decomposition of the anion. An analogous situation exists among the reduced species of the 2:18 heteropolyanions, where the maximum charge is −10, and it has been shown by titration that the reduced acid, $H_{12}[P_2Mo_{18}O_{62}]$, has only ten replaceable protons.[35]

Some ambiguity exists with the tungstoferrate blues concerning the oxidation state of the central atom. Simmons[14] has studied the reduction of 12-tungstocobaltate(III) to 12-tungstocobaltate(II), and, using her value for the formal reduction potential, +0.77 v, she estimated[36] a reduction potential of −1.4 v for the corresponding Fe(III)–Fe(II) reduction. She predicted that the tungstate network of 12-tungstoferrate(III) would be reduced before the central atom, as has been found in the present work. By analogy with the other anions studied, tungstoferrate should, in acidic solutions, be able to accept a total of four electrons. Since in fact it accepts five, it is reasonable to assume that the three-electron reduction (wave at −0.5 v, pH 1.67) involves reduction of the central atom to Fe(II) as well as addition of two electrons to the tungstate network. This may not be the case above pH 5, however, and further study of the reduced compounds is underway to establish the oxidation state of the iron.

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[36] The difference in the potentials derives mainly from the difference in the third ionization potentials of Fe and Co, modified by the appropriate ligand field stabilization energies [see P. George and D. S. McClure, *Progr. Inorg. Chem.*, **1**, 381 (1959)].

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Redistribution Equilibria of Substituents between the Methyl- and Trimethylsilicon Moieties

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Scrambling equilibria resulting from the exchange of pairs of monofunctional substituents (halogen, methoxyl, methylthio, and dimethylamino) between the methyl- and trimethylsilicon moieties have been studied by proton nuclear magnetic resonance. Unexpectedly, these equilibria deviate greatly from the case corresponding to ideal random sorting of the substituents. The experimental data are evaluated in terms of three equilibrium constants—two for the scrambling of the two kinds of substituents on the methylsilicon moiety and an intersystem equilibrium constant describing the distribution of the substituents between the methyl- and trimethylsilicon moieties. The observed deviations from randomness are attributed to π-bonding effects.

Recent communications[1–3] from this laboratory have dealt with equilibria involving redistribution of two kinds of monofunctional substituents on two kinds of central atoms or moieties. In view of the observed unexpected preference of one kind of substituent for one of the central moieties in systems with silicon and germanium as the two kinds of central atoms, a study was undertaken to determine the equilibria between moieties of silicon of varying functionality. In a related paper[4] equilibria in systems of the general type CH_3SiZ_3 *vs.* $(CH_3)_2SiT_2$ have been reported. In these studies, Z and T were monofunctional exchangeable substituents and the CH_3 groups remained fixed to silicon under the reported reaction condition. This paper deals with the related equilibria in systems CH_3SiZ_3 *vs.* $(CH_3)_3SiT$.

Experimental Section

Materials.—Methyltrimethoxysilane and trimethylchlorosilane were purchased from Alfa Inorganics, Inc., Beverly, Mass., and distilled before use. Methyltribromosilane[1] and methyltris(dimethylamino)silane[5] were prepared according to methods described in the literature. Methyltris(methylthio)silane was prepared by refluxing methyltrichlorosilane with lead methylmercaptide in benzene, bp 105° (10 mm); yield, 47%. Trimethylbromosilane was obtained by passing dry hydrogen bromide into a methylene chloride solution of hexamethyldisilazane, bp 77–79°; yield, 69%.

