¢

SDe

Bowling Green State

Center for Photochemical Sciences.

Hyper-Rayleigh Scattering: A Spectroscopic Tool for Nonlinear Optical Property Characterization, Charge Transfer Symmetry Investigation, and Nanoscale Interface Interrogation

Robert C. Johnson and Joseph T. Hupp Department of Chemistry and Center for Nanofabrication and Molecular Self-Assembly Northwestern University

Introduction

Second harmonic generation from isotropic solution was first observed over three decades ago.¹ While coherent second harmonic generation (SHG) is cancelled in isotropic media due to symmetry,² incoherent second harmonic scattering, known as hyper-Rayleigh scattering (HRS), is weakly allowed. Though HRS lay relatively dormant for the quarter-century following its discovery, its popularity was revived when it was appreciated that HRS reports directly on the magnitude of the first hyperpolarizability tensor, β , of molecules in solution.³ β describes second-order nonlinear optical (NLO) activity, an important characteristic of molecules designed for use in emerging technological applications such as photonics, the photon-based analog of electronics.⁴ Over the last ten years, HRS has emerged as the method of choice for solution phase measurement of β . HRS circumvents the need to pole the sample electrically, a sometimes severe limitation of the more common technique for determining β in solution, electric-field-induced second harmonic generation (EFISHG). This versatility permits investigation of both ionic and non-dipolar molecules, neither of which are generally accessible to EFISHG experiments. Furthermore, no other data are needed in order to extract β from an HRS experiment; in contrast, in an EFISHG experiment the analyte's ground state dipole moment, μ , and second order hyperpolarizability, γ , must be determined (or estimated) independently in order to determine β .

The information provided by HRS experiments, however, can be used for more than simply predicting intrinsic frequency doubling efficiencies. For example, symmetry information regarding optical electron transfer can be deduced by observing the polarization of the HRS signal from chargetransfer chromophores under resonance or near-resonance conditions. HRS has also been applied to colloidal solutions of nanoparticles, an increasingly popular class of materials with interesting optical properties. The experiment's unique characteristics allow interrogation of particle/solution interfaces that are invisible to conventional SHG measurements. HRS studies of colloidal metal nanoparticles have revealed enormous hyperpolarizabilities resulting from partial resonance with the colloid's intense surface plasmon absorption bands. Further experiments with metal particles have yielded symmetry information about particle clusters and aggregates.

Experimental Implementation

In an HRS experiment, laser light of frequency ω is directed into an isotropic sample and the incoherently scattered second harmonic (i.e. frequency-doubled) light of frequency 2ω is collected (Scheme 1). This scattered light is HRS. The microscopic origin of the scattering is in the first hyperpolarizability tensor, $\beta_{ijk'}$, which is the coefficient of the second-order term in the expansion of the field-induced dipole moment (eq 1). In this expression, α and γ represent the polarizability and second hyperpolarizability tensors, respectively; the indices i, j, k, l, etc. represent molecular coordinates; and *E* represents the incident field strength. Repeated indices imply summation over those indices.

$$\mu_{\text{ind}} = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots$$
(1)

Continued on page 3

Volume 13 . Issue 2

From the Executive Director

D. C. Neckers, Executive Director, Center for Photochemical Sciences, Bowling Green State University

As editor of the *Journal of the American Chemical Society*, Cheves Walling had more than the usual cadre of enemies. For one thing, he wanted to eliminate the "Communications to the Editor". "Publish the experimental details," he argued, "or don't publish the work at all." In addition, he said, facetiously but semiseriously, that the experimental sections of journals should be published in archival form, and the discussion sections published on paper that dissolved after five or ten years. Melvin S. Newman, another organic chemist of the same era, said it in another way, "If you make a mistake, make it in the discussion section; never report an incorrect experimental result."

On a recent visit to Kodak, Samir Farid and I were talking about how poly(vinyl cinnamates) became the first commercial photoresists. Louis Minsk discovered that these soluble polymers were converted to insoluble solids with ultraviolet light. The first patents appeared in the early 1950s. Poly(vinyl cinnamates) became the first photochemical route to an imaged pattern that later became a semiconductor surface. Minsk, himself, believed that the solidification came about because he was initiating a chain polymerization in the cinnamate that led to crosslinking. Arnost Reiser, who has written on more than one occasion for *The Spectrum*, was a staff scientist at Kodak/Harrow (England) at the time, and ferreted out all of the products in the Minsk poly(vinyl cinnamate) system. He showed, using careful studies of small compounds, that the likely reason for solidifying poly(vinyl cinnamates) into an insoluble solid was because cyclobutane dimers formed between cinnamates on adjacent polymer chains. Minsk never believed this, but his commercial products made lots of money anyway.

I am currently the senior editor of *Advances in Photochemistry*. This august series, started in the early 1960s by Jim Pitts, George Hammond and W. Albert Noyes, Jr., contains stimulating discussions and partial reviews of many topics of pressing concern to contemporary photoscientists. At the time that they were published many of the reviews stimulated discussion, new experiments, and sometimes controversy.

Though we spend most of our lives trying to understand chemical reactions and photochemical processes in greater and greater detail, in the end it's the basic observation that counts—not the current rationale for how the reaction occurs. All we need to do is read those reviews we wrote for *Advances* in the 1960s or the elegant discussion sections in our papers of the 1970s. Many of the arguments that were raging at that time are not important now. In many cases, the fundamental questions that were being asked have been answered. Techniques and experimental methods have changed, so those hard questions from earlier times are easily addressed today.

It's totally irrelevant that Lou Minsk never believed in cinnamate dimerization. If his resist system were competitive, resolution and speed wise, with current commercial systems, we'd be using it in the latest microprocessors. As Walling liked to point out, facts count more than the current theories used to explain them.

In This Issue

Hyper-Rayleigh Scattering: A Spectroscopic Tool for Nonlinear Optical Property Characterization,	
Charge Transfer Symmetry Investigation, and Nanoscale Interface Interrogation	1
From the Executive Director	2
Photosensitized Oxygenation of Small Ring Olefins	9
Something New in Transition Metal Complex Sensitizers: Bringing Metal Diimine Complexes and	
Aromatic Hydrocarbons Together	.17
Center for Photochemical Sciences Publications	. 22

Continued from page 1



Scheme 1. HRS is *incoherent* second-harmonic generation.

At first glance, the experiment would appear to be impossible: the inherently random nature of the distribution of molecular dipoles (candidate nonlinear scatterers) in an isotropic environment (Scheme 1) would imply the complete self-cancellation of the nonlinear response. Importantly, however, while the *net* orientation of molecular dipoles with respect to incoming electromagnetic radiation is clearly zero, the *variance* in the orientation is not. It follows that the variances in the field-induced polarizations are similarly nonzero.^{5,6} These give rise to small, but measurable, HRS signals. For a two-component (solute plus solvent) system, a plot of HRS intensity (corrected

for absorption of incident or scattered light by the sample, if necessary) versus solute concentration yields a straight line with an intercept due to HRS from the solvent and a slope proportional to $|\beta_{solute}|^2$. (More complicated behavior is expected if increases in concentration are accompanied by ordered chromophoric association.⁷)

The incident light for HRS experiments is usually provided by a mode-locked Ti:sapphire laser⁸ (i.e. high repetition rate femto- or picosecond pulses, tunable from 720 nm to 1100 nm) or a Q-switched Nd:YAG laser⁵ (typically 10 Hz; 1064 nm). HRS experiments at longer wavelengths have been performed by introducing an optical parametric oscillator⁹ or a Raman shifter¹⁰ to a YAG-based setup. Pulsing is needed in order to achieve the very high (transient) light intensities necessary to induce detectable frequency doubling. Typically, the fundamental beam is passed through a half-wave plate followed by a polarizer; in addition to providing linearly polarized incident light, this allows for easy modulation of the incident power. A small fraction of the beam is then separated and focused into a doubling crystal, the output of which is recorded by a photodiode. This serves as a reference for beam power and laser mode-locking quality during the experiment. The remainder of the fundamental beam is directed through the sample, and the scattering is detected perpendicular to the incident beam by a cooled photomultiplier tube. Appropriate optical filters are inserted at the detector to ensure that only second harmonic scattering is collected.

Though the Ti:sapphire and YAG setups are similar, the data collection methods differ because of the fundamental differences between the lasers. Since the YAG is a low repetition rate, pulsed laser source, amplification and gated integration are used to collect the signal resulting from every pulse. On the other hand, the Ti:sapphire is treated as a continuous light source for the purposes of the HRS experiment. The beam (and, consequently, the scattering from the sample) is mechanically chopped at ~1 kHz. The chopper frequency is read by a digital lock-in amplifier wired to the detector, allowing retrieval of the very weak HRS signal.

Additional experiments are necessary to ensure that the measured signal arises only from HRS. The spectral characteristics of HRS are used to distinguish it from signals due to competing NLO processes. For example, the possibility of contributions from residual coherent SHG (for example, from particle surfaces; see below) can be tested by evaluating the solute concentration dependence of the measured signal. Authentic HRS exhibits a linear dependence on chromophore number density, while coherent SHG scales quadratically. A more subtle contaminating signal is that due to two-photon-induced emission. Like HRS and coherent SHG, the emission signal intensity depends quadratically rather than linearly on the incident power and is thus immune to detection by power dependence analysis. However, the very different lineshapes inherent to these phenomena allow the emission to be easily discerned. Emission, if present, will appear as a broad background signal on which the essentially monochromatic HRS peak is superimposed. As a practical matter, the emission problem can often be eliminated by shifting the wavelength of the incident light. Alternatively, advantage can be taken of the instantaneous nature of HRS by separating the signal in the time domain¹¹ or the frequency domain (via high-frequency demodulation).¹²

Traditional NLO Studies Involving Donor/Acceptor Molecules

A well-known mechanism for achieving first-order NLO activity is virtual (nonresonant) or real (resonant) excited state charge transfer (CT). While typically many excited states contribute significantly to the NLO response, a useful two-state (ground and nearest excited state) approximation for β is given in eq 2.¹³ Note that β is proportional to $\Delta \mu_{12}$,

$$\beta = \frac{3\mu_{12}^2 \Delta \mu_{12} E_{op}^2}{2(E_{op}^2 - E_{inc}^2)(E_{op}^2 - (2E_{inc})^2)}$$
(2)



the change in dipole moment upon excitation, and to the square of the transition dipole moment, $\mu_{12'}$ which is closely related to the oscillator strength. (E_{op} and E_{inc} denote the energies of the optical transition and of the incident light, respectively.) Accordingly, conjugated organic donor/bridge/acceptor molecules with strongly allowed CT transitions are good NLO targets. In particular, stilbene, polyene, and azobenzene-bridged molecules typically provide long donor/acceptor separation distances (large $\Delta\mu$ values) and correspondingly strong NLO responses.¹⁴⁻¹⁹ Porphyrin-bridged compounds often fulfill these

criteria as well, but their potential as NLO chromophores has been less thoroughly examined.²⁰⁻²² We have measured $|\beta|$ of the porphyrin-bridged compound **1** in chloroform by HRS at 820 nm as 3000 x 10⁻³⁰ esu.²³ By comparison, β of the common NLO chromophore *para*-nitroaniline is 17 – 35 x 10⁻³⁰ esu, depending on the identity of the solvent.

