported the driving force and solvent dependence of the rates of forward and back ET in the series of rhenium-based donor dyads **6** (Figure 4).<sup>34,35</sup> The driving force for both ET reactions is varied by changing the substituents on the diimine ligands in a manner similar to that used by Meyer for the rhenium-phenothiazine series **5**. The most significant difference between these two donor dyad systems lies in the oxidation potentials of the organic donors. Thus, the dimethylaminobenzoate donor in **6** is more difficult to oxidize by approximately 300 mV compared with the phenothiazine donor in **5**. The greater oxidation potential renders forward ET less exothermic in **6** compared to **5**; therefore, forward ET is slow enough in **6** to allow the application of time-resolved luminescence techniques to determine the rate. Figure 5 illustrates plots of the forward ET rate data for donor dyad system **6** in three solvents; the experimental rate data is fitted by using semi-classical theory with  $k^0 = 1.3 \times 10^{10} \text{ s}^{-1}$  ( $H_{AB} = 7 \text{ cm}^{-1}$ ) and  $\lambda = 0.8 \text{ eV}$  ( $\text{CH}_2\text{Cl}_2$ ),  $0.9 \text{ eV}$  (DMF) or  $1.0 \text{ eV}$  ( $\text{CH}_3\text{CN}$ ).<sup>27</sup> Clearly forward ET in **6** is modeled well by the semi-classical ET formalism; moreover, the theoretical analysis suggests that the solvent dependence is due to the solvent dependence of the outer sphere reorganization energy. MacQueen and Schanze also determined rates of back ET in the donor dyad system **6** and found that k<sub>BET</sub> varies from 10<sup>6</sup> to 5 × 10<sup>7</sup> s<sup>-1</sup> for driving



forces ranging from  $-2.6$  to  $-1.7$  eV. Importantly,  $k_{\text{BET}}$  in **6** decreases as the driving force increases, consistent with Marcus inverted region behavior.

The foregoing indicates that forward ET in acceptor and donor dyads **3** - **6** varies in accord with semi-classical ET theory. However, inspection of the rate-free energy correlations for back ET in the acceptor and donor dyads reveals some unusual features (Figure 6). First, for all of the metal-organic systems that have been studied,  $k_{\text{BET}}$  increases as the driving force decreases, consistent with the Marcus inverted region. Second, the back ET rate data for the acceptor and donor dyads follow very different correlations. Thus, rates of back ET in donor dyads **5** and **6** follow a nearly linear semi-logarithmic correlation over a 1.2 eV range of driving force. The back ET rates for acceptor dyads **4** follow an entirely separate correlation-- indeed, for a similar driving force, back ET is  $10^2$  -  $10^3$  times faster in the acceptor dyads.

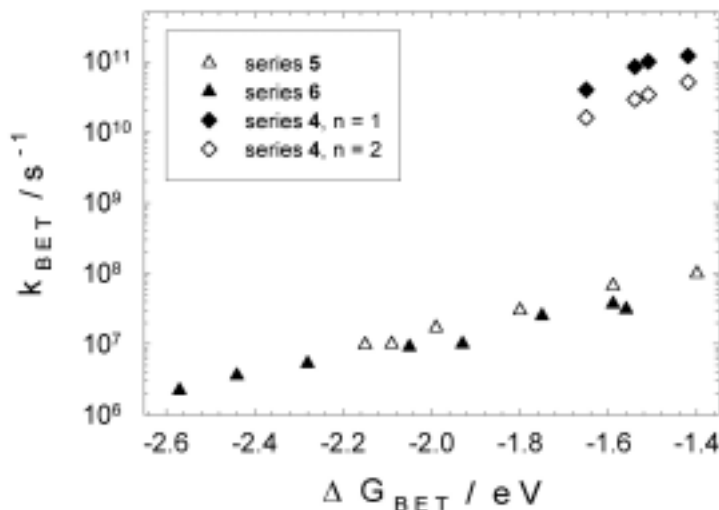


Figure 6. Back ET in metal-organic dyads.