Equilibrations.—The desired proportions of the starting materials (the methylsilicon compound and the trimethylsilicon compound) were sealed in three-quarters filled, 5-mm o.d. precision nuclear magnetic resonance (nmr) tubes and heated at 120°. The time required for reaching equilibrium at this temperature was determined in pilot runs. Equilibrium was considered to be attained when the nmr pattern did not change upon additional

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TABLE I

PROTON NMR CHEMICAL SHIFTS OF THE METHYL- AND TRIMETHYLSILICON MOIETY OBSERVED IN EQUILIBRATED SAMPLES OF EQUIMOLAR AMOUNTS OF CH_3SiZ_3 *vs.* $(CH_3)_3SiT$ (IN PPM RELATIVE TO TMS AS INTERNAL STANDARD IN THE NEAT LIQUIDS)

Z	T	CH_3SiT_3	CH_3SiT_2Z	CH_3SiTZ_2	CH_3SiZ_3	$(CH_3)_3SiT$	$(CH_3)_3SiZ$
Br	Cl	−1.083	−1.217	−1.362	−1.521	−0.392	−0.538
OCH_3	Cl	...[a]	...[a]	−0.342[b]	+0.008[c]	−0.394	−0.063[d]
SCH_3	Cl	...[a]	−0.983[e]	−0.842[f]	−0.697[g]	−0.394	−0.281[h]
SCH_3	Br	...[a]	−1.123[i]	−0.976[j]	−0.692[k]	−0.537	−0.263[l]
$N(CH_3)_2$	Cl	...[a]	...[a]	−0.317[m]	+0.021[n]	−0.373	0.000[o]
$N(CH_3)_2$	Br	...[a]	...[a]	−0.450[p]	+0.017[q]	−0.517	0.000[r]

[a] Not observed. [b] OCH_3, −3.503. [c] OCH_3, −3.433. [d] OCH_3, −3.324. [e] SCH_3, −2.159. [f] SCH_3, −2.118. [g] SCH_3, −2.058. [h] SCH_3, −1.924. [i] SCH_3, −2.220. [j] SCH_3, −2.108. [k] SCH_3, −2.053. [l] SCH_3, −1.919. [m] $N(CH_3)_2$, −2.392. [n] $N(CH_3)_2$, −2.333. [o] $N(CH_3)_3$, −2.325. [p] $N(CH_3)_2$, −2.454. [q] $N(CH_3)_2$, −2.383. [r] $N(CH_3)_2$, −2.373.

heating. The reported equilibrium data correspond to times longer than those required to reach equilibrium. The heating periods for attaining equilibrium in the various systems are given below, with the time at which the equilibrium data were obtained being given in parentheses. For Z = Br and T = Cl: 39 hr at 120° (114.5 hr); Z = OCH_3 and T = Cl: 19 hr at 120° (51 hr); Z = SCH_3 and T = Cl: 396 hr at 120° (512 hr); Z = SCH_3 and T = Br: 210 hr at 120° (326 hr); Z = $N(CH_3)_2$ and T = Cl: 14 days at room temperature (37 days); Z = $N(CH_3)_2$ and T = Br: 13 days at room temperature (22 days). Attempts to study equilibria in the system $CH_3Si(OCH_3)_3$ *vs.* $(CH_3)_3SiBr$ were abandoned due to formation of methyl bromide upon heating of the reactants.

Nmr Measurements.—Proton nmr spectra of the equilibrated mixtures were obtained on a Varian Model A-60 spectrometer immediately after quenching the samples to room temperature. The measurements were performed on the neat liquids with the probe of the spectrometer being near 30°. The samples were diluted with one to three parts of dry benzene only in the systems involving dimethylamino groups in order to achieve better resolution of some of the signals. The proton nmr chemical shifts of the methylsilicon and trimethylsilicon moieties in the species observed at equilibrium are reported in Table I. Peak areas were determined by electronic integration and only in those cases where signals were overlapping, by cutting out and weighing Xerox copies of the spectra. Referencing with tetramethylsilane (TMS) was carried out at the completion of the studies.

Data Treatment.—The general principle of calculating equilibrium constants in systems of the type QZ_ν *vs.* MT_μ (with ν and μ being the number of sites for monofunctional substituents Z and T on the central moieties Q and M) has been reported in detail elsewhere.[1-3,6] Calculations and statistical data evaluations were performed by an IBM 7040 computer.

