

A Tribute to George S. Hammond in Celebration of His 80th Birthday

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In seeking an introduction to a tribute to George S. Hammond in honor of his 80th birthday, it seemed fitting to start with a quotation about the joys and beauty of chemistry and photochemistry by Sir C. N. Hinshelwood, on the occasion of the 100th anniversary of the Chemical Society of London:

“...Chemistry, that most splendid child of intellect and art. Chemistry provides not only a mental discipline, but an adventure and an aesthetic experience. Its followers seek to know the hidden causes which underlie the transformations of our changing world, to learn the essence of the rose’s color, the lilac’s fragrance and the oak’s tenacity and to understand the secret paths by which the sunlight and the air create these wonders.

And to this knowledge they attach an absolute value, that of truth and beauty. The vision of Nature yields the secret for power and wealth, and for this may be sought by many. But it is most often revealed only to those who seek it for itself.”

This quote captures the love and excitement of chemistry, and especially photochemistry, that George Hammond instilled in his students, in his collaborators and colleagues and in those who followed his distinguished and remarkable career.

Hammond, Scientific Revolutions and Thermodynamics.

According to Kuhn’s “Structure of Scientific Revolutions”, a paradigm shift in science occurs when a scientist or group of scientists change the way that other scientists think. By this definition, George Hammond has been a paradigm shifter many times over! In particular, George’s research during the late 1950s, 1960s and 1970s caused paradigm shifts which created the platform for the way organic photochemistry is done today. Kuhn suggested that not only do revolutionary scientists change the way that other scientists think, but exceptional scientists provide splendid exemplars of their research that serve as models for emulation and rapid progress in the field. George’s research during the golden age of photochemistry at Caltech provided exemplar after exemplar for the community to study and to imitate.

There is an amusing analogy between the rules of thermodynamics and the impact that George Hammond has had on the field of photochemistry. Thermodynamics teaches that the entire universe evolves under the influence of two conflicting tendencies: the drive towards chaos (entropy) and the drive towards organization (enthalpy). It is this conflict and the resulting balance of these two driving forces of evolution that determine the richness of diversity we observe in the world around us. Students of science never fail to wonder at the art with which nature continuously interweaves these two great themes into an effective mode of action we chemists call free energy and which has led to the incredible rich array of animate and inanimate objects that constitute our Universe. When George entered the field of photochemistry, the system was entropy rich and in need of organizational enthalpy. George provided the intellectual and scientific leadership that gave structure to the field and yet allowed for the expansion of the discipline as complexity and new methods, ideas and structures emerged and evolved.

Hammond and Dynamics.

How was it possible for mechanistic organic photochemistry to have developed so rapidly with George at the helm? Thermodynamics determines the evolution of chemical systems toward equilibrium, but is silent to the rates and kinetics of the achievement of equilibrium. What can be said about the incredibly rapid rate at which groundbreaking research and outstanding photochemists were produced under George’s guidance? Thermodynamics is

determined by average conditions. Kinetics are determined by fluctuations of energy and occasional dramatic departures from the average. These exceptional departures characterize the stuff of Kuhn's revolutionary science and paradigm shifts. The presence of a great individual of action or thought determines the location and time of such revolutions. So it was with George and his group at Caltech.

George, we all thank you and love you for your mentoring, your insights, your dedications and your ability to imprint your scientific attributes on your students and collaborators.

Peter Leermakers, the Caltech Recruiter.

For the remainder of this report, I would like to present a brief set of recollections of my years with the Hammond group during 1960-1963.

I started my chemical career as an analytical chemist working summers in the Connecticut State Water Laboratory at Wesleyan University. It was there that I met Peter Leermakers who was a Wesleyan student two years my senior and who also worked in the water lab during the summers when he was an undergraduate. Peter left for graduate school at Caltech in the fall of 1958. During the summer before my senior year, Peter returned and informed me that Caltech was the place I had to go for my Ph.D. and furthermore, that I had to work for George Hammond! With typical respect for my elders, that's exactly what I did. I turned out to be the second in a series of Wesleyan graduates who went west to work with George. Bill Herkstroeter, Don Valentine, and Dave Eaton were to follow.

Sandy and I drove across the country and landed in Pasadena at the end of August of 1960. Peter was there waiting for us and helped us settle into the >100° Southern California temperature by inviting us to his apartment which was equipped with a wonderful swimming pool and with margaritas, so powerful that your lips began to curl as the glass of tequila approached them. Peter's apartment complex in northern Pasadena housed a number of Caltech graduate students in chemistry and in physics.

The Caltech Years in the Hammond Group (1960-1963).

The Triplet State Raises Its Three-Pronged Head and Photochemistry Is On Its Way Off the Launching Pad.