Symmetry Effects in Electron Transfer

While HRS is most often used simply to determine the magnitude of $|\beta|$ for molecules, it can also shed light on the symmetry of optical electron transfer reactions—especially if measurements are made under conditions of two-



Figure 1. Typical HRS depolarization data (circles) and fit to eq 3 (curve). The x-axis is the angle of a polarizer placed between the sample and detector. The plot is normalized to b = 1.0, and a is the amplitude (peak-to-valley) of the plot. D is the ratio of the signals at the peak and valley (eq 4). For this data $D \approx 1.5$.

photon resonance (energetic coincidence of charge-transfer absorption and nonlinear scattering) such that the properties of a single excited state dominate β . Important symmetry information, such as the point group of the molecule in the upper state, is accessible because the polarization of the HRS signal contains information about several components of the β tensor.²⁴ The polarization profile of the HRS signal resulting from vertically polarized incident light, for example, can be fit to eq 3, where *y* is the detected HRS signal at polarization angle Θ .

$$= a \cos^2 (\Theta - c) + b$$
 (3)

A typical depolarization plot is shown in Figure 1. The depolarization ratio D is defined as the ratio of vertically- to horizontally-polarized HRS and is given by

$$D = \frac{a+b}{b} \tag{4}$$

D is also related to the ratio of two β tensor components²⁴

¥ =

$$D = \frac{\langle \beta_{zzz}^2 \rangle}{\langle \beta_{xzz}^2 \rangle}$$
(5)

where the z-axis coincides with the charge-transfer axis for a dipolar molecule. β_{zzz} is generally the major component of the β tensor. Regardless of the magnitude of β , D contains excited-state

symmetry information for molecules.²⁴ For example, if Kleinmann symmetry is valid,²⁵ D = 5.0 for a purely dipolar symmetric process (e.g. C_{2v} symmetry), while D = 1.5 in the case of purely octupolar symmetry (e.g. D_{3h} symmetry). Thus for CT chromophores the HRS depolarization ratio serves as a monitor of the symmetry associated with the charge transfer, as described in the examples below.

Crystal violet (CV⁺, **2**) is a common reference chromophore for HRS experiments. Note that it is ionic and nondipolar, rendering it inaccessible to EFISHG analysis. It still possesses a donor-acceptor motif, but instead of a one-to-one









Scheme 2. Localized vs. delocalized charge transfer in bis(diimine) copper (I) complexes.

linear arrangement as in *para*-nitroaniline, three donors are arranged around one acceptor in an *octupolar*-symmetric fashion. HRS depolarization measurements on CV⁺ at 820 nm reveal D = 1.5 ± 0.1 , clearly indicative of octupolar excited state symmetry. In other words, upon excitation, electron density is symmetrically and simultaneously transferred from the three donor moieties to the central electron acceptor site.

Another example is the inorganic coordination compound **3**. While the ground state symmetry is $D_{2d'}$ the symmetry of the metal-to-ligand excited state could be either C_{2v} or $D_{2d'}$, depending on whether charge transfer occurs to a single ligand (localized) or symmetrically to both ligands (delocalized with no dipole moment change; see Scheme 2). (A third possibility that cannot be fully discounted here is a single intraligand charge transfer.) Polarized HRS measurements, obtained near resonance, indicate that D is

 2.7 ± 0.3 .²⁶ This, in turn, indicates that the excited-state symmetry is lower than the ground-state symmetry and that the CT excited-state is instantaneously electronically localized, despite the availability of two equivalent chromophoric ligands. Similar findings (localized CT excited state formation) are described in detail elsewhere²⁷ for compound **4**.

Nanoscale Interfaces

In addition to various molecular systems, HRS is usefully applicable to nanoscale materials systems—for example, colloidal suspensions. Given the technique's sensitivity to molecular symmetry, it is not surprising that it is also sensitive to symmetry, or changes in symmetry, at nanoparticle surfaces. Conventional second harmonic generation is commonly used to investigate surfaces and interfaces,²⁸ but as a coherent process, its application is limited to size regimes greater than about 10 to 20% of the wavelength of incident light.²⁹ In contrast, HRS is an incoherent process; thus, it can be used to probe interfaces on a much smaller scale. In particular, HRS has been used to interrogate SiO₂ nanoparticle/water interfaces.³⁰ Initial HRS studies on aqueous colloidal suspensions of 10 nm diameter SiO₂ nanoparticles have uncovered hyperpolarizabilities that correspond to $|\beta| = 60 - 250 \times 10^{-30}$ esu per SiO₂ formula unit. If, in fact, the net HRS response is generated only at the SiO₂/water interface, while the response from SiO₂ units within the nanoparticles is cancelled by symmetry, the $|\beta|$ value per formula unit would be even greater.

Interestingly, HRS is sensitive to pH-induced chemical changes on the nanoparticle surface. The HRS signal decreases as the pH decreases (i.e as the degree of surface protonation increases), with sharp decreases in signal occurring near the nanoparticle surface pK_a's of 1 and 12 (Figure 2). If $|\beta|$ is also decreasing under these conditions, one explanation may be that surface protonation decreases the degree of *pre*resonance with high energy electronic transitions on the nanoparticle surface. The reasoning is as follows. To contribute to β , an electronic transition must induce charge redistribution (i.e. $\Delta\mu$ or higher multipole changes), in which case the transition's contribution to β scales roughly as $1/E_{op}^{2}$, where E_{op} is the energy of the transition (see eq 2). Oxo-to-silicon transitions (for example, in SiO⁻



Figure 2. HRS response from aqueous solutions of 10 nm diameter SiO_2 nanoparticles as a function of solution pH. Adapted from ref. 30.

surface functionalities) are perhaps the most likely candidates. If this is the case, conversion of surface oxo groups to hydroxy moieties would increase E_{op} and thus reduce $|\beta|$. Subsequent studies have shown that HRS responses can also be elicited from nanoscale semiconductor/solution interfaces, where the semiconductors include $SnO_{2'}$, $TiO_{2'}$ and $ZrO_{2'}$.³¹ The observation of HRS has also recently been reported for quantum-confined CdS^{32,33} and CdSe³⁴ (zinc blende and wurtzite structures). Given the noncentrosymmetric nature of both of these structures, however, the particle interior, in addition to the interfaces, might well contribute to the response.

Gold and Silver Nanoparticles: HRS and Aggregation Effects

Another class of nonmolecular materials with interesting NLO behavior consists of nanoparticles of free-electron metals, such as gold and silver. The fascinating linear optical properties of small metal particles were explained nearly a century ago;³⁵ only



Scheme 3. Quadrupolar polarization of a free-electron metal particle.

recently has HRS been used to investigate their nonlinear optical properties.³⁶⁻³⁹ Unprecedented hyperpolarizabilities—ca. 650,000 x 10⁻³⁰ esu per particle, or 2500 x 10⁻³⁰ esu per atom^{1/2} with 820 nm incident light—have been obtained for aqueous suspensions of 13 nm diameter colloidal gold particles via HRS.³⁷ (Because HRS signal intensities scale as β^2 , the quantity (β^2/a tom)^{1/2} is a more meaningful figure of merit than β/a tom in most instances.) The signal appears to originate from an extremely efficient *quadrupolar* polarization enhancement mechanism (Scheme 3);^{40,41} this

mechanism, unlike the dipolar and octupolar mechanisms, is operative even when the scatterer possesses an inversion center (as with a spherical particle, for example). Excitation wavelength dependence studies clearly show that the large hyperpolarizability is due to partial resonance of the second harmonic frequency of the incident light with the surface plasmon absorption of the gold particles. Smaller $|\beta|$ values (800 x 10⁻³⁰ esu per atom^{1/2}) have been found for silver nanoparticles based on non-resonant HRS experiments.³⁶

The HRS signal from gold nanoparticles responds dramatically to aggregation of the particles in solution.³⁷ In fact, HRS is considerably more sensitive to particle aggregation than is Rayleigh scattering, the typical spectroscopic monitor of aggregate particle size (see Figure 3). The aggregates need only be large enough to break the center of symmetry in order to generate HRS enhancement. The smallest such aggregate would contain only three particles in a triangular arrangement, similar to the octupolar chromophores mentioned earlier. The familiar dipolar HRS mechanism presumably switches on in such assemblies and in larger aggregates of yet lower symmetry. In any case, the HRS aggregation experiments demonstrate that assemblies of gold nanoparticles behave as *low*-symmetry "super-chromophores" rather than as clusters of independent *high*-symmetry (i.e. nominally centrosymmetric) chromophores.

A Potential Bioanalytical Application

The sensitivity of the nanoparticles' HRS response to aggregation presents the possibility for analytical chemical applications. The particles are highly colored, with extinction coefficients as high as $10^{10} - 10^{11}$ M⁻¹ cm⁻¹ per particle. A solution of unaggregated particles is red; upon sufficient aggregation the solution becomes purple or blue. One can envision a detection scheme involving gold nanoparticles in which the species to be detected induces nanoparticle linking, aggregate formation, and concurrent readily detectable changes in optical properties. Indeed, a colorimetric detection scheme for DNA in solution has been reported, in which nanoparticles modified with a specific DNA oligomer are linked only in the presence of the complimentary DNA strand.⁴² The highly specific nature of DNA binding allows for detection of single-base defects by this method,⁴³ this is potentially useful in the diagnosis of genetic disorders. In principle, the sensitivity of this method can be improved by using HRS detection, and, indeed, Vance has reported modest improvements.⁴⁴ HRS is more sensitive than linear light scattering and absorption because it re-



Figure 3. Rayleigh (open circles) and hyper-Rayleigh (filled circles) response of 13 nm gold particles during intentional salt-induced aggregation. Note the immediate response of the HRS signal upon aggregate formation. Adapted from ref. 37.

sponds to the formation of smaller particle aggregates; thus, the onset of HRS enhancement should be observable before any visible color change occurs. If further developed, this could be particularly advantageous in the analysis of extremely small amounts of material, for which the simplest colorimetric detection scheme might be insufficient.

Conclusions

Though most commonly used to quantify the second-order NLO response of molecular chromophores for potential NLO applications, hyper-Rayleigh scattering (HRS) is a versatile technique with a variety of applications. HRS has been used to investigate the symmetry of light-induced intramolecular electron transfer reactions. HRS is applicable to colloidal materials as well as molecules. We have taken advantage of this flexibility, using HRS to probe semiconductor nanoparticle/solution interfaces and to investigate the intense NLO response of free-electron metal particles. Studies of particle/solution interfaces on a very small size scale provide surface chemistry information that is

unattainable via conventional second-harmonic generation (SHG) experiments (albeit, perhaps attainable by other techniques). The intense HRS signal from colloidal gold particles in solution responds dramatically to particle aggregation; this phenomenon has potential applicability for the detection of extremely small amounts of material. While these nonstandard applications are intriguing, the range of applications of HRS presumably has yet to be fully discovered.

Acknowledgments

We gratefully acknowledge the indispensable efforts of Prof. Michael Therien, Dr. Fred Vance, Dr. Buford Lemon, and Dr. Youngjin Kim in many of the studies described here. This research was supported by the U.S. Department of Energy (molecular studies), the Army Research Office - Multidisciplinary University Research Initiative (free-electron metal particles), and the Office of Naval Research (nanoscale interfaces).

