

## INTERVIEW



### Professor Jose Manuel Riveros, whose important research achievements in chemistry are internationally recognized, recently gave an interview to BrJAC

Jose Manuel Riveros Nigra  

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Jose Manuel Riveros Nigra, better known as Professor Riveros, is an Emeritus Professor at the Institute of Chemistry of the University of São Paulo (IQ-USP), Brazil, where he was the Director from 1982 to 1986, and Head of the Fundamental Chemistry Department twice, from 1981 to 1982 and from 1992 to 1993. Prof. Riveros has been an advisor to the Brazilian Association of Synchrotron Light Technology – ABTLuS, and a former member of the Editorial Boards of *Spectrochimica Acta A*, *Journal of Mass Spectrometry*, *Mass Spectrometry Reviews*, *International Journal of Mass Spectrometry* and *Journal of the Brazilian Chemical Society*, and President Emeritus of the Brazilian Society of Mass Spectrometry.

Born and raised in Asunción, Paraguay, Prof. Riveros obtained his Bachelor's degree in Chemistry from the University of California at Berkeley in 1962, and his Ph.D. degree in Chemistry from Harvard University in 1966, under the supervision of Professor E. Bright Wilson Jr., a world renowned physical and quantum chemist of the 20<sup>th</sup> century. Prof. Riveros is internationally known for his important contributions to the field of gas phase ion-molecule reactions using a combination of mass spectrometric techniques and electronic structure calculations.

Prof. Riveros continues to contribute to the IQ-USP as a Senior Professor and his research has been primarily dedicated to the study of chemical reactions in the gas phase. His studies have primarily involved the chemistry of gas-phase ions, mechanisms of gas-phase ionic reactions, semiclassical molecular dynamics of simple reactions, gas-phase ion solvation, the thermodynamic characterization of solvated ions in solution and pKa calculations, molecular spectroscopy using various techniques and applications of multiphoton infrared excitation using lasers and blackbody radiation in the study of gas-phase ions.

With more than one hundred publications, his contributions in the field of physical chemistry have earned him, in addition to a reaction known in the literature as the “Riveros reaction”, several awards and honors including election to full membership in the Brazilian Academy of Sciences in 1980 and the National Order of Merit, Category “Grão Cruz”, in 2005. In addition, his work has been recognized by a Special Issue in his honor of the *International Journal of Mass Spectrometry* (Volume 418, July 2017) and a Special Issue of the online journal ARKIVOC (Volume 2020(ii)).

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### **Would you tell us a little about your childhood and early school years?**

I did my primary and secondary studies at the “Colégio San José” in Asunción, Paraguay, a school of French origin that emphasized a strong classical education, various sporting activities, and what the French define as “esprit de corps”.

### **What early influences encouraged you to study science? Did you have any influencers, such as a teacher?**

I consider my physics and chemistry teachers of the last two years of high school to be the main motivators of my interest in these areas. I was particularly attracted to issues related to atomic structure, the development of nuclear physics and the discovery of new chemical elements (transuranium elements).

### **When did you decide to study chemistry? What motivated you? How was the beginning of your career?**

By the end of my high school years I was interested in pursuing studies in Physics or Chemistry. However, there were no specific courses in Paraguay at that time (1957-1958) directed toward further education in Physics or Chemistry as pure sciences. In the end, I opted to enter the Faculty of Chemistry and Pharmacy of the University of Asunción in 1958. While the Faculty of Chemistry and Pharmacy offered courses leading to degrees in Industrial Chemistry or Biochemistry and Pharmacy, I was very much aware that these major areas were not exactly what I had in mind.

### **What has changed in your profile, ambitions, and performance since the beginning of your career?**

The big change came in early 1959. I had applied for a scholarship offered annually by the United States Embassy in Paraguay. These scholarships had little or almost no demand because they were only for one North American academic year (September to June). I was fortunate to be awarded a scholarship specifically for the University that I had indicated as my first choice: the University of California at Berkeley. For me, it was very exciting to know that I was going to the institution where Ernest Lawrence developed the cyclotron, and where Glen Seaborg triggered the discovery of transuranium elements. I was highly successful academically during the term of the scholarship, so it was extended until I completed my undergraduate studies at Berkeley. Furthermore, I was honored as the top student of the 1962 Chemistry class. Reflecting on my studies at Berkeley, I can particularly highlight an undergraduate research project carried out in the laboratory of Prof. Bruce Mahan, the Quantum Chemistry classes of Prof. Dudley Herschbach (Nobel Prize 1986), and the Physical Organic Chemistry course given by Prof. Donald Noyce.