When I spoke to George Hammond about a research project, he mentioned that he was working on the "triplet state" (how to visualize the "three states" was a puzzle to me at the time and has remained a theme for our research group over the decades) and something about catalyzed formation of triplets by metal complexes. Three states sounded better than one to me, but I really had no idea of what this was all about and was afraid that it might be way too physical chemical-ish for me. Nevertheless, I was very impressed with George and his wonderful reputation for working with students, and I was delighted that he accepted me into the group. I was also lucky to have some wonderful classmates such as Jack Saltiel and other lab mates such as Peter Leermakers, Bob Foss, Karl Kopecky, Jim Clovis, Fred Fischer and Lee Mahoney.

Metal-Complex-Catalyzed-Decomposition of Alkyl Pyruvates

My initial project was not photochemical, but was the investigation of a thermolysis that might involve a triplet state. The idea was to study the thermolysis of methyl pyruvate and see if it could be catalyzed by paramagnetic metal complexes. If the decomposition proceeded through a triplet and collisions with the paramagnetic species, it could lower the A factor and cause a catalyzed rate acceleration. There was some evidence in the literature from measurement of Arrhenius parameters that the *cis-trans* isomerization of ethylenes might go through a triplet state and that certain catalysts of the *cis-trans* isomerization might operate by "catalyzing" formation of the triplet.

My first lab experiment was to synthesize methyl pyruvate. Eagerly, I went to the library and found an Organic Synthesis prep involving the reaction of diazomethane with pyruvic acid. Unfortunately, the storeroom did not stock diazomethane so I had to make some. To my amazement, diazomethane was described in the literature as a yellow gas. That sounded neat. I went to chem stores and signed out the equipment required to prepare diazomethane. I forgot the details, but I remember it required a decomposition that produced this remarkable yellow gas that could then readily be distilled and collected in a cold trap.

I set up the equipment, started the reaction according to the Organic Synthesis recipe and everything went like gangbusters! The yellow gas came bubbling out of the round bottom flask containing the reactants and condensed into a cooled ether solvent in the collection flask. I was so proud of all this that I rushed down the hall to see if there was someone from Robert's group to whom I could show off the set-up. John Baldwin, a second year graduate student working for Jack Roberts, came and looked at the set-up, turned ashen white and raced out of the room screaming, "You should never use ground glass joints when distilling diazomethane in ether! The ground glass can cause the

diazomethane to decompose uncontrollably and set off an explosion!!!!” John was a real scholar and knew all this stuff. Hey, I was just a rookie; how was I to know? Anyway, the reaction worked well as did the synthesis of methyl pyruvate, so now I could start decomposing it in the presence of the metal complexes.

Interestingly, at the same time that I was using metal complexes to decompose methyl pyruvate, Peter Leermakers was using the same metal complexes to quench benzophenone triplets and looking for a correlation with paramagnetic properties. As it turned out, the thermolysis experiments did not show a correlation with paramagnetic properties but were a lot easier to run than photochemical quenching experiments. It turned out that the metal complexes that “catalyzed” the decomposition of methyl pyruvate were also excellent quenchers of benzophenone triplets. Pretty soon I was predicting which metal complexes would quench and which would not, in the photochemical experiments and doing this without a photon in sight!

One of Those Serendipitous, Career-Defining Events. The Friday Night Lecture Demonstration at Caltech.

After about six months of research on the metal complex catalyzed decomposition of methyl pyruvate, a serendipitous twist made a critical impact on my career. As an undergraduate at Wesleyan, I had discovered the luminol chemiluminescence experiment and would show it off any opportunity I could get. One day I was showing it off in the lab. George Hammond was about to present a “Friday demonstration lecture” to the Pasadena community and I needed him about the demonstration that he might be presenting, assuming that there would be none. George nailed me with, “Nick, why don’t you show the luminol experiment. It’s sort of photochemical and that’s what I’m going to talk about.” With a combined feeling of anxiety and excitement, I accepted. As I expected, George gave a fabulous lecture on the research that Peter, Bob Foss, Bill Baker and others had been doing on the photochemical reactions of benzophenone and his beautiful method for demonstrating the involvement of triplets. What I didn’t expect is that when he introduced my demonstration he jokingly termed me an “anti-photochemist” because my results on the catalyzed decomposition of methyl pyruvate were contrary to current paradigms about the effect of paramagnetism on photoreactivity. The demonstration went well (I still remember someone in the audience saying, “Wow! This is just like Disneyland!!!”).

The Saturday Morning After Experiment. The Beginning of Triplet Sensitized Photoreactions in Solution. Triplet Energy Transfer Becomes a Household Word.

