

Directional Photoinduced Charge Transfer in Thin Polymeric Porphyrin Films

Carl C. Wamser, Department of Chemistry, Portland State University

Introduction

Photoinduced electron transfer is at the heart of numerous important reactions, biological processes, and technological applications.¹ Artificial photosynthesis, for example, refers to solar energy conversion approaches that take inspiration from the molecules or the strategies of natural photosynthesis.² Natural photosynthesis includes light-harvesting chromophores that ultimately lead to electron transfer within a carefully structured reaction center, followed by sequential electron transfers across a photosynthetic membrane. As a simple analog of the photosynthetic membrane, we have been studying novel polymeric films made from porphyrins by interfacial polycondensation.^{3,4} These films display a unique structural and redox asymmetry that generates directional photopotentials and photocurrents. In this paper, we summarize these effects and offer our current interpretations.

Interfacial Polymerization

Many chemists are familiar with the "nylon rope" demonstration as a simple example of interfacial polymerization.⁵ Two immiscible solvents each contain a reactive monomer, typically an aqueous solution of a diamine and an organic solution of a diacyl chloride, which generates a thin polyamide film at the interface. We have adapted this approach to use tetrasubstituted porphyrins as the monomers, specifically an acid chloride derivative (TCCPP – 5,10,15,20-tetra(4-chlorocarbonylphenyl)porphyrin) and either an amino or hydroxy derivative (TAPP – 5,10,15,20-tetra(4-aminophenyl)porphyrin or THPP – 5,10,15,20-tetra(4-hydroxyphenyl)porphyrin). These monomers are allowed to react undisturbed over a period of hours, during which time they generate a thin film of polymer at the interface. The film is extremely thin (10-500 nm) because the film itself creates a barrier that hinders diffusional contact of the reactive monomers with one another. Film thickness can be controlled by adjusting reaction time and/or monomer concentrations. The interfacial polymer film can be carefully removed, washed to remove excess monomers and to hydrolyze excess acid chloride groups, and deposited onto an appropriate substrate for further study.

A unique aspect of such films, illustrated in Figure 1, is the structural asymmetry. The surface formed in contact with a given monomer will have a higher concentration of that monomer incorporated into the polymer. We designate opposite sides as N and C, indicating an excess of amine substituents or carboxy substituents, respectively. Films made with the hydroxy monomer have H and C surfaces. The presence of unequal concentrations of monomers on opposite surfaces has been demonstrated by contact angle pH titrations⁶ and XPS studies of films made from metalloporphyrins.⁷ The presence of porphyrins with different substituents at different locations within the polymer film leads in turn to a unique redox asymmetry. Substituent effects on the redox properties of tetraphenyl porphyrins have been quantitatively correlated with Hammett constants.^{8,9} Since amino (or hydroxy) groups are electron-donating and carboxy groups are electron-withdrawing, a gradient of redox potentials across the film is predicted. The presence of porphyrins with various mixes of amide and amine or amide and carboxy substituents creates a

Continued on page 3

From the Executive Director

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

This year marked the 13th anniversary of the Advisory Board of the Center for Photochemical Sciences. It's hard to describe how much helpful advice we have gotten from our Board members over the years. For me, the enthusiastic support of colleagues has been one of the most gratifying parts of both starting the Center and seeing it grow to its current level of activity. In this small way, I again thank each member of the Advisory Board past and present for your service to the Center.

The Center for Photochemical Sciences got its start over lunch during a torrential downpour in July in Bowling Green. Somehow I had convinced Samir Farid, from Kodak, to come give us a talk. During lunch on that rainy day Samir, Chris Dalton, Dean of Arts and Sciences Ken Baker, Vice President for Academic Affairs Betsy Clark, and I talked about a Ph.D. authority for the Chemistry Department. Samir said, "Why don't you start a Center for Photochemical Sciences?"

So that's what we did. With approval from the University (took a while) and a letterhead logo designed by Chris Dalton's daughter (age 8), I announced to the world the birth of the Center. The headline on the story in C & E News said "Bowling Green Focuses on the Photosciences." A writer from the SPIE Newsletter came around and did another story. The SPIE Newsletter story introduced me to Kelly Swainson, an inventor of three-dimensional imaging, a designer from Ford Design by the name of Sucatta who said there's a use for that, and Chuck Hull, the man who invented and coined the word for *stereolithography*. From thence came the Center's interaction with 3D Systems, rapid prototyping, and the rest.

The Advisory Board had its start when Chris Dalton and I invited several friends to Bowling Green for a weekend in October to talk about our fledgling Center. I had football tickets for the perfect October college weekend. (It poured again so everybody went home!) Fred Lewis, Dave Eaton and Samir Farid graciously gave of their time on a miserable Friday/Saturday in northwest Ohio to help us get started. Dick Wright, of the former Mead Imaging, arrived in my office early on that Friday afternoon and said "Have you had lunch?" I had not so we went to Bowling Green's finest, the Holiday Inn, where Dick asked for the daily specials. The one which Dick ordered was eggs Benedict, wherein the waitress asked "Sir, would you like that with zucchini or mashed potatoes?" So began the Advisory Board meetings.

It's incredible that the Center survived all this, but survive it did. (And it doesn't ALWAYS rain in Bowling Green.) The next year we discussed with the Advisory Board our proposal for a Ph.D. in the photochemical sciences. Approximately sixth months later the modified proposal, strengthened by their input, was approved by the Ohio Board of Regents. The rest, as they say, is history.

Besides honoring our Advisory Board members, I want to publicly acknowledge the tremendous contributions of Pat Green. No one, including yours truly, has been more important to the growth and development of the Center for Photochemical Sciences than Pat Green.

Some years ago I gave a talk at the Honors banquet in the Chemistry Department at the University of Kansas, my alma mater. I don't remember much that I said then, save one thing. I was sure that "had Ludwig van Beethoven been alive today, he would have been a chemist." He would have relished the challenges of the profession even more than writing symphonies. *Sic ergo* Pat Green.

Pat, from all of us at the Center as well as in the photochemical sciences worldwide, and specifically from those in Bowling Green we say, sincerely, "Thank you." You may not be a photochemical scientist but you are, for sure, an honorary member of the clan and a very important one.

