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Publisher *Taylor & Francis*

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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

### Preface

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**To cite this Article** Veiderma, Mihkel(1990) 'Preface', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, xli — xliii

**To link to this Article:** DOI: 10.1080/10426509008038904

**URL:** <http://dx.doi.org/10.1080/10426509008038904>

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## PREFACE

### Phosphorus Chemistry in 1989, a review of the Tallinn Conference

International conferences on phosphorus chemistry have lasting traditions. The first of them was held in Heidelberg in 1964, the 11th—25 years later in Tallinn.

Traditionally, phosphorus and its compounds have been used mainly in fertilizers, in matches, as chemical reagents etc. The manufacture of these materials at present exceeds 20 million metric tons per year as calculated to elemental phosphorus. During the last decades, however, a significant qualitative change has taken place in the phosphorus chemistry.

First, the important role of phosphorus in biochemical processes of the metabolism and energy exchange of living matter as well as in intellectual activities of humans has become better known. In good reason, phosphorus can be called the element of life and intellect.

On the other hand, the negative sides of phosphorus as a life stimulant have made themselves obvious in the forms of ever-increasing eutrophication of water-bodies and environmental pollution in the places where phosphorus containing materials are excavated or processed.

Second, the extraordinary ability of phosphorus to form a large variety of chemical bonds and compounds has become widely established. We could like here to point to the importance of research in the chemistry of mono- and di-coordinated phosphorus and organophosphorus ligands, the fast-growing application of phosphorus compounds in biochemical studies and organic synthesis.

Third, phosphorus has become an element of many uses in new materials for modern technologies. To name just a few: extractives, ion exchangers, complexing agents, liquid membranes, selective catalysts, synthetic hormones, artificial biomaterials, pesticides, functional ceramics and bonding materials, solid state lasers, fiber optics and electronics.

Phosphorus has become an element bringing together scientists of many different fields. The phosphorus chemistry has become more and more interdisciplinary.

The 11th Conference of Phosphorus Chemistry was organized by the Estonian Academy of Sciences (Institute of Chemical Physics and Biophysics) and Tallinn Technical University together with the Academy of Sciences of the USSR (the Scientific Council of Organoelement Compounds, A. N. Nesmeyanov Institute of Organoelement Compounds in Moscow and A. E. Arbuzov Institute of Organic and Physical Chemistry in Kazan) and the Academy of Sciences of the Ukrainian SSR (Institute of Organic Chemistry in Kiev). The Conference was held under the IUPAC sponsorship.

By number of participants the Tallinn Conference was the largest—503 scientists from 32 countries attended the conference, 207 from the USSR among them. The number of 30-minute lectures was 141 and posters—350. The Opening Lecture on the topics “Principles of Phosphorus Chemistry: the Reality of Molecular States” was presented by Professor H. Bock (FRG).

The abstracts of lectures and poster communications in three volumes were given to the participants at the registration. From the contributions received, the National Scientific Board rejected 15 as not corresponding with the theme of the conference. The accepted presentations were subdivided in five sections: Synthesis, Structure, Stereochemistry and Reactivity of Organophosphorus Compounds (53 lectures and 161 posters), Chemistry of Phosphorus Compounds in Particular Coordination and Bonding (27 lectures and 20 posters), Chemistry of Phosphorus Coordination Compounds (18 lectures and 38 posters), Biochemical Aspects of Phosphorus Chemistry (21 lectures and 61 posters), Chemistry of Phosphates, Including Condensed Phosphates and Apatites, and Other Inorganic Phosphorus Compounds (22 lectures and 70 posters). The level of the scientific program, according to the opinion of International Board, was high in both basic and applied research areas. In the following we give some examples of the new scientific results presented at the conference, in a small overview which in no means is complete and of course may reflect the individual interests and impressions of the organizers.

In synthesis the methods of phosphorylation for making organophosphorus compounds of nontraditional structures have been developed, including the syntheses on the basis of 1,3,2λ<sup>5</sup>-dioxaphospholanes, the preparation of 1,4-diphospha-2,3,5,6-tetrahydroxycyclohexanes etc. The chemistry of making tertiary phosphines through phosphinous complexes has been carefully studied. A number of cyclic structures with phosphorus-containing groups in the main chain or as a substituent have been obtained.

