

TABLE 1

PROPERTIES OF CYCLIC PERMETHYLPOLYSILANES

| Compound | M.p. | NMR, ppm (δ) | Anal. ^a | | | Mol. wt. | |
|----------------------------------|---------|-----------------------|--------------------|-------|-------|----------|-----------------------------------|
| | | | C | H | Si | Calcd. | Found |
| Me ₁₀ Si ₅ | 186-189 | -0.135 | 41.09 | 10.29 | 48.39 | 290.8 | 285 ^b 290 ^c |
| Me ₁₂ Si ₆ | 252-255 | -0.132 | 41.19 | 10.41 | 48.33 | 349 | 341 ^b |
| Me ₁₄ Si ₇ | 228-232 | -0.125 | 41.08 | 10.40 | — | 407 | 400 ^b |

^a Calcd. for (C₂H₆Si)_n: C, 41.30; H, 10.40; Si, 48.30. ^b By osmometry. ^c By mass spectroscopy

217 m μ (shoulder on end absorption) and λ_{max} 242 m μ ($\epsilon = 2100$). The infrared spectra of both compounds show no absorption in the siloxane region, but the cyclopentasilane undergoes air oxidation easily with appearance of a siloxane infrared band at 1050 cm⁻¹. Some properties of the cyclic permethylpolysilanes are summarized in Table 1.

Preliminary experiments, indicate that Me₁₀Si₅ forms a delocalized anion-radical like that obtained from Me₁₂Si₆¹⁰.

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The redistribution of chlorine, fluorine, or methoxy with hydrogen on silicon

Several studies during recent years have dealt with the distribution of products at equilibrium in the redistribution of ligands about a silicon atom*. These studies have generally shown a random distribution of products when both redistributing ligands are organic substituents^{2a, 3} or hydrogen^{2b}. Quite nonrandom distributions are observed with many other combinations such as the redistribution of an alkoxy or an

* For recent reviews of this subject see reference 1.

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amino substituent with halogen⁴. In all of these latter cases the deviations from random distribution are in the direction favoring the compounds containing the most equal number of dissimilar ligands; *i.e.*, the equilibrium in equation (1) lies far to the right.

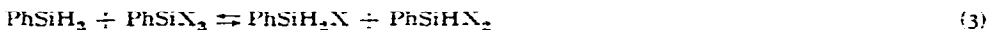


Although these studies clearly demonstrate a dependence of the ligand-silicon bond energy on the remaining substituents on silicon, they do not provide a clear picture of the nature or the source of these bond energy variations. We now wish to report some equilibrium constants in the redistribution of hydrogen, a ligand incapable of π -bonding, with various potentially π -bonding ligands. These data show an increased stability associated with the accumulation of oxygen or fluorine about a silicon atom.

We recently reported the catalysis of the redistribution of hydrogen and chlorine on silicon by tetraalkylammonium halides⁵. These catalysts and, particularly, tetrabutylammonium fluoride, are also effective in the redistribution of fluorine and hydrogen on silicon, and the redistribution of hydrogen and methoxy is catalyzed by lithium methoxide. This latter base-catalyzed reaction was first noted by Friedel and Ladenburg⁶ and later extended by Bailey⁷. By use of these catalysts, the equilibrium distribution of hydrogen with methoxy, fluorine and chlorine has been examined in a system containing two organic substituents per silicon (reaction 2) as shown in Table 1.



Preliminary data in a system with one organic substituent per silicon (reaction 3),



show a similar phenomenon; the equilibrium again lies far to the left when X is fluorine or methoxy. Very similar distributions were noted in several examples where the phenyl group was replaced by a methyl group in reaction (2) and (3).

Table 2 gives the equilibrium constants for reaction (2) and also the ΔF_{dev} , where:

$$\Delta F_{\text{dev}} = -1/2RT \ln K_r/K_r$$

Since K_r is the equilibrium constant expected for a random distribution of exchange products (4 for reaction 2), the ΔF_{dev} should represent the ΔH per mole of silane for these redistributions. A preliminary value of -1.6 kcal/mole was obtained by calorimetry at 40°C for reaction (2) (X = fluorine) which compares very favorably with the ΔF_{dev} of ± 1.9 kcal/mole.

The exchanges involving fluorine and methoxy represent the largest deviations from random distributions yet reported which favor the accumulation of one ligand on the silicon*, and are in sharp contrast to the hydrogen-chlorine system and other previously reported studies which show deviations in the opposite direction. We suggest that this greater stability of the combination of products having an accumulation of methoxy or fluorine on silicon reflects an increase in the bond energy of the silicon-fluorine or silicon-oxygen bond with an increasing number of fluorine or methoxy substituents on silicon. An alternative explanation, which would involve the strengthening of the silicon-hydrogen bond is not consistent with the data of Smith and Angelotti⁸, which shows the Si-H stretching frequency to increase with the increasing electronegativity of the substituents on silicon. Consideration of the Si-H

* A significant but somewhat smaller deviation from random distribution favoring the accumulation of similar ligands has been observed in the redistribution of OMe and SMe groups on Me_2Si (Ref. 1a, Table IV, p. 210).