In This Issue

Directional Photoinduced Charge Transfer in Thin Polymeric Porphyrin Films	1
From the Executive Director	2
Photochemistry and Photophysics of Xanthy and Thioxanthy Carbocations	6
Center for Photochemical Sciences Publications	12

Continued from page 1

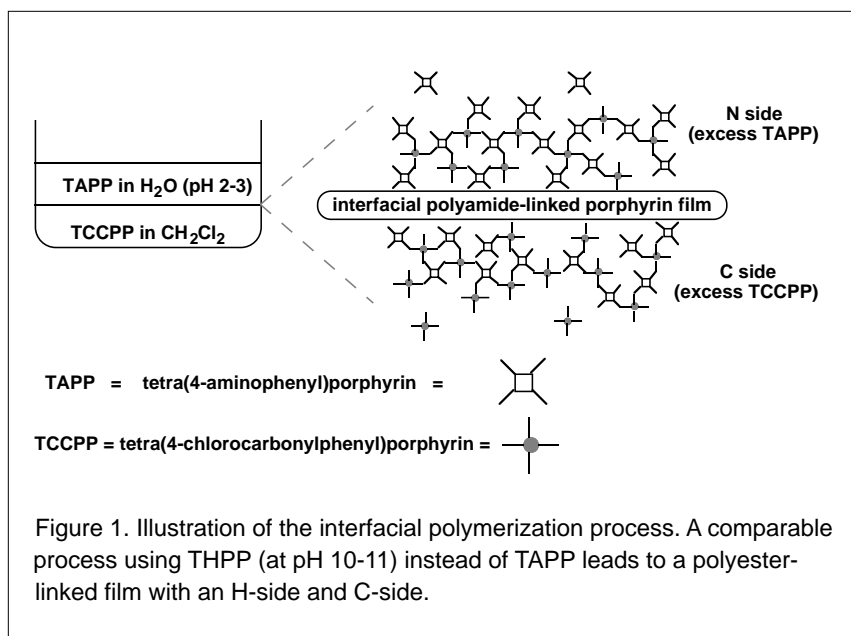


Figure 1. Illustration of the interfacial polymerization process. A comparable process using THPP (at pH 10-11) instead of TAPP leads to a polyester-linked film with an H-side and C-side.

with white light designed to simulate the solar spectrum. The direction of the light and the attachment of the leads were noted with a two-letter acronym in the following manner: the first letter indicated the side of film towards the light and the second letter the side of the film probed, i.e., the side **not** electrically grounded. For example, **CC** indicates that the C side of the film faced the laser and the sign of the photopotential indicated the relative potential on the C side. Figure 2 illustrates a set of laser-induced photopotentials for the four possible configurations of a thin porphyrin polyamide film.

Note that a negative potential develops on the C side of the film regardless of the direction from which the laser impinges (**CC** and **NC** configurations). Monitoring the opposite side in each case simply gives a mirror image trace indicating the relatively positive potential on the N side (**CN** and **NN**). This directionality is as predicted based on the different redox potentials within the porphyrin film.

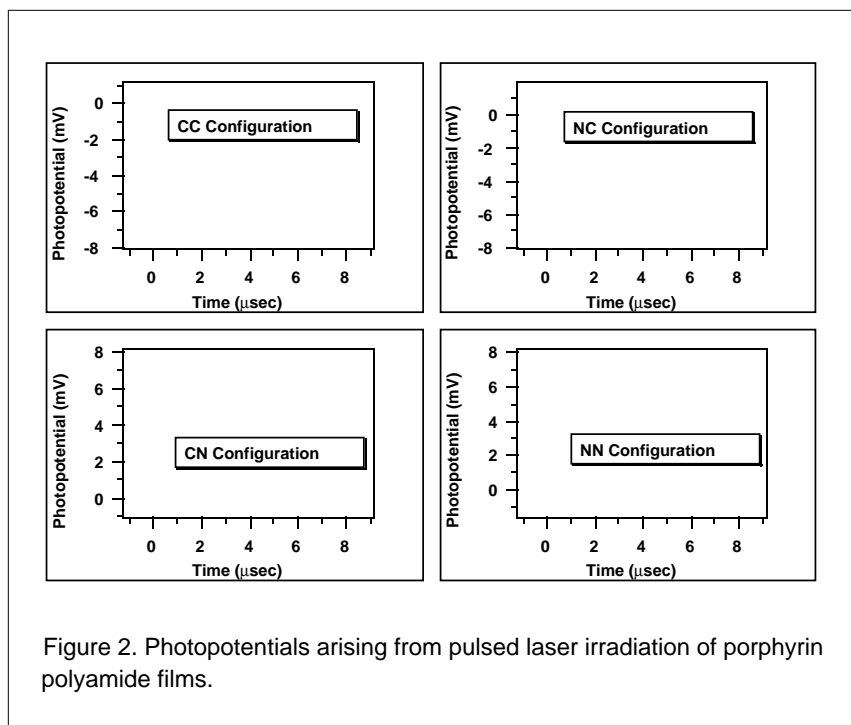


Figure 2. Photopotentials arising from pulsed laser irradiation of porphyrin polyamide films.

rich mixture of redox potentials, which consistently point to a preferred direction for electron transfer away from the N (or H) side towards the C side. We probed this prediction of a preferential directionality for electron transfer by studying photopotentials generated by laser pulses.

Photoinduced Charge Transfer

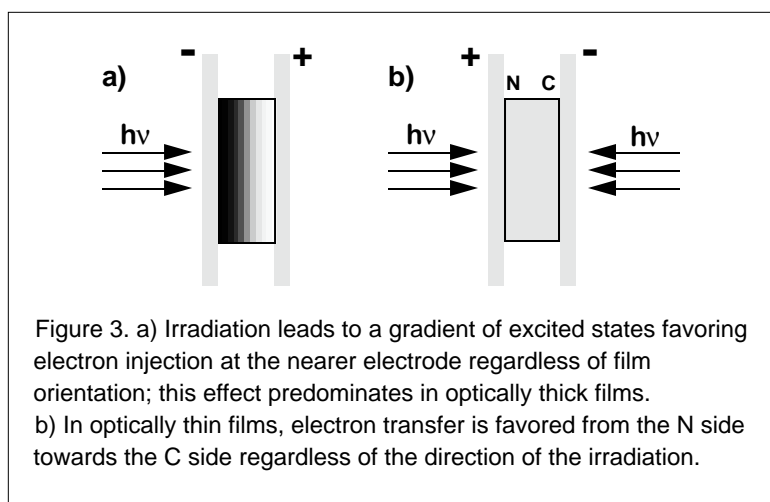
Polymer films were washed, deposited onto a transparent electrode, and sandwiched between a second identical transparent electrode. For fast kinetic studies, the cell was irradiated with a pulsed dye laser (450 nm) with pulse duration < 1 nsec and pulse power 0.2 mJ per pulse (PTI 2300 and 201). Photopotentials were monitored by a high-speed oscilloscope (Tektronix 11402). Irradiations were also carried out