References

- 1. Terhune, R. W.; Maker, P. D.; Savage, C. M. Phys. Rev. Lett. 1965, 14, 681-684.
- 2. Giordmaine, J. A. Phys. Rev. 1965, 138, A1599-A1606.
- 3. Clays, K.; Persoons, A. Phys. Rev. Lett. 1991, 66, 2980-2983.
- 4. Prasad, P. N.; Williams, D. J. Introduction to Nonlinear Optical Effects in Molecules and Polymers; Wiley-Interscience: New York, 1995.
- 5. Clays, K.; Persoons, A.; de Maeyer, L. In *Modern Nonlinear Optics, Part 3*; Evans, M., Kielich, S., Eds.; Wiley: New York, 1994; pp 455-498.
- 6. Clays, K.; Persoons, A. Rev. Sci. Instrum. 1992, 63, 3285-3289.
- 7. Guan, H. W.; Wang, C. H. J. Chem. Phys. 1993, 98, 3463-3468.
- 8. Clays, K.; Persoons, A. Rev. Sci. Instrum. 1994, 65, 2190-2194.
- 9. Stadler, S.; Dietrich, R.; Bourhill, G.; Bräuchle, C.; Pawlik, A.; Grahn, W. Chem. Phys. Lett. 1995, 247, 271-276.
- 10. Pauley, M. A.; Wang, C. H. Chem. Phys. Lett. 1997, 280, 544-550.
- 11. Noordman, O. F. J.; van Hulst, N. F. Chem. Phys. Lett. 1996, 253, 145-150.
- 12. Olbrechts, G.; Strobbe, R.; Clays, K.; Persoons, A. Rev. Sci. Instrum. 1998, 69, 2233-2241.
- 13. Oudar, J. L.; Chemla, D. S. J. Chem. Phys. 1977, 66, 2664-2668.
- 14. Marder, S. M.; Cheng, L.-T.; Tiemman, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhøj, J. *Science* **1994**, *263*, 511-514.
- 15. Song, O. K.; Woodford, J. N.; Wang, C. H. J. Phys. Chem. A 1997, 101, 3222-3226.
- 16. vanWalree, C. A.; Franssen, O.; Marsman, A. W.; Flipse, M. C.; Jenneskens, L. W. J. Chem. Soc. Perkin Trans. 2 1997, 799-807.
- 17. Hendrickx, E.; Clays, K.; Persoons, A.; Dehu, C.; Bredas, J. L. J. Am. Chem. Soc. 1995, 117, 3547-3555.
- 18. Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. J. Phys. Chem. **1991**, *95*, 10631-10643.
- 19. Cheng, L.-T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. J. Phys. Chem. **1991**, 95, 10644-10652.
- 20. LeCours, S. M.; Guan, H.-W.; DiMagno, S. G.; Wang, C. H.; Therien, M. J. J. Am. Chem. Soc. 1996, 118, 1497-1503.
- 21. Albert, I. D. L.; Marks, T. J.; Ratner, M. A. Chem. Mater. 1998, 10, 753-762.
- 22. Suslick, K. S.; Chen, C. T.; Meredith, G. R.; Cheng, L.-T. J. Am. Chem. Soc. 1992, 114, 6928-6930.
- 23. Johnson, R. C.; Therien, M. J.; Hupp, J. T. Unpublished work.
- 24. Kaatz, P.; Shelton, D. P. J. Chem. Phys. 1996, 105, 3918-3929.
- 25. Kleinmann, D. A. Phys. Rev. 1962, 126, 1977-1979.
- 26. Johnson, R. C.; Kim, Y.; Hupp, J. T. Unpublished work.
- 27. Vance, F. W.; Hupp, J.T. J. Am. Chem. Soc. 1999, 121, 4047-4053.
- 28. Corn, R. M.; Higgins, D. A. Chem. Rev. 1994, 94, 107-125.
- 29. Wang, H.; Yan, E. C. Y.; Borguet, E.; Eisenthal, K. B. Chem. Phys. Lett. 1996, 259, 15-20.
- 30. Vance, F. W.; Lemon, B. I.; Ekhoff, J. A.; Hupp, J. T. J. Phys. Chem. B 1998, 102, 1845-1848.
- 31. Lemon, B. I. Ph.D. Thesis, Department of Chemistry, Northwestern University, 1999.
- 32. Fu, D.; Li, M.; Wang, X.; Cheng, J.; Zhang, Y.; Lu, Z.; Cui, Y. Supramol. Sci. 1998, 5, 495-498.
- 33. Santos, B. S.; Pereira, G. A. L.; Petrov, D. V.; de Mello Donegá, C. Opt. Commun. 2000, 178, 187-192.

- 34. Jacobsohn, M.; Banin, U. J. Phys. Chem. B 2000, 104, 1-5.
- 35. Mie, G. Ann. Phys. 1908, 25, 377-445.
- 36. Clays, K.; Hendrickx, E.; Triest, M.; Persoons, A. J. Mol Lig. 1995, 67, 133-155.
- 37. Vance, F. W.; Lemon, B. I.; Hupp, J. T. J. Phys. Chem. B 1998, 102, 10091-10093.
- 38. Galletto, P.; Brevet, P. F.; Girault, H. H.; Antoine, R.; Broyer, M. Chem. Commun. 1999, 581-582.
- 39. Galletto, P.; Brevet, P. F.; Girault, H. H.; Antoine, R.; Broyer, M. J. Phys. Chem. B 1999, 103, 8706-8710.
- 40. Agarwal, G. S.; Jha, S. S. Sol. State Commun. 1982, 41, 499-501.
- 41. Hua, X. M.; Gersten, J. I. Phys. Rev. B 1986, 33, 3756-3764.
- 42. Elghanian, R.; Storhoff, J. J.; Mucic, R. C.; Letsinger, R. L.; Mirkin, C. A. Science 1997, 277, 1078-1081.
- 43. Storhoff, J. J.; Elghanian, R.; Mucic, R. C.; Mirkin, C. A.; Letsinger, R. L. J. Am. Chem. Soc. 1998, 120, 1959-1964.
- 44. Vance, F. W. Ph.D. Thesis, Department of Chemistry, Northwestern University, 1999.

About the Authors

Joseph T. Hupp is a Morrison Professor in the Chemistry Department at Northwestern University. He earned a B.S. degree in chemistry from Houghton College in western New York and a Ph.D. from Michigan State University. His interests include inorganic photophysics and photochemistry, mesoporous molecular materials chemistry, interfacial electrochemistry, and parenting of twins. His address is Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illnois 60208, e-mail: jthupp@chem.nwu.edu, web: http://www.chem.nwu.edu/~hupp/index.html.

Robert C. Johnson is pursuing his Ph.D. in chemistry at Northwestern University. He received his M.S. in chemistry from Northwestern in 1998 and B. S. degrees in chemistry and mathematics from Miami University in 1997.

©Copyright 2000 by the Center for Photochemical Sciences *The Spectrum* is a quarterly publication of the Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403. Phone 419-372-2033 Fax 419-372-0366 Email photochemical@listproc.bgsu.edu WWW http://www.bgsu.edu/departments/photochem/ Executive Director: D. C. Neckers Principal Faculty: D. C. Neckers F. N. Castellano, M. E. Geusz,

D. C. Neckers, M. Y. Ogawa,

V. V. Popik, M. A. J. Rodgers,

D. L. Snavely

Pat Green

Alita Frater

The Spectrum Editor: Production Editor:

COPYRIGHT PERMISSION

A person may make a single copy of any or all articles in this issue for personal use. Copying beyond that permitted by the U.S. Copyright law is allowed provided that the appropriate per copy fee is paid through the Copyright Clearance Center, Inc., 27 Congress St., Salem, MA 01970. For reprint permission, please write to the Center for Photochemical Sciences.

EDITORIAL POLICY

The Spectrum reserves the right to review and edit all submissions. The Spectrum is not responsible for contents of articles.

Articles submitted to The Spectrum will appear at the discretion of the editorial staff as space is available.

Photosensitized Oxygenation of Small Ring Olefins

Aryeh A. Frimer Department of Chemistry, Bar-Ilan University

Electronic Structure of Dioxygen

Although the discovery of oxygen by Lavoisier, Priestly, and Scheele¹ took place over two centuries ago, the scientific community continues to be fascinated by the sixteenth element. This intrigue stems in part from the complicated role molecular dioxygen and its derivatives play in a variety of autoxidative, photooxidative and metabolic processes. Oxygen is involved not only in the "breath of life," but more interestingly in what might be poetically called "the breath of death"²—oxygen toxicity.³

Rather uniquely, molecular oxygen is a ground state triplet state (${}^{3}O_{2}$), with its two electrons of highest energy bearing parallel spins and located one each in the degenerate π^{*}_{2p} orbitals.⁴ This triplet character is responsible for the paramagnetism and diradical-like properties of ground state molecular oxygen. More importantly, this triplet electronic configuration (${}^{3}\Sigma_{g}$) only permits reactions involving one-electron steps. Thus, despite the exothermicity of oxygenation reactions, a spin barrier prevents ${}^{3}O_{2}$ from reacting indiscriminately with the plethora of singlet ground-state organic compounds surrounding it. One could well argue that it is this spin barrier that permits life to be maintained.

The two lowest excited states of oxygen are both singlets, in which the two highest-energy electrons have antiparallel spins; no spin barrier exists for their concerted reaction with organic substrates. In the lower of the two, a ${}^{1}\Delta_{g}$ state which lies 22.5 kcal mol⁻¹ above the ground state, both of the highest-energy electrons occupy the same π^{*}_{2p} orbital. In the second, a ${}^{1}\Sigma^{*}_{g}$ state lying 15 kcal mol⁻¹ yet higher, each of the π^{*}_{2p} orbitals is half full (Table 1). In the gas phase the lifetimes of ${}^{1}\Delta$ and ${}^{1}\Sigma$ oxygen are 45 min and 7s, respectively. However, in solution these lifetimes are dramatically reduced through collisional deactivation to approximately 10⁻³ and 10⁻⁹ s, respectively.⁵ Because the reactions that concern us are generally carried out in solution, it is longer-lived ${}^{1}\Delta$ state that is involved as the active oxygen species. We shall, henceforth, refer to this longer lived species as singlet oxygen. A simplified picture of the three lowest electronic states of molecular oxygen and a comparison of some of their properties is presented in Table 1.

				Lifetime (s) ^{2,3}	
Electronic State	Relative Energy (kcal/mol ⁻¹)	Configuration of II^*_{2p}	Gas Phase	Liquid Phase	
${}^{1}\Sigma^{+}_{g}$	37.5	\uparrow \downarrow	7-12	10-9	
$^{1}\Delta_{g}$	22.5	<u>↑↓</u>	2700	10-3	
³ Σ ⁻ _g	0	\uparrow \uparrow	∞	∞	

Table 1. The Three Lowest Electronic States of Molecular Oxygen and Selected Properties.

Singlet Oxygen Sources - Photosensitization

An impressive variety of physical and chemical sources of ${}^{1}O_{2}$ are now available for laboratory-scale purposes.⁶ These include photosensitization, oxidation of $H_{2}O_{2'}$ decomposition of phosphite ozonides and endoperoxides, and microwave discharge. Photosensitization is clearly the most convenient technique available for generating ${}^{1}O_{2}$ and, by far, the most commonly used, since it is applicable to a large spectrum of reaction temperatures, solvents and sensitizers (including those which are polymer or resin based). Most importantly for unreactive substrates, this physical method, unlike the chemical methods mentioned above, requires no additional reagents—merely longer photolysis times.

There are two major classes of photosensitized oxidative processes, appropriately called "type I" and "type II".⁷ In the former, the sensitizer triplet (sens³), formed via intersystem crossing of the excited singlet state sensitizer (sens^{1*}; eq 1), interacts directly with a molecule of **substrate**. This interaction can lead down either of two different pathways. The first is hydrogen atom abstraction, which initiates free radical autoxidative processes ("type Ia", eqs 2 and 3). Alternatively, electron transfer from substrate to excited sensitizer may occur, in which case the oxygenation products result from the coupling of the substrate cation radical with superoxide anion radical ("type Ib", eqs 4-6). Irrespective of whether the mechanism of oxygenation is a photoinitiated autoxidation or an electron transfer photooxidation,⁸ only ground state triplet molecular oxygen (³O₂) is involved.