Results and Conclusions

The equilibria involving scrambling of monofunctional substituents Z and T between methyl- and trimethylsilicon moieties are represented by

$$CH_3SiZ_3 + 3(CH_3)_3SiT \rightleftharpoons CH_3SiT_3 + 3(CH_3)SiZ \quad (1)$$

Exchange of substituents Z and T proceeds well below the temperature[7] where methyl groups directly attached to silicon participate in the exchange processes. Therefore, it is valid to conclude that in these studies the methylsilicon moiety, $CH_3Si{<}$, and the trimethylsilicon moiety, $(CH_3)_3Si–$, will remain intact under the relatively mild conditions of the equilibration of eq 1. This conclusion is supported by the nmr spectra of equilibrated samples where no products were detected which could have originated from the exchange of methyl groups bonded directly to silicon.

In addition to the equilibrium described by eq 1, there are other equilibria to be considered. These deal with the distribution of the monofunctional substituents, Z and T, on the methylsilicon moiety and are described by

$$2CH_3SiZ_2T \rightleftharpoons CH_3SiZ_3 + CH_3SiZT_2 \quad (2)$$

$$2CH_3SiZT_2 \rightleftharpoons CH_3SiT_3 + CH_3SiZ_2T \quad (3)$$

The set of three equilibria represented by eq 1–3 is sufficient to describe the systems CH_3SiZ_3 *vs.* $(CH_3)_3SiT$. These equilibria are expressed in quantitative terms by means of the corresponding equilibrium constants given in eq 4–6

$$K_I = [CH_3SiT_3][(CH_3)_3SiZ]^3/[CH_3SiZ_3][(CH_3)_3SiT]^3 \quad (4)$$

$$K_1 = [CH_3SiZ_3][CH_3SiZT_2]/[CH_3SiZ_2T]^2 \quad (5)$$

$$K_2 = [CH_3SiT_3][CH_3SiZ_2T]/[CH_3SiZT_2]^2 \quad (6)$$

The constant, K_I, the intersystem constant, relates quantitatively the distribution of Z and T between the $CH_3Si{<}$ and $(CH_3)_3Si–$ moieties. The constants K_1 and K_2 describe the scrambling equilibria of Z and T on the $CH_3Si{<}$ moiety.

The experimental nmr data obtained on the equilibrated systems were evaluated in terms of the constants K_1, K_2, and K_I, the values of which are listed in Table

TABLE II

EQUILIBRIUM CONSTANTS IN THE SYSTEM CH_3SiZ_3 *vs.* $(CH_3)_3SiT$ AT 120°

Z	T	K_1	K_2	K_I
Br	Cl	0.42[a] (0.43)[b,c]	0.36 (0.40)[c]	10.32 ± 1.4
OCH_3	Cl	...[d] (1.8×10^{-2})[e]	...[d] (4.2×10^{-2})[e]	$(7 \pm 3) \times 10^{-10}$
SCH_3	Cl	6.6×10^{-2} (0.1)[f]	...[d] (0.16)[f]	$(7 \pm 2) \times 10^{-7}$
SCH_3	Br	7.2×10^{-2} (4.1×10^{-2})[f]	...[d] (8.6×10^{-2})[f]	$(4 \pm 3) \times 10^{-6}$
$N(CH_3)_2$	Cl[g]	...[d] (5×10^{-4})[e]	...[d] (5×10^{-4})[e]	$(1 \pm 0.2) \times 10^{-10}$
$N(CH_3)_2$	Br[g]	...[d] (1.6×10^{-4})[f]	...[d] (1.4×10^{-3})[f]	$(6 \pm 1) \times 10^{-12}$
Ideal randomness		0.333	0.333	1.00

[a] Data not in parentheses were obtained in the system CH_3SiZ_3 *vs.* $(CH_3)_3SiT$. [b] Data in parentheses were obtained in the system CH_3SiZ_3 *vs.* CH_3SiT_3. [c] See ref 1. [d] Constants could not be calculated owing to insufficient number of components present at equilibrium. [e] See ref 8. [f] Unpublished results. [g] Data correspond to room temperature.