Photopotential Lifetimes

The observed risetime and lifetime of the photopotential varied substantially depending on the specific history of the film. Figure 2 illustrates typical examples of the relatively simple traces that consisted of just a rapid initial spike, with the majority of the photopotential arising within < 1 μsec, and a very long decay time, limited by the instrumental response (> 200 μsec). We interpret these phenomena to represent a directional charge transfer between different porphyrin units within the polymer, leading to charge separation that can be observed as a photopotential. The charge separation is relatively rapid, but not rapid enough to be attributable to the singlet state of the porphyrins, which typically have lifetimes < 10 nsec (free base TPPs in dilute solution). Thus we suggest that it is triplet excited porphyrins that undergo electron

transfer from TAPP (or THPP) to TCPP units within the polymer. The resultant charge separation is surprisingly long-lived, suggesting that the charges have settled into deep traps not readily reversed. Steady-state irradiation with white light leads to photopotentials up to 250 mV, representing the accumulation of the long-lived component of the photopotential. Decay times are still long, limited by the RC time constant of the detection system—in the case of steady-state irradiation, over several seconds. Larger photopotentials arise if the film is soaked in a solution of methyl viologen, a good electron acceptor, suggesting that charge trapping is an important part of the photopotential generation. Comparable long-lived charge trapping in liquid crystal porphyrin films has been observed, in which case the effect has been suggested as a possible information storage mechanism.^{10,11}

Other porphyrin polymer films display more complex photopotential traces, including multiple risetimes and decay times.¹² These observations suggest the presence of an additional mechanism for charge separation, which operates on a much faster time scale for both risetime and decay time. The additional effect is, we surmise, the mechanism ordinarily observed in porphyrin films, namely exciton dissociation at the porphyrin/electrode interface.^{13,14} In this case, singlet state excitons that migrate to the porphyrin/electrode interface inject electrons into the transparent conductive electrode. The risetime corresponds to the rate of exciton dissociation, which is very rapid (< 1 nsec); recombination, or partial recombination, also occurs relatively quickly. This behavior is consistent with TPP characteristics as a p-type semiconductor.



consistent with normal porphyrin film behavior; in general, irradiation of symmetrical films of crystalline¹³ or liquid crystalline¹⁴ porphyrins leads to a negative photopotential at the nearer electrode, since there is a greater probability of excitons reaching the front electrode for electron injection.

In contrast, optically thin films have a relatively uniform distribution of excited states across the film regardless of the light direction. In these cases, the inherent redox asymmetry of the film is observed as a preferred electron transfer from the N side towards the C side (electron-rich porphyrins to electron-deficient porphyrins), i.e., the CC and NC (or HC) configurations give consistently negative photopotentials for optically thin films. For the typical laser irradiation wavelength of 450 nm, close to the intense porphyrin Soret band, optically thin corresponds to films less than 100 nm in thickness, with $A < 1$. We would predict that this effect should be wavelength-dependent, following the porphyrin absorption spectrum, in which case the redox gradient could control the directionality in even thicker films when light of lesser absorbance is used. A similar wavelength-dependent effect has been observed in thin liquid crystal porphyrin films, where high optical densities lead to decreased photoeffects.¹⁴

Future Work

Although photopotentials as high as 250 mV have been obtained using steady-state white light approximating the solar spectrum, typical photocurrents have been below a nanoampere and very irreproducible. We suspect that the manner of applying a wet film onto the electrodes does not lead to effective or uniform electrical contact. Thus for solar energy conversion, we have turned to electrode systems that offer the possibility of covalent binding of porphyrins, in particular using TCPP adsorption onto TiO_2 as in the Grätzel cell.³ Nevertheless, the unique structural asymmetry of these interfacial films has been intriguing, leading to a variety of potential applications.^{15,16}

Photopotential Directionality

Competition between the two mechanisms for electron transfer can be followed in a number of ways. It is observed that thicker films, which absorb light more strongly, do not necessarily lead to greater photopotentials, but in fact lead to different patterns of directional photopotentials. Figure 3 illustrates the different patterns of directionality that could be observed as a function of light direction and film orientation. When we use thick porphyrin polymer films, the nearer electrode displays the negative potential regardless of the film orientation, i.e., the CC and NN (or HH) configurations give consistently negative photopotentials for optically thick films. This is

Acknowledgements

Financial support from the U.S. Department of Energy, Basic Energy Sciences, Solar Photochemistry Program (DE-FG06-90ER-14131) is gratefully acknowledged. Coworkers who contributed the majority of the experimental work described include Velu Senthilathipan and Wen Li.

The author would like to express his deep gratitude to George Hammond for the inspiration he has provided over many years. He would also like to express the great pleasure he feels in welcoming George and Eve as new neighbors in Portland.

References

1. *Photoinduced Electron Transfer*; Fox, M.A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Vol. A-D.
2. Gust, D.; Moore, T.A.; Moore, A.L. *Acc. Chem. Res.* **1993**, *26*, 198-205.
3. Wamser, C.C.; Lebzelter, J.; Ryu, C.-H. *ACS Polym. Prepr.* **1996**, *37*, 384-385.
4. Li, W.; Wamser, C.C. *Langmuir* **1995**, *11*, 4061-4071.
5. Summerlin, L.R.; Ealy, J.L., Jr. *Chemical Demonstrations: A Sourcebook for Teachers*; American Chemical Society: Washington, D.C., 1985.
6. Wamser, C.C.; Gilbert, M.I. *Langmuir* **1992**, *8*, 1608-1614.
7. Wamser, C.C.; Bard, R.R.; Senthilathipan, V.; Anderson, V.C.; Yates, J.A.; Lonsdale, H.K.; Rayfield, G.W.; Friesen, D.T.; Lorenz, D.A.; Stangle, G.C.; van Eikeren, P.; Baer, D.R.; Ransdell, R.A.; Golbeck, J.H.; Babcock, W.C.; Sandberg, J.J.; Clarke, S.E. *J. Am. Chem. Soc.* **1989**, *111*, 8485-8491.
8. Ransdell, R.A.; Wamser, C.C. *J. Phys. Chem.* **1992**, *96*, 10572-10575.
9. Kadish, K.M.; Morrison, M.M. *J. Am. Chem. Soc.* **1976**, *98*, 3326-3328.
10. Liu, C.-Y.; Pan, H.L.; Fox, M.A.; Bard, A.J. *Science* **1993**, *261*, 897-899.
11. Liu, C.-Y.; Hasty, T.; Bard, A.J. *J. Electrochem. Soc.* **1996**, *143*, 1914-1918.
12. Wamser, C.C.; Senthilathipan, V.; Li, W. *SPIE Proc.* **1991**, *1436*, 114-124.
13. Kampas, F.J.; Gouterman, M. *J. Phys. Chem.* **1977**, *81*, 690-695.
14. Gregg, B.A.; Fox, M.A.; Bard, A.J. *J. Phys. Chem.* **1990**, *94*, 1586-1598.
15. Lonsdale, H.K.; Wamser, C.C. U.S. Patent 4,917,800, April 17, 1990.
16. Lonsdale, H.K.; Babcock, W.C.; Friesen, D.T.; Smith, K.L.; Johnson, B.M.; Wamser, C.C. U.S. Patent 4,948,506, August 14, 1990.