An important question concerns the origin of the exceptional difference in the rates of back ET for the acceptor and donor dyads. One possible explanation is that electronic coupling is considerably larger in the acceptor dyads. In fact, Mallouk and co-workers fit back ET rate data for **4** by using a quantum mechanical expression with  $H_{\text{DA}} = 100 \text{ cm}^{-1}$ .<sup>28</sup> By contrast, MacQueen and Schanze fit back ET rates for dyads **6** by using the same theoretical expression with  $H_{\text{DA}} = 0.7 \text{ cm}^{-1}$ .<sup>35</sup> This one hundred-fold apparent difference in  $H_{\text{DA}}$  for back ET is surprising in view of the fact that electronic coupling for forward ET (*vide supra*) is *not* significantly different in the two dyad systems. Moreover, we suggest that the apparent  $H_{\text{DA}}$  observed for the back ET in the donor dyads is unreasonably small. (Note that the  $H_{\text{DA}}$  values for back ET in acceptor dyad system **4** are in accord with those observed for all-organic donor-acceptor systems).<sup>36,37</sup>

It is likely that electronic spin-state factors are the origin of the exceptionally low electronic coupling for back ET in the donor dyads. Equations 2 and 3 provide schemes for photoinduced ET in the acceptor and donor dyads. However, these equations are incomplete because they leave out the effects of electronic spin-state on the ET processes. Spin-state factors may be important, because studies of ruthenium and rhenium diimine complexes indicate that the MLCT state that is involved in the photoinduced ET reactions has predominantly triplet spin character.<sup>12-15</sup> Because the MLCT state is a triplet, the charge separated states formed by forward ET (CT in eqs. 2

and 3) will have triplet spin character as well. Therefore, since the ground state is a singlet, the rate of back ET will depend upon the extent of singlet-triplet mixing in the CT state (i.e., stronger singlet-triplet mixing will afford faster back ET).<sup>38,39</sup> For the reasons outlined below, we believe that in the acceptor dyads there is significant singlet-triplet mixing in the CT state, but in the donor dyads there is little singlet-triplet mixing. Because of the considerable singlet-triplet mixing in the acceptor dyads, spin-state factors do not play a role and back ET occurs at rates that are “typical” for dyads where photoinduced ET involves singlet states.<sup>36,37</sup> By contrast, since singlet-triplet mixing is weak in the donor dyads (i.e., the CT state is a “pure triplet”) back ET is impeded by spin-state factors.

The different extent of singlet-triplet mixing in the acceptor and donor dyads arises because the electronic structure of the CT state differs in the two systems. Thus, as described earlier, in the acceptor dyads the CT state consists of a  $d^5$  metal ion linked to an organic radical ion. In this case the CT state has spin-density in an orbital that has a large degree of metal character, thereby introducing substantial spin-orbit coupling and singlet-triplet mixing. The situation is very different for the donor dyads, because in these systems the CT state consists essentially of a covalently linked organic radical anion and organic radical cation (i.e., the metal is  $d^6$ ). Spin-orbit coupling is weak because the spin density is in orbitals having little metal character. The weak spin-orbit coupling gives rise to a CT state which is nearly a “pure” triplet; consequently the rate of back ET is retarded by spin-state restrictions. Importantly, the unfavorable spin-state factors appear in the rate expression as a weak electronic coupling factor.

#### IV. Distance Dependence of Intramolecular ET in Metal-Organic Dyads

Relatively little work has been carried out concerning the distance dependence of “long range” (non-adiabatic) ET in metal-organic dyads. This stems mainly from the difficulty associated with chemical synthesis of spacer assemblies that are suitably functionalized to coordinate the metal center and to hold an electron donor or acceptor at a pre-defined distance from the metal. Moreover, analysis of distance dependence of ET data is complicated by the fact that the overall distance dependence of  $k_{ET}$  arises from at least two factors that vary with donor-acceptor separation: (1) the donor-acceptor electronic coupling ( $H_{DA}$ ) decreases with increasing separation distance; (2) the outer-sphere reorganization energy ( $\lambda_s$ ) increases with increasing separation distance. In principle it is possible to separately determine the distance dependence of these two terms; however, in practice this separation is, at best, problematic.<sup>40,41</sup> Therefore, in this article we survey the metal-organic systems that have been examined and report the overall distance dependence of  $k_{ET}$  as a  $\beta$  value which is extracted from a plot of  $\ln k_{ET}$  as a function of donor-acceptor separation.

