# Sidney W. Benson

1918–2011

BIOGRAPHICAL *Memoirs*

*A Biographical Memoir by*
*David M. Golden*



NATIONAL ACADEMY OF SCIENCES

# SIDNEY WILLIAM **BENSON**

*September 26, 1918–December 30, 2011*

Elected to the NAS, 1981

Photograph by Anna Benson.

*By David M. Golden*

My friend and mentor Sid Benson died at the age of 93 on December 30th, 2011. In this memorial I will attempt to summarize some of Sid's many accomplishments, and try to convey a sense of Sid as a person as well. Sid himself wrote expansively about his career in science; he was among the first to contribute when *The Journal of Physical Chemistry* began a program of inviting prominent physical chemists to write feature articles summarizing their current research. (*J. Phys. Chem*. 85:3375, 1981) The *Annual Reviews of Physical Chemistry*, which since 1965 has selected a prominent physical chemist to write about his scientific history, featured Benson in their 1988 issue. (*Annu. Rev. Phys. Chem*. 39:1, 1988) Additional interesting insights into Sid's career are contained in a video made at USC. http://www.youtube.com/watch?v=t8etN_rqtbc.

My own sense of Sid Benson as a person and as a mentor was summarized in my introductory remarks in the *Journal of Physical Chemistry A* issue that celebrated Sid's 80th birthday. I wrote:

> *I was privileged to work with Sidney Benson for thirteen years and in that time and since, I have come to know all of his junior colleagues. It is striking that there always existed among us a unanimous affection that goes far beyond scientific collaboration.*

When I was told about Sid's passing I reached out to some colleagues who I knew shared my feelings. These were some responses:

> *He did more for me than even my Father did. Therefore there is a void in my heart which is inevitable.*
>
> *–R. "Sri" Srinivasan (PhD student Benson)*
> *Inventor of LASIK surgery*

*I was never able to thank him enough for the inspiration he was for me and for the influence he had on my scientific career. When I look back it is hard to overestimate how lucky we were to have had Sid almost to ourselves for 2 years.*

*–Robin Walsh (Post-doctoral fellow at SRI),*
*Reading University, UK*

*A most important part of my professional life was the relatively short but emphatic association with Sid. He was for me not only a brilliant mind and great teacher but also a real friend.*

*–Kurt W. Egger (Post-doctoral fellow at SRI)*

*am very sorry to hear about Sid's passing away. We all owe him a lot and deeply miss him. We certainly will keep him firmly in our memories.*

*–Jürgen Troe*
*Georg-August-Universität Göttingen, Germany*

*I know you will miss him; so will I. His work was an important part of both of our lives.*

*–Robert G. Bergman*
*University of California Berkeley*

*I count Sid Benson among my important mentors. He had a major effect on both my research and my teaching.*

*–John I. Brauman*
*Stanford University*

Sidney W. Benson was born on September 26, 1918, in New York City. He was a product of the New York City Public School System, including the spawning ground for scientists that was Stuyvesant High School, from which he graduated in 1934. He went on to do his undergraduate work at Columbia College and graduated with honors in chemistry, physics, and mathematics in 1938. His Ph.D. was obtained at Harvard University in 1941, working under the guidance of George B. Kistiakowsky. He then spent another year at Harvard as a postdoctoral fellow for Professor G. S. Forbes.

He established himself as Chairman, Department of Thermochemistry and Chemical Kinetics. (An important insight into Sid Benson comes from the knowledge that SRI did not have departments and did not have titles such as "chairman." Sid never lacked chutzpah!)

Benson started his professional career as an instructor at the College of the City of New York in 1942. In 1943 he joined the Manhattan Project (Kellex) as a group leader, and then in 1944 he traveled to California to begin a long career at the University of Southern California (USC). After 6 months of teaching, he was recruited to defense work at USC under Division 9 of the NDRC. He received a certificate of merit for his contributions to the war effort. At USC he was promoted from assistant professor to associate professor in 1948 and to professor in 1951.