TABLE 1
 REDISTRIBUTION EQUILIBRIA

| Reagent ^a | Reaction conditions ^b | | Products ^a | |
|---------------------------------------------|----------------------------------|---------------|---------------------------------------|----------------------------------------|
| | Catalyst | Reaction time | | |
| PhMeSiHF ^c (0.07) (± 0.01) | Bu ₃ NF | 48 h | PhMeSiH ₂ (0.47) | PhMeSiF ₂ (0.47) |
| PhMeSiH(OMe) (0.087) (± 0.01) | BuLi ^d | 96 h | PhMeSiH ₂ (0.456) | PhMeSi(OMe) ₂ (0.456) |
| PhMeSiHCl (0.59) | Bu ₄ NCl | 96 h | PhMeSiH ₂ (0.20 ± 0.01) | PhMeSiCl ₂ (0.20 ± 0.01) |

^a Mole fraction at equilibrium given in parentheses. Equilibrium concentrations represent the limiting concentrations after at least four half-lives and were confirmed by approach from the reverse direction. ^b From 0.5 to 1.0 ml of the reagent with 1 to 3% by weight of the indicated catalyst were heated at 100°C in sealed NMR sample tubes. Analyses were obtained by ¹H NMR and GLC. ^c 0.036 at 25°C. ^d Butyl lithium (15%) in hexane serves as a source of lithium methoxide *via* reaction with the methoxysilane.

 TABLE 2
 $\Delta F_{dev.}$ FOR $\text{PhMeSiH}_2 + \text{PhMeSiX}_2 \rightleftharpoons 2 \text{PhMeSiXH}$

| X | K ^a | $\Delta F_{dev.}$ ^b |
|-----|----------------|--------------------------------|
| F | 0.023 ± 0.01 | +1.9 ± 0.1 kcal/mole |
| OMe | 0.037 ± 0.007 | +1.7 ± 0.1 kcal/mole |
| Cl | 8.5 ± 0.3 | -0.28 ± 0.01 kcal/mole |

^a At 100°C from the data in Table 1, where $K = \frac{[\text{PhMeSiXH}]^2}{[\text{PhMeSiH}_2][\text{PhMeSiX}_2]}$
^b $\Delta F_{dev.} = -\frac{1}{2}RT \ln K/4$.

stretching frequencies, in fact, suggests that the strongest SiH bond in eqn. 2 (X = F) is in phenylmethylfluorosilane where the hydrogen and fluorine are sharing a silicon atom*.

This increase in the Si-F or Si-O bond energy may represent an increasing π interaction of these ligands with the silicon atom; an accumulation of these electro-negative substituents should favor π -bonding by lowering the energy of the vacant interacting orbital of the silicon atom. Similar explanations have recently been proposed^{9,10} for the strong preference of the dimethylamino or methoxy group for the most electron deficient silicon in redistributions with chlorine between differently substituted silanes. The consideration of only the ionic contributions to the bond energy would lead to the incorrect prediction that the sharing of a fluorine and hydrogen by the silicon should be preferred. A very similar enhanced stability is observed on accumulation of oxygen or fluorine on carbon and has been interpreted as a π interaction of these ligands with carbon *via* no bond resonance** (Ref. 11). The similarity of these phenomena with carbon and silicon raises many interesting questions on the relative importance of σ^* or $3d$ orbitals in any interpretation based on a π interaction.

* The Si-H stretching frequencies are: PhMeSiH₂³ (2140 cm⁻¹), PhMeHSiF (2167 cm⁻¹), PhMeHSiCl (2169 cm⁻¹), and PhMeHSiOMe (2115 cm⁻¹).

** A formulation, equivalent to no bond resonance, would involve π interaction with the σ^* orbital at carbon.

The more nearly statistical distributions with chlorine and hydrogen are consistent with the decreased tendency of second-row elements to form π -bonds¹². The comparison of bond lengths^{12,13} and dipole moments¹⁵ certainly suggests a much stronger π interaction in fluorosilanes than with chloro- or bromosilanes. The change in direction of these deviations from a random distribution on proceeding from oxygen or fluorine to chlorine, in fact, suggests a different controlling factor for the second-row ligands. Either electrostatic or steric interactions between the halogen atoms would favor the silane with dissimilar ligands.

The generality of the above considerations, which suggest that first row, π -bonding ligands should prefer the most electron deficient silicon, is being explored.

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Chelation and isomerism in organotin oxinates

A variety of studies¹⁻³ have provided uniformly strong support for the suggestion of Holmes and Kaesz⁴ that changes in the hybridisation of the tin bonding orbitals in methyltin compounds will be reflected in variations in the tin-proton spin coupling constants. In particular, as the s-character of the bonding orbitals of tin increases,

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