In 1962, I was admitted as a graduate student at Harvard University with a full scholarship. There, I undertook my Ph.D. thesis on molecular structure studies by microwave spectroscopy under the supervision of Prof. Bright Wilson. My experience at Harvard, from 1962 to 1966, was very stimulating because of the opportunity to interact with some of the great names in Chemistry and Physics. I also had the great pleasure of sharing an apartment in Cambridge, MA, USA, with two other graduate students and great friends, one of whom, Tom Steitz, would earn the Nobel Prize in Chemistry in 2009. I must also mention the support and encouragement that I always received from my father, Dr. Manuel Riveros, who is considered the master of surgery in Paraguay.



Jose M. R. Nigra and Thomas A. Steitz at Harvard University in 1963.

### Could you briefly comment on recent developments in analytical chemistry, considering your contributions?

I will mention four areas that are of current importance and to which I believe we have made some fundamental contributions. Obviously, many other areas at the forefront of chemical research such as the chemistry of biomolecules, the chemistry and properties of nanoparticles, the enormous growth of computational chemistry, the revival of electrochemistry, advances in catalysis, among others.

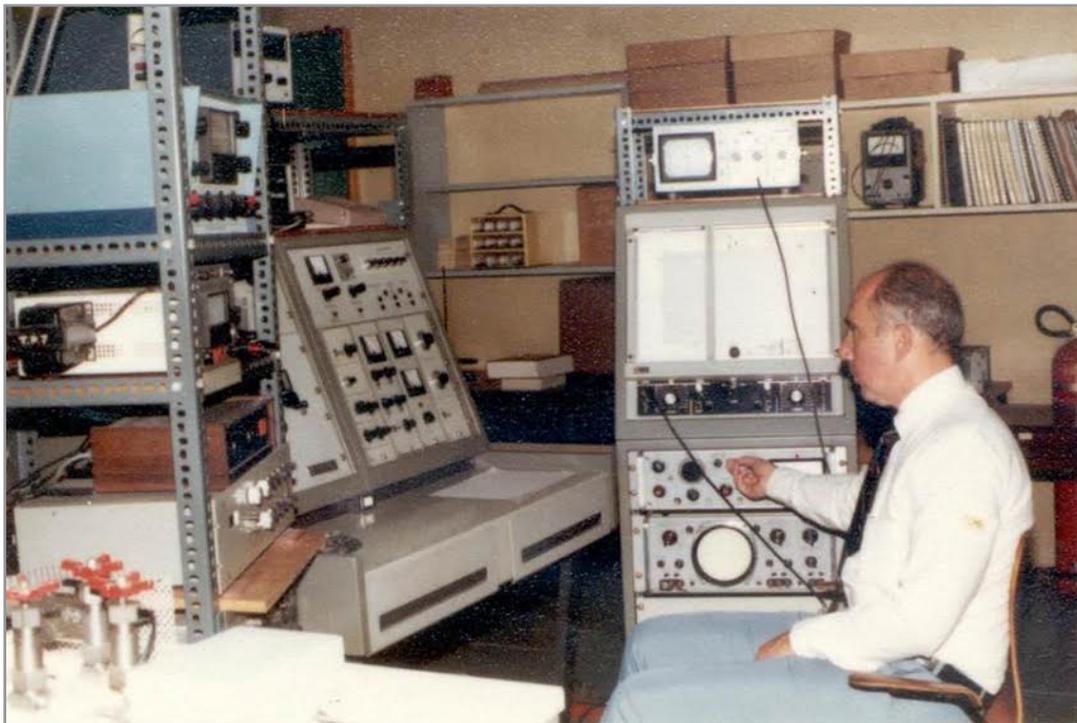
- The elucidation of reaction mechanisms from an intrinsic point of view has had a huge impact on our understanding of reactions of interest on the interface of chemistry and biology. In this respect, our paper published in 1978 (Takashima, K.; Riveros, J.M. "Gas Phase Pathways for Ester Hydrolysis", *J. Am. Chem. Soc.* **1978**, *100*, 6128), and other later papers related to this (Pliego, J.R.Jr.; Riveros, J.M. "The Gas Phase Reaction between Hydroxide Ion and Methyl Formate: A Theoretical Analysis of the Energy Surface and Product Distribution", *Chem. Eur. J.* **2001**, *7*, 169), represent a breakthrough in the interpretation of the mechanisms of simple biochemical model systems.
- The experimental article published in 1973 (Riveros, J.M.; Breda, A.C.; Blair, L.K. "Formation and Relative Stability of Chloride Cluster Ions in the Gas Phase by Ion Cyclotron Resonance", *J. Am. Chem. Soc.* **1973**, *95*, 4066) represents a historic milestone in the theoretical development of the potential energy surfaces of ionic reactions in the absence of a solvent. This is a subject that has had enormous development since the 1980s. Progressively higher-level computational methods have been widely used in recent years, and have even allowed for the simulation of reaction dynamics that do not strictly obey traditional statistical theories (for example, de Souza, M.A.F.; Correira, T.C.; Riveros, J.M.; Longo, R.L. "Selectivity and Mechanisms Driven by Reaction Dynamics: The Case of the Gas-Phase  $\text{OH}^- + \text{CH}_3\text{ONO}_2$  Reaction", *J. Am. Chem. Soc.* **2012**, *134*, 19004).
- Vibrational ion spectroscopy based on dissociation induced by infrared multiphoton absorption, is now widespread. Some of the potential applications have stemmed from our early papers [for example, (a) Gaumann, T.; Riveros, J.M.; Zhu, Z. "The Infrared Multiphoton Dissociation Spectra of Bromopropene Isomeric Cations", *Helv. Chim. Acta* **1990**, *73*, 1215; (b) Gaumann, T.; Zhu, Z.; Kida, M.C.; Riveros, J.M. "Kinetic and Spectroscopic Characterization of the Allyl Bromide Molecular Ion", *J. Am. Soc. Mass Spectrom.* **1991**, *2*, 372. (c) Morgon, N.H.; Linnert, H.V.; Giroldo, T.; Riveros, J.M. "The Isomerization of the Molecular Ion of Allyl Bromide", *J. Phys. Chem.* **1996**, *100*, 18048].
- Theoretical modeling of reactions in solution, and particularly those involving ions in aqueous solution, has represented a huge challenge and a subject of increasing interest. The development of a robust methodology to calculate the Gibbs energy of ion solvation (Pliego, J.R.Jr.; Riveros, J.M. "The cluster-continuum model for the calculation of the solvation free energy of ionic species", *J. Phys. Chem. A* **2001**, *105*, 7241) has been hugely successful and has been extensively used to calculate aqueous phase  $\text{pK}_a$ 's and the energy profile of reactions in solution (for example, Pliego, J.R.Jr.; Riveros, J.M. "A Theoretical Analysis of the Free Energy Profile for the Different Pathways in the Alkaline Hydrolysis of Methyl Formate In Aqueous Solution", *Chem. Eur. J.* **2002**, *8*, 1945).

