THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 108, NUMBER 45, NOVEMBER 11, 2004

Personal and Professional History of Tomas Baer

Tom Baer was born in Zurich, Switzerland on August 27, 1939. His parents, George and Maly Baer and family arrived in New York Harbor on the ocean liner, La Liberte, in the early fifties. Tom's father was a master bookbinder and had a job at Cuneo Press in Chicago. The family settled in a suburb nearby, where Tom stayed until he left for college. The challenges and experiences he had as an eleven year old in a new country, learning a new language, gave him an appreciation of the importance and value of American public education. During his high school years, classical music was his passion. As an aspiring musician, he often set his alarm to wake himself-up in the middle of the night to hear a particular piece of music broadcast from WFMT Radio Chicago. Since bookbinding provided a modest income at best, Tom spent his summers trimming trees in Morton Arboretum to pay for his college education. Little did he know how much his tree trimming skills would be needed in hurricane prone North Carolina. Tom married Carol McAninch on July 21, 1962 and has three children: Susan (1963), Allison (1966), and Jefferson (1971).

Tom received his undergraduate degree in mathematics in 1962 from Lawrence College in Appleton, Wisconsin. It is a well kept secret that he majored in math to avoid retaking organic chemistry, the one course he lacked for a degree in chemistry. Nevertheless, he eventually established his chemistry credentials by obtaining a masters degree (1964) at Wesleyan University in Middletown, CO, where he studied the denaturization of globular proteins by optical rotory dispersion. He then moved to Cornell University for his doctoral work, where he worked with Professor Simon Bauer on the reaction of diazomethane with HCl to produce $CH_3Cl + N_2$, the methyl chloride being highly vibrationally excited. The hope that these nascent excited molecules would exchange H for D when reacting with D_2 was not realized, but these experiments did instill in Tom a lifelong interest in chemical kinetics.

A thousand mile move due west brought Tom to Northwestern University, where he joined the research group of Professor Edward W. Schlag, who at that time was working on fluorescence of photoexcited molecules and photoelectron spectroscopy using threshold electrons. Tom made his first major contributions to science during his two years with Ed Schlag and graduate student Bill Peatman. In a key paper (1969), they demonstrated that threshold electrons could be collected with near unit efficiency by passing them through a long pipe with small apertures. Threshold photoelectron spectroscopy (TPES) was the forerunner of pulsed field ionization (PFI) or ZEKE spectroscopy.

Tom moved from Northwestern to the University of North Carolina in Chapel Hill in 1970, where he began his independent

10.1021/jp0405761 CCC: $27.50 © 2004 American Chemical Society

career and developed a love for the university and town that would keep him at UNC for over 30 years. He initiated a project in threshold photoelectron photoion coincidence (TPEPICO) spectroscopy, a technique for energy selecting ions. The use of threshold electrons in PEPICO was key to achieving high resolution and the ability to carry out dynamical studies on energy selected ions. During the 1970s, Tom embarked on a research project that measured unimolecular decay rates of energy selected ions and modeled these with the statistical theory of unimolecular decay. He also studied bimolecular reactions, reported in a series of papers discussing the use of TPEPICO to energy select the vibrational levels of reactant ions, including Xe^+, O_2^+, NO^+, and $CH_2Br_2^+$.

TPEPICO has remained a key research area of the Baer group. Through the development of new experimental methods and the application of ever more sophisticated theoretical techniques, TPEPICO has remained a vital research area. A particularly interesting series of papers involved organic ions, including the pentene isomers and many simple esters, which were found to dissociate via two-component decay rates. This was attributed to a competitive dissociation/isomerization mechanism. In a number of cases, all of the dissociation and isomerization rate constants could be extracted from the data and modeled with RRKM theory. Those that involved H atom transfer steps, required tunneling to yield quantitative agreement with experiment.

The recent application of velocity focusing optics and the experimental elimination of “hot” electron contamination has permitted the Baer group to model quantitatively sequential and parallel reactions involving several dissociation steps. Among these are organometallic ions that can be dissociated all the way to the bare metal ion. An example of such a reaction is $CrBz_2 + h\nu \rightarrow CrBz^+ + Bz \rightarrow Cr^+ + 2Bz$ (Bz = benzene). By determining the energy required to fully dissociate this ion to products, whose heats of formation are well-known, it was possible to determine the heat of formation of the neutral molecule. The experimental advances have also resulted in highly accurate dissociation onset measurements with error limits below 10 meV.