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(6) L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964).

(7) K. Moedritzer, *Organometal. Rev.*, **1**, 179 (1966).

(8) J. R. Van Wazer and K. Moedritzer, *J. Inorg. Nucl. Chem.*, **26**, 737 (1964).

II. It is seen that in the cases where K_1 and K_2 could be determined from the experimental data, good agreement is observed with the values for these constants obtained separately in a study[8] of the corresponding systems CH_3SiZ_3 *vs.* CH_3SiT_3. The latter data are listed in parentheses in Table II. In most of the cases, however, an insufficient amount of components was seen at equilibrium for the systems CH_3SiZ_3 *vs.* $(CH_3)_3SiT$ so that, unfortunately, direct calculation of values for K_1 and K_2 was not possible.

The intersystem constants, $K_{\rm I}$, also listed in Table II, deviate in all cases more or less from the values expected for ideal random distribution of substituents, $(K_{\rm I})_{\rm rand} = 1.00$. The nonrandom value of $K_{\rm I}$ indicates that at equilibrium there is a definite preference of a given substituent for one kind of central moiety. When the two monofunctional substituents are chlorine and bromine atoms, the chlorines prefer to be associated with the $CH_3Si<$ moiety rather than the $(CH_3)_3Si-$ group. A more striking preference is observed when halogen atoms are exchanged with groups such as OCH_3, SCH_3, and $N(CH_3)_2$, respectively. In the latter cases, the halogen atoms, chlorine, as well as bromine, greatly prefer to be linked to the $(CH_3)_3Si-$ moiety. This tendency is strongest for the $N(CH_3)_2$ group, is also strong for the OCH_3 group, and is somewhat weaker for the SCH_3 group.

The constants K_1, K_2, and $K_{\rm I}$ of Table II have been used to calculate the relative proportions of the components at equilibrium for the compositions for which nmr data were obtained. The good agreement between the experimental and calculated proportions is shown by the data of Table III. In the cases where K_1 and K_2 could not be determined, the appropriate values of these constants, listed in parentheses in Table II, were used for the calculations.

Discussion

The systems discussed in this paper are a special example of the exchange of two kinds of monofunctional substituents between two kinds of central moieties. Since in the cases reported here the functionalities of the two central moieties differ from each other, it was desirable to calculate composition diagrams showing the equilibrium concentrations of all species present for various typical cases. The graphs in Figure 1 display diagrams for systems QT_3 *vs.* MZ for various values of the intersystem constant $K_{\rm I} = [QT_3][MZ]^3/[QZ_3]\cdot[MT]^3$, with the values of the constants $K_{Q_1} = [QT_3]\cdot[QZ_2T]/[QZT_2]^2$ and $K_{Q_2} = [QZ_3][QZT_2]/[QZ_2T]^2$ having the random value of 0.333. Somewhat different curves, of course, are to be expected when K_{Q_1} and K_{Q_2} deviate from the values calculated for random sorting of the substituents Z and T on Q. The graphs show the kinds of distributions when $K_{\rm I}$ ranges from a very small value, $K_{\rm I} = 10^{-20}$, to a very large value, $K_{\rm I} = 10^{+20}$, with the case for random distribution of Z and T between Q and M denoted by $K_{\rm I} = 1.00$.