In the early 1940s, USC leadership sought to make the school, at the time a collection of professional schools, into a major research university. Benson believed that he was hired as part of this program. The end of World War II accelerated this program as the G.I. Bill of Rights led to massive increases in the student population at USC. The campus doubled in size. There were so many students, USC had to borrow 20 barracks from the U.S. Department of Defense for housing. Benson's labs and classrooms were also in barracks. Benson felt that some of his best work was done in those barracks.

Relatively early in his career at USC Sid was involved with a faculty group, which after a tumultuous time negotiated a pay raise for full-time faculty with the USC President. At the time, salary for full-time professors ranged from $1,900 to $4,000 a year. After much effort, the fledgling senate secured an initial 10 percent raise. Activities of this nature are not a surprise to Sid's friends. I once heard him described as someone who liked to be in the eye of a hurricane, watching the tumult around him, and if the hurricane showed signs of slowing down, Sid would give it a poke!

In 1963 he began a 13-year stay at SRI International. (Then known as The Stanford Research Institute.) The move was prompted by breathing difficulties that his late wife, Natasha, had in Los Angeles. He established himself as Chairman, Department of Thermochemistry and Chemical Kinetics. (An important insight into Sid Benson comes from the knowledge that SRI did not have departments and did not have titles such as "chairman." Sid never lacked chutzpah!) Sid's first group consisted of two post docs, Kurt W. Egger and me, David M. Golden. We were assigned some empty space in

Sid Benson at SRI in 1964.
(Photo courtesy David M. Golden.)

which to build laboratories. Robin Walsh joined as a post doc a year later. The three of us would have extraordinary weekly tutorial meetings in which Sid enlightened us in all areas of thermochemistry and kinetics. These sessions remained a highlight for the three of us all through our careers! In the thirteen-year period during which I had the good fortune to be a co-worker of Sid's we were joined by a series of postdocs and several regular staff members. The thermochemistry and chemical kinetics group performed experiments involving gas phase reactions, often with halogen compounds. Benson was involved with well over one hundred publications during his time at SRI.

Sid returned to USC in 1976. He became emeritus in 1994, but remained active until shortly before his death. In 1977, the University made him Distinguished Professor of Chemistry. In 1977, Benson helped to recruit George Olah, now Distinguished Professor of Chemistry and Chemical Engineering and Materials Science, and Donald P. and Katherine B. Loker Chair in Organic Chemistry. Olah and Benson in 1977 established the Hydrocarbon Research Institute and both became scientific co-directors. Later named after the Lokers, the institute is the nation's only university-based institution devoted to hydrocarbon research and training, and the only privately funded research center of its kind. Olah's research at the institute earned him a Nobel Prize in Chemistry in 1994.

Sidney Benson had a distinguished career in chemistry as a teacher, in making basic contributions to the field, and in providing results fundamental to a number of fields of practical, social, and economic significance. Benson was dearly loved by his undergraduates, graduates, and post-doctoral researchers. He was a pioneer in employing the concepts of dimensional analysis and conversion factors in teaching elementary chemistry, and developed these ideas in the first edition of his 1952 book *Chemical Calculations*. He was founder and editor (1969-1983) of the *International Journal of Chemical Kinetics*.

Benson's textbook *The Foundations of Chemical Kinetics*, first published in 1960, remains a seminal contribution to the field. Among his other books, *Atoms, Molecules and Chemical Reactions: Chemistry from a Molecular Point of View* and *Thermochemical Kinetics* (2nd ed., 1976) are regarded as significant contributions to chemistry. The latter being essentially the bible for the area that takes its name as a descriptor.

He was honored for his contributions on many occasions: elected to the National Academy of Sciences (1981), honorary member of Phi Kappa Phi, Fellow of the Japanese Society for Advancement of Science (1980), and recipient of the National Science Foundation's Citation for Creative Research (1982).

