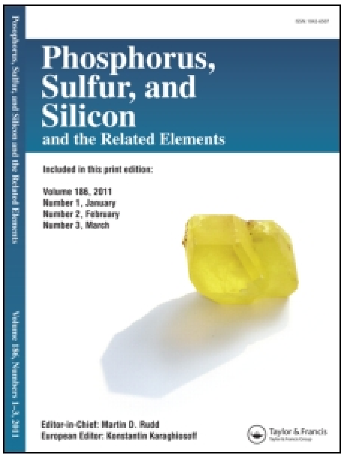

Phosphorus, Sulfur, and Silicon and the Related Elements

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FOREWORD

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FOREWORD

Professor Robert R. Holmes

Gordon and Breach wishes to take this opportunity to honor Professor **Robert R. Holmes**, the Editor-in-Chief of this journal, by publishing a selection of his foremost papers, which have appeared primarily in ACS journals over the last three decades. We are indeed grateful to the American Chemical Society for giving us permission to compile this issue, and also to the American Institute of Physics. The papers are listed in chronological order and thus follow the course of his investigations in the chemistry of main group elements.

Robert Holmes' early work had its impetus based on the latter part of his Ph.D. thesis under Professor Herbert C. Brown at Purdue University. It was an exploratory area at the time and dealt with the Lewis acid-base properties of the Group 3 and Group 5 halides. In a calorimetric study, it was learned that the order of acidities of the boron halides was $BBr_3 > BCl_3 > BF_3$, opposite from electronegativity considerations: H. C. Brown and R. R. Holmes. "The Heats of Reaction of Pyridine and Nitrobenzene with Boron Trifluoride, Trichloride and Tribromide. The Relative Acceptor Properties of Boron Halides," *J. Am. Chem. Soc.*, **78**, 2173–2176 (1956).

Professor Holmes began his academic career at Carnegie Institute of Technology, now Carnegie Mellon University, at the age of 24. His initial studies involved work on the phosphorus trihalides with amines. This led to the formation of very interesting cage compounds. Both $P_4(NMe)_6$ and $S_4P_4(NMe)_6$ were reported from his laboratory to have structures analogous to the adamantyl forms of P_4O_6 and P_4O_{10}, respectively. While extending the chemistry of this class of substances, work was started on Lewis acidities of the Group 5 pentahalides. This opened the way to a long-term interest in pentacoordinate molecules of main group elements, especially those of Groups 4 and 5. At this juncture, in 1962, Dr. Holmes accepted a position at Bell Telephone Laboratories in Murray Hill, New Jersey where he continued to develop the structural and spectroscopic chemistry of the series of phosphorus chlorofluorides, PCl_nF_{5-n}. Interestingly, no analogous series is known with the isoelectronic anionic series with silicon, $SiCl_nF_{5-n}^-$.

Prof. Holmes then moved to his present position as Professor of Chemistry at the University of Massachusetts in Amherst in 1966 and pursued a broad program of research that explored the structure and molecular dynamics of nonrigid pentacoordinate molecules of main group elements. This led to the formation of structures extending from trigonal bipyramidal to square pyramidal for five-coordinate cyclic derivatives of phosphorus, arsenic, antimony, silicon, germanium, and tin. Solid state displacement coordinates typified by those described in the oft-cited paper on cyclic phosphorane structures [R. R. Holmes and J. A. Deiters. "Structural Distortions of Cylic Phosphoranes and the Berry Exchange Coordinate. A Quantitative Description," *J. Am. Chem. Soc.*, **99**, 3318–3326 (1977)] favored the Berry exchange process for pseudorotation and not the "turnstile" process. As a result of his extensive investigations in phosphorus chemistry, Professor Holmes was asked to write an ACS monograph on the topic. By the time the task was completed, the monograph was issued in two volumes: R. R. Holmes. "Pentacoordinated Phosphorus-Structure and Spectroscopy," Volume I, ACS Monograph 175, American Chemical Society, Washington, D.C., 1980, 479 pp.; and R. R. Holmes. "Pentacoordinated Phosphorus-Reaction Mechanisms," Volume II, ACS Monograph 176, American Chemical Society, Washington, D.C., 1980, 237 pp.

Work was then more heavily concentrated on the role of pentacoordinated phosphorus in nucleophilic substitution reactions in both enzyme and nonenzyme environments. A molecular mechanics model was developed that reproduced X-ray structures of nonrigid phosphorane molecules that allowed for structural change along the Berry pseudorotational coordinate. This was particularly successful in interpreting active site interactions in the phosphoryl transfer enzymes, ribonuclease and staphylococcal nuclease.

In the last few years, his research has diverged to include the formation of new organooxotin clusters described in a series of papers with tin nuclearities up to seven, e.g., tin in a rare double cube geometry, studies of pentaoxyphosphoranes with varying ring sizes, from five- to eight-membered, and companion studies of isoelectronic anionic silicates. *Ab-initio* molecular orbital calculations have complemented the experimental approach in establishing factors favoring the greater reactivity of hypervalent silicon compared to phosphorus.

These studies have been followed by the structural characterization of a series of phosphorus compounds with P—S coordination giving geometries between square pyramidal and octahedral. Efforts to induce silicon to enter into higher coordination are underway as well as the use of nitrogen donor atoms, important as potential coordinating agents at enzymatic active sites. In this regard, the theoretical and experimental work of Dr. Holmes' group on cyclic pentaoxyphosphoranes has led to a discrimination among models for the active site geometry of cAMP (cyclic adenosine monophosphate) in phosphodiesterases and protein kinases.

The complete publication list of Professor Holmes and his coworkers is presented here with an asterisk placed beside those that are reprinted in full in this volume. Prof. Holmes would like to express thanks to his students, post-doctoral associates, and to visiting scientists with whom he has worked closely. It is because of their dedication and interest that his achievements were possible. Particular thanks are due Professor Roberta O. Day who performed the X-ray structural investigations, Professor Joan A. Deiters of Vassar College who carried out many of the theoretical studies; and his wife, Joan, who assisted not only in computational work but also in editing this journal. Dr. Holmes gives his heartfelt thanks in appreciation of their fine work that has made his academic career so enjoyable.