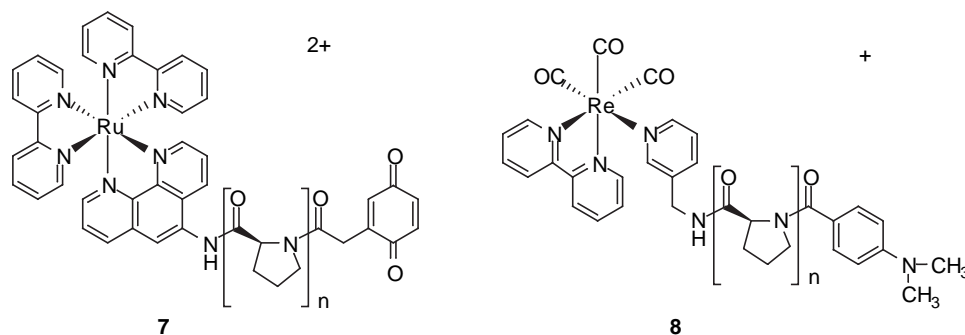


Figure 7. Chemical formulas of oligo-proline bridged metal-organic dyads.

Schanze and Sauer were the first to report a detailed study of long-range photoinduced ET in a series of metal-organic dyads. These authors examined the rate of photoinduced forward ET in dyad series **7** which consists of a  $\text{Ru}(\text{bpy})_3^{2+}$  chromophore covalently linked to a p-benzoquinone acceptor using a series of oligo-L-proline peptide spacers.<sup>42</sup> The oligo-prolines are conformationally restricted and hold the  $\text{Ru}(\text{bpy})_3^{2+}$  and quinone units at a reasonably well-defined separation distance.<sup>43</sup> Rates of forward ET from the MLCT excited state of the  $\text{Ru}(\text{bpy})_3^{2+}$  chromophore to the quinone in **7** ( $\Delta G = -0.35$  eV) vary from  $1 \times 10^9 \text{ s}^{-1}$  ( $n = 0$ ) to  $4 \times 10^5$  ( $n = 4$ ). Although the kinetic studies were complicated owing to the fact that the proline spacers adopt a range of conformations in the aprotic solvent used in the study, a  $\beta$  value of  $0.75 \text{ \AA}^{-1}$  was estimated for series **7** (see Figure 8). Several years later Schanze and Cabana reported a study of the distance dependence of photoinduced ET in a second series of oligo-proline bridged dyads **8**.<sup>44,45</sup> Rate constants for photoinduced forward ET in **8** ( $\Delta G = -0.23$  eV) vary from  $1 \times 10^8 \text{ s}^{-1}$  ( $n = 0$ ) to  $4 \times 10^5$  ( $n = 2$ ) and an overall distance dependence of  $\beta = 1.0 \text{ \AA}^{-1}$  is obtained from the rate data. By examining the temperature dependence of  $k_{\text{FET}}$  in **8**, Schanze and Cabana demonstrated that the primary term that decreases with separation distance in **8** is the donor-acceptor electronic coupling ( $H_{\text{DA}}$ ).

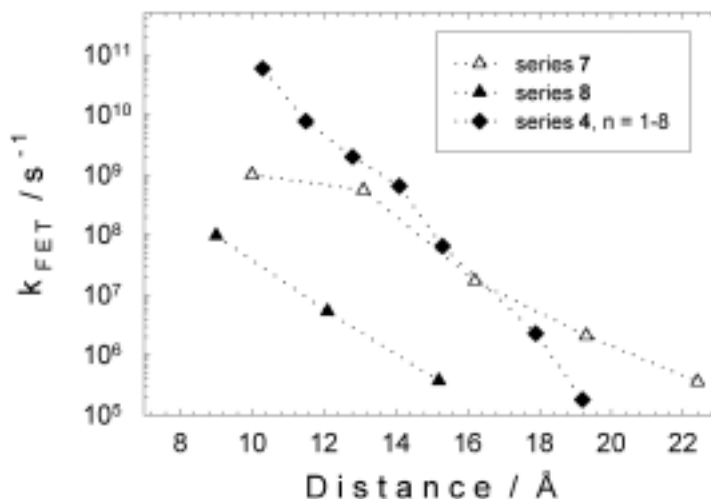


Figure 8. Distance dependence of forward ET in metal-organic dyads.

Mallouk and co-workers reported an extensive study of the spacer and driving force dependence of the rate of ET in a series of dyads consisting of a  $\text{Ru}(\text{bpy})_3^{2+}$  chromophore covalently linked to a paraquat acceptor via a methylene chain of variable length (**4**,  $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{CH}_3$ ,  $n = 1 - 8$ ).<sup>46</sup> Rates of photoinduced forward ET in **4** ( $\Delta G = -0.42$  eV) decrease with increasing spacer length and vary from  $6 \times 10^{10} \text{ s}^{-1}$  ( $n = 1$ ) to  $1.8 \times 10^5 \text{ s}^{-1}$  ( $n = 8$ ). Several interesting conclusions are drawn from the distance dependence rate data on **4**. First, the rate of forward ET decreases strongly and monotonically as the length of the poly-methylene spacer increases and the experimental distance dependence affords an effective  $\beta$  value of  $1.38 \text{ \AA}^{-1}$ . Interestingly, the experimental data imply that the poly-methylene spacers adopt primarily extended conformations in **4**; this may be a consequence of the strong Coulombic repulsion between the ruthenium and paraquat units (both feature a 2+ charge).

