TABLE I

Compound	Ion	A_p, e.v.	$D(X_3Si-SiX_3)$, kcal. mole^{-1}
Si_2H_6	SiH_3^+	11.85 ± 0.05	81.3 ± 4
	SiH_2^+	11.94 ± 0.04	......
Si_2Cl_6	$SiCl_3^+$	11.55 ± 0.1	$\leqslant 85 \pm 6$

measured using a Consolidated Electrodynamics Corporation Model 21-103C mass spectrometer modified to allow magnetic scanning. The method used to evaluate the appearance potential data has been described previously.[6]

The silicon–silicon bond dissociation energy in disilane can be calculated from the appearance potentials of the SiH_3^+ ion from silane (12.40 e.v.)[6] and disilane (Table I) and the heats of formation[3] of the two compounds. Thus, if

$$SiH_4 + e^- \longrightarrow SiH_3^+ + H + 2e^- \qquad (1)$$

and

$$Si_2H_6 + e^- \longrightarrow SiH_3^+ + SiH_3 + 2e^- \qquad (2)$$

then

$$\Delta H_f(SiH_3) = A_p(2) - A_p(1) + \Delta H_f(Si_2H_6) - \Delta H_f(SiH_4) + \Delta H_f(H)$$

assuming the SiH_3^+ ions are energetically identical in both reactions. The resulting value of $\Delta H_f(SiH_3) = 49.2$ kcal. mole^{-1} is in excellent agreement with the previous value of 49.5 kcal. mole^{-1} determined by consideration of hydrocarbon ions from several alkylsilanes.[6] This value for the heat of formation of the silyl radical, taken with the heat of formation of disilane,[3] leads to a value of $D(H_3Si-SiH_3) = 81.3$ kcal. mole^{-1}. The appearance potential of the SiH_2^+ ion from disilane also has been measured. Assuming formation by the process

$$Si_2H_6 + e^- \longrightarrow SiH_2^+ + SiH_4 + 2e^- \qquad (3)$$

the heat of formation of SiH_2^+ is calculated to be 285 kcal. mole^{-1}, in good agreement with the value of 282 kcal. mole^{-1} derived from silane.[6]

Since the heat of formation of hexachlorodisilane is not known, the above procedure cannot be applied to this compound. However, the Si–Si bond dissociation energy can be calculated from the $SiCl_3^+$ appearance potential (Table I) and the ionization potential of the trichlorosilyl radical (7.88 e.v.).[6] The resulting value is $D(Cl_3Si-SiCl_3) = 85$ kcal. mole^{-1}. The near equality of the silicon–silicon bond strengths in Si_2H_6 and Si_2Cl_6 is interesting, being consistent with the observation that Si–Si bond lengths in the two compounds are very similar,[7] as are the silicon–hydrogen bond dissociation energies in silane and trichlorosilane.[6]

The higher values for D(Si–Si) reported here permit a better understanding of recent observations of the properties of several substances with silicon-silicon bonds[2,8] than do the earlier results.

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[6] W. C. Steele, L. D. Nichols and F. G. A. Stone, *J. Am. Chem. Soc.*, in press.

[7] L. O. Brockway and J. Y. Beach, *ibid.*, **60**, 1836 (1938).

[8] F. G. A. Stone, "Hydrogen Compounds of Group IV Elements," Prentice-Hall, Englewood Cliffs, N. J., 1962.

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FERROSILOXANES AND FERROSILICONATE ANIONS[1]

Sir:

Monomeric alkylsiloxanes of definite composition, in which the silicon-atoms are partly replaced by transition metals of the VIII group are practically unknown.[2] We now have succeeded in sythesizing a representative of the series of ferrosiloxanes and wish to describe its preparation, properties and derivatives, while further work on this class of compounds is in progress.

Three moles of an alkali trimethylsilanolate react in ethereal solution with one mole of anhydrous ferric chloride to give a brownish precipitate of alkali chloride (containing ferric oxides) and a brown solution of tris-trimethylsiloxy-iron, according to the equation[3]

$$3(Me_3SiO)Na + FeCl_3 \longrightarrow 3NaCl + (Me_3SiO)_3Fe$$

Evaporation of the solvent and sublimation of the residue *in vacuo* affords a 45% yield of the new compound with the analytical composition $Me_9Si_3O_3Fe$ (Fe calcd. 17.27; found, 17.73).