TABLE III

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA (IN MOLE PER CENT) IN THE SYSTEM QZ_3 *vs.* MT WHERE $Q = CH_3Si$ AND $M = (CH_3)_3Si$

(A) System CH_3SiBr_3 vs. $(CH_3)_3SiCl$

R ≡ Br/Si	R' ≡ Q/Si	QBr_3	QBr_2Cl	$QBrCl_2$	QCl_3	MBr	MCl
0.407[a] (0.394)[b]	0.136[a] (0.126)[b]	0.0 (0.1)[c]	1.2 (1.3)	4.0 (5.1)	7.4 (7.0)	33.0 (32.5)	54.4 (54.0)
0.903 (0.913)	0.301 (0.324)	4.0 (3.8)	10.6 (10.2)	12.6 (11.4)	5.2 (4.6)	45.5 (46.9)	22.1 (22.9)
1.380 (1.395)	0.460 (0.457)	16.4 (15.4)	18.6 (19.0)	9.0 (9.8)	1.7 (1.8)	44.1 (44.0)	10.2 (9.9)
1.897 (1.906)	0.632 (0.647)	36.9 (36.2)	21.7 (21.3)	4.9 (5.2)	1.2 (0.5)	31.6 (33.2)	3.7 (3.6)
2.442 (2.448)	0.814 (0.821)	65.2 (65.1)	15.1 (14.9)	1.8 (1.4)	- (0.0)	17.2 (17.9)	0.8 (0.7)

(B) System $CH_3Si(OCH_3)_3$ vs. $(CH_3)_3SiCl$

R ≡ Cl/Si	R' ≡ Q/Si	QCl_3	QCl_2-(OCH_3)	QCl-$(OCH_3)_2$	Q-$(OCH_3)_3$	MCl	$M(OCH_3)$
0.173[a] (0.200)[b]	0.827[a] (0.793)[b]	- (0.0)[c]	- (0.0)	5.4 (5.7)	73.9 (76.9)	14.6 (11.6)	6.1 (5.8)
0.348 (0.393)	0.652 (0.622)	- (0.0)	- (0.0)	8.9 (7.6)	53.3 (57.5)	30.4 (27.2)	7.4 (7.7)
0.508 (0.547)	0.492 (0.479)	- (0.0)	- (0.0)	9.4 (8.1)	38.5 (41.1)	45.3 (42.7)	6.9 (8.1)
0.679 (0.688)	0.321 (0.327)	- (0.0)	- (0.0)	8.0 (7.4)	24.7 (24.6)	60.8 (60.4)	6.5 (7.5)
0.851 (0.848)	0.147 (0.144)	- (0.0)	- (0.1)	4.3 (5.3)	10.1 (9.5)	80.5 (74.7)	5.2 (5.4)

(C) Systém $CH_3Si(SCH_3)_3$ vs. $(CH_3)_3SiCl$

R ≡ Cl/Si	R' ≡ Q/Si	QCl_3	QCl_2-(SCH_3)	QCl-$(SCH_3)_2$	Q-$(SCH_3)_3$	MCl	$M(SCH_3)$
0.176[a] (0.166)[b]	0.824[a] (0.825)[b]	- (0.0)[c]	- (0.0)	5.8 (7.1)	76.7 (75.2)	10.8 (10.3)	6.8 (7.3)
0.342 (0.347)	0.658 (0.661)	- (0.0)	- (0.2)	9.9 (9.4)	56.2 (56.2)	24.8 (24.5)	9.2 (9.7)
0.517 (0.519)	0.483 (0.494)	- (0.0)	- (0.3)	10.7 (9.9)	38.7 (38.1)	41.2 (41.1)	9.3 (10.5)
0.681 (0.690)	0.319 (0.317)	- (0.0)	- (0.4)	9.7 (8.9)	22.0 (22.6)	59.3 (58.3)	9.1 (9.8)
0.859 (0.871)	0.164 (0.152)	- (0.0)	0.8 (0.7)	7.5 (7.1)	6.9 (8.6)	78.0 (77.4)	6.8 (6.2)