In summary, although there are a limited number of studies of the distance dependence of photoinduced ET in metal-organic systems, the available rate data reveal overall rate-distance dependences that are consistent those observed in organic donor-acceptor systems.

## V. Conclusion

It is clear that much has been learned about fundamental aspects of ET through studies of covalently linked metal-organic dyads. The survey of photoinduced forward ET rate data reveals that in this process metal-organic dyads are "well-behaved", i.e., their performance is in accord with modern theories of ET reactions. By contrast, the survey of charge recombination rate data reveals that the kinetics for back ET in the donor dyads is unusually slow compared to other systems. This unusual behavior is attributed to effects of electron spin-multiplicity on the charge recombination process.

Current research efforts in many of the laboratories which are responsible for the work described herein is focused on more complex supramolecular assemblies, including metal-organic based triads and tetrads.<sup>18,20,21,47,48</sup> Other groups are taking the small-molecule dyads and incorporating them into complicated molecular assemblies and materials such as zeolites, SiO<sub>2</sub>, TiO<sub>2</sub>, DNA and organic polymers.<sup>49-53</sup> These studies are taking the knowledge base that has been created through the fundamental studies described herein and applying it to the construction of useful materials and devices for future technologies.

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$$k_{ET} = v_n \kappa_{el} \kappa_n$$
, where  $v_n \kappa_{el} = \frac{2H_{DA}^2}{\hbar} \sqrt{\frac{\pi^3}{\lambda \kappa_B T}}$  and  $\kappa_n = \exp - \frac{(\Delta G_{ET} + \lambda)^2}{4\lambda \kappa_B T}$ . In this expression,  $H_{DA}$  is the donor-acceptor electronic coupling matrix element,  $\lambda$  is the reorganization energy and the other terms have their usual meaning. Many experimentalists use a simplified version of this expression in which  $v_n \kappa_{el} = k^o$ , where the latter term is the "maximum" ET rate (in the limit where electronic coupling is strong enough such that ET is adiabatic). See refs. 1 and 2 for a more detailed discussion of electron transfer theory.
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## Upcoming Meetings

An up-to-date version of this list is posted on the I-APS website (<http://www.chemistry.mcmaster.ca/~iaps/index.html>). Please send new meeting announcements to: [wsjenks@iastate.edu](mailto:wsjenks@iastate.edu) and [iaps@mcmaster.ca](mailto:iaps@mcmaster.ca).

◆ **VIII INTERNATIONAL SYMPOSIUM ON LUMINESCENCE SPECTROMETRY IN BIOMEDICAL AND ENVIRONMENTAL ANALYSIS**

May 26 - 29, 1998

University of Las Palmas, Spain

Information: Prof. Dr. Jose Juan Santana Rodrigues, Dept. of Chemistry, Faculty of Marine Sciences, University of Las Palmas de G.C., 35017 Las Palmas de G.C., Spain, [josejuan.santana@quimica.ulpgc.es](mailto:josejuan.santana@quimica.ulpgc.es), <http://www.ulpgc.es/novedades/cmm>.

◆ **INTERNATIONAL CONFERENCE ON REACTIVE INTERMEDIATES AND REACTION MECHANISMS**

July 12 - 17, 1998

Ascona, Switzerland

Information: Professor Peter Chen (Chair), Laboratory for Organic Chemistry, ETH Zentrum, Universität 16, CH-8092 ZÜ, Switzerland. Phone +41-1-632-2898, Fax +41-1-632-1280, [chen@org.chem.ethz.ch](mailto:chen@org.chem.ethz.ch)

◆ **XVIII IUPAC SYMPOSIUM ON PHOTOCHEMISTRY**

July 19 - 24, 1998

Sitges (Barcelona), Spain

Information: Dr. Jose L. Bourdelande, Secr. Organ. Comm., Dep. de Quimica, Universitat Autonoma de Barcelona, 08193 Bellaterra (Barcelona) Spain, [JFONT@correu.gencat.es](mailto:JFONT@correu.gencat.es), <http://cc.uab.es/photoiupac98/>.