### What are your lines of research? You have published many scientific papers. Would you highlight any?

My research activities at the Institute of Chemistry at the University of São Paulo have gradually decreased since 2010, after I reached compulsory retirement. However, I have maintained my interest in the characterization of chemical reactions at the fundamental level, of which some examples have been illustrated above. As I no longer have a laboratory under my responsibility, I have carried out both experimental and theoretical work in collaboration with other researchers from Brazil and abroad. In addition

to the articles previously cited, I would like to cite four papers that have been particularly rewarding for me and that have been internationally recognized:

- Riveros, J.M. "Anharmonic of the Out-of-Plane Vibration of the Methyl Radical", *J. Chem. Phys.* **1969**, *51*, 1269. This is my first paper published as a faculty member at the University of São Paulo and was helpful in elucidating the planar structure of the methyl radical.
- Faigle, J.F.G.; Isolani, P.C.; Riveros, J.M. "The Gas Phase Reaction of F<sup>-</sup> and OH<sup>-</sup> with Alkyl Formates", *J. Am. Chem. Soc.* **1976**, *98*, 2049. This is the fundamental article that describes what would become known as the 'Riveros reaction'. Much credit should be given to Prof. Paulo Celso Isolani who did a lot of the groundwork on these reactions during his Ph.D. thesis under my supervision.
- Riveros, J.M.; Ingemann, S.; Nibbering, N.M.M. "Formation of Gas Phase Solvated Br<sup>-</sup> and I<sup>-</sup> in Ion/Molecule Reactions of Halobenzenes. Revised Heat of Formation of Benzyne", *J. Am. Chem. Soc.* **1991**, *113*, 1053. The work described in this publication was originally started in our laboratory in 1976 and resulted in the demonstration that benzyne has a much higher thermochemical stability than originally proposed. This paper opened new paths in the study of benzyne-related reactions.
- Giroldo, T.; Xavier, L.A.; Riveros, J.M. "An Unusually Fast Nucleophilic Aromatic Displacement Reaction: The Gas-Phase Reaction of Fluoride Ions with Nitrobenzene", *Angew. Chem. Int. Ed.* **2004**, *43*, 3588. A pioneering work that demonstrated the possibility of a concerted mechanism in nucleophilic aromatic reactions and that has led to the discovery of a series of similar reactions in condensed phases.