In 1977, he was awarded the American Chemical Society Award in Petroleum Chemistry in recognition of his accomplishments in the measurement of bond dissociation energies, free radical studies, and his "invention" of "thermochemical kinetics", empirical methods for the quantitative estimation of thermochemical and kinetic data. In that same year the Tolman Award in Chemistry was given to him by the Southern California Section of the American Chemical Society (ACS). In 1986 he was awarded the Irving Langmuir Award in Chemical Physics by the ACS. In the same year, he became the fifth awardee of the Royal Chemical Society's Michael Polanyi Prize in Chemical Kinetics.

In 1989, the Chemistry Department of the University of California at Berkeley invited him to deliver their G. N. Lewis Lecture. In December 1989, he was awarded an Honorary Doctor of Science Degree (*Honoris Causa*) by the University of Nancy in France. In 1990, he was elected to membership in the Indian Academy of Sciences.

Benson also received many honors and accolades at USC. In 1984, he received the USC Associates Award for Creativity in Research and Scholarship. In 1986, he was awarded the USC Presidential Medallion, the university's top recognition for those who have brought honor and distinction to the campus. He received the USC Faculty Lifetime Achievement Award in 1990, four years before his retirement.

I would summarize Benson's work by saying that he performed experiments and theoretical work that have enabled the codification and extrapolation of chemical kinetic and thermochemical data. This allows us to examine problems of real interest ranging, in my own experience, from atmospheric to combustion chemistry. Complex problems such as these can only be said to be understood if a numerical model made up of individual chemical steps can be used to reproduce laboratory experiments carried out under a variety of conditions, followed by the extrapolation of the model parameters to the real

conditions of interest. This extrapolation is the key to the above understanding and Sid Benson's work has taught us how to think about this process.

It is largely due to Benson that one finds that physical organic chemistry texts now routinely contain tables of thermochemical quantities such as bond dissociation energies.

Benson emphasized the global nature of chemical processes. He pointed out that individual chemical reactions are not universes unto themselves, but must be thought about in concert with others. The impact of these ideas on the chemistry community is easily seen by the enormous number of citations to Benson's work that appear in the literature.

He has often been among the most cited chemists in the world, a testament to the broad impact his work has had. He made significant contributions to physical chemistry, organic chemistry, inorganic chemistry, and biochemistry, covering a wide spectrum of areas. His contributions have been fundamental and practical. His work has not only become an integral part of advanced textbooks in physical and organic chemistry but is also of industrial and economic importance. His work in thermochemistry, enhanced in recent years by advances in computational capabilities, has transformed a once esoteric field into an active branch of modern chemistry. Everyone who works at modeling complex chemical processes such as air pollution, the ozone layer, combustion, or explosions is familiar with and makes use of the fundamental contributions of Benson to these fields.

His "group additivity" concepts provided fundamental methods for obtaining accurate estimates of thermochemical properties such as heats of formation, entropies, bond energies, and heat capacities of organic molecules and radicals. These techniques have become standard among scientists and engineers estimating thermochemical properties.

In addition to his own research, Benson stimulated the research directions of many peers. He asked questions and made assertions in print and at conferences that were both interesting and could be answered experimentally. Sometimes his assertions were confirmed and sometimes not, but in either case they stimulated a quantitative view of chemistry that was previously lacking. It is largely due to Benson that one finds that physical organic chemistry texts now routinely contain tables of thermochemical quantities such as bond dissociation energies.

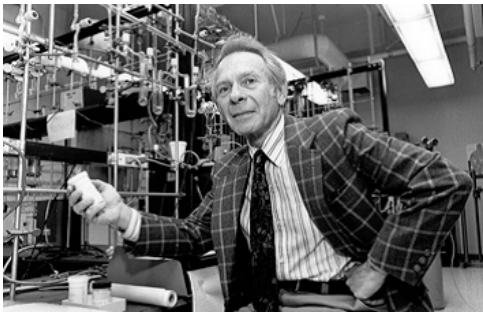
From left to right: David Golden, Robin Walsh (at rear), Sid Benson, and Kurt Egger in Bordeaux, France, 1986. (Photo courtesy David M. Golden.)