◆ **THE JABLONSKI CENTENNIAL CONFERENCE ON LUMINESCENCE AND PHOTOPHYSICS**

July 23 - 27, 1998

N. Copernicus University, Torun, Poland

Information: Dr. Piotr Targowski, Secr. Org. Comm., Instytut Fizyki, Uniwersytetu N. Kopernika, ul. Grudziadzka 5, PL-87-100 Torun, Poland, [lum98@phys.uni.torun.pl](mailto:lum98@phys.uni.torun.pl), <http://www.phys.uni.torun.pl/~lum98>

◆ **15<sup>TH</sup> INTERNATIONAL CONFERENCE ON RADICAL IONS**

August 5 - 8, 1998

Rochester, NY

Information: Debbie Shannon, Center for Photoinduced Charge Transfer, Department of Chemistry, University of Rochester, Rochester NY 14627. Phone (716) 275-8286, Fax (716) 242-9485

◆ **IPS-12. TWELFTH INTERNATIONAL CONFERENCE ON PHOTOCHEMICAL CONVERSION AND STORAGE OF SOLAR ENERGY**

August 9 - 14, 1998

Berlin, Germany

Information: The Secretariat IPS-12, Hahn-Meitner-Institut Berlin. Department of Physical Chemistry, Glienicke Str. 100, D-14109 Berlin, ips-12@hmi.de.

◆ **CELEBRATION OF THE "PHOTOCHEMICAL TIE TO 1938"**

August 23 - 27, 1998

Boston, MA, USA (Fall ACS National Meeting)

Information : V. Ramamurthy, Department of Chemistry, Tulane University, New Orleans, LA, USA, Voice (504) 862-8135, Fax (504) 865-5596, <http://www.chem.fsu.edu/photo38.htm>, [murthy@mailhost.tcs.tulane.edu](mailto:murthy@mailhost.tcs.tulane.edu). The program for this meeting is given at the end of this section and will honor the 60<sup>th</sup> birthdays of R. S. H. Liu, D. C. Neckers, J. Saltiel, N. J. Turro, P. J. Wagner, and D. G. Whitten.

**HOTELS (add ~12% tax to the rate below); All rates are per night (!) NOTE: ACS GETS A DISCOUNTED RATE FOR SOME OF THESE HOTELS AND WILL BE PUBLISHED IN CHEM. ENG. NEWS. YOU CAN TRY TO GET THE DISCOUNTED RATE BY CALLING 202-872 6008. ACS IS UNLIKELY TO GIVE THE RATE TILL THEY PUBLISH IN CHEM. ENG. NEWS.**

Sheraton, Copley Square, 617-236-2000, few minutes from convention center, \$309

Marriott, Copley Square, 617-236 5800, few minutes from convention center, \$ 299

The Bostonian, 5 minutes from the financial district, 800-343-0922, \$285

The Lenox Hotel, one block from the convention center, 800-225-7676, doubles/singles \$269 (S & D)

The Colonnade, across from the convention center, 800-962-3030, \$250 (S & D)

The Eliot Hotel, minutes from the Copley place, 800-44eliot, Single \$ 235, double \$ 255

Hilton, next to the convention center, 800-874-0663, Single \$ 235, double \$ 255

Copley Sq Hotel, walking distance to the convention center, 1-800-225-7062, \$ 225 (S & D)

Howard Johnson Hotel, Kenmore Square, 800-654-2000. \$ 195 (S & D); 30 mts walk; a bit far away.

The MidTown Hotel, an easy walk to the convention center, 800-343-1177, \$149 single

The Copley Inn, minutes from the financial center, 1-800-232-0306, \$ 125 (5 mts walk) \$159 double

Howard Johnson Lodge, 800-654-2000. \$120 (S), \$130 (D); 4 blocks from Copley Sq and convention center



Chandler Inn, short walk to the convention center, 800-842-3450, Singles from \$99 and doubles 109. 15 mts walk to Convention center.

The Buckminster, Boston's Back Bay, 800-727-2825 \$ 99 (S), 10-15 minutes walk.

Here is a web site with 5 or 6 listings of bed and breakfasts as well as an 800 number to call. They put you on hold, so you have to be patient.

<http://bbreserve.com/listings.htm>

To contact Bed & Breakfast Reservations, North Shore, Greater Boston & Cape Cod toll free, dial 1-800-888-5515, then select the option for Boston by Phone (toll free in USA and Canada) and after Boston by Phone is on the line, enter the Speed Select code \*118.

