

Professor José Manuel Riveros

A Tribute



Dedicated to Prof. José Manuel Riveros on the occasion of his 80th anniversary

Published on line 12-15-2019

In this issue of Arkivoc, colleagues, friends and admirers have contributed manuscripts honoring Dr. José Manuel Riveros Nigra, Emeritus Professor of the Institute of Chemistry of the University of São Paulo, Brazil.^{1,2}

Born and raised in Asunción, Paraguay, the son of a prominent Paraguayan medical doctor³ and an Italian mother, Prof. Riveros learned English in New York at the age of seven during his father's specialization in cancer surgery as a Guggenheim fellow. Deciding on a career in science during high school, he entered the School of Chemistry and Pharmacy of the University of Asunción as an undergraduate in 1958. Desiring a greater intellectual challenge than he encountered during his coursework in Paraguay, he applied through the American Embassy in Asunción for a one-year scholarship at the University of California, Berkeley, where he was admitted as a sophomore in 1959. His academic performance resulted in the extension of his fellowship for two more years in order to finish his Bachelor's Degree in Chemistry, graduating at the top of the College of Chemistry class of 1962. Undergraduate research in the laboratory of Professor Bruce Mahan on Xe-photosensitized photolysis of methane provided him with experience in photophysics, atoms and small molecules in the gas phase, vacuum techniques, glassblowing and gas chromatography. These skills and interests would prove to be of practical importance in his later research career in Brazil.

After graduating from UC Berkeley, he pursued Ph.D. studies in physical chemistry at Harvard University from 1962-1966 as a fellow of the Organization of American States under the supervision of Professor E. Bright Wilson Jr., one of the twentieth century icons of physical and quantum chemistry. For his Ph.D. thesis, Riveros concentrated on the determination of the molecular structure and conformation of small molecules such as nitric acid and ethyl formate in the gas phase using microwave spectroscopy, an area in which his interest has been recently renewed, in large part due to the enormous advances in computational capabilities and instrumentation since the 1960s. During his graduate studies at Harvard, he made numerous friendships with colleagues who would later become prominent scientists in their own right, and in addition met the Bostonian Deborah Cutler who was destined to become, in 1967, his wife and lifelong companion. After one year at Cornell as a postdoctoral fellow developing methodology for the spectroscopic and structural characterization of small alkyl radicals with Professor George Fraenkel, Riveros was obliged by his visa status to leave the USA for at least two years, precluding an academic career in the USA for the moment.

The lack of academic research opportunities in Paraguay led Dr. Riveros to contact the University of São Paulo, which was in the process of a restructuring that would transform it into one of the premier research and teaching universities in Latin America. Prof. Simão Matias, the forward-thinking Director of the Institute of Chemistry at the University of São Paulo (IQ-USP), showed immediate interest and Dr. Riveros and his wife arrived in São Paulo in December, 1967, to begin his career in academia. Initially supported as a Visiting Professor by the São Paulo Research Foundation (FAPESP) and the Ford Foundation, he was hired shortly thereafter as a faculty member in the Department of Fundamental Chemistry. Rising to the rank of Full Professor in 1977 after acquiring Brazilian citizenship, Professor Riveros served two terms as Department Chair (1981-1982; 1992-1993) and, from 1982-1986, as Director of the IQ-USP, overseeing the scientific and administrative activities of both departments (Fundamental Chemistry and Biochemistry), consisting of 105 professors, ca. 250 non-academic staff, and ca. 600 undergraduate and graduate students. Other significant contributions to Chemistry in Brazil include: coordinating a FAPESP-US NSF Special International Brazil-USA Undergraduate Student Exchange Program (2007-2013); serving as President of the Brazilian Society of Mass Spectrometry (2005-2013); and serving as a member of the Scientific Board of the Brazilian National Synchrotron Laboratory (1999-2015). During his career, he was a Visiting Professor or Visiting Scientist at the École Polytechnique Federale de Lausanne, the University of Amsterdam, the Institute of Molecular Sciences, Okazaki, Japan, the MIT Regional Laser Center, the University of California at Irvine, Stanford University, the City University of New York, Harvard University, UNICAMP and the Federal Universities of São Carlos and

Bahia, in addition to serving on the Editorial Boards of *Spectrochimica Acta A*, the *Journal of Mass Spectrometry*, *Mass Spectrometry Reviews*, the *International Journal of Mass Spectrometry* and the *Journal of the Brazilian Chemical Society*. Following compulsory retirement in 2010 at age 70, Professor Riveros continued to contribute to the Institute as a Senior Professor and, as a Brazilian Senior Research Fellow, to the consolidation of the graduate research program at the newly created Federal University of the ABC in Santo André, SP. Recognition of his career achievements include a Fulbright fellowship in 1977, a Founding Member of the São Paulo State Academy of Science in 1976, election to full membership in the Brazilian Academy of Sciences in 1980, the Rheinboldt-Hauptmann Prize, Rhodia/IQ-USP in 1998, the Simão Mathias Medal of the Brazilian Chemical Society in 2001 and the National Order of Merit, Category Grã Cruz, in 2005. In 2015, Professor Riveros and two retired colleagues from the Biochemistry Department were the first to be elevated to the status of Emeritus Professor in appreciation of their contributions to the Institute. Since 2015, Prof. Riveros and his wife have lived a life of semi-retirement between São Paulo and Sarasota, Florida, while maintaining scientific contacts with Prof. Correra, his successor at the Institute, and several intellectual collaborators in the USA.

