

## Book reviews

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*Organosilicon Chemistry*, by S. Pawlenko, de Gruyter, Berlin, New York, 1986, xii + 186 pages, £70, ISBN 3-11-010329 X.

This is, I am sorry to say, a very bad book. The author rightly saw that there is a need for a monograph presenting the most important aspects of organosilicon chemistry in a simple form, but he has failed badly in his attempt to meet that need.

The main faults of the book can be roughly classified as: (1) invalid assertions, including very inaccurate generalizations; (2) misjudgements of the relative importance of various aspects of the subject; and (3) errors of English so serious as to be confusing or misleading. Examples of each type are as follows:

(1) (a) "All silicon bonds spontaneously convert to silicon-oxygen bonds."

(b) "The hydrolysis of C-I and C-Br bonds, which are easily polarized, also proceeds by an  $S_N2$  reaction mechanism, and is also rapid."

(c) (In a discussion in the case of heterolytic fission of the Si-C bond.) "The Si-C bond is always polarized with the partial positive charge on the Si atom. Depending on the substituent group on the silicon and carbon, the polarization may be enhanced or weakened. Positively charged groups on the carbon (especially hydrogen) and negatively charged groups (especially oxygen) on the silicon decrease the bond polarization and stabilize the bond."

(d) "The rate of chloroorganosilane hydrolysis is the same as that of an ionic reaction. The rate of hydrolysis is the same for bromo- and iodoorganosilanes."

(e) "Silicon can form a double bond to carbon but only if certain rather bulky groups are substituents of the carbon."

(f) "There is an important ( $d \leftarrow p$ ) $\pi$  component in the Si-N bond of organosilyl nitrogen compounds. Nucleophilic attack on the silicon atom is therefore enhanced."

(g) "Stable tris(tri-*t*-butylsilyl)ammonium bromide  $\{(H_3C)_3C)_3Si\}_3N^+ HBr^-$  precipitates from a pentane solution of amino-tri-*t*-butylsilane through which hydrobromic acid is bubbled at 0°C." (The product is actually  $[(H_3C)_3C)_3SiNH_3Br]$ .)

(h) "Organosilyl ethers are liquids which can be distilled."

(i) Base-catalysed solvolysis of organosilicon hydrides is stated to involve rate-determining formation of the pentacoordinated intermediate followed by rapid loss of hydride ion. (In fact the slow step involves the breaking of the Si-H bond.)

(j) (Of silanetriols) "Only aryl organosilanetriols are known, e.g. phenylsilanetriol." (In fact the crystal structure of cyclohexylsilanetriol has been determined.)

(2) (a) In the account of the preparation of  $R_4Si$  species attention is concentrated (with a detailed diagram of the complex vacuum train) on their formation by treatment of  $SiH_4$  (produced within the system from  $SiCl_4$ ) with  $RLi$  compounds; this is possibly the last method a practising organosilicon chemist would use, except perhaps for the reaction of  $SiCl_4$  with an alkyl halide and aluminium in a fused salt, which is described as "a convenient process"!

(b) In the discussion of preparation of  $R_xSiH_{4-x}$  compounds, the one method for which detailed instructions (again with a detailed diagram of the apparatus) are given involves the reaction of  $H_2SiCl_2$  and  $Me_2Zn$ , which no-one would dream of using these days.

(c) For the preparation of organosilicon pseudohalides, the preferred procedure is said to be that involving the reactions of organosilicon chlorides with alkali metal pseudohalides in a fused salt mixture, and again a detailed sketch of the apparatus is given. I doubt whether anyone other than the originator of this method has ever used it.

(d) In the discussion of application of ESR spectroscopy to organosilicon compounds, the two examples considered both involve radical anions,  $[(Me_3Si)_2-C=C=C(SiMe_3)_2]^\ddagger$  and  $[R_2Si=SiR_2]^\ddagger$ , and there is no mention of simple silicon-centred radicals such as  $R_3Si^\cdot$ .

(3) (a) (In the discussion of the transition state in  $S_N2$  hydrolysis of organic bromides). "It was supposed that the orbital of the free electron pair in the hydroxyl ion and the back-lap of the C-Br antibonding orbital might be overlapped. The HO-C bond could thus be formed before the C-Br bond was dissolved."

(b) "Dimethylmethylenesilane can be identified and preserved at  $-196^\circ C$ , or collected from some reactive compounds."