(D) System $CH_3Si(SCH_3)_3$ vs. $(CH_3)_3SiBr$

R ≡ Br/Si	R' ≡ Q/Si	QBr_3	QBr_2-$(SCH_3)_2$	QBr-$(SCH_3)_2$	Q-$(SCH_3)_3$	MBr	$M(SCH_3)$
0.186[a] (0.189)[b]	0.814[a] (0.835)[b]	- (0.0)[c]	- (0.1)	10.6 (10.5)	72.9 (70.8)	8.3 (7.9)	8.2 (10.7)
0.373 (0.385)	0.627 (0.645)	- (0.0)	0.4 (0.3)	14.1 (14.3)	50.0 (48.1)	23.6 (22.3)	12.0 (15.0)
0.557 (0.552)	0.443 (0.471)	- (0.0)	0.6 (0.5)	14.1 (14.7)	32.4 (29.1)	39.9 (39.9)	13.1 (15.8)
0.628 (0.645)	0.372 (0.386)	- (0.0)	0.4 (0.6)	13.7 (14.0)	24.5 (22.5)	50.0 (47.6)	12.3 (15.3)
0.897 (0.899)	0.103 (0.115)	- (0.0)	0.4 (0.9)	5.4 (6.3)	5.7 (3.1)	82.8 (81.5)	5.7 (8.1)

(E) System $CH_3Si[N(CH_3)_2]_3$ vs. $(CH_3)_3SiCl$

R ≡ Cl/Si	R' ≡ Q/Si	QCl_3	QCl_2-NMe_2	QCl-$(NMe_2)_2$	Q-$(NMe_2)_3$	MCl	$MNMe_2$
0.189[a] (0.180)[b]	0.811[a] (0.827)[b]	- (0.0)[c]	- (0.0)	14.7 (15.4)	68.0 (65.7)	3.3 (3.6)	14.1 (15.4)
0.356 (0.380)	0.644 (0.650)	- (0.0)	- (0.0)	24.6 (23.0)	40.4 (41.5)	13.4 (12.6)	21.5 (23.0)
0.524 (0.555)	0.476 (0.447)	- (0.0)	- (0.0)	24.6 (25.0)	20.1 (22.6)	30.9 (27.4)	24.4 (25.0)
0.689 (0.715)	0.311 (0.336)	- (0.0)	- (0.0)	24.0 (21.5)	9.6 (9.6)	47.5 (47.4)	18.9 (21.5)
0.797 (0.829)	0.203 (0.236)	- (0.0)	- (0.0)	19.9 (16.2)	3.7 (4.1)	63.0 (63.4)	13.5 (16.3)

(F) System $CH_3Si[N(CH_3)_2]_3$ vs. $(CH_3)_3SiBr$

R ≡ Br/Si	R' ≡ Q/Si	QBr_3	QBr_2-NMe_2	QBr-$(NMe_2)_2$	Q-$(NMe_2)_3$	MBr	$MNMe_2$
0.206[a] (0.206)[b]	0.794[a] (0.775)[b]	- (0.0)[c]	- (0.0)	15.5 (14.7)	62.0 (64.8)	5.1 (5.9)	17.4 (14.7)
0.379 (0.381)	0.621 (0.638)	- (0.0)	- (0.0)	22.1 (20.3)	41.7 (41.8)	16.0 (17.6)	20.2 (20.3)
0.554 (0.515)	0.446 (0.481)	- (0.0)	- (0.0)	22.8 (21.2)	25.3 (23.3)	28.7 (34.2)	23.2 (21.2)
0.712 (0.693	0.283 (0.323)	- (0.0)	- (0.0)	19.3 (17.7)	13.0 (10.6)	50.0 (53.6)	18.0 (18.2)
0.860 (0.866)	0.140 (0.157)	- (0.0)	- (0.0)	11.9 (11.1)	3.8 (2.9)	74.7 (75.0)	9.7 (11.1)

[a] From the ingredients

[b] Values in parentheses are calculated from the n.m.r. data

[c] Values in parentheses are calculated from the equilibrium constants K_1, K_2, and $K_{\rm I}$ in Table II.

