The Journal of Physical Chemistry A

 VOLUME 102, NUMBER 44, OCTOBER 29, 1998

S. W. Benson

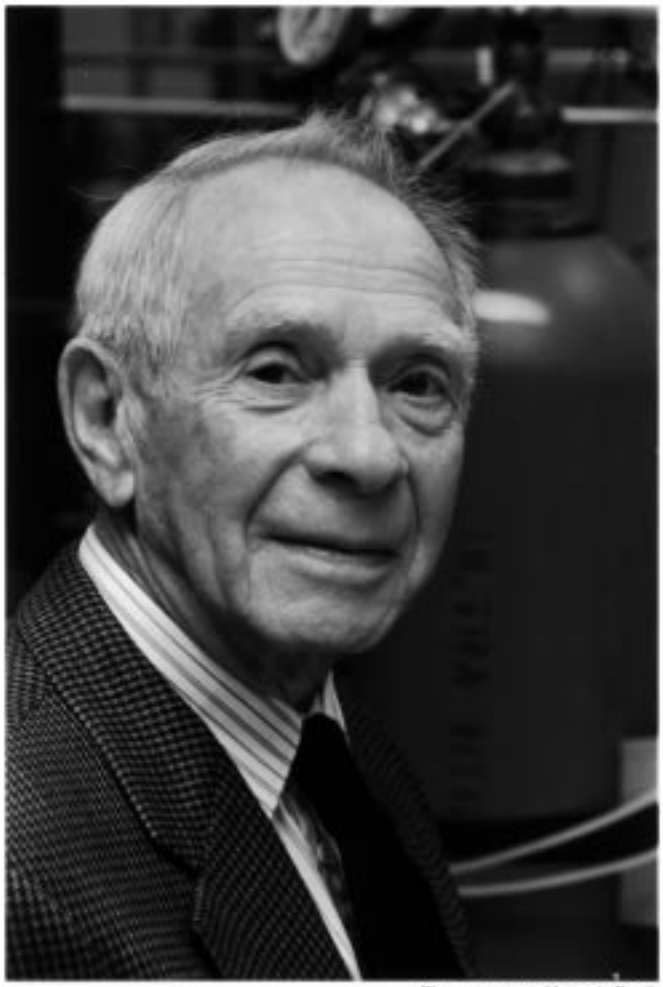

Photo courtesy of Irene A. Ferth

Biography

Sidney W. Benson was born on September 26, 1918, in New York City. He is 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.

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 Group Leader, and then in 1944 he traveled to California to begin a long career at the University of Southern California. After 6 months of teaching, he was recruited to Defense Work at USC under Div. 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 1963 he began a 13-year stay at SRI International (then known as The Stanford Research Institute) where the under-

10.1021/jp9832488 CCC: $15.00
Published on Web 10/29/1998

signed began as a postdoctoral fellow in 1963. Professor Benson returned to USC in 1976 and remains active in an emeritus role today. In 1977, the University made him Distinguished Professor of Chemistry and established the Loker Hydrocarbon Research Institute, which has gained worldwide recognition as a center of important hydrocarbon and energy research.

Sidney Benson has had a distinguished career in chemistry—as a teacher, in basic contributions to the field, and in providing results fundamental to a number of fields of practical, social, and economic significance. He was a pioneer in employing the concept of dimensional analysis and conversion factors in teaching elementary chemistry, and this was developed in the first edition of his book in 1952 *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.

He has been honored for his contributions on many occasions: 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 an entirely new field, 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 ACS. *The Journal of Physical Chemistry* began a program of inviting prominent physical chemists to write feature articles summarizing their current research. Professor Benson was among the first invited to contribute. 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.

In 1986 he was awarded the Irving Langmuir Award in Chemical Physics by the American Chemical Society. In the same year, he became the fifth awardee of the Royal Chemical Society's Michael Polanyi Prize in Chemical Kinetics. Earlier that year, the University of Southern California gave him its most prestigious faculty award, the Presidential Medallion, honoring his research, teaching, and service to the University, dating back to 1944.

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.

He has been among the top 25 most cited chemists in the world since 1965, a testament to the broad impact his work has had so far. Very few chemists in this century have made as significant contributions as those of Sidney Benson to physical chemistry, organic chemistry, inorganic chemistry, and biochemistry, covering a wide spectrum of areas. His contributions have been fundamental and practical and rank among the most important developments in this century. 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 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 have 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 methods of choice among scientists and engineers for estimating thermochemical properties.

Professor 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 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 chemistry related to the fact that ozone has been widely used around the world in place of chlorine for the purification of drinking water reflects another area of Benson's contributions. He and 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 has 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 quantitative properties of biradicals and the biradical mechanism in ring-opening reactions, and further 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. This period included the invention of the very low pressure pyrolysis technique, which made possible the quantitative measurement of free radicals at high temperatures with no complicating secondary reactions.

Professor Benson has been involved in solving one of the most baffling paradoxes 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, for the first time, the mechanisms of hot ignition and his ideas on the molecular mechanisms for knock inhibition by lead.

In 1970 he was able to formulate 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.

Benson had an 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 have now been 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.

One of his most significant experimental developments in this period has been 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. It has made possible studies of equilibria and yielded heats of formation of some radicals to 0. 15 kcal/mol, an order of magnitude improvement over earlier studies. VLPR is a unique tool for chemical kinetics experiments. Total mass balances to 3% can be obtained by simultaneously observing all species, reactants, and products in a complex chemical reaction including atoms and free radicals.

In 1976 Benson began a study of the thermochemistry of molecules and free radicals containing sulfur, which has done much 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 has 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.

Much of his work has been devoted to energy-related problems. He and his colleagues have succeeded in establishing a thermochemical data base for use in predicting stability and reactivity of polynuclear aromatic compounds, which has great importance in coal gasification and liquefaction as well as pollution-related problems.

One of the important practical areas of Professor Benson's research has been the investigation of a method for directly converting methane to ethylene and acetylene, and polymerizing methane and ethylene to larger hydrocarbons in one simple step. An extremely important byproduct of this research has been the development of a detailed molecular model of the kinetics of soot formation in flames. On a related note, he has set forth a mechanism for the free-radical chemistry of acetylene at high temperatures that is consistent with the findings of shock-tube experiments. Additionally, two papers, one on the mechanism of acetylene polymerization and a second on the mechanisms of the reaction of nitric oxide (NO) with acetylene (C_2H_2) above 1000 K, have accounted quantitatively for the production of polymers (below 1000 K) in pure acetylene and for the production of HCN and H-atoms from the reaction of NO with C_2H_2.

It remains to be pointed out, speaking for many of the colleagues of Sidney Benson listed on the following pages, that all of us who have had the privilege of working with him have come away from that experience as better scientists and with an enormous love and respect for the man!

David M. Golden