Туре Іа	
$Sens^1 + hv \rightarrow Sens^{1^*} \rightarrow Sens^3$	(1)
$Sens^3 + RH \rightarrow SensH + R$	(2)
$R^{\cdot} + {}^{3}O_{2} ROO^{\cdot} \rightarrow Oxygenation$	(3)

Type Ib

- $\operatorname{Sens}^{3} + R \to \operatorname{Sens}^{-} + R^{+}$ (4)
- $\begin{array}{ll} \operatorname{Sens}^{\cdot} &+ & {}^{3}\operatorname{O}_{2} \to \operatorname{Sens} &+ & \operatorname{O}_{2}^{\cdot} \\ \operatorname{R}^{+} &+ & \operatorname{O}_{2}^{\cdot} \to & \operatorname{Oxygenation} \end{array} \tag{5}$

"Type II", on the other hand, is characterized by initial interaction between the sensitizer triplet and a molecule of **oxygen**. The traditional "type II" (sometimes called "type IIa")⁹ involves transfers of the sensitizer's excitation energy to molecular oxygen generating singlet molecular oxygen ($^{1}O_{2}$), which is the oxygenation species (eqs 7 and 8). (The direct absorption of light by $^{3}O_{2}$ to produce $^{1}O_{2}$ is a spin-forbidden process.) Recently, however, two additional type II processes have been observed, which results in oxygenation via radical processes. In "type IIb", triplet sensitizer interacts with dioxygen via electron transfer to yield superoxide; the latter, or more likely its derivatives,¹⁰ initiate oxygenation (eqs 9 and 10).^{9,11} Research in the case of Rose Bengal has suggested, however, that the source of the superoxide is in fact a reaction between the sensitizer and singlet oxygen.^{9,12} Finally and most recently, a third "type II" reaction (which we will refer to as "type IIc") has been observed with n- π^* sensitizers, in which the triplet sensitizer (generally an excited carbonyl) reacts with molecular oxygen generating a diradical peroxy species (e.g., \cdot O-CR₂-OO[.]). The latter may initiate radical processes itself or via its derivatives (eqs 11 and 12).¹³

Type IIa

$Sens^3 + {}^3O_2 \rightarrow Sens^1 + {}^1O_2$	(7)
---	-----

 $RH + {}^{1}O_{2} \rightarrow Oxygenation$ (8)

Type IIb

$$\operatorname{Sens}^{3} + {}^{3}\operatorname{O}_{2} \to [\operatorname{Sens}^{1} + {}^{1}\operatorname{O}_{2}] \to \operatorname{Sens}^{+} + \operatorname{O}_{2}^{-}$$
(9)

$$RH + O_2^{-}$$
 (or HOO) \rightarrow Oxygenation (10)

Type IIc

$$\begin{array}{ll} \text{Sens}^3 + \ ^3\text{O}_2 \rightarrow \ \text{Sens-OO} & (11) \\ \text{RH} + \ \text{Sens-OO} \rightarrow \ \text{Oxygenation} & (12) \end{array}$$

Photosensitized oxygenations as a rule, and this is particularly true in the case of the small ring compounds discussed below, can involve ${}^{1}O_{2}$ and/or free-radical processes. Hence, several tests have been developed to discern between the two mechanisms:^{6c} (1) ${}^{1}O_{2}$ reactions are quenched by DABCO. (2) On the other hand, radical mediated processes will be inhibited by free-radical inhibitors such as 2,6-di-*t*-butylphenol. (3) Because of their low activation energies, the rate of singlet oxygenations are well known to be *insensitive* to reaction temperature; such is not the case with free radical autoxidations. (4) The reaction results should be compared with those obtained when ${}^{1}O_{2}$ is chemically generated from triphenyl phosphite ozonide.

Modes of ¹O₂ Reaction with Olefins⁶

Unlike ${}^{3}O_{2}$, which displays a biradical character, all the electrons in ${}^{1}O_{2}$ are paired. Hence, the type of reaction it undergoes is expected to involve electron pairs. Additionally, it is convenient to think of ${}^{1}O_{2}$ as the oxygen analogs of ethylene. Indeed, each of the three modes in which ${}^{1}O_{2}$ reacts with unsaturated compounds finds a precedent in one of the reaction pathways of olefins.

The first of these modes is a [2+2] cycloaddition to a double bond to form a 1,2-dioxacyclobutane or dioxetane (eq 13). These cyclic peroxides are sometimes of moderate stability but readily cleave thermally or photochemically into two carbonyl-containing fragments. The cleavage is quite often accompanied by the generation of an excited carbonyl moiety and chemiluminescence. The second mode bears a striking resemblance to the Alder "ene" reaction. In the ${}^{1}O_{2}$ ene reaction, olefins containing an allylic hydrogen are oxidized to the corresponding allylic hydroperoxides in which the double bond has shifted to a position adjacent to the original double bond (eq 14). The third and final mode involves a [4+2] Diels-Alder-type addition of singlet oxygen to a diene producing an endoperoxide (eq 15). The question of the mechanism in these three reaction types has been the subject of much heated debate over the past decade. The highlights of this long-standing controversy have been reviewed.⁶



A variety of factors control all singlet oxygen reactions.⁶ Singlet oxygen is mildly electrophilic and the rate of reaction within a homologous series of compounds is generally inversely proportional to their ionization potential. Solvent has only a minimal effect on the rate of reaction; changes in rate are commonly due to solvent effects on the lifetime of singlet oxygen. Because of the low activation energy for singlet oxygen processes (0.5-8 kcal), little if any temperature effect on the rate of reaction is observed. Regarding the mode of reaction, electron-rich olefins as well as sterically hindered alkenes tend to prefer dioxetane formation, though two modes often compete. Finally, the direction of singlet oxygen attack is predominantly, if not exclusively, from the less hindered side of the molecule.

Photosensitized Oxygenation of Small Ring Olefins

Over the past two decades, we have been exploring the effect of strain on the rate, mode and direction of singlet oxygen reactions.¹⁴ In particular, we have focused on various small ring olefin systems in which ring-strain decreases or develops as we proceed towards product. We summarize our findings below; some of these are new, while others are reaffirmations of previously stated observations.

Singlet oxygen is insensitive to the relative thermodynamic stability of the final product.

We first came across this phenomenon in our studies on vinyl cyclopropanes. In the singlet oxygen "ene" reaction of dicyclopropyl olefins **1** and **4** (eq 16), allylic hydrogen abstraction occurs **both** from the methyl group (to give **2** and **5**) and from the three-membered ring (giving **3** and **6**, respectively). This is despite the fact that, in the latter case, the formation of an alkylidenecyclopropane requires an investment of 11.4 kcal of strain energy.^{14a,c} We, therefore, concluded that in the product-determining transition state, ${}^{1}O_{2}$ is insensitive to the strain developing in the final product. This conclusion is consistent with prior evidence that singlet oxygen reactions have very small activation energies (0.5-8 kcal/mol)¹⁵ and that the product-determining transition state is reactant-like and occurs quite early.⁶



The relative rate data determined for **1** and **4** ($k_{rel} = 0.041$ and 0.33, respectively) are also quite interesting, for it indicates that the substitution of the methyl groups in trimethylethylene ($k_{rel} = 0.024$) and tetramethyethylene (TME; $k_{rel} = 1.00$) by a cyclopropyl moiety does not dramatically affect the rate of reaction. This suggests that the reputed electron donating ability of a cyclopropyl group only comes into play when an electron deficient center is created, which is not the case in these ${}^{1}O_{2}$ ene reactions. 14c,14e

The ${}^{1}O_{2}$ "ene" reaction is sensitive to the interatomic distance between the α -olefinic carbon and the γ -allylic hydrogen.

In the photosensitized oxygenation of alkylidenecyclopropane derivatives (eqs 17 and 18),^{14b,14e} we discovered that the allylic ring hydrogens were inert to ene-reaction, even when no other allylic hydrogens were available for abstraction. When exocyclic allylic hydrogens were available, they alone reacted via an ${}^{1}O_{2}$ "ene" reaction (eq 18). However, the relative rate of oxygenation was quite sluggish—ca. 180 times slower than TME.



Similarly, while oxidation products are obtained in the photosensitized oxygenation of tetraalkylkylcyclopropenes (**11**, eq 19), these products result exclusively from free radical, not from singlet oxygen, processes. By contrast, both alkylidenecyclobutanes and alkylcyclobutenes react with singlet oxygen.^{14e}



For the reasons noted in the previous section, we were hesitant to attribute the inertness of the allylic ring hydrogens in 7 and 9 to the 8-10 kcal/mol increase in strain energy in going from an alkylidenecyclopropane (7) to a cyclopropene (8). Indeed, the insensitivity of ${}^{1}O_{2}$ to strain was further affirmed by the slow oxygenation rate of 9, despite the fact that there is a release of 35 kcal/mol of strain energy in going from isopropylidenecyclopropane 9 to cyclopropyl hydroperoxide **10**. We must, therefore, look elsewhere for an explanation.

We have suggested^{14b,14e,14i} that the interatomic distance between the α -olefinic carbon and the γ -allylic hydrogen, the distance which the attacking ${}^{1}O_{2}$ must span in the ene reaction irrespective of mechanism, may be a pivotal consideration in determining whether the hydrogen is abstractable. Too great a distance may well place legitimate candidates "out of reach." Using bond lengths and angles from literature data, we have calculated the C_{α} -H_{allylic} distance for isobutylene, methylenecyclobutane, methylcyclobutene, methylenecyclopropane, and methylcyclopropene. It should be noted that in these calculations, the preferred ${}^{1}O_{2}$ ene reaction orientation⁶ was used whenever possible, i.e., the



Scheme 1. Calculated $C_{\alpha}\text{-}H_{allylic}$ Distances for Isobutylene and Various Cycloolefins

abstracted γ -allylic hydrogen was aligned in a plane perpendicular to the plane of the double bond. The necessary bond rotations were accomplished using Gaussian 76.¹⁶ As shown in Scheme 1, the reactive cycloolefins all have a C_{α}-H_{allylic} distance below 3.09 Å, while for those which are unreactive this value is above 3.24 Å. It may be these crucial 0.15 Å which, in the latter case, place the abstractable γ -allylic hydrogen "out of reach."

The ${}^1\text{O}_{_2}$ "ene" reaction is sensitive to the the orientation of the $\gamma\text{-allylic}$ hydrogen.

Trisubstitutedcyclopropenes (**12**, eq 20) undergo facile photosensitized oxidation; however, careful analysis reveals that, again, only free radical processes are involved. This lack of reactivity to ${}^{1}O_{2}$ cannot stem from any "out of reach" considerations. There must yet be another factor at play in these small-ring compounds.

It has been well documented that in the ${}^{1}O_{2}$ ene reaction, there is a strong preference for the abstraction of those allylic hydrogens aligned in a 90° dihedral angle with respect to the plane of the double bond *in the low*

energy conformations of the olefin.^{6,14f} Similarly, in cyclic systems, the abstraction of pseudo-axial hydrogens are greatly preferred over pseudo-equitorial ones. Even the more rigid systems, e.g. cyclobutenes and alkylidenecyclobutanes,^{14e} can react via a ¹O₂ ene process presumably because they are flexible enough to permit even a normally equatorial hydrogen to attain a pseudo-axial position (via "flipping" or "puckering"), if necessary. There are, however, systems in which a pseudo-axial position is completely precluded, and indeed no singlet oxygen **ene** reaction is observed. Thus, the allylic ring hydrogens of both alkylidenecyclopropanes¹⁷ and cyclopropenes¹⁸ are displaced ca. 33° from the perpendicular and both resist abstraction in a singlet oxygen process.