In 1992, Tom spent a year in France where he wrote a book (with William Hase as coauthor) entitled *Unimolecular Reactions; Theory and Experiments*, published by Oxford University Press in 1996. This comprehensive work on energy selected systems combines theory and experiment, as well as ionic and neutral systems.

An important component of Tom’s photoionization work has centered on the use of synchrotron radiation. He spent a sabbatical year as a John Simon Guggenheim Foundation Fellow at the University of Paris in Orsay in 1976−7 and again in 1982, where he collaborated with Paul Guyon, developing a coincidence experiment in which the threshold electrons were energy selected, not only by their angular properties but also by their time-of-flight. This yielded a resolution of 5 meV, with complete suppression of hot electrons. They concentrated their efforts on the dissociation of small ions, such as O_2^+, N_2O^+, and CO_2^+. One of the key discoveries resulting from this work was the mechanism for the production of low energy electrons in Franck−Condon gaps. Dissociation onsets lying in Franck−Condon gaps had been reported for many years. However, no one addressed the problem of how ions could be produced at these energies. By noting the similarities between neutral fluorescence and the production of threshold electrons, Baer and Guyon showed that the production of threshold electrons was related to the neutral dissociation continua lying in these Franck−Condon gap regions. A number of bimolecular reactions were also investigated in collaboration with Tom Govers.

As a result of his synchrotron radiation work, Tom emerged as an early expert among chemists in the use of synchrotron radiation. He has served on review and advisory committees at synchrotron facilities in Brookhaven, the Swiss Light Source, and the Advanced Light Source in Berkeley, where he and his students continue to carry out experiments.

In 1982, Tom and his student Keith Cole began studies on multiphoton ionization using pulsed lasers. These investigations eventually led to the study of conformational energies of alkyl substituted cyclic ethers and ketones. They noted regular patterns in the $n \rightarrow 3s$ transition energies of these compounds as methyl groups were substituted at various locations. In addition, axial and equatorial alkyl groups had widely different transition origins. This permitted them to readily distinguish conformations that were frozen out in the pulsed molecular beam. All the evidence indicated that the equatorial and axial conformations of a molecule, such as 3-methyl cyclohexanone, were instantly frozen out upon expansion in the molecular beam, so that the transition origin intensities for these two molecules was a good measure of their relative concentration in the room-temperature valve. By measuring the peak intensities as function of the valve temperature, they were able to obtain van’t Hoff plots and thus to extract gas-phase enthalpy differences between these conformations. This work was extended to rotational conformations in molecules such as ethyl-cyclohexanones.

An interesting additional finding emerged from modeling the cooling dynamics in the molecular beam. All indications were that the cooling takes place over several microseconds during the expansion. However, RRKM calculations of the isomerization process indicated that the reaction should have rate constants well in excess of 10^9 s^{-1}. How then can the isomers be instantly frozen at the concentrations characteristic of the valve temperature? They concluded that the isomerization rate constant is much slower than predicted by the statistical theory (RRKM). It was rather surprising that the statistical theory should fail for molecules as flexible and large as methyl cyclohexanone. However, Tom has argued that it is precisely in this energy and size regime that non-RRKM behavior should be expected. Low energy and temperature processes mean that few vibrational oscillators are excited much above $v = 1$. Thus, most of the energy flow dynamics takes place with the oscillators in the harmonic region of their potential energy surfaces, where energy flow is inhibited. These conclusions are slowly being confirmed by other experiments, as well as by theory.

Tom’s most recent departure from TPEPICO has been through his collaboration with Roger Miller in a broad range of mass spectrometric aerosol studies. This rapidly growing field has been motivated by the need to develop new tools for the analysis of aerosol particles, their concentration, their composition, and their size. The unique contribution from the Baer/Miller group has been the separation of the vaporization and ionization steps in the aerosol particle analysis. This has permitted them to gently vaporize particles containing organic species and to gently ionize them with a pulsed vacuum UV laser. This approach is ideal for studies involving gas surface reactions of organic aerosols, in which the progress of the reaction can be followed by both the depletion of the organic reagent and the formation of product.

A quick review of Tom’s publication list and his list of collaborators, students, and postdoctoral associates makes clear the great impact that he has had on Physical Chemistry. His love for science is evident from his life in science. We would like to join with all those who have contributed to and will benefit from this Festschrift in thanking Tom for all he has done to make science exciting for us as well.

Bill Hase
Roger Miller
Guest Editors