On the Saturday morning after the Friday demonstration lecture, I went into the lab and talked to Peter Leermakers about George’s comment the night before about my being an anti-photochemist. Peter had a great idea to get me into photochemistry: mix up ethyl pyruvate (my project) and benzophenone and irradiate (Peter’s project) the brew and see what happens! In fact, the experiment was set up by noon. We noticed that upon irradiation, bubbles of gas came streaming out of the photolysis setup. The bubbles stopped immediately when the lamp was off and started up again when the lamp was turned back on. This was so exciting that we called George at home, and in minutes he was in the lab to proclaim this was a sensational result. Neither Peter nor I had much of a clue why he was so excited, but it was the beginning of the use of triplet energy transfer to sensitize photoreactions, and George, with his typical insight, sensed where he could go with it. Little did Peter and I realize that this was the humble beginning of “triplet photosensitized photoreactions in solutions”. George had obviously grasped its importance immediately and within a few weeks half the group was working on some form of photosensitized reaction.

Peter and I then went to work immediately on trying to photosensitize the Diels-Alder reaction of a diene with maleic anhydride, a topic of considerable controversy at the time. We went to the storeroom to find an appropriate 1,3-diene to add to the maleic anhydride, which we already had in hand. The chemical storeroom at Caltech had a bottle labeled “purified 1,3-pentadiene”, affectionately known as piperylene. That sounded pretty good so we used piperylene as the diene in an attempt to photosensitize Diels-Alder. Checking the attempted photosensitized reaction by vpc indicted no reaction of the maleic anhydride, but the piperylene appeared to isomerize. We assumed that the “purified” piperylene was *trans* and that the isomerization was *trans* to *cis*. However, we discovered that the bottle actually was PURE *cis*-piperylene. Checking into the source of the *cis*-piperylene (remember, in 1960 there was no Aldrich and students often left chemicals in the chem stores after they finished their thesis work), we found that a student of a former Caltech faculty member had prepared it. The amazing thing was that the preparation involved taking a mixture of *cis* and *trans*-piperylene with maleic anhydride!! Obviously a scholar, the student, knew that the *trans*-piperylene reacted rapidly with maleic anhydride in a Diels-Alder reaction at room temperature, but *cis*-piperylene did not react at all due to simple steric hindrance considerations! Had Peter and I known that, we probably would not have used piperylene for our photosensitization experiments!!

Shortly after the discovery of triplet photosensitization, Karl Kopecky showed how to produce triplet carbenes from photosensitization of diazomethane decomposition, Jack Saltiel launched the photosensitized isomerization of stilbene, John Fox did the photosensitized decomposition of azo compounds, and Fred Fischer and I got involved in the norbornadiene to quadracyclene valence isomerization. Wow! This was a fabulous period of activity and excitement.

As a result of the prodigious research generated by George's group, the period 1960-1963 was one of tremendous excitement in the field of photochemistry and scientifically as the field of mechanistic organic photochemistry was expanding in an exciting and explosive manner. What a group of colleagues! In addition to Peter, there was Angelo Lamola, Jack Saltiel, and Bob Liu who went on to blaze their own trails in photochemistry; Karl Kopecky, who synthesized and isolated the first 1,2-dioxetanes when he started his academic career at Alberta, was a labmate. Downstairs in Crellin Laboratory, Wilse Robinson was helping to put the ideas of molecular spectroscopy into photochemistry with postdocs like Mostafa El-Sayed.

Fond Memories of Photochemistry at Caltech and Many Thanks.

Everyone who was in George's group during the golden years at Caltech recalls with fondness the incredible highs that were had as George led discussions in which new ideas crackled like sparks. It seems that after an hour's discussion on the little blackboard near the entrance to the lab, within days new and exciting results were produced.

George showed us all how to share his love and excitement with his muse, chemistry. We all owe many thanks and enormous gratitude to George for creating so much new knowledge and for changing the way we think. Perhaps this feeling for George is captured in another quote from Hinshelwood:

"But of that most important kind of knowledge, that which does not seem to relate to any existing field, it is harder to speak on the basis of anything but faith. And yet in this knowledge lies the true seed of the future. It will come only from the least conforming of minds, and the discoveries of the greatest ultimate moment are the least likely to have been favored by official encouragement or support. They must be like the flowers of the poet

...daffodils,
That come before the swallow dares, and take
The winds of March with beauty."

Such thoughts have united the Hammond clan for decades and will continue to do so for decades to come.

Respectfully submitted,
Nick Turro
Hammond group graduate and very proud of it!

About the Author

Nicholas Turro received his undergraduate degree from Wesleyan University (CT) in 1960 and his Ph.D. from Caltech in 1963 under the direction of George S. Hammond. After a year's postdoc at Harvard with P. D. Bartlett, he began his career in 1964 at Columbia University where he is currently the William P. Schweitzer Professor of Chemistry, Professor of Chemical Engineering and Applied Chemistry, and Professor of Earth and Environmental Engineering. He is the author of 2 books and over 670 scientific papers. He is a member of the National Academy of Sciences and the American Academy of Arts and Sciences. Recent awards include the ACS Award in Colloids and Surface Chemistry and the J. Willard Gibbs Medal awarded by the Chicago Section of the ACS. He can be reached at Columbia University, Department of Chemistry, 3000 Broadway, MC 3119, New York, New York 10027, e-mail: njt3@columbia.edu.