Relating the results obtained in this study to the data reported[4] for the systems CH_3SiZ_3 *vs.* $(CH_3)_2SiT_2$ and unpublished results in the system $(CH_3)_2SiZ_2$ *vs.* $(CH_3)_3SiT$, some general conclusions may be drawn with regard to the affinity of a given pair of

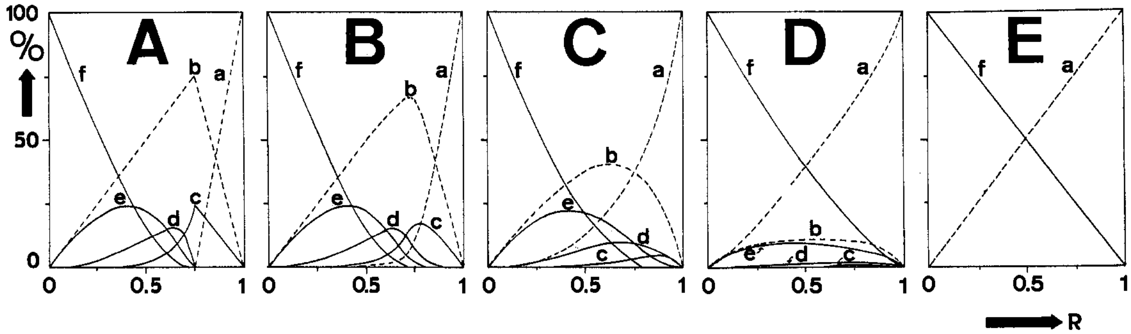

Figure 1.—Theoretical equilibrium curves in systems QT_3 *vs.* MZ for $K_1 = K_2 = 0.333$ (ideal randomness) and varying K_I. A: $K_I = 10^{-20}$; B: $K_I = 10^{-5}$; C: $K_I = 1.00$ (ideal randomness); D: $K_I = 10^{+5}$; E: $K_I = 10^{+20}$. a = MZ, b = MT, c = QZ_3, d = QZ_2T, e = QZT_2, f = QT_3, with $R = Z/(Q + M)$, and $R' = M/(Q + M)$.

monofunctional substituents for various methylsilicon moieties. Considering the pair chlorine–bromine, it is found that, at equilibrium in each of the three types of systems, the chlorine atoms tend to associate with the silicon moiety containing the lesser amount of methyl groups. On the other hand, in relation to all other substituents used in these studies, chlorine as well as bromine atoms prefer to be with the silicon moiety containing the larger number of methyl groups. A similar trend also has been observed[9] for the equilibria involving exchange of chlorine with hydrogen, thus placing the hydrogen on the silicon atom bearing the least number of organic substituents.

Estimations of the enthalpy of the reaction of eq 1 based on the bond energy approach[2] show that the values of ΔH assuming only σ-bond contributions differ considerably from ΔH values that were calculated from the intersystem constant K_I according to the approximation[10] given by

$$\Delta H \approx \delta\Delta F = -RT \ln [K_I/(K_I)_{\text{rand}}] \qquad (7)$$

These differences are attributable to π-bonding effects which, therefore, appear to be the major driving force for the nonrandom equilibrations of eq 1. Quantum mechanical calculations[11] support the concept of the major influence of π contributions in these reactions.

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The Mass Spectra of Lithiomethyltrimethylsilane and Lithium *t*-Butoxide[1]

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The mass spectra of lithiomethyltrimethylsilane, I, and lithium *t*-butoxide, II, have been observed in the vapor phase, using a time-of-flight mass spectrometer and a direct inlet sample system. The data show that I is essentially entirely in the form of tetramers; II, on the other hand, consists entirely of hexamers. Molecular weight data on II obtained from freezing point lowering measurements on benzene solutions also indicate hexameric association.

It was shown in a study of the mass spectrum of ethyllithium[3] that the association observed in solution[4] is reflected in the vapor composition. Ions produced by electron impact provided evidence for the existence of tetrameric and hexameric species. Since that time a determination of the crystal structure[5] of ethyllithium has also revealed the existence of association in the solid state.

It is our intent to extend the range of mass spectral

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