The ferrosiloxane forms yellow-green waxy crystals with m.p. 179–181° and subl. temp. 130°/1 mm. It shows extremely high solubility in common organic solvents, but is quite sensitive even against traces of moisture and is quickly hydrolyzed, trimethylsilanole and ferric hydroxide being formed. The pure compound, however, is thermally stable up to its melting point, after which its color slowly turns to red-brown with decomposition. According to cryoscopic molecular weight determinations in benzene as a solvent the compound is strictly dimeric (calcd., 646.6; found, 636), a result which was to be expected from our earlier investigations of analogous alumino- and gallo-siloxanes.[1] We therefore propose the structure I, which is supported by the infrared spectrum (in Nujol mull), with strong bands at 7.95, 8.02, 10.00 and 10.57 (ν Si–O–Fe), 11.80, 13.17 and 13.38 μ. The typical infrared lines of the bridging siloxy groups appear at 12.32 and 13.20 μ and are in good agreement with the corresponding lines in the spectra of the Al- and Ga-compounds. The structure of the latter has in turn been confirmed by n.m.r. spectra.[1] N.m.r. investigations in CCl_4 solutions of I and TMS as an internal standard, however, resulted only in quite broadened and unsharp proton signals with very high chemical shifts up to higher fields and proved the paramagnetic character of I.

Among the chemical properties of the new ferrosiloxane the reactions with alkalitrimethylsilanolates are most remarkable. Equimolar solutions of I and a sodium or potassium trimethylsilanolate in CCl_4 undergo an exothermic reaction at room temperature and quantitative yields of the alkali salts of the new tetrakis-trimethylsiloxy-iron-III-

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[1] Heterosiloxanes, IX; Part VIII: H. Schmidbaur and M. Schmidt, *Angew. Chem.*, **74**, 328 (1962).

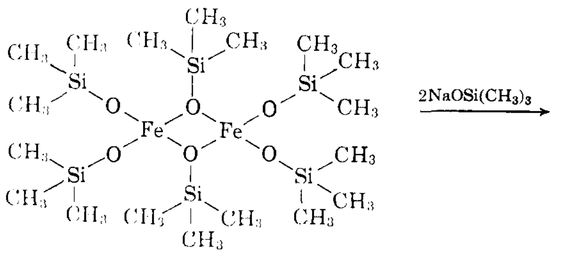
[2] K. A. Andrianov and A. A. Zhdanov, *Izvest. Akad. Nauk SSR, Otdel. Khim. Nauk*, 1590 (1959); *C. A.*, **54**, 8687 (1960).

[3] It is important that the ferric chloride solution is added to the silanolate solutions (and not *vice versa*), otherwise, only poor yields if any, are obtained. With the potassium trimethylsilanolate and homologous alkylsilanolates the reaction proceeds in the same manner.

anion are precipitated. Calcd. for $Na[Fe(OSiMe_3)_4]$: Na, 5.28; Fe, 12.82. Found: Na, 5.47; Fe, 13.20. Calcd. for $K[Fe(OSiMe_3)_4]$: K, 8.66; Fe, 12.37. Found: K, 8.71; Fe, 12.51.

Not melting up to more than 200° and insoluble in organic solvents these "heterosiliconates" are typical salt-like substances. The infrared spectra of the sodium and potassium salt (in Nujol mull) show a new and characteristic [ν Si–O–Fe]- band at 11.05 and 10.92 μ, respectively. All the bands of the spectra are almost independent of the cation and exhibit the existence of a discrete $[Fe(OSiMe_3)_4^-]$ anion, as proposed in formula II.