Similarly, alkylidenecyclobutenes react only at the exocyclic double bond, while the allylic ring hydrogens are inert to ene reaction abstraction (eq 21).^{14f-h} Here we are dealing with cyclobutyl rings containing three trigonal carbons which are constrained to be planar. The remaining ring methylene hydrogens—the only available allylic hydrogens on the ring—are displaced ca. 36° from the perpendicular¹⁹ and there is no way these allylic ring hydrogens can attain anything even approximating a pseudo-axial position. In the absence of exocyclic allylic hydrogens, as in the case of 1,1'-bi(benzocyclobutenylidene)^{14f} and cyclopropylidenecyclobutenes,^{14j} no ¹O₂ reaction is observed, though free-radical autoxidative processes may well occur (eq 22).





The rate of singlet oxygenation is correlated with the olefinic ionization potential.

We noted previously that the relative rate of oxygenation (k_{rel}) of isopropylidenecyclopropane **9** was ca. 180 times slower than TME. We also fail to see singlet oxygen products in the case of alkylcyclopropenes. Several authors have

(23)

found a good general correlation between olefin HOMO energies (or ionization potentials) and the relative rates of ${}^{1}O_{2}$ ene reaction, 6e,6f,20 i.e., the higher $E_{(olefin-HO)}$ (or the lower the I.P.) the greater the rate. As shown in Table 2, the ionization potential (IP) of cyclopropene is substantially higher than that of its homologs.²¹ We suggest, therefore, that in the case of cyclopropene and alkylidenecyclopropane, the rate of the singlet oxygenation²² has slowed in both cases because of the high I.P.; in the former case, free radical autoxidative processes compete favorably. We are presently exploring the effect of I.P. lowering substituents on the course of these reactions.

Table 2. Ionization Potential and Relative ¹O₂ Reactivity of Small Ring Cycloaklenes



The approach of ${}^{1}O_{2}$ is from the less hindered face of the ring.

The photosensitized oxygenation of alkylidenecyclobutanes **13a-d** are undoubtedly singlet oxygen processes: no reaction occurs in the absence of oxygen, sensitizer or light or in the presence of the ${}^{1}O_{2}$ quencher DABCO;^{6a,23} nor are the rate or mode of reaction affected by the addition of the radical inhibitor 2,6-di-t-butylphenol.^{6a,24} As outlined in equation 23, each of these olefins reacts via a ${}^{1}O_{2}$ -ene mode, involving the abstraction of an allylic hydrogen from the isopropylidene methyl groups, and yields a pair of geometric isomers.

$R^{"} \xrightarrow{H}_{3 4} 1. {}^{1}O_{2}$ $R \xrightarrow{I}_{8} X$	R - 2 1 R - 2	+ R" <u>2 1</u> R <u>R</u> '
13	14	15
a: R=R"=-(CH ₂) ₄ -; R'=H	15%	85%
b: R= <i>n-</i> C ₄ H ₉ ; R'=R"=H	40%	60%
c: R=Ph; R'=R"=H	40%	60%
d: R=Me; R'=vinyl; R"=H	40%	60%

The predominance of epimer **15**, in which the hydroxyl group is *trans* to the substituent "R" at C-3, indicates that ${}^{1}O_{2}$ approached **13** preferentially *trans* to this substituent. The preferential formation of **15** is indeed consistent with singlet dioxygen's well known propensity to undergo ene attack from the less sterically encumbered face of a substrate.⁶

Conclusion

The above data indicates that ${}^{1}O_{2}$ is relatively insensitive to strain considerations present in either the substrate or product. More important seem to be the ionization potential of the reacting double bond and the ground state geometry of the olefin—in particular, the relative orientation of the allylic hydrogen and the C_{α}-H_{allylic} interatomic distance. Strain does, however, play a crucial role in the secondary rearrangements of the primary oxygenation products.²⁵

References

- 1. Cassebaum, H.; Schufle, J. A. J. Chem. Ed. 1975, 52, 442-444.
- 2. Frimer, A. A.; Rosenthal, I. In Foreward to Active Oxygen Part A. Isr. J. Chem. 1983, 23, 398.
- 3. (a) Fridovich, I. *Science* **1978**, *201*, 875-880. (b) Fridovich, I. *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic Press: New York, 1972; Vol. I, p 239.
- 4. Slater, J. C. Quantum Theory of Molecules and Solids; McGraw-Hill: New York, 1983; Vol. 1.
- (a) Arnold, S. J.; Kubo, M.; Ogryzlo, E. A. Adv. Chem. Ser. 1968, 77, 133. (b) Merkel, P. D.; Kearns, D. R. J. Am. Chem. Soc. 1972, 94, 1029.
- 6. (a) Frimer, A. A. In *The Chemistry of Peroxides*; Patai, S. Ed.; Wiley: Chichester, 1983; pp 201-234. (b) Frimer, A. A. *Chem. Rev.* 1979, 79, 359-387. (c) Frimer, A. A.; Stephenson, L. M. In *Singlet O*₂ -*Volume II: Reaction Modes and Products. Part I*; Frimer, A. A., Ed.; Chemical Rubber Company: Boca Raton, Florida, 1985; Chapter 3. (d) Frimer, A. A., Ed., *Singlet O*₂; Chemical Rubber Company: Boca Raton, Florida, 1984-1985; Vols. 1-4. (e) Gollnick, K.; Kuhn, H. J. In *Singlet Oxygen*; Wasserman, A. A., Murray, R. W. Eds.; Academic Press: New York, 1979; pp 287-427. (f) Denny, R. W.; Nickon, A. Org. *React.* 1973, 20, 133-336.
- (a) Schenk, G. O.; Koch, E. Z. Electrochem. 1960, 64, 170. (b) Rosenthal, I. In Singlet O₂ Volume I: Physical-Chemical Aspects; Frimer, A. A. Ed.; Chemical Rubber Company: Boca Raton, Florida, 1985; pp 13-38.
- (a) Lopez, L. In *Photoinduced Electron Transfer* (Topics in Current Chemistry 156), Mattay, J. Ed.; Springer Verlag: Berlin, 1990; Vol. I, pp 117-166. (b) Lewis, F. D. In *Photoinduced Electron Transfer. Part C. Photoinduced Electron Transfer Reactions: Organic Substrates*, Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; pp 1-69.
- 9. Jefford, C. W.; Boschung, A. F. Helv. Chim. Acta 1977, 60, 2673-2685.
- (a) Superoxide turns out to be a poor radical on all accounts, rarely initiating free radical autoxidative processes via H-abstraction or addition to double bonds.^{10b,10c} Its conjugate acid HOO, or another of its derivatives HO, are well documented radical initiators. (b) Frimer, A. A. In *Superoxide Dismutase*; Oberley, L. W. Ed.; Chemical Rubber Company: Boca Raton, Florida, 1982; Vol. II, pp 83-125. (c) Frimer, A. A. In *The Chemistry of Peroxides*; Patai, S. Ed.; Wiley: Chichester, 1983; pp 429-461.
- 11. Neckers, D. C. J. Photochem. Photobiol., A: Chem. 1989, 47, 1-29.
- 12. Jefford, C. W.; Estrada, M. J.; Barchietto, G. Tetrahedron 1987, 43, 1737-1745; see also references therein.
- (a) Shimizu, N.; Bartlett, P. D. J. Am. Chem. Soc. 1976, 98, 4193-4200. (b) Mori, A.; Takeshita, H. Chem. Lett. 1978, 395-396. (c) Bartlett, P. D.; Becherer, J. Tetrahedron Lett. 1978, 2983-2986. (d) Koo, J.-Y.; Schuster, G. B. J. Org. Chem. 1979, 44, 847-851. (e) Sawaki, Y.; Ogata, Y. J. Am. Chem. Soc. 1981, 103, 2049-2053. (f) Shepherd, J. P. J. Org. Chem. 1983, 48, 337-342. (g) Clennan, E. L.; Speth, D. R.; Bartlett, P. D. J. Org. Chem. 1983, 48, 1246-1250. (h) Sawaki, Y.; Foote, C. S. J. Org. Chem. 1983, 48, 4934-4940. (i) Sawaki, Y.; Ogata, Y. J. Org. Chem. 1984, 49, 3344-3349.
- (a) Frimer, A. A.; Roth, D.; Sprecher, M. *Tetrahedron Lett.* **1977**, 1927-1930. (b) Frimer, A. A.; Farkash, T.; Sprecher, M. J. Org. Chem. **1979**, 44, 989-995. (c) Frimer, A. A.; Roth, D. J. Org. Chem. **1979**, 44, 3882-3887. (d) Frimer, A. A.; Antebi, A. J. Org. Chem. **1980**, 45, 2334-2340. (e) Frimer, A. A. Isr. J. Chem. **1981**, 21, 194-202. (f) Frimer, A. A. J. Photochem. **1984**, 25, 211-226. (f) Frimer, A. A.; Weiss, J. J. Org. Chem. **1993**, 58, 3660-3667. (g) Frimer, A. A.; Weiss, J.; Gottlieb, H. E.; Wolk, J. L. J. Org. Chem. **1994**, 59, 780-792. (h) Frimer, A. A.; Pizem, H. *Tetrahedron* **1999**, 55, 12175-12186. (i) Frimer, A. A.; Afri, M.; Baumel, S. D.; Gilinsky-Sharon, P.; Rosenthal, Z.; Gottlieb, H. E. J. Org. Chem. **2000**, 65, 1807-1817. (j) Frimer, A. A.; Sharon, O. Unpublished work.
- 15. (a) Koch, E. *Tetrahedron* **1968**, 24, 6295-6318. (b) Ashford, R. D.; Ogryzlo, E. A. *J. Am. Chem. Soc.* **1975**, 97, 3604-3607.