(c) (In an outline of the preparation of organosilanols.) "The reaction medium may remain neutral or nearly neutral during the preparation, and the organosilanols may be separated immediately into a solvent phase."; and (of organosilyl esters of inorganic acids) "They fume intensely in the open air and may be prepared in the absence of moisture." (In each case *may* should be replaced by *must*.)

(d) "Some organosilanediols are isomorphous. Bis(pentafluorophenyl)silanediol, for example, has melting points between  $115$  and  $165^\circ C$ ." (The correct term is polymorphic.)

(e) "The ability of an organosilicon atom to form a silicon-metal bond is differential."

(f) "Unlike inorganic monosilane  $SiH_4$ , the hydroorganosilanes are all non-inflammable in the open air." (What is meant is that they do not ignite spontaneously in the air.)

There are also numerous spelling and typographical errors. Among the many well known names incorrectly presented (with correct versions in parentheses) are: Amstage (Armitage), Aulett (Aylett), Brock (Brook), Equidie (Escudié), Fowlis (Fowles), Gasper (Gaspar), Gilmann (Gilman), Gragg (Cragg), Harrad (Harrod), Jaekson (Jackson), Lippert (Lappert), MacDiarmed (MacDiarmid), Mitehell and Mitsell (Mitchell), Pidcook (Pidcock), Rubottúm (Rubottom), Sheldric (Sheldrick), Shipperfield (Chipperfield), and Showen (Schowen). (I myself appear as Elaborn.) Where surnames are correct, the initials frequently are not.

I have written at such length to demonstrate that this book should be kept out of the hands of anyone other than well-informed and discerning organosilicon chemists (who will not be misled, and who could find it a useful source of references). It would be especially harmful to students, particularly those embarking upon research in organosilicon chemistry. I regret having to criticize it so severely, because the author has previously served organosilicon chemists well in his work for the Houben-Weyl series. Moreover, his objective was a good one, and with a little help from specialists, he could have produced a useful monograph; given some guidance

from a practising organosilicon chemist, attention to the English by an appropriate British or American chemist, and careful proof-reading it could have been transformed with relatively little effort. Indeed, I hope that the publishers will even now consider producing an appropriately amended version, which could find a good market.

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*The Periodic Table of the Elements*; by R.J. Puddephatt and P.K. Monaghan, 2nd edition, Clarendon Press, Oxford, 1986. x + 102 pages. £6.95. ISBN 0-19-855516-4.

The expressed aim of this book is to present, at a level suitable for first year students in universities and technical colleges (and for senior secondary school students), the periodic behaviour of the elements and their compounds. This is an exceptionally difficult task, guaranteed to produce universal criticism. Surely, every lecturer in inorganic chemistry reading this book feels that it is so like a course that they have given/are giving/are about to give, that they could have made a much better job of it themselves; after all, it would have been *so* much better if the authors had missed out A, expanded B and included C. This, of course, boils down to the fact that they did not have the courage to do what Dick Puddephatt and Paddy Monaghan have done, which is to present a clear and concise description of periodicity in 100 pages, at a price that all students (even those with outstanding bar bills) can afford. It is easy to criticize a book like this (I'll prove this in the next paragraph), but it is more meaningful to praise it. It gently takes the student, in a non-mathematical manner, through simple atomic structure into the Aufbau principle, via the Schrödinger wave equation. Having discussed the Group classification, the periodic effects upon atomic and bonding properties of the main-group elements are presented, including such topics as ionization energies, electron affinities, covalent and ionic radii, electronegativity, polarizability, ionic and covalent bonding, and oxidation state. The structures and binding energies of the main-group elements are then discussed, followed by examples of periodicity manifest in the halides, hydrides, methyls, oxides and sulfides of these elements. Catenation is examined, as is the diagonal relationship and the anomalous behaviour of the first row elements. Similar, but briefer, consideration is then given to the transition elements, the lanthanides and the actinides. Each chapter is concluded by a (very small) number of rather trivial problems, and the inclusion of some more probing questions would have strengthened the already impressive pedagogical value of this book.

This text is outstandingly good when describing trends, the heart of periodicity, and the excellent illustrations support the lucid text. Both authors are demonstrably experienced teachers, and this text could be understood by the weakest of students. Nevertheless, this book does have a serious weakness, and this relates to the use of valence bond theory throughout the volume. This out-dated, erroneous and misleading theory (in the populist version presented here) is poison to the minds of impressionable students, and (like pornography) they should only be exposed to it