In the studies of kinetics and mechanisms of the reactions with phosphorus compounds, thion-thiol rearrangements, phosphotropic tautomerism, enolization of phosphoryl group have been addressed. Many interesting contributions dealing with the application of physical methods and quantum chemistry calculations in the elucidation of structure and reactivity of organophosphorus compounds have been presented.

In Section 2 the results obtained in the field of phosphorus in lower coordination states were presented dealing with the reactivity of these compounds in coordination chemistry which seems to remain one of the most promising areas of phosphorus chemistry in near future. New approaches to initiation and stabilization of the compounds of 3-valent two-coordinated phosphorus, 5-valent three-coordinated and 5-valent two-coordinated phosphorus have been created, cations with two-coordinated phosphorus have been obtained and their reactivity established.

The main trends in the chemistry of phosphorus coordination compounds (Section 3) included the studies of the new ways of stabilization of labile phosphorus-containing structures in the coordination sphere of a metal, use of new types of phosphorus-containing complexones for coordination binding of metal ions and search for new catalysts for chemical and biochemical processes. Very impressive in this field were studies on the ways of synthesis of coordination compounds using "bare" phosphorus ligands, i.e. the structures which are based on linear as well as cyclic phosphorus units P<sub>2</sub>–P<sub>6</sub> without substituents at phosphorus. This new area in coordination chemistry is very important from theoretical point of view and it promises new achievements in the synthesis of phosphorus compounds based on extraordinary reactivity of coordinated P-ligands.

Biochemical aspects of phosphorus chemistry at the conference were represented with studies in three areas—the synthesis of oligonucleotides and their analogues, the synthesis of phosphoaminoacids and elucidation of the mechanisms of their biological activity, the studies on the mechanisms of the reactions of organophosphorus substrates and inhibitors with enzymes. New interesting data were presented on antiviral effects of organophosphorus compounds.

In Section 5 the work on synthesis, structure and application of inorganic compounds of phosphorus was discussed, including apatites, monomeric and polymeric phosphates, N-, S- and F-substituted phosphates. The interest towards apatite has greatly increased because of the new technological applications of this material in ion exchangers, luminophores, catalysts, special ceramics and, as a biocompatible carrier material, in medicine. In preparative chemistry of phosphates the studies on the compounds with P-N, P-S and P-F as well as the compounds with low oxidation level have largely replaced the work with traditional phosphorus-oxygen substances. The most interesting types of these materials were nitridophosphates, fluorophosphates, thiophosphates, borophosphides, P-N-B-polymers, alkyl- and aryl-substituted phosphazenes and other polymers on their basis. By oxidation of phosphorus with oxygen in gas phase, pure  $P_4O_6$  has been obtained and can be used as a phosphorylating agent in the synthesis of various organophosphorus compounds. The main contribution in the chemistry of monomeric and polymeric phosphates was given by the work on the synthesis of the compounds with several different metal cations in combination with new forms of phosphate anions with ring-shape, chain-like and branched structures. The synthesis of the double ultra-phosphates was announced at the conference. Many of the synthesized compounds have useful properties.

An agreement between IUPAC and Gordon and Breach made it possible to publish these proceedings in *Phosphorus, Sulfur and Silicon*. They consist of 4-page synopses of the lectures as well as the abstracts of the posters which were presented. The proceedings reflect the latest scientific achievements and the future trends in the chemistry of phosphorus and undoubtedly will be a valuable tool in the hands of phosphorus chemists.

The organizers wish to express their sincere thanks to all those who contributed to making this conference a success: the speakers, the chairpersons, the members of the International and National Scientific Boards and many helpful colleagues in the Institute of Chemical Physics and Biophysics and Tallinn Technical University.

We hope that in addition to the active participants, the 44 accompanying ladies and guests enjoyed the social events: the get-together party, concerts and sight-seeing excursions, the conference dinner which contributed to renewing old and forming new friendships. We hope that all participants will remember these interesting and stimulating days in Tallinn and we are looking forward to our next Phosphorus family meeting in Toulouse in 1992.

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