

Beyond the traditional confines: Physical organic chemistry in the 21st century

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Biography: Marye Anne Fox is the M. June and J. Virgil Waggoner Regents Chair in Chemistry and Vice President for Research at the University of Texas. She was born in Canton, Ohio in 1947 and received a bachelor's degree from Notre Dame College and a Ph. D. from Dartmouth College, both in chemistry. She is a member of the National Academy of Sciences and of the American Philosophical Society and a fellow of American Academy of Arts and Sciences and of the American Association for the Advancement of Science. She is the recipient of several national and international awards in chemistry and in science policy. She currently serves on the editorial boards of seven journals and has published over 300 papers and three books in the general area of physical organic chemistry, focussing on photochemistry, electrochemistry, and the characterization of reactive intermediates.

I began my professional career in the early 1970's, when the claim that "physical organic chemistry was dead" was widely being disseminated among the chemical community. And I must agree that, by all rights, if physical organic chemistry were restricted to the increasingly narrow, incremental studies being undertaken by some at that period, that field was, and indeed deserved to be, dead. A more reasonable conception of the goals of physical organic chemistry, however, is the study of the relationship between structure and properties of organic and organometallic molecules of both low and high molecular weight. This definition thus unites this intellectually based area with the newly emerging fields of bioorganic chemistry and organic materials science, and provides the key means by which the techniques of physical and analytical chemistry can be brought to bear on practical problems. This is an alliance that would convince even the most hardened skeptic that, far from being dead, physical organic chemistry holds the key to future advances.

In many ways, physical organic chemists can be thought of as the generalists of the discipline. (This is probably the reason that, compared with other fields, relatively few of our students are facing unemployment in an era when breadth as well as depth is increasingly valued by so many prospective employers.) I suspect I am not the only physical organic chemist who causes problems for people who are doing introductions to seminars: "What kind of chemist are you, anyway?" In any case, the approach of physical organic chemistry in addressing interdisciplinary problems in molecular science is likely to be the most promising means for attaining a deep understanding of the fundamental science underlying molecular design, electronic interactions, and intermolecular associations.

One important part of our discipline that never ceases to amaze our non-chemist scientific colleagues in physics and biology is our willingness, and ability, to make specific new molecules with unusual structures. We can then use them to test the operation of basic electronic interactions within and among molecules and their aggregates. The ability to do synthesis, even simple synthetic conversions, will always assure physical organic chemists of a niche in the solution of cross-disciplinary problems and, hence, of a role in evolving interdisciplinary teams. I am sufficiently adamant about the importance of synthesis that no student has received a Ph. D. under my supervision without making and fully characterizing at least one new molecule. Each one of my students also develops his/her own scientific problem, but always within the context of an almost familial group of peers who are interested in the same overriding kinds of scientific questions. In my research group, I have had successful students from every sub-disciplinary area of chemistry (organic, physical, inorganic, and analytical) except biochemistry.

My own approach to physical organic chemistry has been to explore the use of photochemical and electrochemical methods to define the reactions of probe molecules in unusual, non-homogeneous environ-

ments and to describe the chemical characteristics of species normally thought of as reactive intermediates. This general approach has led us to investigate how surfaces might perturb the reactivity of ions, radicals, and ion radicals and how these intermediates might behave in their excited states. We've been especially interested in how visible and infra-red light can induce chemical changes in organic molecules that ordinarily do not absorb these photons. In the process, we've uncovered some important basic principles regarding electronic coupling and photoinduced electron transfer. We've studied colloids, micelles, self-assembled monolayers on metallic surfaces, semiconductor clusters and powders, supercritical fluids, and liquid crystals: all toward understanding how macroscopic or microscopic organization can influence the electronic properties of the component molecules. We've measured reaction kinetics directly by laser flash photolysis and pulse radiolysis and indirectly by product analyses of newly discovered reactions. Recently, we've compared new classes of self-organizing macromolecules with those prepared by rational synthesis in an effort to learn how the gap between microscopic and macroscopic properties might be breached.

The implications of this work have immediate consequence in solar energy conversion, in environmental chemistry, and in materials science. They lead, for example, to new means for the design of new functional polymers and of novel optoelectronic materials whose properties can be anticipated, and improvements projected, on the basis of theories grounded in experimental observation. Our most recent work addresses new methods for non-silver-based imaging and for the production of materials in which the conductivity and magnetic and optical properties can be switched rapidly. In focussing our work on fundamental properties, as is appropriate to investigations in basic science, we have learned important practical consequences that likely would have eluded us if we had tried to focus initially on the application. Physical organic chemistry demands a knowledge of the most fundamental of basic research areas, but has broad consequences throughout the practice of chemistry.

Where is the field to go? The political realities associated with current modes for external support of sponsored projects, together with vast improvement in the productivity of chemistry within the last several decades, suggest that research groups will be smaller. This means we will have to choose scientific problems with more thought and careful evaluation of implications of the research objective. I see our work becoming increasingly collaborative, not necessarily with my colleagues in chemistry, but more likely with experts in materials science, mechanical or chemical engineering, or even non-scientific areas like business or the law. Certainly we can expect closer scientific interactions with focussed chemical partners in industry and in other countries. Inherently, the problems that we choose with our partners will be increasingly interdisciplinary and relevant to specific societal needs. And, of course, academic research will continue to focus on the synergistic integration of the achievement of our research objectives with education of a group of impressively talented students.

Perhaps in such speculations we should recall the words of Yogi Berra, the great baseball philosopher, who said "the future ain't like it used to be."