

## George Andrew Olah (1927–2017)

George A. Olah, the recipient of the 1994 Nobel Prize in Chemistry for his groundbreaking work on superacids that led to isolation and observation of long lived carbocations, passed away on 8 March 2017 at his home in Beverly Hills, California.

Olah was one of the pre-eminent scientists in the second half of the twentieth century and the early part of the 21st century. His pioneering contributions to Chemistry span through one of the most magnificent era of science. Olah was born on 22 May 1927 in Budapest, Hungary to Julius Olah, a lawyer and Magda Krasznai. He finished his school years in the Gymnasium of the Piarist Fathers (one of the best schools in the Roman Catholic religious teaching order) while the World War II was raging. In his autobiography<sup>1</sup>, *A Life of Magic Chemistry*, he describes his horrifying experiences of the time. He and his parents survived, but he lost his older brother, Peter. After the war, he studied chemistry at the Technical University of Budapest and completed his Ph D in 1949 under the supervision of Geza Zemplen, a carbohydrate chemist, trained under the legendary chemist, Emil Fischer. In 1949, he married Judith Lengyel, a technical secretary at the University, who later studied chemistry and became his partner in research and life. He began his academic career as an Assistant Professor in the same department at the Technical University and was promoted in 1954 as the Head of Department of Organic Chemistry and Associate Scientific Director of Central Research Institute of the Hungarian Academy of Sciences. However, those years in Hungary were really tumultuous in his life due to the post-war Soviet rule. Amid the turmoil and aftermath of a failed uprising against Soviet rule in 1956, future seemed bleak and he decided to join the torrent of about 200,000 Hungarian refugees and fled his native Hungary with his wife and two-year old toddler son. With a brief stay in Vienna and England, he moved to Canada.

Olah, was a true legendary chemist and a great visionary, who had a prophetic approach for solving challenging problems. In 1957, he joined the Dow Chemicals at Sarnia in Canada and continued his research work. One of the major areas at Dow Chemicals at that time

was Friedel-Crafts-type chemistry for the production of ethylbenzene from benzene and ethylene (for the conversion to styrene for polystyrene manufacture), which involves arenium (Wheland) cation intermediates. It was during this period (1957–1964), that his breakthrough work on long-lived carbocations, such as *tert*-butyl and isopropyl cations in superacids was carried out<sup>2,3</sup>. This work later won for him his Nobel Prize in 1994.



In 1965, Olah was recruited to academia as a professor in Western Reserve University, which later became Case Western Reserve University by merging with Case Institute of Technology. Based on the work<sup>4</sup> of Ron Gillespie in Canada, he had realized that fluorinated Brønsted superacids such as HF and FSO<sub>3</sub>H in combination with Lewis superacids led to conjugate Brønsted superacids<sup>5</sup>, which are billions and even trillion times stronger than 100% sulphuric acid. In the late 1950s he had demonstrated that in such superacid systems at low temperatures long-lived carbocations can be generated. He coined the name ‘Magic Acids’ for the ones made from the combination of anhydrous FSO<sub>3</sub>H and SbF<sub>5</sub> that cleaved Christmas candle paraffin wax into long lived *tert*-butyl cation (like magic!)<sup>5</sup>. Prior to his pioneering work, carbocations were inferred as only fleeting intermediates (with microseconds to nanoseconds life-time) in acid catalysed hydrocarbon transformations. It was Olah’s genius that led to the stabilization of carbocations in superacids and their structural elucidation by low temperature NMR spectroscopy and later on by even X-ray structural analysis<sup>5</sup>. His exhaustive structural studies on longlived carboca-