- 16. Binkley, J. S.; Whiteside, R. A.; Hariharan, B. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D., Gaussian Inc., Pittsburgh PA, 1976.
- 17. Laurie, V. W.; Stiglani, W. M. J. Am. Chem. Soc. 1970, 92, 1485-1488.
- 18. Allen, F. H. Tetrahedron 1982, 38, 645-655.
- 19. (a) Lebedev, V. L.; Bagatur'yants, A. A.; Taber, A. M.; Kalechits, I. V. *Russ. J. Phys. Chem.* 1978, *58*, 633-635.
 (b) Goldish, E. J. Chem. Ed. 1959, *36*, 408-416.
- 20. (a) Kearns, D. R. J. Am. Chem. Soc. 1969, 91, 6554-6563. (b) Paquette, L. A.; Liotta, D. C.; Baker, A. D. Tetrahedron Lett. 1976, 2681-2684. (c) Adam, W.; Carballiera, N.; Cheng, C.-C.; Sakanishi, K.; Gleiter, R. J. Org. Chem. 1979, 44, 851-853. (d) van den Heuvel, C. J. M.; Verhoeven, J. W.; de Boer, Th. Recl. Trav. Chim. Pays-Bas 1980, 99, 280-284. (e) Hurst, J. R.; Schuster, G. B. J. Am. Chem. Soc. 1982, 104, 6854-6856. (f) Reference 6e, Table II, pages 291-295 and 298ff. (g) Monroe, B. M. In Singlet O₂ Volume I: Physical-Chemical Aspects; Frimer, A. A. Ed.; Chemical Rubber Company: Boca Raton, Florida, 1985; pp 177-224; see especially pp 201-206. (h) Ref. 6c, p 71. (i) We note, however, that the I.P./rate correlation is far from perfect,^{20e-h} primarily because ionization potential is by no means the sole determinant of reaction rate.
- (a) Bischof, P.; Heilbronner, E. Helv. Chim. Acta 1970, 53, 1677-1682. (b) Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. Helv. Chim. Acta 1977, 60, 2213-2233. (c) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J.; Brundle, C. R.; Kuebler, N. A. J. Am. Chem. Soc. 1976, 98, 7179-7182. (d) Turner, D. W. In Molecular Photoelectron Microscopy; Wiley Interscience: New York, 1970. (e) Aue, D. H.; Mishishnek, M. J.; Shelhammer, D. F. Tetrahedron Lett. 1973, 4799-4802.
- 22. (a) Foote, C. S. Accounts Chem. Res. 1968, 1, 104. (b) Jefford, C. W.; Rimbault, C. G. Tetrahedron Lett. 1981, 22, 91-94. (c) Matsuura, T.; Horinaka, A.; Nakashima, R. Chem. Lett. 1972, 887-890. (d) Wilkinson, F.; Brummer, J. G. J. Phys. Chem. Ref. Data 1981, 10, 809-1000.
- 23. (a) Ouannes, C.; Wilson, T. J. Am. Chem. Soc. 1968, 90, 6527-6528. (b) Davidson, R. S.; Trethewey, K. R. J. Am. Chem. Soc. 1976, 98, 4008-4009. (c) Davidson, R. S.; Trethewey, K. R. J. Chem. Soc. Perkin Trans. II 1977, 178-182. (d) Monroe, B. M. J. Phys. Chem. 1977, 81, 1861-1864. (e) Deneke, C. F.; Krinsky, N. I. Photochem. Photobiol. 1977, 25, 299-304.
- 24. Foote, C. S. In Free Radicals in Biology; Pryor, W. A., Ed.; Academic Press: New York, 1977; Vol. II, pp 85, 101.
- 25. See Frimer, A. A. J. Photochem. 1984, 25, 211-226 and the papers cited in note 14.

About the Author

Aryeh A. Frimer is The Ethel and David Resnick Professor of Active Oxygen Chemistry at Bar-Ilan University, Ramat Gan, Israel, and Senior Research Associate at NASA Glenn Research Center, Cleveland, Ohio. He received his Ph.D. in chemistry from Harvard University in 1974 under the tutelage of Paul D. Bartlett. His address is Department of Chemistry, Bar-Ilan University, Ramat Gan 52900, Israel, e-mail: frimea@mail.biu.ac.il.

The Spectrum on the World-Wide Web

The Spectrum is available on the Center's Web site: http://www.bgsu.edu/departments/photochem/. You can access via Acrobat Reader. There are instructions for downloading a free copy of Acrobat Reader from the Adobe Web site.

If you plan to access *The Spectrum* electronically, please send an e-mail to: photochemical@listproc.bgsu.edu. We will remove you from our paper mailing list. Please browse our Web site for up-to-date information about the Center and its programs.

Something New in Transition Metal Complex Sensitizers: Bringing Metal Diimine Complexes and Aromatic Hydrocarbons Together

Russell Schmehl, Department of Chemistry, Tulane University

Introduction

The oil embargo of the early 1970s sent a shock through western nations and served as a wake up call for the development of alternative fuels. In the years that followed, the United States invested heavily in a variety of technologies which included active solar energy conversion. One appealing approach pursued was the development of photochemical systems for the conversion of light energy into storable fuels such as hydrogen.¹ A variety of schemes were contrived for such multi-electron redox processes and many involved molecular photosensitizers, PS, in reaction sequences like the one shown below (Scheme 1). Through a single photoinduced electron transfer reaction (or a series of photoredox reactions) reducing equivalents accumulate in a catalyst capable of reducing water to hydrogen. The photosensitizers used in such schemes must meet several criteria including (a) the PS must absorb visible light over much of the solar spectrum at energies high enough to carry out useful photoredox reactions, (b) the excited state lifetime must be long enough for photoinduced electron transfer reactions to compete effectively with other decay processes, (c) photoredox reactions of PS* with suitable electron acceptors (or donors) must be thermodynamically favorable, (d) the radical ion of PS formed following the photoredox reaction must be stable long enough to allow for efficient regeneration of the sensitizer and (e) the PS must be stable to photolysis for prolonged periods (i.e. no side photoreactions). These stringent criteria for the photosensitizer greatly narrow the number of candidate molecular systems. Among the more promising chromophores are the diimine complexes of Ru(II) and Os(II); the acknowledged parent of this now enormous group of chromophores is $[Ru(bpy)_2]^{2+}$ (bpy = 2,2'-bipyridine).

General Photophysical and Photochemical Properties of Ru(II) Diimine Complexes

The thermally equilibrated excited state of this class of complexes is metal-to-ligand charge transfer (MLCT) in nature.² The complexes absorb to varying degrees in the visible and many have red luminescence (600-750 nm) with excited state lifetimes that range from a few nanoseconds to a few microseconds in solution at room temperature. The thermally equilibrated excited state is believed to be predominantly of triplet spin multiplicity and the radiative rate constant is within a factor of two of 10⁵ s⁻¹ for the majority of complexes of this type.³ While only a few complexes have been examined in detail, the available data suggest intersystem crossing efficiencies for population of the ³MLCT state are close to unity. The excited complexes are generally reasonably good one electron oxidants and reductants. For $[(bpy)_3Ru]^{2+}$ the potentials for one electron oxidation and reduction of the excited state are approximately 0.8 V each (vs. SCE) and the ions formed $[(bpy)_3Ru(III)]^{3+}$ and $[(bpy)_2(bpy)Ru(II)]^+$ are stable in several solvents. The parent chromophore ($[(bpy)_3Ru]^{2+}$), however, undergoes reasonably efficient photoinduced ligand loss in many organic solvents; the reactive excited state is a ligand field (d-d) state reached via thermally activated internal conversion from the MLCT state. Investigations of other complexes showed that population of the reactive ligand field state can be circumvented by designing heteroleptic (mixed diimine ligand) complexes with one diimine ligand having a significantly lower energy LUMO (and therefore MLCT transition) than the other diimine ligands. For example, Paul Rillema's





group examined the photochemistry of $[(bpy)_2Ru(bpz)]^{2+}$ (bpz = 2,2'-bipyrazine) and found that the complex does not undergo photosubstitution and the barrier to population of the ligand field state was high enough that it is not the predominant thermally activated process for relaxation of the MLCT state.⁴

During the 1980s fundamental aspects of the photophysical behavior of Ru(II) and Os(II) diimine complexes were explored in detail. One important result from Tom Meyer's group was



constants as a function of the magnitude of the electron-vibrational coupling constant, S_M , for an excited state having an energy of 16,000 cm⁻¹ (46 kcal) and $\hbar\omega$ of 1400 cm⁻¹ (4 kcal).

the observation that nonradiative relaxation in a series of closely related complexes follows the energy gap law.⁵ That is, as the energy of the MLCT excited state decreases, the rate constant for nonradiative relaxation increases (the relationship is exponential). This may seem to pose practical problems for use of Ru(II) diimine complexes as sensitizers since the parent complex [(bpy)₃Ru]²⁺ is yellow and efforts to design derivatives that absorb a larger portion of the visible spectrum (and thus have lower energy MLCT states) will be hindered by the fact that nonradiative relaxation will dominate excited state decay. However, nonradiative relaxation rate constants also depend on the electron-vibrational coupling constant, S_{M'} and the average vibrational frequency coupling ground and excited states ($\hbar \omega_{M'}$ eq 1). The magnitude of S_M is directly proportional to the average bond displacement between the ground and excited state ($\Delta r \propto S_M^{-1/2}$).

$$k_{nr} \propto \exp(-S_M) \exp(-\frac{\gamma E_0}{\hbar \omega_M})$$

$$\gamma = \ln(\frac{E_0}{S_M \hbar \omega_M}) - 1$$
(1)

Equation 1 indicates that the nonradiative decay rate constant will increase with increasing excited state distortion as long as the energy gap, $E_{0'}$ is significantly greater than the averaged vibrational frequency. Figure 1 shows the relative magnitude of k_{nr} as a function of increasing S_M for a system having an energy gap of 16,000 cm⁻¹ (46 kcal) and $\hbar \omega$ of 1400 cm⁻¹ (4 kcal), values typical of Ru(II) diimine complexes. Thus, one means of minimizing increases in the nonradiative decay rate constant with decreasing E_0 is to design systems having minimal (or decreasing) distortion between ground and excited states. Meyer and coworkers provided an elegant example of this in studies of complexes of *trans*-1,2-bis-(4-(4'-methyl)-2,2'-bipyridyl)ethene. They illustrated the concept that, as the degree of delocalization of the ligand localized electron in the MLCT state is increased (through extended conjugation), the average degree of distortion relative to the ground state decreases and the nonradiative decay rate constant decreases.⁶ This approach has proved useful in making a variety of sensitizers with excited states that are longer lived than other sensitizers that emit at the same frequency but lack extended conjugation in the electron accepting ligand.⁷ However, often the ligand with extended conjugation has a ligand localized triplet excited state that is lower in energy than the MLCT state.^{8,9} Such systems are fundamentally different sensitizers and generally do not meet the criteria stated above.



Figure 2: Accessible excited states and decay processes for supramolecular complexes having both MLCT and ${}^{3}(\pi-\pi^{*})$ states. Shown also is a ${}^{3}MC$ (d-d) state that is thermally accessible from the MLCT state.

Supramolecules With Nearly Iso-Energetic MLCT and ${}^{\rm s}\!(\pi\to\pi^*)$ States

Another approach for making sensitizers that absorb throughout the visible and have long lived excited states is to exploit reversible intramolecular energy transfer processes between the MLCT state and an independent chromophore having a long lived triplet excited state. Figure 2 shows a diagram of the relative energies of the states involved for a typical metal diimine complex covalently linked to an aromatic hydrocarbon having a $3(\pi \rightarrow \pi^*)$ excited state of nearly the same energy. Many aromatic hydrocarbons have very large singlet-triplet splitting with triplet energies comparable to Ru(II) diimine 3 MLCT states; generally the aromatic hydrocarbons have long lived ${}^{3}(\pi \rightarrow \pi^*)$ states. Selective excitation into the visible light absorbing MLCT transition is followed by efficient intersystem crossing to the 3 MLCT state. Subsequent relaxation of the complex to the ground state depends on the magnitude of the rate constants for energy transfer to the



Figure 3: Excited state decay for MLCT and ${}^{3}(\pi-\pi^{*})$ states in rapid equilibrium as a function of the decay rate constant of the ${}^{3}(\pi-\pi^{*})$ state. The energy gap between the sates is -500 cm⁻¹ (K_{eq} = 11) and the lifetime of the MLCT state is 1 µs.

 ${}^{3}(\pi \to \pi^{*})$ state (k_{en} and k_{-en}) and relaxation of both of the excited states (k_{CT} and k_{pi}). The kinetics can be evaluated exactly and the solution has been published in several texts on photophysics.^{10,11} In the particular case where the ¹MLCT state intersystem crosses to the ³MLCT state exclusively, population of the ${}^{3}(\pi \to \pi^{*})$ state depends on the relative values of k_{en} and k_{CT} . If $k_{en} >> k_{CT}$, the two states will be in equilibrium if $k_{-en} >> k_{pi}$. Of course, the relative magnitude of k_{-en} depends on the energy gap between the ³MLCT and ${}^{3}(\pi \to \pi^{*})$ states. As the energy gap increases, the back energy transfer rate constant will decrease until eventually back energy transfer is unimportant in the decay dynamics.