Prof. Riveros at work on the ICR instrument at the IQ-USP laboratory, 1984.

**Do you keep yourself informed about the progress of research in chemistry? What is your opinion about the current progress of chemistry research in Brazil? What are the recent advances and challenges in scientific research in Brazil?**

I continue to follow the main Chemistry journals, both those that are of a general scope and those that are more specialized in physical chemistry. I also continue to be asked to be a referee of manuscripts submitted to first rate journals such as the *J. Am. Chem. Soc.*, *Chem. Eur. J.*, *J. Phys. Chem. A and B* and others.

It is clear that issues related to biomolecules occupy the greatest emphasis today, but there are important advances in the area of materials, in the area of organic synthesis and the functionalization of molecules, and in the introduction of new analytical methodologies. I understand that there has been a great advance of research in Chemistry in Brazil, especially in the last 20 years, covering all areas of Chemistry. This can be easily illustrated by the large number of publications by Brazilian researchers in a variety of journals dedicated to all areas of Chemistry. It is particularly noteworthy that this advance is observed across the country, from North to South, despite the differences in research conditions and the support available in the different Brazilian regions.

*"I understand that there has been a great advance of research in Chemistry in Brazil, especially in the last 20 years, covering all areas of Chemistry."*

I believe that the great challenge, in addition to the continuous support necessary for the progress of research, is to achieve greater international insertion. This is increasingly important because Brazil is geographically far from the major centers of scientific strength. Brazilian researchers often find it difficult to attend international meetings, with the exception perhaps of those in the State of São Paulo, where financial support from the São Paulo Research Foundation (FAPESP) has been significant. On the other hand, and despite the need to give due credit to the work carried out in the country, I am sometimes concerned by the occasional exaggerated local "radio broadcasting" of results claiming miraculous applications that are based on circumstantial evidence.

**For you, what have been the most important recent achievements in analytical chemistry research? What are the landmarks?**

Research in Analytical Chemistry has had a spectacular development in the last 30 years, to the point where *Analytical Chemistry* – an American Chemical Society journal – has a large following by the whole chemical community. This journal, along with other main journals covering analytical chemistry, have reached high relevance and notoriety among international journals.

From the present major areas of analytical chemistry, I can highlight the evolution of mass spectrometry as an analytical tool applicable to a wide range of problems. The advances in instrumentation and in ionization methods in mass spectrometry presently allow for qualitative and quantitative analyses with great selectivity, sensitivity and reliability, with applications ranging from simple substances to highly complex biomolecules.

**There are in Brazil, and in the world, several conferences on chemistry. To you, how important are these meetings to the scientific community? How do you see the development of national chemistry meetings in Brazil?**

Scientific meetings, in Brazil and around the world, are extremely important for several reasons, such as: updating of the researcher; opportunity to openly expose results; opportunity to establish contacts with other researchers; and the possibility of stimulating new ideas and new areas of research based on works presented at these meetings. There are currently excellent meetings in Brazil, especially those dedicated to specific areas of Chemistry. It has been possible to attract renowned scientists from different countries as Invited Lecturers and the topics discussed have covered the frontiers of the different areas. Large meetings, such as the annual meeting of the Brazilian Chemical Society or the six-monthly meetings of the American Chemical Society have become huge, and I believe that the mini-symposia embedded in these meetings turn out to be the most important events.

**Would you mention the recognitions have you received for your professional achievements?**

- Full Member of the Brazilian Academy of Sciences since 1980.
- Founding Member of the São Paulo State Academy of Sciences in 1976.
- Rheinboldt-Hauptmann Prize, 1998.
- Simão Mathias Medal of the Brazilian Chemical Society, 2001.
- National Order of Scientific and Technological Merit, Category “Grão Cruz”, 2005.
- Emeritus Professor at the Institute of Chemistry, University of São Paulo, 2015.
- Special issue of the International Journal of Mass Spectrometry in my honor, Volume 418, July 2017.
- Special issue of the journal ARKIVOC (Archive for Organic Chemistry) in my honor, Volume 2020.