tions gave rigour and new dimension to hydrocarbon reaction mechanisms under acid catalysis. Olah’s studies on carbocations created clear demarcation between the trivalent ‘carbenium ions’, planar ions of the CH<sub>3</sub><sup>+</sup> type, and the penta- or higher coordinated ‘carbonium ions’ of the CH<sub>5</sub><sup>+</sup> type, analogous to other ‘onium ions’<sup>6</sup>. While trivalent carbenium ions are the key intermediates in electrophilic reactions of  $\pi$ -donor unsaturated hydrocarbons, penta-coordinated carbonium ions are the key to electrophilic reactions of  $\sigma$ -donor saturated hydrocarbons through the ability of C–H or C–C single bonds to participate in 2e–3c bond formations. The non-classical bonding in 2-norbornyl cation [C<sub>7</sub>H<sub>11</sub>]<sup>+</sup> suggested by Saul Winstein in the 1940s and 1950s necessitated a higher-coordinate carbon<sup>7</sup>. This was the topic of the so-called classical–nonclassical ion controversy, involving the late H. C. Brown (1979 Nobel Laureate). The nonclassical structure of the 2-norbornyl cation was finally resolved by Olah’s <sup>13</sup>C labelling work using low temperature NMR spectroscopy and subsequent solid state NMR at 5 K (ref. 8). The structure of the nonclassical 2-norbornyl cation was later unequivocally established by low temperature X-ray structural analysis in 2013 by the collaboration of German and American groups<sup>9</sup>. His studies on higher-coordinate carbon compounds led to a new area of ‘hypercarbon chemistry’<sup>10</sup>. He also showed that in superacids, electrophiles can be further activated to superelectrophiles by protosolvation (superelectrophilic activation) that can initiate electrophilic reactions on weakly basic substrates<sup>11</sup>.

His early work in the 1950s in the area of fluorine chemistry in Hungary helped many researchers in the study and development of many fluorinated drugs. He also developed pyridinium polyhydrogen fluorides (known as the Olah’s reagent), which is widely used as an ionic liquid substitute for volatile HF, stable at ambient temperature. Many novel and practical fluorination protocols have been developed using the Olah’s reagent<sup>12</sup>. The same type of reagent was later (in the 1990s) commercialized to produce high octane gasoline in an environmentally safe process termed ‘ALKAD’.

In 1977, Olah moved to the University of Southern California, with one of the authors (G.K.S.P.), and founded the Loker Hydrocarbon Research Institute with the generous support of Donald and Katherine Loker, where he stayed for the rest of his extraordinary life. He continued his research activities that included synthetic methods, catalysis, oxidations, organosilicon and organofluorine chemistry and computations. He also became impressed with the predictive power of the computational chemistry with the prodding of his theoretician friends and used it to make important discoveries. In 1994, he was bestowed with the solo Nobel Prize in Chemistry for his seminal work on carbocations.

During his post-Nobel Prize years, Olah focused on remediation of mankind's fossil fuel based greenhouse problem. His solution to the carbon conundrum was a new approach developed with the author known as 'The methanol economy'<sup>13</sup>. The concept is based on the use of liquid methanol as an energy carrier and a convenient substitute fuel for gasoline and diesel. Moreover, it can be used as a feedstock for producing ethylene and propylene leading to all petroleum-derived products. The joint work with NASA-JPL also paved the way for a direct liquid methanol fuel cell (DMFC), a highly efficient portable source of electricity. He also developed new methods for converting existing natural/shale gas (methane) and CO<sub>2</sub> to syngas for making methanol<sup>14</sup>. He proposed that the renewable methanol can be produced by the reaction of hydrogen (generated from water electrolysis using renewable energy) with carbon dioxide from both anthropogenic and natural sources, liberating mankind from dependence on fossil fuels. Conversion of carbon dioxide to methanol is now commercially practised in the George Olah Renewable Methanol Plant in Iceland.

More recently, based on reports of astrophysical observations of carbocations and molecules including methanol in space, Olah suggested that methanol could have played a key role in the evolution of complex molecular building blocks that eventually led to life<sup>15</sup>.

Olah's work had a lasting impact on chemistry. His work on carbocations is

discussed in all elementary organic chemistry textbooks. His hero in chemistry was the late Hans Meerwein of Marburg. Olah was a friend/collaborator of many notable chemists: M. Saunders, N. Arnett, R. Huisgen, R. Grubbs, K. C. Nicolau, B. Sharpless, K. Houk, H. Schwarz, J. Rabo, G. Somorjai, P. J. Stang, K. Christe, A. de Meijre, R. Gillespie, G. Schrobilgen, the late chemists: H. Prinzbach, R. E. Williams, K. Wade, P. Schleyer, I. Ugi, J. Pople, D. J. Cram, J. D. Roberts, J. Kochi, C. Nenitzescu, A. Cotton, and others. One of the authors, G.K.S.P., had the privilege of working with Olah for 43 years, first as a graduate student and subsequently as a colleague, not only on carbocations and fluorine chemistry, but also on the methanol economy topics.