Since the focus of this article is on exploiting reversible energy transfer to extend the lifetime of ³MLCT states of metal diimine complexes, it is worthwhile to present calculated decay curves for a few hypothetical cases. MLCT states of Ru(II) diimine complexes generally have lifetimes of around 1 µs in nonaqueous solutions. Using a fixed forward energy transfer rate constant and assuming the energy gap can be used to calculate the equilibrium constant, the value of k_{en} can be determined and the relative concentrations of the ³MLCT and ³($\pi \rightarrow \pi^*$)

states can be evaluated at any time during the relaxation. The lifetime of the ³MLCT state becomes a weighted average of the lifetimes of the two equilibrated states; as the energy gap becomes larger, the concentration of the ³MLCT state at any time during the decay decreases, but the lifetime increases.

For systems with a fixed energy gap, the rate constant for decay of the equilibrated excited states decreases as the lifetime of the ${}^{3}(\pi \rightarrow \pi^{*})$ state increases. Figure 3 shows luminescence decays for several kinetic cases where forward and reverse energy transfer are rapid relative to relaxation of either of the states involved ($k_{en} = 2.2 \times 10^{8} \text{ s}^{-1}$ and $\Delta E_{en} = -500 \text{ cm}^{-1}$).



Figure 4: Decay of the excited MLCT/ ${}^{3}(\pi-\pi^{*})$ states as a function of the rate constnt for energy transfer. The energy gap is -500 cm⁻¹ and the lifetimes of the MLCT and $(\pi-\pi^{*})$ states are fixed at 1 µs and 20 µs, respectively.

The decay curves shown indicate the effect of changes in the lifetime of the ${}^{3}(\pi \rightarrow \pi^{*})$ state $(1/k_{pi})$ on the observed decay of the 3 MLCT state. The top portion of the figure shows that, following an initial rapid equilibration period, the ratio of the ${}^{3}(\pi \rightarrow \pi^{*})$ state to 3 MLCT state remains constant and is equal to the equilibrium ratio (i.e. the two states are in *thermodynamic* equilibrium). The important feature is that the observed lifetime of the 3 MLCT state increases as the lifetime of the ${}^{3}(\pi \rightarrow \pi^{*})$ state increases *up to a limit*. Beyond the limit the observed decay lifetime will not change as the lifetime of the ${}^{3}(\pi \rightarrow \pi^{*})$ state becomes longer.

On the other hand, when the rate constant for energy transfer is comparable to the rate of radiative and nonradiative decay of at least one of the states, there is a very significant difference. The ratio of $[{}^{3}(\pi \rightarrow \pi^{*})]_{t}$ to $[{}^{3}MLCT]_{t}$ during the decay *does NOT equal the equilibrium ratio*. For example, Figure 4 shows decay curves and $[{}^{3}(\pi \rightarrow \pi^{*})]_{t}$ to $[{}^{3}MLCT]_{t}$ ratios for a system having k_{CT} and ΔE_{en} fixed at 10^{6} s⁻¹ and -500 cm⁻¹, respectively. When the forward energy transfer rate constant is approaching the equilibrium limit ($k_{en} >> k_{CT}$), the $[{}^{3}(\pi \rightarrow \pi^{*})]_{t}$ to



[³MLCT], ratio approaches the equilibrium value (11 when ΔE_{en} is -500 cm⁻¹). For systems where k_{en} is less than or equal to the decay rate constant of the ³MLCT state, the $[^{3}(\pi \rightarrow \pi^{*})]_{t}$ to $[^{3}MLCT]_{t}$ ratio at times beyond the initial equilibration period is greater than the equilibrium value since the ³MLCT state is depleted faster than the $^{3}(\pi \rightarrow \pi^{*})$ state can back energy transfer and maintain equilibrium. The $[{}^{3}(\pi \rightarrow \pi^{*})]_{t}$ to [³MLCT], ratio remains constant during the decay, but the system is at a kinetic steady state, not equilibrium. As k_{-en} decreases relative to $k_{pi'}$, the overall rate constant for decay of the ${}^{3}(\pi \rightarrow \pi^{*})$ state (and thus the MLCT state) also decreases. Figure 4 illustrates that overall decay times on the

order of the lifetime of k_{pi} can be achieved (i.e. much longer lifetimes than for the rapid equilibrium case). Unfortunately, for a given energy gap, the forward energy transfer rate constant, k_{en} , also decreases, as does the relative concentration of the long lived species formed (as shown in Figure 4).

While the detailed analysis of the kinetics is complex, the qualitative result is always the same: reversible energy transfer between a long lived ${}^{3}(\pi \rightarrow \pi^{*})$ state and a ${}^{3}MLCT$ state will lead to longer lived ${}^{3}MLCT$ emission. Thus, this approach is promising for making complexes with very long lived ${}^{3}MLCT$ emission, apparently defying the energy gap law.

A Case Study: Ru(diimine)₃ / Pyrene Complexes

Over the past decade, several Ru(II) diimine complexes have been covalently linked to pyrene in various ways. Figure 5 shows the structures of seven ligands that have been used in the preparation of these complexes. In a few, the pyrene is tethered to the diimine ligand via a saturated hydrocarbon tether; the other ligands have either a conjugated bridge or no bridge at all. In fact, Mike Rodgers' group at Bowling Green was the first to publish on these complexes.¹² They found that for [(Pyr-C4Am-phen)Ru(bpy)₂]²⁺ the luminescence appears to originate from the ³MLCT state, but the excited state absorption spectrum clearly resembles that of the pyrene triplet. The luminescence decay consists of two components of 7 ns and 11 μ s. From this they concluded that the initially populated ³MLCT state rapidly relaxes to an equilibrium population of the MLCT and π - π * states. The MLCT state lies approximately 600 cm⁻¹ (1.7 kcal) above the pyrene triplet. Subsequent work by Sasse on a reasonably closely related derivative yielded similar results.¹³ Quite recently Castellano and coworkers, also at Bowling Green, made the interesting observation that the photophysical behavior for alkyl tethered complexes depends on the number of coordinated bipyridyl-pyrene ligands.¹⁴ The two complexes [(Pyr-C2OH-bpy)Ru(bpy)₂]²⁺ and [(Pyr-C2OH-bpy)₃Ru]²⁺ have luminescence decays of 3 and 9 μ s, respectively.

The complexes having pyrene linked to a diimine ligand through an acetylene bridge, reported by Harriman and Ziessel, are somewhat different.¹⁵ The complex [(Pyr-CC-bpy)Ru(bpy)₂]²⁺ emits significantly farther to the red and has a two component luminescence decay, with lifetimes of 7 ps and 42 μ s. The system appears to be in rapid equilibrium, with the MLCT state approximately 1200 cm⁻¹ (3.4 kcal) above the π - π * state. The complex [(Pyr-CC-tpy)Ru(tpy)]²⁺ is unique, since it is the only complex of this class having the pyrene π - π * state higher in energy than the MLCT state. The lifetime of the MLCT emission at 698 nm is over 500 ns, nearly 10 times longer than other related Ru(II) terpyridine derivatives.

Our own group, in collaboration with Piotr Piotrowiak (now at Rutgers, Newark) and Randy Thummel (U. Houston), published on this class of complexes a few years ago and reported two relatively peculiar examples.¹⁶ The complex $[(Pyr-phen)Ru(bpy)_2]^{2+}$ has the pyrene linked in the 2 position of the phenanthroline ligand. The crystal structure of the complex shows that the pyrene is held rigidly orthogonal to the phenanthroline and is also π stacked with one of the bipyridine ligands. The photophysical behavior in solution at room temperature reflects the strain on the coordination sphere; the lifetime of the 600 nm emission is only 4 ns and the quantum yield is less than 0.001. Interestingly,

the transient absorption spectrum of the complex resembles that of pyrene and the lifetime of the TA is approximately 70 ns. In matrices at 77 K the steady state emission is very narrow, resembling phosphorescence of *unsubstituted* pyrene. The other complex reported, $[(Pyr-bpy)Ru(bpy)_2]^{2+}$, exhibits strong luminescence in solution at room temperature. The 640 nm emission decays with two components of 1.3 µs and 57.4 µs and the transient absorption spectrum does not resemble that of pyrene. In this case the energy gap is smaller (~ 200 cm⁻¹) and the forward energy transfer from the initially populated ³MLCT state is clearly slower than that measured for other covalently linked Ru(diimine)/pyrene complexes. The slower forward energy transfer dynamics play a role in producing this particularly long lived derivative.

Potential Applications

Little has been done with these complexes beyond photophysical characterization. Recently, however, Sasse and coworkers examined light induced electron transfer from $[(bpy)_2Ru(Pyr-C2-bpy)]^{2+}$ to methyl viologen (paraquat) and found that cage escape from the geminate ion pair formed is much higher than for closely related sensitizers.¹⁷ It is not clear whether the oxidized species is the metal complex or the pyrene (the redox potentials are very similar). Additionally, complexes having long excited state lifetimes are quenched readily by oxygen and can serve as excellent sensors; a chemosensor for O₂ based upon $[(bpy)_2Ru(Pyr-bpy)]^{2+}$ has been investigated in detail.¹⁸ Finally, this concept can be extended to the investigation of complexes having lower energy MLCT states with much shorter excited state lifetimes; in particular, it will be interesting to see if Os(II) diimine complexes covalently linked to appropriate aromatic hydrocarbons will have significantly lengthened excited state lifetimes.

References

- 1. See (a) Bard, A. J.; Fox, M. A. Acc. Chem. Res. 1995, 28, 141-145. (b) Meyer, T. J. Acc. Chem. Ress. 1989, 22, 163-170.
- See (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. Coord. Chem. Rev. 1988, 84, 85-277. (b) Meyer, T. J. Pure Appl. Chem. 1986, 58, 1193-1206. (c) Watts, R. J. Chem. Educ. 1983, 60, 834-842.
- 3. This has been a topic of significant discussion. For a thorough discussion of this issue see: Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 3877-3886.
- 4. Ross, H. B.; Boldaji, M.; Rillema, D. P.; Blanton, C. B.; White, R. P. Inorg. Chem. 1989, 28, 1013-1021.
- (a) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. J. Phys. Chem. 1986, 90, 3722-3734. (b) Caspar, J. V.; Meyer, T. J. J. Phys. Chem. 1983, 87, 952-957. (c) Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. J. Am. Chem. Soc. 1982, 104, 630-632.
- 6. Boyde, S.; Strouse, G. F.; Jones, W. E., Jr.; Meyer, T. J. J. Am. Chem. Soc. 1990, 112, 7395-7396.
- 7. (a) Anderson, P. A.; Strouse, G. F.; Treadway, J. A.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* 1994, 33, 3863-3864.
 (b) Nazeeruddin, Md. K.; Pechy, P.; Gratzel, M. *Chem. Commun.* 1997, 1705-1706.
- 8. (a) Sacksteder, L.; Lee, M.; Demas, J. N.; DeGraff, B. A. J. Am. Chem. Soc. 1993, 115, 8230-8238.
- (a) Baba, A. I.; Ensley, H. E.; Schmehl, R. H. *Inorg. Chem.* **1995**, *34*, 1198-1207. (b) Shaw, J. R.; Schmehl, R. H. J. Am. Chem. Soc. **1991**, *113*, 389-394. (c) Shaw, J. R.; Webb, R. T.; Schmehl, R. H. J. Am. Chem. Soc. **1990**, *112*, 1117-1123.
- 10. Demas, J. N. Excited State Lifetime Measurements; Academic: New York, 1983; pp 59-62.
- 11. Birks, J. B. The Photophysics of Aromatic Molecules; Wiley: New York, 1970.
- 12. Ford, W. E.; Rodgers, M. A. J. J. Phys. Chem. 1992, 96, 2917-2919.
- 13. Wilson, G. J.; Sasse, W. H. F.; Mau, A. W.-H. Chem. Phys. Lett. 1996, 250, 583-88.
- 14. Tyson, D. S.; Castellano, F. N. J. Phys. Chem. 1999, 103, 10955-10960.
- 15. Hissler, M.; Harriman, A.; Khatyr, A.; Ziessel, R. Chem. Eur. J. 1999, 5, 3366-3381.
- 16. Simon, J. A.; Curry, S. L.; Schmehl, R. H.; Schatz, T. R.; Piotrowiak, P.; Jin, X.; Thummel, R. P. J. Am. Chem. Soc. 1997, 119, 11012-11018.
- 17. Wilson, G. J.; Launikonis, A.; Sasse, W. H. F.; Mau, A. W. H. J. Phys. Chem. A 1998, 102, 5150-5156.
- 18. Ji, H.-F.; Shen, Y; Hubner, J. P.; Carroll, B. F.; Schmehl, R. H.; Simon, J. A.; Schanze, K. S. *Appl. Spectroscp.* 2000, in press.