About the Author

Carl C. Wamser is a professor of chemistry at Portland State University. He received his Ph.D. degree at Caltech in 1970 under the direction of George S. Hammond and did a postdoctoral year with Paul D. Bartlett at Harvard. He taught at California State University, Fullerton, from 1970-1983 before moving to Portland and has spent sabbatical leaves working with Melvin Calvin (UC Berkeley) and Michael Grätzel (EPFL, Switzerland). His address is Department of Chemistry, Portland State University, Portland, OR 97207-0751 or WamserC@pdx.edu. Further details about the research program are kept up at <http://chem.pdx.edu/~wamser/>

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.

Photochemistry and Photophysics of Xanthylium and Thioxanthylium Carbocations

Mary K. Boyd, Loyola University of Chicago

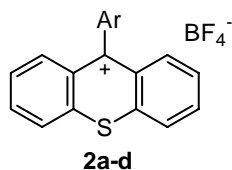
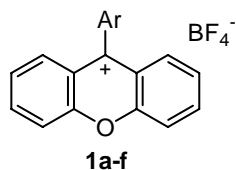
Introduction

Carbocations are important intermediates in an array of organic chemical reactions resulting in extensive investigations of their ground-state chemistry.¹ Recent development of techniques for the photogeneration of transient carbocations has permitted study of cation reactivity at very short time scales.² In addition to the importance of photogeneration methods for these fundamental studies in physical organic chemistry, their numerous practical applications include the photoinitiation of organocationic reactions, the application of photoacids to polymerization, as well as in photoimaging systems and photochromic materials. A separate but intimately related area of carbocation photochemistry studies their excited-state properties and reactivity. This area has received considerably less attention than studies of ground state carbocations, despite the fundamental and practical significance of these species in their excited states. We have studied both areas of carbocation photochemistry: photogeneration and excited-state chemistry. Our complementary approach has enabled us to apply results from our studies to applications of carbocation photochemistry, in particular to synthetic methodology.

The xanthylium cation and related substrates have been the focus of several photochemical and photophysical studies, including ours, due to their relatively long lifetimes and strong fluorescence emission. In particular, these characteristics have permitted use of Stern-Volmer fluorescence quenching techniques to measure rate constants in studies of bimolecular excited-state cation reactivity. For these studies, the cations were usually generated either by treatment of alcohol precursors with strongly acidic media, or through a two laser flash photolysis method. The former method limits the range of quenchers that can be studied, while the latter technique is complicated by the concomitant formation of radicals. We chose instead to thermally generate the xanthylium cations as stable tetrafluoroborate salts by treatment of the corresponding 9-xanthenol with fluoroboric acid. These cation salts are soluble in neutral, inert media such as acetonitrile, permitting us to measure their singlet excited lifetimes in the absence of quenchers and study their fluorescence quenching behavior using the Stern-Volmer approach. A significant advantage of organic cation salts is the elimination of acidic media as solvent, allowing reactivity studies with a wide range of quenchers.

Excited-State Carbocation Reactivity With Nucleophilic Species

Our initial studies focused on substituent effects on the reactivity of singlet excited 9-arylxanthylium cations **1a-f** with nucleophilic quenchers.³ Absorption spectra for the cation tetrafluoroborate salts in acetonitrile were identical to the spectra reported for the same cations generated in aqueous acidic solution or acidified organic solvents, with absorp-



Aryl substituent: **a**=H, **b**=*p*-F, **c**=*m*-F, **d**=*p*-CH₃, **e**=*m*-CH₃, **f**=*m*-OCH₃

tion maxima at 260, 374 and 450 nm. Excitation at 374 nm in acetonitrile gave steady-state fluorescence spectra that were also identical to emission spectra previously reported, with a broad unstructured band centered near 540 nm. Fluorescence lifetimes in acetonitrile solvent ranged from a high of 27.6 ns for the parent 9-phenylxanthylium cation **1a**, decreasing to subnanosecond values as the substituents became more strongly electron donating. Fluorescence from **1a-f** was quenched by the addition of water and alcohols (methanol, isopropyl alcohol and *tert*-butyl alcohol). Stern-Volmer analysis of plots of relative fluorescence quantum yields versus the quencher concentration gave excited-state bimolecular rate constants for reaction of the singlet excited cations with the quenchers. For each of the four quenchers the rate constants vary from a low of approximately 10⁶-10⁷ M⁻¹ s⁻¹ (for **1b**) up to the diffusion limit (for **1f**). Each substituted cation exhibits a

tion of water and alcohols (methanol, isopropyl alcohol and *tert*-butyl alcohol). Stern-Volmer analysis of plots of relative fluorescence quantum yields versus the quencher concentration gave excited-state bimolecular rate constants for reaction of the singlet excited cations with the quenchers. For each of the four quenchers the rate constants vary from a low of approximately 10⁶-10⁷ M⁻¹ s⁻¹ (for **1b**) up to the diffusion limit (for **1f**). Each substituted cation exhibits a

much smaller range of rate constants along the quencher series. Using **1b** as an example, the quenching values range from $8.88 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (quenching by water) to $8.05 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (quenching by isopropyl alcohol).

