The Role of the Solvent in Chemical Reactions

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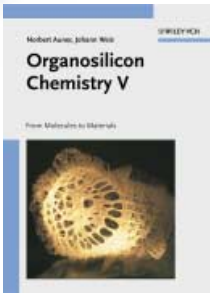
Published in:
Angewandte Chemie

Publication date:
2004

Organosilicon Chemistry V



From Molecules to Materials. By *Norbert Auner* and *Johann Weis*. Wiley-VCH, Weinheim 2003. 838 pp., hardcover € 159.00.—ISBN 3-527-30670-6

Organosilicon Chemistry V is the fifth volume in a series in which Volumes I to IV have already appeared. Those four volumes contained the contributions presented at the "Munich Silicon Days". The conference series has now developed to become the "European Silicon Days", the first of which took place in Munich in 2001, and has led to the present volume, in which the editors have again taken on the task of collecting together the results in this fascinating area of Main Group chemistry that were presented there. The 120 contributions cover a wide range of topics, from the chemistry of single silicon atoms to extended networks. Thus, one can expect to find here a representative cross-section through modern silicon chemistry.

As in the previous volumes, several contributions are devoted to the synthesis of low-valent silicon compounds such as silylenes and unsaturated species and to investigating their properties. One especially fascinating topic is the search for ways to stabilize compounds with a triple bond to silicon (RSi≡E). Possible routes are discussed and some first indications are given. By using thermally generated silicon atoms, it has been shown possible to isolate a number of unusual reactive silicon species in a matrix. Results on the generation of cations with threefold-coordinated silicon have been a topic of controversy in the last few years. Here, in addition to some theoretical considerations, the authors describe several studies on bridged and donor-stabilized silicon cations.

The chemistry of silyl anions ranges from their synthesis to their application in building up silicon-containing polymers. There are articles dealing with silicon–nitrogen compounds, namely hydrazines, hydroxylamines, and cyclosilazanes. Silicon-containing transition-metal complexes constitute a very wide field of research, covering topics that range from silanolates to ferrocenylsilanes, and from applications in catalysis to nonlinear optics.

An important group of articles are those with an industrial background, covering topics as varied as basic considerations about methods for "sustainable production" of silicon, the optimization of the Müller–Rochow synthesis and modified versions of it, and the great variety of uses of silicones and ways of modifying them. For example, one group is investigating the use of polycarbosilanes as building blocks for producing membrane materials. The preparation of nanostructured SiO materials has proved to be an especially fruitful area of investigation, and the production of SiO_2 particles by various techniques is leading to many new possibilities. Aluminosiloxanes are discussed as molecular models for aluminum silicates, and the results on spinel-type Si/Al/O/N compounds form a link to solid-state chemistry. Another important aspect that must not be forgotten is that of the biological, medical, and pharmaceutical applications of silicon compounds and related studies.

Thus, the book could be said to present a good overview of silicon chemistry. However, the full scope of the subject cannot be easily grasped in this form, as the editors have not grouped the contributions according to topic areas, for example under chapter headings. Consequently, after reading the editors' introduction in which they discuss the most important directions of current research in silicon chemistry, the reader seeking a specific topic must scan through the titles of the articles or use the subject index. Furthermore, one expects to find guidance in the literature citations that will direct one to further reading on a topic, but some of the authors fail to help the reader in that respect. Most of the articles, in accordance with the year in which the symposium took place, cover the literature up to 2000, and some have even added publications from 2002. On the other hand, a few of them give no references at all. However, to sum up, the book provides readers with the opportunity to get a good overview of current research on silicon chemistry.

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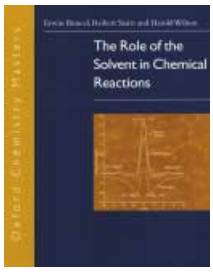

(Series: Oxford Chemistry Masters, Vol. 6). By *Erwin Buncel*, *Robert Stairs* and *Harold Wilson*. Oxford University Press, Oxford 2003. ix + 159 pp., paperback £ 27.50.—ISBN 0-19-85110-0

Recent decades have witnessed an enormous increase in our understanding of medium effects on a large variety of chemical processes. It is now fully recognized that the reaction environment exerts a dominating influence on reaction kinetics and thermodynamics and on catalytic efficiencies. Comparisons of analogous reactions in the gas phase and in the liquid phase have been illuminating. Experiment and theory went hand in hand in these developments, and most recently the rapidly growing contributions of molecular dynamics computer simulations have greatly contributed to an in-depth understanding

of medium effects at a molecular level. The present book, written by three Canadian chemists, provides a useful introduction to solvent effects on chemical reactions. Of course, the topic is much too broad and extensive to be handled comprehensively and profoundly in a book of only 159 pages.

After a general introduction (Chapter 1), attention is given to the solvent as a medium, emphasizing noncovalent interactions and solvation of ionic and uncharged solutes (Chapter 2). Chapter 3 considers the solvent as a reaction participant, with particular attention to acid–base properties and oxidation–reduction processes. Empirical correlations of solvent effects (chemometrics) employing a wide variety of solvent parameters are treated in Chapter 4. In Chapter 5 theoretical approaches to solvent effects (semi-empirical and ab initio quantum-mechanical methods, as well as Monte Carlo/molecular dynamics computer simulations) are briefly reviewed. Chapters 6 and 7 are devoted to case studies: dipolar aprotic solvents (Chapter 6), and acidic/basic/chiral solvents and ionic liquids (Chapter 7). Lastly, Chapter 8 contains some concluding observations and references to more comprehensive handbooks. Some chapters give a few problems; no answers to these problems are provided. The appendix (7 pp.) contains tables of properties of selected solvents, solvent property parameters, and other relevant data. The bibliography (13 pp., about 450 references, even a few from 2003) contains both book and journal references.

Overall the book is rather conventional in its approach, and I have some doubts about whether it will generate much enthusiasm among present-day chemistry students. For example, the thrilling computational results obtained by Jorgensen and co-workers for the identity reaction of chloride ions with chloromethane in the gas phase, in DMF, and in water (shown on the cover of the book) are discussed in only four sentences. The book does not even pay any attention to the enormous kinetic consequences of going from the gas phase to a liquid reaction medium.

Although some novel developments are briefly discussed (ionic liquids, density-functional theory), other exciting recent topics are largely ignored (including organic chemistry in water, the application of microwaves in suitable media, supercritical fluids, etc.). The rather strong emphasis on chemometrics is, in my view, not fully warranted, since it may give undergraduates the impression that the understanding of medium effects depends substantially on statistical analyses of data sets for (selected) solvents. It must also be regretted that the outcome of these correlations receives too little attention with regard to their meaning and usefulness. For those interested in water and mixed binary aqueous solvent systems (the media used in most reaction mechanistic studies) the brief and sometimes vague discussion of hydrophobic hydration is hardly satisfactory, because some modern developments have not been taken into account. Hydrophobic interactions are hardly discussed at all. Minor weak points include the absence of a clear distinction between transition state and activated complex, the use of both the terms free energy and Gibbs energy, the absence of dipole moments in the table of solvent properties, and the statement that volumes of activation are inherently more accurate than entropies of activation.

In summary, the book can be a useful companion for undergraduate students in their first attempts to grasp the importance of solvent effects. Within a relatively brief format, a wide variety of relevant topics are mentioned and briefly introduced. But after this initiation the student should rapidly proceed to more comprehensive and in-depth treatments of the important issue of environmental effects on chemical processes.

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DOI: 10.1002/anie.200385110