Olah was quite prolific with close to 1500 publications, 160 patents and 25 edited books and monographs. He was a kind and generous mentor, who trained more than ~300 graduate students, post-docs and colleagues from many corners of the world (many from India also), who have done exceptionally well in their chosen careers. He was a highly cited chemist with an *h*-index of 102! In the course of his career, besides the Nobel Prize, he won innumerable awards, including the ACS Priestley Medal, Cope Award, Roger Adam's Prize, and Israel's Eric and Sheila Samson Prime Minister's Prize for Alternatives to Transportation Fuels. He received more than 15 honorary doctorates. He was a member of many US and international academies, including the US National Academy of Sciences, US National Academy of Engineering and Indian National Science Academy.

Olah is survived by his wife Judy, two sons, George Jr and Ronald and three grand children. He was a true hero of chemistry, a great role model and a caring human being. He will be deeply missed by the chemistry community.

1. Olah, G. A. (with Mathew, T.), *A Life of Magic Chemistry, Autobiographical Reflections including Post-Nobel Years and the Methanol Economy*, John Wiley and Sons, Hoboken, New Jersey, 2015, 2nd updated edn.
2. Olah, G. A., Tolgyesi, W. S., Kuhn, S. J., Moffatt, M. E., Bastien, I. J. and Baker, E. B., *J. Am. Chem. Soc.*, 1963, **85**, 1328.

3. Olah, G. A., Baker, E. B., Evans, J. C., Tolgyesi, W. S., McIntyre, J. S. and Bastien, I. J., *J. Am. Chem. Soc.*, 1963, **86**, 1360.
4. Gillespie, R. J., *Acc. Chem. Res.*, 1968, **1**, 202.
5. Olah, G. A., Prakash, G. K. S. and Sommer, J., *Science*, 1979, **206**, 13; Olah, G. A., Prakash, G. K. S., Molnar, A. and Sommer, J., *Superacid Chemistry*, John Wiley and Sons, Hoboken, New Jersey, 2009, 2nd edn.
6. Olah, G. A., *J. Am. Chem. Soc.*, 1972, **94**, 808.
7. Winstein, S., Trifan, D. S., *J. Am. Chem. Soc.*, 1949, **71**, 2953; 1952, **74**, 1147, 1149.
8. Olah, G. A., Prakash, G. K. S., Arvanaghi, M. and Anet, F. A. L., *J. Am. Chem. Soc.*, 1982, **104**, 7105; Olah, G. A., Prakash, G. K. S. and Saunders, M., *Acc. Chem. Res.*, 1983, **16**, 440.
9. Scholz, F., Himmel, D., Heinemann, F. W., Schleyer, P. v. R., Meyer, K. and Krossing, I., *Science*, 2013, **341**, 62.
10. Olah, G. A., Prakash, G. K. S., Wade, K. N. and Molnar, A., *Hypercarbon Chemistry*, John Wiley and Sons, Hoboken, New Jersey, 2011, 2nd edn.
11. Olah, G. A. and Klumpp, D. A., *Superelectrophiles and their Chemistry*, John Wiley and Sons, Hoboken, New Jersey, 2008.
12. Olah, G. A. and Li, X.-Y., In *Synthetic Fluorine Chemistry* (eds Olah, G. A., Chambers, R. D. and Prakash, G. K. S.), John Wiley and Sons, Hoboken, New Jersey, 1992.
13. Olah, G. A., Goepfert, A. and Prakash, G. K. S., *Beyond Oil and Gas: The Methanol Economy*, Wiley-VCH, Weinheim, 2009, 2nd edn.
14. Olah, G. A., Goepfert, A., Czaun, M., Mathew, T., May, R. B. and Prakash, G. K. S., *J. Am. Chem. Soc.*, 2015, **137**, 8720.
15. Olah, G. A., Mathew, T., Prakash, G. K. S. and Rasul, G., *J. Am. Chem. Soc.*, 2016, **138**, 1717; Olah, G. A., Mathew, T. and Prakash, G. K. S., *J. Am. Chem. Soc.*, 2016, **138**, 6905; 2017, **139**, 566.

G. K. SURYA PRAKASH\*  
THOMAS MATHEW

Loker Hydrocarbon Research Institute,  
Department of Chemistry,  
University of Southern California,  
837 Bloom Walk, Los Angeles,  
CA 90089-1661, USA  
\*e-mail: gprakash@usc.edu