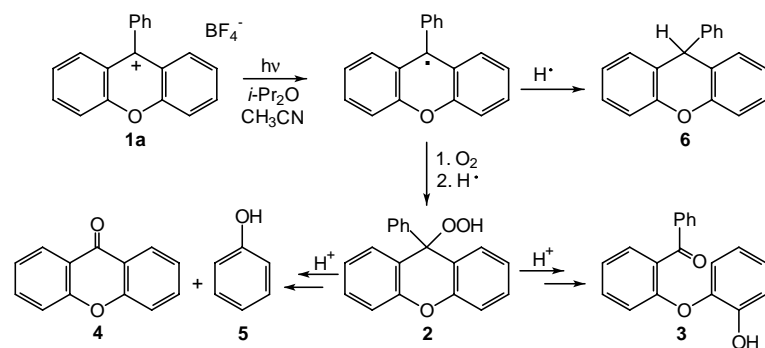
The quenching rate constant dependence of the 9-aryl substituent demonstrates that the rate constants increase (up to the diffusion limit) as the substituents become more strongly electron donating. The substituent effects were further examined through a Hammett analysis. Correlations were first attempted versus the σ and σ^+ substituent parameters, with very poor results for each of the four quenchers. The poor correlations were mainly due to scatter from the meta-substituted cations whose points fell above the line, indicative of their enhanced excited-state reactivity. Excellent correlations were instead obtained with σ^{hv} , a substituent parameter for excited-state reactivity.⁴ Plots of $\log [k_q(\text{X})/k_q(\text{H})]$ versus σ^{hv} for each of the four quenchers gave excellent linear plots with correlation coefficients of 0.98 or better, with the exception of the point corresponding to **1c**, the *m*-F substituted cation. The point for **1c** falls below the line, with the extent of the deviation increasing with the steric bulk of the alcohol alkyl group. Values calculated for ρ gave a negative value for each quencher, opposite to the substituent dependence observed for quenching of the ground-state 9-arylxanthyl cations by nucleophiles.⁵ The ground-state substituent effects can be explained by electronic stabilization of the positively charged species by electron-donating substituents, with the effect somewhat attenuated owing to twisting of the 9-aryl group away from the planarity of the xanthyl backbone.

The relative quenching order for the excited-state cations also differs from the order observed for nucleophilic reactions of ground-state cations in acetonitrile solvent. In an effort to elucidate the excited-state quenching mechanism we had hoped to isolate photoproducts from reaction of the excited-state cations with the water or alcohol quenchers. Unfortunately, we were unable to isolate photoproducts from these reactions due to competing thermal reactions resulting from the higher quencher concentrations necessary for preparative irradiations.

Instead we turned to quenching of the 9-arylxanthyl cations by dialkyl ethers, in order to explore the nature of substituent effects on excited-state cation quenching with a variety of quenchers.⁶ Fluorescence from **1a-f** was quenched by the addition of each of four dialkyl ethers (diethyl ether, isopropyl ether, *tert*-butyl methyl ether and *tert*-butyl ethyl ether). Stern-Volmer analysis of fluorescence quenching data with the measured cation fluorescence lifetimes gave values for the excited-state bimolecular quenching rate constants. Values for the rate constants range from 10^6 to $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, and are comparable in magnitude to the rate constants determined for quenching of these singlet excited cations by water and alcohols. As with the water and alcohol quenchers, the ether quenching rate constants increase in magnitude as the electron-donating ability of the substituent increases. Excited-state Hammett analysis using the σ^{hv} substituent parameter gave negative ρ values for quenching of cations **1a-f** by the four ethers. These ether quenching results demonstrate the generality of the substituent effect reversal between the ground and excited state for quenching of the 9-arylxanthyl cations.

With both the substituent effect and water/alcohol quenching order different from ground state cation-nucleophile reactions, we considered the possibility of a different mechanism operating in the excited state, namely electron transfer. Application of the Rehm-Weller equation shows that cation $E_{1/2}^{\text{red}}$ values must account for the substituent effect on the quenching rate constants should an electron transfer mechanism be operating.⁶ Values of $E_{1/2}^{\text{red}}$ show substituent effects too small to account for the observed three order of magnitude difference in cation quenching by water, alcohols and ethers, eliminating the possibility of an electron transfer mechanism.

We successfully isolated photoproducts **2-6** from irradiation at 350 nm of the 9-phenylxanthyl cation **1a** in acetonitrile solvent in the presence of isopropyl ether. These photoproducts suggest the intermediacy of the 9-phenylxanthyl radical, with a mechanism as outlined in Scheme 1. Conversion of the hydroperoxide **2** to the ring-opened product **3**



Scheme 1

or xanthere **4** in acidic media has been established.⁷ Since electron transfer from the ethers to the xanthyl cation is ruled out as the quenching mechanism, an alternate possibility is nucleophilic attack of the ether on the cation to generate an intermediate oxonium ion. Subsequent homolytic cleavage of the oxonium ion would generate the xanthyl radical and the ether radical cation. Overall, the mechanism is formally an electron transfer process, and may be viewed as an inner-shell electron transfer.

Huckel molecular orbital calculations provide a possible explanation for the excited-state substituent dependence on the quenching rate constants.⁸ The calculations showed that in S_1 there is negligible positive charge at C_9 , and the lobe and MO coefficient at C_9 in S_1 increase as the substituents become more strongly electron donating. The larger quenching rate constants associated with the more strongly electron donating substituents can then be explained by invoking frontier orbital theory, as the larger lobes would provide better overlap with the incoming nucleophile lone pair.