The compounds I and the anion II again[1,4,5] are examples for a class of "complex silicones," which give evidence that the siloxy group, in spite of its strong $d\pi p\pi$ bond character between silicon and oxygen is able to act as a mono- and divalent ligand to form stable complex compounds. The preparation, properties, n.m.r. and infrared investigations of analogous alumino- and gallo-siliconate anions will be reported elsewhere.[5]



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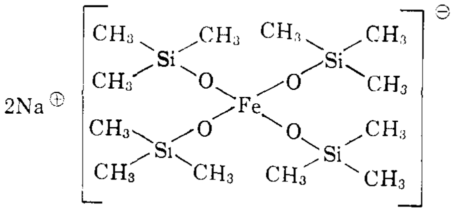

II

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(4) H. Schmidbaur and M. Schmidt, *J. Am. Chem. Soc.*, **84**, 1069 (1962).

(5) H. Schmidbaur and M. Schmidt, *Angew. Chem.*, **74**, 589 (1962).

BOOK REVIEWS

Notes on Molecular Orbital Calculations. By JOHN D. ROBERTS, Professor of Organic Chemistry, California Institute of Technology. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1961. ix + 156 pp. 15 × 23 cm. Price, $4.95.

This small book very effectively shows how the organic chemist can use Hückel LCAO molecular orbital theory in its simplest form to obtain values of bond orders, atomic charges, free-valence indexes, and other quantities and conclusions of importance to him. Numerous exercises give opportunity for helpful practice in the application of methods and rules.

The chapters are entitled "Atomic Orbital Models" (22 pages), "Molecular Orbital Calculations. Electronic Energy Levels" (30 pages), "Bond Orders, Free-Valence Indexes, and Charge Distributions" (8 pages), "Application of Group Theory to Simplification of MO Determinants" (12 pages), "Aromaticity" (4 pages), "Molecules with Heteroatoms" (5 pages), "Nonplanar Systems" (9 pages), "Molecular Orbital Theory and Chemical Reactivity" (14 pages), "Approximate Methods" (10 pages) and "Higher-Order Calculations (3 pages). Following these are three Appendices, one on solutions of typical exercises, the second including reprints of two articles, the third a brief bibliography of reference books.

The appearance of the book is very attractive, and diagrams (prepared by the author personally) are numerous, clear and helpful. Only a few unimportant misprints were noted. In a few places terminology seems to be rather unorthodox or confusing. Thus on p. 28, a secular equation (that is, a secular determinant equated to zero) seems to be called a "secular determinant." On p. 59, "self-consistent field" is used in what seems to the reviewer a strange way. On p. 66, the author describes the operations of a symmetry group which he calls D_{2v}, although others call it D_2; however, the group which he actually needs for π-electron systems is C_{2v} (one rotation and two reflections instead of three rotations); but by ignoring the fact that two of the rotations turn π-orbitals upside-down, correct results are obtained. Similarly, on p. 70 the group C_2 (with one rotation) is described instead of C_s (with one reflection), but again correct results are obtained. But, if "a rose by any other name would smell as sweet," the above-mentioned deviations do not matter. They do not affect the value of the book as an extremely useful, practical primer for the application of Hückel theory to organic chemical problems. However (though again this does not affect the usefulness of the book), the reviewer does not see why on p. 56 the author uses "trimethylenemethane" with three double bonds from a central carbon atom, hence for the latter a valence of six, as a reference standard for the free valence index.

The author might have provided helpful orientation for those wishing to go deeper, if in the last chapter he had briefly pointed out certain characteristic quantitative faults of the simple Hückel theory, such as that it exaggerates the charges on atoms when charges are present, and exaggerates the bond orders of conjugated "single" bonds, like the central bond in butadiene.

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Progress in High Polymers. Volume 1. Editors, J. C. ROBB, PH.D., D.SC., and F. W. PEAKER, PH.D. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1961. vii + 340 pp. 16.5 × 25.5 cm. Price, $12.00.

This work, intended to be the first of a new series, is a collection of critical review articles in the field of polymer chemistry. The diversity of topics covered is such that at least portions of the book should be useful to anyone active in polymer research.

The first article, "The Theory of High Polymer Solutions" by T. B. Grimsley, rather than being primarily a review of the literature in the broad field defined by the title, presents a systematic, concise exposition of the theory. The author