**◆ SINGLET MOLECULAR OXYGEN: CHEMICAL, BIOLOGICAL AND MEDICAL ASPECTS**

September 2 - 5, 1998

Caraguatatuba, Tabatinga Beach, Sao Paulo

Information : Professor Paulo Di Mascio, Instituto de Quimica, Universidade de Sao Paulo, Caixa Postal 26.077, 05599-970 Sao Paulo, Brazil. Fax (++5511)8187970.

## A Symposium on Molecular and Supramolecular Photochemistry — August 23 – 26, 1998 — Boston ACS National Meeting

Time	Sunday, August 23	Monday, August 24	Tuesday, August 25	Wednesday, August 26
8:30 – 9:00 a.m.	CHAIR: A. LAMOLA G. S. Hammond	CHAIR: R. SRINIVASAN T. Gilbro	CHAIR: H. ROTH J. Michl	CHAIR: M. GARCIA-GARIBAY R. G. Weiss
9:00 – 9:30 a.m.	M. Kasha	Y. Shichida	R. A. Caldwell	J. R. Scheffer
9:30 – 10:00 a.m.	K. Nakanishi	M. Tsuda	D. I. Schuster	Y. Ito
10:00 – 10:30 a.m.	H. E. Zimmerman	W. J. DeGrip	L. Tolbert	Y. Inoue
BREAK		BREAK		
10:45 – 11:15 a.m.	CHAIR: E. CHANDROSS M. A. El Sayed	CHAIR: A. TROZZOLO E. R. Gaillard	CHAIR: R. SCHMEHL D. C. Nocera	CHAIR: G. HEFFRON R. E. Schwerzel
11:15 – 11:45 a.m.	F. D. Lewis	J. Saliel	M. D.E. Forbes	M. B. Sponsler
11:45 – 12:15 p.m.	G. B. Schuster	R. S. H. Liu	E. F. Hlinski	W. F. Jager
12:15 – 12:45 p.m.	J. K. Barton			
LUNCH		LUNCH		
1:45 – 2:15 p.m.	CHAIR: D. F. EATON H. B. Grey	CHAIR: I. KOCHEVAR R. S. Givens	CHAIR: G. JONES S. Farid	CHAIR: A. BRAUN F. C. De Schryver
2:15 – 2:45 p.m.	T. J. Meyers	I. Bronstein	L. B. Johnston	J. K. Thomas
2:45 – 3:15 p.m.	M. A. Fox	C. Turró	J. L. Goodman	K. S. Schanze
3:15 – 3:45 p.m.	N. C. Yang	C. V. Kumar	H. Inoue	BREAK (3:00 – 3:15)
BREAK		BREAK	BREAK	CHAIR: C. DALTON
4:00 – 4:30 p.m.	CHAIR: K. SCHAFFNER S. C. Shim	CHAIR: K. DESHAYES M. Irie	CHAIR: M. ZIMMT I. R. Gould	P. F. Barbara (3:15 – 3:45) D. C. Neckers
4:30 – 5:00 p.m.	H. A. Morrison	R. G. Zepp	D. H. Waldeck	D. G. Whitten
5:00 – 5:30 p.m.	D. R. Arnold	R. C. Zafriou	W. S. Jenks	N. J. Turro
5:30 – 6:00 pm	P. J. Wagner			

# INTER-AMERICAN PHOTOCHEMICAL SOCIETY MEMBERSHIP FORM



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Postdoctoral Fellow*	\$15 (22)	\$27 (36)	—	_____
Student*	\$8 (11)	\$8 (11)	—	_____
Voluntary Contribution to support student travel				_____
			TOTAL	_____

\*Name of current advisor \_\_\_\_\_

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<input type="checkbox"/> Imaging Systems (Silver) (PG)	<input type="checkbox"/> Photoconductivity (PN)
<input type="checkbox"/> Imaging Systems (Nonsilver) (RG)	<input type="checkbox"/> Photoelectrochemistry (PL)
<input type="checkbox"/> Lasers (LS)	<input type="checkbox"/> Photoionization (PI)
<input type="checkbox"/> Macromolecular (CC)	<input type="checkbox"/> Photolithography (PT)
<input type="checkbox"/> Mechanistic (MP)	<input type="checkbox"/> Photomedicine (PM)
<input type="checkbox"/> Ordered Media (OM)	<input type="checkbox"/> Photosynthesis (PS)
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<input type="checkbox"/> Polymer (CY)	<input type="checkbox"/> Vision (VS)