Benson's early work (1946-1964) ranged over broad areas of physical chemistry and included several landmark contributions. In 1955, he showed that the classical bimolecular reaction of $H_2$ and $I_2$ is in fact largely a radical chain reaction. Major contributions during this period also came in the areas of kinetics and mechanism. In 1956, he helped to establish the correctness of the Chapman mechanism for ozone chemistry in the atmosphere. Ozone reflects another area of Benson's contributions. He and his co-workers made detailed analysis of the mechanism for the interaction of ozone with organic molecules, and the subsequent decomposition of the polyoxides and ozonides formed. His quantitative predictions of the stability of alkyl trioxides and hydro-trioxides have since been confirmed by other laboratories.

He made many important contributions to the study of free radical kinetics and bond-dissociation energies. A major accomplishment was reported in a series of papers that succeeded in unraveling the mechanisms of alkyl iodide pyrolysis and reactions with HI. These led to values of radical heats of formation and bond-dissociation energies. This work also led to the "iodination" method for obtaining bond-dissociation energies and "stabilization" energies in conjugated free radicals. A well-cited paper on bond-dissociation energies was published at the request of the American Chemical Society Committee on Chemical Education. Benson contributed to the solution of the baffling paradox of combustion chemistry, the mechanism of cool flames. In 1986, he was an invited plenary lecturer at the International Combustion Symposium in Munich where he presented his ideas on the mechanisms of hot ignition and on the molecular mechanisms for knock inhibition by lead.

Always looking for simple classical explanations, Sid formulated a semi-ion pair model for four-center concerted reactions, which permitted calculations of their activation energies and quantitatively explained the Markownikoff rule for the four-center addition of HX species to substituted olefins as an effect of the polarization of the substituent

groups. He had some initial success in formulating a formal charge model for predicting the heats of formation of hydrocarbons and their free radicals. Failures to extend this to highly polar molecules were resolved with the development of a new electronegativity scale, which permits quantitative estimation of the heat of formation of any organic molecule RX from the heat of formation of the methyl derivative $CH_3X$.



Benson at USC.
(Photo by Wendy Rosin Malecki, courtesy USC University Archives.)

One of his most significant experimental developments was the use of the very low pressure reactor (VLPR) for the study of the thermochemistry of free radicals. This technique, an extension of earlier work on very low pressure pyrolysis, consists of studying atom-molecule reactions in a well-stirred reactor (at low temperatures) under conditions where secondary reactions are minimal and can be studied independently if needed.

Benson studied the thermochemistry of molecules and free radicals containing sulfur in an attempt to clarify the mechanisms of reaction of sulfur-containing compounds in oxidation, in air pollution, and in the generation of sulfuric acid in the atmosphere leading to the "acid rain" phenomenon. In the related chemistry of the stratosphere, he postulated the potential importance of metals and metal oxides, either from micrometeorites or, if added independently, in scavenging halogen atoms in the stratosphere and stabilizing the ozone layer.

Sid took full advantage of the sporting opportunities in California. He skied for many years and was an avid tennis player until very late in life. It remains to point out that Sid took a measure of delight in being contrary to conventional thinking. This was reflected in his being a Trotskyite while at Harvard and political conservative in his later years. It also led him to make light of the possibility that CFC's could threaten the ozone layer and to even more stridently debunk the general consensus about climate change. He was often confrontational at meetings, but always with a pure heart. He never felt that disagreeing strongly with you on a scientific topic meant you couldn't have a beer together after the meeting.

In addition to his wife Anna Bruni Benson, Sid Benson is survived by his son Nicholas; his daughter Jeannette Hamilton; stepchildren Mara Lee Maltauro, Sumishta Brahm, and Mark Seldis; granddaughter Sydney; brother Albert; and sister Rhoda.

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