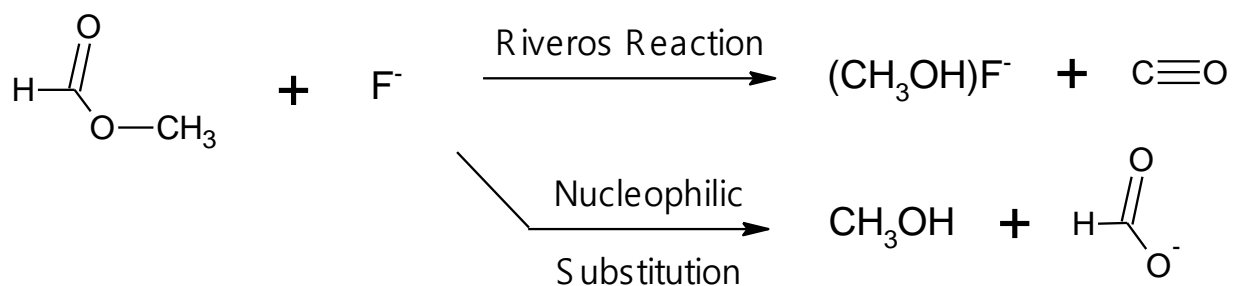
The arrival of Prof. Riveros in São Paulo was serendipitously timed for the future directions of his research career at the Institute since it coincided with the final negotiations for the creation of a novel international cooperative program, financed by the US National Academy of Science (NAS) and the Brazilian National Research Council (CNPq), and designed to accelerate the advancement of Chemistry in Brazil. In its 8-year existence, the NAS-CNPq Program established a select group of laboratories in São Paulo and Rio de Janeiro in collaboration with a US counterpart, providing the Brazilian laboratory with state-of-the-art instrumentation, expeditious acquisition of parts and chemicals from the USA and a post-doctoral researcher from US collaborators to participate *in situ* in the consolidation of the new laboratory. Prof. John Baldesweiler convinced Prof. Riveros, whom he had known at Harvard, to partner with him in the emerging field of Ion Cyclotron Resonance (ICR), a specialized mass spectrometric technique that permits the isolation of ionic species for relatively long times in the gas phase and hence allows studies of the kinetics and energetics of their unimolecular chemical and photochemical reactions together with their interaction with other ionic and molecular species.



Prof. Riveros at work on the ICR instrument in his laboratory, 1984. (photograph courtesy of Prof. Henrique Toma, IQ-USP)

Given his prior experience in studies of the structure of small molecules in the gas phase, the entry into the field of ICR in collaboration with Profs. Baldesweiler and Brauman and Dr. Larry Blair (from the Brauman group at Stanford) provided the impetus for the subsequent internationally recognized research career of Prof. Riveros. Employing ICR as a tool combined, when germane, with quantum chemical calculations, Prof. Riveros, together with his undergraduate (>30) and graduate students (19 Ph.D. theses and 12 MSc dissertations), postdoctoral fellows (9) and faculty collaborators, investigated a number of fundamental questions and themes of importance in modern physical chemistry. This work, reported in more than 150 scientific publications,¹ includes seminal studies of: (a) the intrinsic acidity and basicity of organic molecules in the gas phase that demonstrated that the relative acidities or basicities of functional groups like alcohols and amines in solution are the consequence of modulation of the intrinsic acidity and basicity by solvation effects; (b) the formation and stability of solvated ions in the gas phase and the mechanisms of a range of ionic reactions in the gas phase, which included experimental and theoretical characterization of species related to benzyne and ionic reactions of organosilanes; (c) chemical reactions initiated by multiphoton absorption; (d) spectroscopy and unimolecular fragmentation reactions of ions induced by black body radiation; (e) quantum chemical methodology combined with thermodynamic cycles and gas phase data of ions to predict pK_a values and reaction profiles of organic molecules in solution. Particularly emblematic is the reaction now known in the literature as the Riveros reaction.⁴

The Riveros reaction is an anion-induced decarbonylation of a methyl ester that leads to the methanol-solvated anion (fluoride ion in this case) in the gas phase in competition with nucleophilic attack of the anion at the methyl group:



In closing, two short quotations provide insight into the vision of Prof. Riveros with regard to our mission and responsibilities as professors and scientists in a developing country.⁵ In an ACS Graduate Education Newsletter (Fall, 2007), he emphasized the challenges and opportunities for science in Brazil: "Economic forecasts predict that Brazil will become a major economic force by 2050, surpassing all of the individual Western European economies. Yet, to achieve this status, Brazil must overcome major changes in the years ahead and make giant strides toward a knowledge-based economy." In an undergraduate commencement address at the Institute, he emphasized that the most important teaching goal for a professor at an institution like the Institute of Chemistry is "to awaken the ability of students to learn how to learn, to know how to deal with new scientific technologies and methodologies, and to deal with that which never was and with that which could be."

Notes and References

1. See Riveros, J. M. *Int. J. Mass Spectrom.* **2017**, *418*, xiii-xxv, for a more detailed autobiographical sketch and publication list.
2. Readers with an aural comprehension of Portuguese will appreciate the research seminar “Reatividade química ao nível molecular: experimento e teoria” [“Chemical reactivity at the molecular level: experiment and theory” (slides mostly in English)] presented by Prof. Riveros in the graduate seminars at the Institute of Chemistry of the Federal University of Rio de Janeiro in **2013**, available on YouTube (Accessed 09/09/2019): <https://www.youtube.com/watch?v=80xzjuzuJqs>.
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(b) Riveros, J. M. “Reactions of Organic Molecules with Organic Ions: Riveros And Related Reactions”, in *Encyclopedia of Mass Spectrometry, Vol 4*, Ed. N. M. M. Nibbering, Elsevier Science, 2004, pp 475–483.
5. Quoted by Galembeck, F., laudatory address at the ceremony awarding the title of Emeritus Professor to Prof. Riveros, Reitoria, University of São Paulo, October 19, 2015 (text kindly provided by Prof. Galembeck, IQ-UNICAMP).

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