

## Peter J. Wagner



Photograph taken by Bruce Fox

Peter Wagner received his B.S. degree in Chemistry from Loyola University, Chicago, in 1960 and his Ph.D. in Chemistry from Columbia University in 1963, where he was a Westinghouse Fellow and a NSF Cooperative Fellow. His Ph.D. research mentor was Cheves Walling. He was a NSF postdoctoral fellow with George Hammond at Caltech before joining the Chemistry faculty at Michigan State University in 1965. He was promoted to Associate Professor in 1968, Professor in 1970, and currently is University Distinguished Professor. He was named an Alfred P. Sloan Fellow in 1968 and in 1971 received an NSF Senior Postdoctoral Fellowship for research with Mostafa El-Sayed at UCLA. He received a J. S. Guggenheim Foundation Fellowship in 1983 for research at the National Research Council in Canada. He also has won several awards from MSU. He has been generous in devoting time to professional matters, especially as an Associate Editor of the *Journal of the American Chemical Society* from 1975 through 1986. (He claims that this job was necessary preparation for his career as a soccer referee.)

Peter Wagner has authored or co-authored over 170 research publications including seven reviews; his 1971 paper in *Accounts of Chemical Research* summarizing mechanistic knowledge of the Norrish type II reaction was named a "Citation Classic" in 1987 to recognize its receiving over 400 (now 500) citations. He has presented over 100 invited lectures on his research and has been a plenary lecturer at over 30 national and international conferences. He served as American organizer for the 1980 IUPAC Conference on Organic Photochemistry and chairman of the 1985 Gordon Conference on Organic Photochemistry. Forty-two students have obtained graduate degrees under his mentorship.

Peter Wagner's early research dealt mainly with ketone photoreactions and energy transfer. He is probably best known for his thorough study of the Norrish type II reaction and for creative use of this reaction to establish fundamental aspects of excited state reactivity. These studies began during his postdoctoral stint with George Hammond, where they demonstrated that the Norrish type II cleavage of aliphatic ketones occurs from both excited singlet and triplet states. Among his

accomplishments are the following: demonstrating that the quantum efficiencies of most triplet ketone reactions do not reflect relative reactivities of the excited states but rather the partitioning of biradical intermediates between product formation and reversion to ketone; showing that the reactivity of excited ketones and structural effects thereon mimic those of alkoxy radicals; demonstrating that thermal interconversion of excited triplets can allow efficient photochemistry to occur from upper excited states; producing a thorough analysis of how hydrogen abstraction by triplet ketones is affected by varying degrees of charge transfer; measuring relative rates of  $\beta$ -cleavage of radicals based on product ratios formed from  $\delta$ -substituted valerophenones; and development of a clear understanding of how rates and product distributions for intramolecular bifunctional reactions depend on the competition among reaction, bond rotations, and excited state decay. Allowing other reactions to intramolecularly compete with hydrogen abstraction allowed him to measure rate constants for triplet  $\alpha$ -cleavage reactions, for the well-known photoenolization of *o*-alkylphenyl ketones and the previously unknown photoenolization of  $\alpha$ -diketones, and for various intramolecular energy transfer and charge transfer processes. Study of the enolization of *o*-alkyl ketones settled another controversy. By comparing tolyl alkyl ketones to methyltetralones, he discovered that only the former form two distinct triplets, undoubtedly *syn-anti* conformers, and that rotation of the latter to the former is a rate-determining step in enolization. This led to a collaborative 1977 paper with Jacob Wirz that for the first time allowed proper identification of the various intermediates detectable by flash kinetics. In 1991 Wagner discovered that many *o*-alkylphenyl ketones that were thought to undergo reversible photoenolization (via  $\gamma$ -hydrogen abstraction) as their only photoreaction instead efficiently form benzocyclobutenols that are stable below 50 °C. These are formed from the *o*-xylylene photoenols, many stereoselectively. Very recent work has confirmed the idea that the geometry of the lowest energy twisted enol triplet determines product stereochemistry.

With respect to energy transfer, Wagner has made several major findings. In 1967 came an explanation of nonvertical

energy transfer; rate constants for energy transfer to biphenyl are intermediate between those predicted by biphenyl's absorption and emission energies, since energy transfer involves a significant change in biphenyl's geometry. Next came the demonstration that rate constants for exothermic triplet energy transfer are lower than diffusion controlled in common, non-viscous organic solvents, in contrast to the then universal assumption that exothermic energy transfer is totally diffusion controlled. Later, Wagner demonstrated that energy transfer between chromophores in a mixture modifies the lifetimes measured for any of their excited states, a fact that has wide implications. Most recently, he has demonstrated how intramolecular energy transfer between chromophores affects Stern-Volmer quenching plots and that triplet energy transfer between two chromophores on each end of a flexible chain is dominated by through space energy transfer from an ensemble of coiled conformations, a nice counterpoint to Closs' demonstration of through bond energy transfer in rigid molecules.

Wagner has addressed other questions, such as the excited state behavior of transition metal complexes, as revealed by the behavior of photoreactive organic ligands. His current interests include how molecular geometry affects the chemical behavior of excited states and the intersystem crossing of biradicals and the reactions of triplet benzenes, especially their 2 + 2 cycloaddition to alkenes and the radical cleavage of various ring substituents. He is also addressing the question of how electron density in excited states, radicals, and biradicals is manifested in the activation parameters for their reactions.

In addition to his scientific accomplishments, Peter Wagner is known for his gardening enthusiasm, especially for orchids, for his witty conversation, and for his relentless pursuit of birdies (in golf). His colleagues all are relieved that his many endeavors, both personal and professional, have not been lessened by his futile belief that his beloved Chicago Cubs could yet win the World Series.

**Irene E. Kochevar**  
*Harvard Medical School*