Carbocation Photophysics

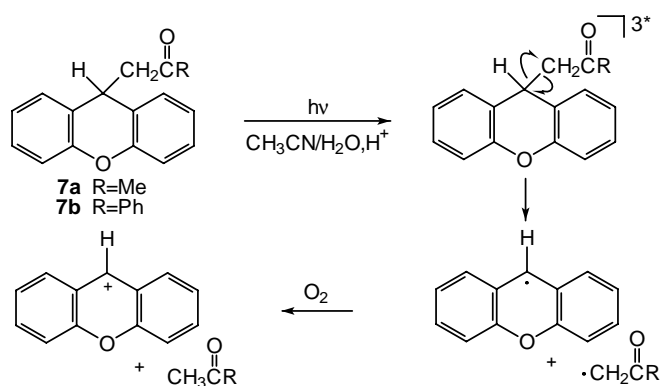
Measurement of fluorescence quantum yields and lifetimes has allowed a detailed analysis of the photophysical properties of 9-arylxanthyl and 9-arylthioxanthyl carbocations.⁹ The cations were studied as their tetrafluoroborate salts in acetonitrile. Rate constants for total decay and fluorescence as well as non-radiative rate constants were calculated from the fluorescence quantum yields and lifetimes. In the 9-arylxanthyl series, a dramatic substituent effect is observed, with an increase in the electron-donating ability of the substituents resulting in a decrease in the fluorescence lifetimes and quantum yields. The total decay rate constants increased as the substituents became more strongly electron donating, with values ranging from $\sim 10^7 \text{ s}^{-1}$ for the parent 9-phenylxanthyl cation **1a** to $\sim 10^9 \text{ s}^{-1}$ for the *m*-methoxy substituted cation **1f**. A dramatic substituent effect is similarly observed on the non-radiative rate constants. In contrast, the fluorescence rate constants exhibit only a modest substituent effect. The possibility of a substituent effect on the rate constant for intersystem crossing was suggested to account for the substituent dependence on the photophysical parameters for the xanthyl cations.

In contrast, the 9-arylthioxanthyl cations **2a-d** exhibited little or no substituent effect in similar measurements. There is apparently no substituent effect on the fluorescence lifetimes with each cation exhibiting a lifetime of $\sim 1 \text{ ns}$, and only a very modest effect on the fluorescence quantum yields. No substituent effect is seen on the total decay rate constants, with each cation exhibiting values of $\sim 10^9 \text{ s}^{-1}$ that are at the upper end of the range observed for the xanthyl cations. There is only a very modest variation in the fluorescence rate constants, with no substituent effect observed for the non-radiative rate constants. A possible explanation offered to account for the short lifetimes and rapid non-radiative decay for the thioxanthyl cations is a second excited state that is close in energy to the fluorescent state. Alternatively, the absence of a substituent effect on the thioxanthyl cations may be attributed to the sulfur heteroatom causing an enhanced intersystem crossing to the triplet state, an influence which might overwhelm any effects due to the 9-aryl substituent. A third possibility that may account for the different photophysical behavior of the thioxanthyl cations is a structural change due to the presence of a sulfur heteroatom in the central xanthyl ring resulting in a greater twisting of the 9-aryl ring away from planarity, decreasing potential conjugative interactions from substituents on the 9-aryl ring. To investigate this possibility, we carried out geometry optimization calculations on the 9-phenylxanthyl and thioxanthyl cations at the AM1 level. The minimized structures show that the 9-phenyl ring is twisted 59° out of planarity in the xanthyl case, where a 90° twist represents the structure with the 9-phenyl ring perpendicular to the xanthyl backbone. In comparison, the 9-phenyl ring in the thioxanthyl cation has a twist angle of 68° . These results suggest less conjugative interactions in the thioxanthyl system, in accord with the experimental results.

Xanthyl Cation Photogeneration Via Carbon-Carbon Bond Cleavage

We are interested in novel methods and substrates for the photogeneration of carbocations, particularly those involving carbon-carbon bond cleavage. We were intrigued by a report that the xanthyl cation is ejected from protonated xanthyl alcohols and ketones in strongly acidic solutions.¹⁰ Mechanistic studies on 9-xanthylacetone **7a** and 9-xanthylacetophenone **7b** suggest an A1 mechanism for cation formation involving initial protonation on the carbonyl oxygen with subsequent heterolytic carbon-carbon bond cleavage to generate the xanthyl cation, although a concerted mechanism could not be ruled out.

We reasoned that this bond cleavage might be promoted by irradiation, due to the enhanced excited-state stability exhibited by the xanthyl cation. Indeed, irradiation at 300 nm of 9-xanthylacetone or 9-xanthylacetophenone in dilute aqueous acidic solution with acetonitrile cosolvent resulted in rapid quantitative formation of the xanthyl cation, with no thermal reaction under these photolysis conditions.¹¹ Cation formation is not subject to acid catalysis over the acid range studied (5-30% H_2SO_4), ruling out a proton-assisted bond cleavage mechanism analogous to the ground-state reaction mechanism. Laser flash photolysis studies of xanthyl ketones **7a-b** in aqueous acidic acetonitrile demonstrate that the xanthyl radical is formed as the primary photoproduct. In the presence of both oxygen and acid, this



Scheme 2

radical undergoes subsequent clean conversion to the xanthylic cation. Based on the laser flash photolysis results and the lack of acid catalysis, we proposed the mechanism shown in Scheme 2. An initial homolytic carbon-carbon bond cleavage produces the xanthylic radical and the corresponding α -keto radical. Oxidation of the xanthylic radical by oxygen, in an energetically favored process, generates the xanthylic cation in a subsequent step. The mechanism is further supported by the isolation of the radical-derived photoproduct bixanthylic.

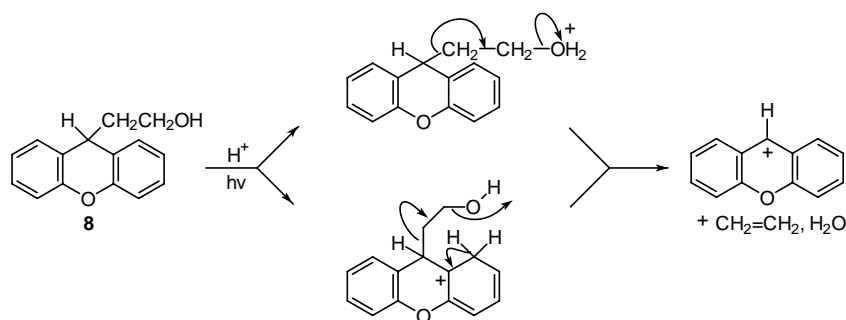
Our studies on 9-xanthylic acetone and 9-xanthylic acetophenone demonstrate that stable cations can be photogenerated through selective carbon-carbon bond cleavage processes, albeit through a homolytic cleavage

mechanism different from the mechanism operating in the ground state. We were particularly interested in the design of substrates that would generate cations through direct photoheterolysis of carbon-carbon bonds. We chose to modify our initial substrates by altering the leaving group in an effort to promote heterolytic bond cleavage. We selected 2-(9-xanthylic)ethanol **8** as a potential candidate, since it forms the xanthylic cation thermally in strongly acidic solution. We also studied 9-xanthylic methanol **9** for comparative purposes. Preparative irradiation of either alcohol in mildly acidic aqueous solution with acetonitrile cosolvent, demonstrates rapid quantitative xanthylic cation formation, under conditions where no thermal reaction occurs.¹² The quantum yield for cation formation from **9** is independent of acid concentration, and the radical coupling product bixanthylic was isolated following irradiation in nitrogen-purged solutions. These results suggest a homolytic bond cleavage mechanism for **9** analogous to that proposed for the xanthylic ketones.