About the Author

Russell Schmehl received his Ph.D. from the University of North Carolina in 1980 under the direction of David Whitten. Following a year as a postdoctoral associate with Royce Murray, also at UNC, he joined the faculty at Tulane University in 1982. He is an active member of the Inter-American Photochemical Society, serving as organizer of the 10th Winter Conference in 1998 and as Secretary of the society from 1998-2000. Dr. Schmehl may be contacted at the Department of Chemistry, Tulane University, New Orleans, Lousiana, 70118; email: russ@mailhost.tcs.tulane.edu.

Center for Photochemical Sciences Publications 1998-2000

- 352. Sarker, A. M.; Lungu, A.; Mejiritski, A.; Kaneko, Y.; **Neckers, D. C.** Tetraorganylborate salts as convenient precursors for photogeneration of tertiary amines. *J. Chem Soc.*, *Perkin Trans.* **2 1998**, *10*, 2315-2321.
- 353. Hu, S.; Popielarz, R.; Neckers, D. C. Fluorescence probe techniques (FPT) for measuring relative efficiencies of free radical photoinitiators. *Macromolecules* **1998**, *31*, 4107-4113.
- 354. Strehmel, B.; Sarker, A. M.; Malpert, J. H.; **Neckers, D. C.** Photoinduced crosslinking of diacrylates for a series of ammonium alkyltriphenylborates using the fluorescence cure monitor. Presented at the 216th ACS National Meeting, Boston, MA, August 1998.
- 355. Sarker, A. M.; Malpert, J. H.; Strehmel, B.; **Neckers, D. C.** Synthesis and photoluminiscence studies of fluorinated oligophenylenevinylenes. Presented at the 216th ACS National Meeting, Boston, MA, August 1998.
- Sarker, A. M.; Kaneko, Y.; Neckers, D. C. Photochemistry and photophysics of novel photoinitiators: N,N,N-tributyl-N-(4-methylene-7-methoxycoumarin) ammonium borates. *J. Photochem. Photobiol. A* 1998, 117, 67-74.
- 357. Morlino, E. A.; **Rodgers, M. A. J.** The photoinduced dissociation of nitric oxide from nitrosyl metalloporphyrins. *Prog. React. Kinet.* **1998**, *23*, 91-115.
- 358. Hu, S.; Neckers, D. C. Mechanism of alkyl phenylglyoxylates photoreaction in the presence of oxygen. *J. Photochem. Photobiol.* **1998**, *118*, 75-80.
- 359. Hu, S.; Sarker, A. M.; Kaneko, Y.; **Neckers, D. C.** Reactivities of chromophore-containing methyl tri-n-butylammonium organoborate salts as free radical photoinitiators: dependence on the chromophore and borate counter ion. *Macromolecules* **1998**, *31*, 6476-6480.
- 360. Zang, H.; Neckers, D. C. Photochemical reactions of 2,4-diethyl-2,4-diphenyl-1,3-cyclobutanedione in benzene and in isopropyl alcohol. *J. Org. Chem.* **1999**, *64*, 2103-1206.
- 361. Busetti, A.; Soncin, M.; Jori, G.; Kenney, M. E.; **Rodgers, M. A. J.** Treatment of malignant melanoma by highpeak-power 1064 nm irradiation followed by photodynamic therapy. *Photochem. Photobiol.* **1998**, *68*, 377-381.
- 362. Fedorov, A. V.; **Snavely, D. L.** Vibrational overtone spectroscopy of cycloheptatriene-*d*₆ at the third and fourth overtone regions. *J. Phys. Chem. A* **1998**, *102*, 4749.
- 363. Fedorov, A. V.; **Snavely, D. L.** Vibrational overtone spectroscopy of cycloheptatriene chromium tricarbonyl, benzene chromium tricarbonyl, and corresponding hydrocarbon ligands. *J. Phys. Chem. A* **1998**, *102*, 6234-6238.
- 364. Nikolaitchik, O. A.; **Bullerjahn, G. S.** Transcript analysis of the *pcbABC* genes encoding the antenna apoproteins in the photosynthetic prokaryote, *Prochlorothrix hollandica*. *FEMS Microbiol. Lett.* **1998**, *168*, 187-194.
- 365. Hu, S.; Malpert, J. H.; Yang, X.; Neckers, D. C. Exploring chromophore tethered aminoethers as potential photoinitiators for controlled radical polymerization. *Polymer* **2000**, *41*, 445-452.
- 366. Wang, Y.; Petrov, V.; **Ding, Y. J.**; Zheng, Y.; Khurgin, J. B.; Risk, W. P. Ultrafast generation of blue-light by efficient second-harmonic generation in periodically-poled bulk and waveguide potassium titanyl phosphate. *Appl. Phys. Lett.* **1998**, *73*, 873-875.
- 367. Gu, X. H.; Korotkov, R.; **Ding, Y. J.**; Kang, J. U.; Khurgin, J. B. Observation of backward third-harmonic generation in periodically-poled lithium niobate. *Opt. Commun.* **1998**, *155*, 323-326.

- 368. Navarro, J. A.; Hervas, M.; Babu, C. R.; Molina-Heredia, F. P.; **Bullerjahn, G. S.**; De la Rosa, M. A. Kinetic mechanisms of PSI reduction by plastocyanin and cytochrome c₆ in the ancient cyanobacteria *Pseudanabaena* sp. PCC6903 and *Prochlorothrix hollandica*. In *Photosynthesis: Mechanism and Effects*; Garab, G., Ed.; Kluwer Publishers: Dordrecht, 1998; pp 1605-1608.
- 369. Kaneko, Y.; Sarker, A. M.; **Neckers, D. C.** Mechanistic studies of photobase generation from ammonium tetraorganyl borate salts. *Chem. Mater.* **1999**, *11*, 170-176.
- 370. Grinevich, O.; Serguievski, P.; Sarker, A. M.; Zhang, W.; Mejiritski, A.; **Neckers, D. C.** Relative activity of possible initiating species produced from photolysis of tetraphenyl and triphenylbutyl borates as measured by fluorescence probe techniques. *Macromolecules* **1999**, *32*, 328-330.
- 371. Sarker, A. M.; Kaneko, Y.; **Neckers, D. C.** Electron transfer followed by double fragmentation reactions: mechanism of photogeneration of tertiary amines and radicals from tetraorganyl borates. *J. Photochem. Photobiol. A* **1999**, *121*, 83-90.
- 372. Gu, X. H.; Korotkov, R.; **Ding, Y. J.**; Khurgin, J. B.; Risk, W. P. Quasi-phase-matched backward secondharmonic generation and third-harmonic generation in periodically-poled potassium titanyl phosphate waveguide. *Opt. Lett.* **1999**, *24*, 127-129.
- 373. Gu, X. H.; **Ding, Y. J.**; Kang, J. U.; Khurgin, J. B. Backward second-harmonic generation in periodically-poled LiNbO₃. Special issue of *Opics & Photonics News: "Optics in 1998"* **1998**, *9*, 29-30.
- 374. Zhang, W.; Feng, K.; Wu, X.; Martin, D.; **Neckers, D. C.** Photochemical properties of 4-benzoylbenzylammonium borates. *J. Org. Chem.* **1999**, *64*, 458-463.
- 375. Strehmel, B.; Sarker, A. M.; Malpert, J. H.; Strehmel, V.; Seifert, H.; Neckers, D. C. Effect of aromatic ring substitution on the optical properties, emission dynamics and solid state behavior of fluorinated oligophenylenevinylenes. *J. Am. Chem. Soc.* **1999**, *121*, 1226-1236.
- 376. Grinevich, O.; Mejiritski, A.; **Neckers, D. C.** AFM force-distance curve methods for measuring the kinetics of silicon chemical etching and reactions between silylating agents and a silicon surface. *Langmuir* **1999**, *15*, 2077-2079.
- 377. Soncin, M.; Busetti, A.; Biolo, R.; Jori, G.; Kwag, G.; Li, Y.-S.; Kenney, M. E.; **Rodgers, M. A. J.** Photoinactivation of amelanotic and melanotic melanoma cells sensitized by axially substituted Si-naphthalocyanines. *J. Photochem. Photobiol.*, *B: Biol.* **1998**, *42*, 202-210.
- 378. Busetti, A.; Soncin, M.; Jori, G.; **Rodgers, M. A. J.** High efficiency of benzoporphyrin derivative in the photodynamic therapy of pigmented malignant melanoma. *Br. J. Cancer* **1999**, *79*, 821-824.
- 379. Soncin, M.; Busetti, A.; Fusi, F.; Jori, G.; **Rodgers, M. A. J.** Irradiation of amelanotic melanoma cells with 532 nm high peak power pulsed laser radiation in the presence of the photothermal sensitizer Cu(II)-hematoporphyrin: a new approach to cell photoinactivation. *Photochem. Photobiol.* **1999**, *69*, 708-712.
- 380. Babu, C. R.; Volkman, B. F.; **Bullerjahn, G. S.** NMR solution structure of plastocyanin from the photosynthetic prokaryote, *Prochlorothrix hollandica*. *Biochemistry* **1999**, *38*, 4988-4995.
- 381. Hu, S.; Neckers, D. C.; Photocycloaddition and ortho-hydrogen abstraction reactions of methyl arylglyoxylates: structure dependent reactivities. *J. Chem. Soc., Perkin Trans.* 2 1999, 1771-1778.

For reprints of any of these publications, please write or e-mail the Center for Photochemical Sciences and refer to the reprint by number. Reprints of articles in press will be provided upon publication of the article.

Plug Into The Benefits of SPIE Membership

Networking

Stay connected to your professional community. Learn from others willing to share their ideas, and gain access to the people who can help you grow.

Member Discounts

Save money on conference and continuing education fees, SPIE publications, and video courses.

Journal Subscription

You choose one of SPIE's three peer-reviewed journals—available online or in print.

OE Reports

Free subscription to SPIE's monthly newspaper. This paper serves the technical community with news and commentary on cutting-edge technology it's your direct link to colleagues.

SPIE Web

Get Information on upcoming symposia, society news and events, books and journals, membership, and much, much more.

A Voice in the Community

As a member you may vote on society business, hold office, and receive recognition through society awards and fellowships.

Employment Assistance

Visit the career center or attend a professional development seminar at selected SPIE symposia. Post your resume or find a job in OE Reports or on the web at OPTICS.ORG.

Professional Group Benefits

Insurance, discount travel, and no-fee credit card.



Contact SPIE to join:

Phone 1 360 676 3290 • E-mail membership@spie.org • Web www.spie.org