**For you, what is the importance of the national funding agencies for the scientific development of Brazil?**

Funding agencies are essential for the progress of science in the country, and Chemistry in Brazil would not have had the development we see today without this support. In particular, I would like to mention robust programs such as: the Support Program for Scientific and Technological Development (PADCT), the Thematic Grants and the Research, Innovation and Dissemination Centers (CEPIDs) supported by the São Paulo Research Foundation (FAPESP); the National Council for Scientific and Technological Development (CNPq) Millennium Institutes; the Coordination for the Improvement of Higher Education Personnel (CAPES) and the CNPq scholarship programs. On the other hand, I believe that “Ciência sem Fronteiras” (Science Without Frontiers) program did not have the expected impact considering the enormous amount of resources allocated to the program. It is also noticeable that the participation of the private sector in promoting research in Brazil is still very timid despite of the importance of Chemistry to Brazil. Only Petrobras, the Brazilian energy company, has financed projects of various types, and more recently the Serrapilheira Institute, the first private non-profit institution, has been geared towards fostering science in Brazil.

*“There are currently excellent conditions in Brazil to achieve a solid specialization in Chemistry, given the existence of excellent research centers in several universities in the country.”*

**At the moment, the situation for scientific research in Brazil is one of decreasing investment. How do you see this situation, and what would you say to young researchers?**

Everything points to an exceedingly difficult situation in the short term, due to cuts in the budget for science and technology by the federal government. This situation becomes even more dramatic considering the effect that the new coronavirus pandemic will have on Brazil’s economy. The sharp depreciation of the Brazilian currency will also be an unfavorable factor for the purchase of imported supplies and equipment, and which may not be fully accounted by the current research grants. At this moment, I fear that young researchers will have great difficulty in obtaining significant research funds and it may be necessary for them to pool efforts in joint projects with other researchers from Brazil and abroad.

**What advice would you give to a young scientist who wants to pursue a career in analytical chemistry?**

There are currently excellent conditions in Brazil to achieve a solid specialization in Chemistry, given the existence of excellent research centers in several universities in the country. The most important thing at the outset is interest, scientific curiosity and a real motivation for Chemistry. I would recommend that undergraduate students start early participating in a good quality research group to become familiar with current problems, techniques and methodologies in Chemistry, and to see how research projects are actually carried out. Chemistry, like other human activities, requires a lot of dedication. Science has no timetable - when you find a good idea or a good experiment, try to do it completely. It should always be remembered that Chemistry as a successful science is 5% inspiration and 95% effort.

There is also an untapped potential to develop advances in chemistry in the private sector, and for those

with an entrepreneurial spirit, I believe there will be enormous possibilities in Brazil in the future. But above all, a young scientist must have ambition and passion for what she/he does.

### **How would you like to be remembered?**

I hope I have contributed to the education of many generations of chemists in Brazil and have been able to motivate them and encourage a critical spirit, curiosity and enthusiasm for the unknown, both for those who joined the job market after graduation and for those who chose an academic career.

### **How important is it for you to have been a professor and researcher at an institution like the University of São Paulo?**

I joined the University of São Paulo (USP) initially as a Visiting Professor at the former Faculty of Philosophy, Sciences and Letters, in November 1967, after completing a one-year postdoctoral tenure at Columbia University, New York. I became an Assistant Professor in 1968 and in 1970 I joined the newly created Institute of Chemistry at the same university (IQ-USP). I was promoted to Full Professor in 1977.

My experience as a professor and researcher at USP was very rewarding for several reasons: i) I had the satisfaction of participating in the beginning of formal Ph.D. programs at USP starting in 1970; ii) the high quality of USP students; iii) the research tradition established by the pioneers of IQ-USP, among them Professors Paschoal Senise, Ernesto Giesbrecht, Simão Mathias and Giuseppe Cilento; iv) the Ph.D. students, postdocs and undergraduate research interns who have been part of my research group since its creation in 1970 and to whom I am very grateful; v) the incomparable technical assistance received first by Antônio Geraldo Ayrosa, and from 1990 onwards by Jair Menegon, without whom it would not have been possible to develop research and instrumentation in our group.



Prof. Riveros in front of the FT ICR instrument at the IQ-USP laboratory, 2007.