In contrast to the other substrates, the quantum yield for cation formation from 2-(9-xanthylic)ethanol **8** is acid dependent, suggesting that it may undergo a proton-assisted direct photoheterolysis to generate the xanthylic cation. We have proposed two possible mechanisms to account for a heterolytic carbon-carbon bond cleavage (Scheme 3). The first mechanism is a photochemical analogue of the ground-state mechanism, proceeding via initial protonation of the hydroxyl oxygen, with subsequent carbon-carbon bond cleavage in a photochemically induced Grob fragmentation to generate the xanthylic cation, ethylene and water. The second possible mechanism instead proceeds via protonation of the xanthylic aromatic backbone, followed by intramolecular proton abstraction by the hydroxyl oxygen, with rearomatization of the xanthylic backbone and heterolytic bond cleavage to similarly generate the xanthylic cation, ethylene and water. Irradiation of **8** in deuterated solution demonstrated isotope incorporation on the xanthylic backbone, in support of this mechanism. No radical coupling products were isolated following irradiation of **8** in nitrogen or oxygen-purged solutions, suggesting that radical intermediates are not involved in the mechanism.

Synthetic Applications in the Development of Photocleavable Protecting Groups

Trityl and methoxy-substituted trityl functionalities have been used extensively as protecting groups of primary hydroxyl groups in sugar, nucleoside and steroid chemistry.¹³ The 9-phenylxanthylic (pixyl or Px) group has been similarly used to protect the 5'-hydroxy group of nucleosides, however the moderate acidic conditions required for its



Scheme 3

removal can cause undesired side reactions, such as the cleavage of the 2'-tetrahydropyranyl protecting group.¹⁴ It occurred to us that we might be able to take advantage of our photochemical studies of the 9-phenylxanthylic moiety to carry out the deprotection reaction photochemically in neutral solution. Indeed, with the emergence of new synthetic techniques such as oligonucleotide synthesis via combinatorial chemistry, and the light-directed, spatially addressable

synthesis of oligonucleotide arrays, novel photodeprotecting groups for primary alcohols are in high demand.¹⁵ The pixyl moiety is an attractive candidate as a potential photocleavable protecting group for primary alcohols as its highly rigid and planar backbone results in an enhanced excited-state stability. 9-Phenylxanthen-9-ol has been previously shown to undergo photochemically induced heterolytic carbon-oxygen bond cleavage to generate the 9-phenylxanthylium cation in neutral aqueous solution suggesting that the pixyl group has potential as photocleavable protecting group for primary alcohols.¹⁶

We protected five different primary alcohols, including the nucleoside thymidine, by reaction with pixyl chloride. Irradiations in neutral acidic acetonitrile at either 254 or 300 nm resulted in complete removal of the pixyl moiety with very good to excellent yields of the recovered alcohols.¹⁷ Control experiments demonstrated that no thermal reactions or degradations were occurring. We are elaborating our studies through the design of refined substrates with modifications including judicious choice and placement of substituents, and in the development of orthogonal protecting groups.

Acknowledgments

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society for the support of this research. Financial support by the National Science Foundation - Research Experience for Undergraduates (CHE-9619709) is also gratefully acknowledged. I am especially grateful to the many co-workers, listed in the references, who participated in this work.

References

1. Olah, G.A.; Schleyer, P. von R. *Carbonium Ions*; Wiley & Sons: New York, 1970; Vol. I-V.
2. For recent reviews see:
 - a) Boyd, M.K. Photochemistry and Photophysics of Carbocations. In *Molecular and Supramolecular Photochemistry, Volume 1: Organic Photochemistry*; Ramamurthy, V., Schanze, K.S., Eds.; Marcel Dekker: New York, 1997, p 147.
 - b) McClelland, R.A. *Tetrahedron* **1996**, *52*, 6823.
 - c) Das, P.K. *Chem. Rev.* **1993**, *93*, 119.
3. Valentino, M.R.; Boyd, M.K. *J. Org. Chem.* **1993**, *58*, 5826.
4. McEwen, J.; Yates, K. *J. Phys. Org. Chem.* **1991**, *4*, 193.
5. McClelland, R.A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929.
6. Valentino, M.R.; Boyd, M.K. *J. Photochem. Photobiol. A: Chem.* **1995**, *89*, 7.
7. Koorts, J.; Taljaard, B.; Goosen, A. *S. Afr. J. Chem.* **1987**, *40*, 237.
8. Boyd, M.K.; Lai, H.Y.; Yates, K. *J. Am. Chem. Soc.* **1991**, *113*, 7294.
9. Bedlek, J.M.; Valentino, M.R.; Boyd, M.K. *J. Photochem. Photobiol. A: Chem.* **1996**, *94*, 7.
10. a) Deno, N.C.; Sacher, E. *J. Am. Chem. Soc.*, **1965**, *87*, 5120.
 - b) Trudell, M.B. M.S. Thesis, San Francisco State University, 1988.
 - c) Keefe, J.R. Personal communication.
11. Clifton, M.F.; Fenick, D.J.; Gasper, S.M.; Falvey, D.E.; Boyd, M.K. *J. Org. Chem.* **1994**, *59*, 8023.
12. Rost, J.M.; Boyd, M.K. Unpublished results.
13. Greene, T.W.; Wuts, P.G.M. *Protective Groups in Organic Synthesis*; Wiley & Sons: New York, 1991.
14. Cristodoulou, C.; Agrawal, S.; Gait, M.J. *Tetrahedron Lett.* **1986**, *27*, 1521.
15. a) Beaucage, S.L.; Iyer, R. *Tetrahedron* **1992**, *48*, 2223.
 - b) Pease, A.C.; Solas, D.; Sullivan, E.J.; Cronin, M.T.; Holmes, C.P.; Fodor, S.P.A. *Proc. Natl. Acad. Sci. USA*, **1994**, *91*, 5022.
16. Wan, P.; Yates, K.; Boyd, M.K. *J. Org. Chem.* **1985**, *50*, 2881.
17. Mistic, A.; Boyd, M.K. *Tetrahedron Lett.* **1998**, *39*, 1653.

About the Author

Mary K. Boyd received a Ph.D. in chemistry in 1989 from the University of Toronto. She is currently an Associate Professor of Chemistry at Loyola University Chicago. Her address is the Department of Chemistry, Loyola University Chicago, 6525 N. Sheridan Rd., Chicago, IL 60626.

OPOTEK Inc.

Tunable Laser Systems

Tel: 760-929-0770

FAX: 760-929-8782

e-mail: opotek@opotek.com

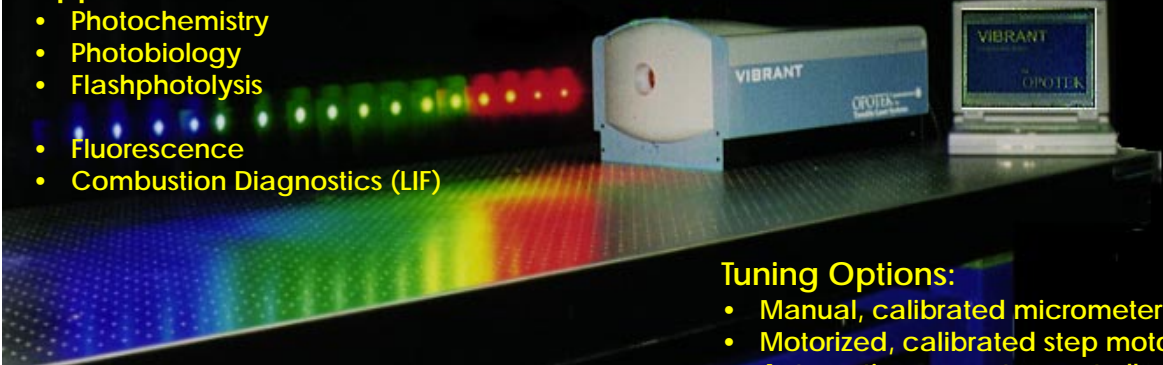
2233 Faraday Avenue, Suite E, Carlsbad, CA 92008

OPOTEK offers a variety of products from stand-alone OPO modules,
to fully computerized Tunable Laser Systems.

Standard products range from 210nm, in the UV, to 2.2 μm in the IR.
Consult OPOTEK for cost-effective custom products.

Applications:

- Photochemistry
- Photobiology
- Flashphotolysis
- Fluorescence
- Combustion Diagnostics (LIF)



Tuning Options:

- Manual, calibrated micrometer
- Motorized, calibrated step motor
- Automatic, computer controlled

Please visit us at: www.opotek.com

If performance, price, and service play a decisive role in
acquiring a reliable Tunable Laser System - consider OPOTEK.

©Copyright 1998 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 419-372-6069
 Email photochemical@listproc.bgsu.edu
 WWW <http://www.bgsu.edu/departments/photochem/>

Executive Director: D.C. Neckers
 Administrative Director: Pat Green
 Principal Faculty: G.S. Bullerjahn, J.R. Cable,
 F.N. Castellano, Y.J. Ding,
 M.E. Geusz, D.C. Neckers,
 M.Y. Ogawa, M.A.J. Rodgers,
 D.L. Snavely

The Spectrum Editor: Pat Green
 Production Editor: Alita Frater

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.

Center for Photochemical Sciences Publications

337. Kaneko, Y.; Neckers, D.C. Simultaneous photoinduced color formation and photoinitiated polymerization. *J. Phys. Chem.* 1998, 102, 5356-5363.
338. Ding, Y.J.; Khurgin, J.B. A new scheme for efficient generation of coherent and incoherent submillimeter to THz waves in periodically-poled lithium niobate. *Opt. Commun.* 1998, 148, 105-109.
339. Ding, Y.J.; Reynolds, D.C.; Lee, S.J.; Khurgin, J.B.; Rabinovich, W.S.; Katzer, D.S. Evidence for strong spatially-localized band-billing effects at interface islands. *Appl. Phys. Lett.*, 1997, 71, 2581-2583.
340. Ding, Y.J.; Khurgin, J.B. Spatial, temporal and spectral effects and conversion efficiencies in second-harmonic generation from mode-locked lasers in surface-emitting geometry. *J. Appl. Phys.* 1997, 83, 4732-4739.
341. Fedorov, A.V.; Snavely, D.L. Vibrational overtone spectroscopy of cycloheptatriene. *J. Phys. Chem. A* 1997, 101, 9042-9049.
342. Leytner, S.; Snavely, D.L.; Grinevich, O. Reversible isomerization of methylcyclopentadienes directed by selective excitation of the methyl out-of-plane fourth overtone transition. *Chem. Phys. Lett.* 1997, 277, 443-449.
343. Kaneko, Y.; Hu, S.; Neckers, D.C. Photochemical reactivities of alkyl thiophenoglyoxylates and alkyl furanylglyoxylates. *J. Photochem. Photobio.* 1998, 114, 173-179.
344. Feng, K.; Zang, H.; Martin, D.; Marino, T.L.; Neckers, D.C. Synthesis and study of iodonium borate salts as photoinitiators. *J. Poly. Sci.* 1998, 36, 1667-1677.

For reprints of any of these publications, please write 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.

Advertising in *The Spectrum*

In the past we have not had any advertisements in *The Spectrum* because we are limited in staff. Corporate sponsors donate money to defray the cost of publishing and mailing *The Spectrum* to over 7,000 people in 50 countries. Those sponsors can place ads, if they wish, in four issues and are acknowledged as a sponsor. Some companies have chosen to remain anonymous. We intend to continue the corporate sponsorship program. This is our preferred way to help with our costs. However, we receive constant inquiries about placing advertisements. Therefore, we are going to offer advertising space on a trial basis.

Size:	Full page	-	\$1,000 per issue
	Half page	-	\$ 500 per issue
Specifications:	Computer file - EPS or PICT file (preferred method)		
	Camera-ready hard copy		
Deadlines:	Fall Issue	-	September 1
	Winter Issue	-	December 1
	Spring Issue	-	March 1
	Summer Issue	-	June 1

We also will reserve the right to limit the number of advertisements per issue based on space. For additional information about the corporate sponsorship or advertisements, please contact Pat Green (pgreen@bgnet.bgsu.edu) at 419-372-2033 (phone) or 419-372-6069 (fax).