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THE REDISTRIBUTION EQUILIBRIA OF SILANIC HYDROGEN WITH CHLORINE ON METHYLSILICON MOIETIES

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SUMMARY

The scrambling equilibria of silanic hydrogen with chlorine atoms on various combinations of mono-, di-, and trimethylsilicon moieties have been determined by proton nuclear magnetic resonance. The data have been evaluated in terms of sets of equilibrium constants which show that at equilibrium, the exchangeable hydrogen atoms prefer to be with the silicon moiety bearing the least number of methyl groups.

INTRODUCTION

The recent discovery of the tetraalkylammonium-catalyzed[1,2] redistribution of silanic hydrogens with halogens on silicon prompted us to extend our previously reported quantitative studies[3-6] of the redistribution equilibria of exchangeable substituents on methylsilicon moieties. This paper, therefore, describes in quantitative terms all of the possible redistribution equilibria between $(CH_3)_3SiCl$, $(CH_3)_3SiH$, $(CH_3)_2SiCl_2$, $(CH_3)_2SiH_2$, CH_3SiCl_3, and CH_3SiH_3 resulting from exchange of silanic hydrogen with chlorine atoms. Unlike other catalysts[7] promoting the exchange of silanic hydrogen with halogens on silicon, tetraalkylammonium salts quite effectively catalyze this exchange process without involving the alkyl groups of the alkyl and alkylhalosilanes.

EXPERIMENTAL SECTION

Reagents

Trimethylsilane, dimethylsilane, and methylsilane were obtained from Peninsular ChemResearch, Inc., Gainesville, Fla., and were used as received. Trimethylchlorosilane was purchased from Alfa Inorganics, Beverly, Mass., dimethyldichlorosilane and methyltrichlorosilane from Columbia Organic Chemicals, Columbia, S.C. The halosilanes were redistilled before use. All reagents contained less than 1% of hydrogen-containing impurities, as determined by proton nuclear magnetic resonance (NMR).

Preparation of samples, equilibration, measurement and determination of equilibrium constants

The samples were prepared by placing 1–5 mole percent of dry tetrabutylammonium chloride and the desired amount of the halosilane in a thick-walled NMR tube (0.7 mm wall thickness, obtained from NMR Specialties, New Kensington, Pa.) and condensing the desired amount of methylsilane into the tube. The tubes were then sealed and heated at 100°. In order to minimize the error in the quantitative NMR determination of the tube contents, due to the fact that considerable amounts of volatile silane would accumulate in the gas phase above the liquid and thus would not be counted by the NMR method, the tubes were filled to more than 9/10 of the available volume. This was accomplished by sealing the tubes while they were kept in a dry-ice bath at −78°. Upon warming to room temperature, the liquid generally expanded so as to leave only a small gas bubble in the tube. Surprisingly, only about 5% of the tubes thus prepared ruptured upon heating at 100°.

TABLE 1

PROTON NMR CHEMICAL SHIFTS (in ppm relative to tetramethylsilane) OBSERVED IN NEAT SAMPLES OF EQUILIBRATED MIXTURES OF METHYLCHLOROSILANES

System	Compound	CH_3–Si		H–Si	
		δ(ppm)	J(HC–SiH) (cps)	δ(ppm)	J(HSi–CH) (cps)
CH_3SiCl_3 *vs.* $(CH_3)_2SiH_2$[b]	CH_3SiCl_3	−1.088			
	CH_3SiCl_2H	−0.827	2.3 (2)[a]	−5.550	2.3 (4)[a]
	CH_3SiClH_2	−0.565	3.6 (3)	−4.725	3.6 (4)
	CH_3SiH_3	−0.158	4.6 (4)	−3.542	4.7 (4)
	$(CH_3)_2SiCl_2$	−0.758			
	$(CH_3)_2SiClH$	−0.475	3.1 (2)	−4.858	3.2 (7)
	$(CH_3)_2SiH_2$	−0.140	4.1 (3)	−3.792	4.2 (7)
CH_3SiCl_3 *vs.* $(CH_3)_3SiH$[c]	CH_3SiCl_3	−1.068			
	CH_3SiCl_2H	−0.797	2.3 (2)	−5.533	2.3 (4)
	CH_3SiClH_2	−0.550	3.6 (3)	−4.700	3.6 (4)
	CH_3SiH_3	−0.138	4.6 (4)	−3.517	4.7 (4)
	$(CH_3)_3SiCl$	−0.392			
	$(CH_3)_3SiH$	−0.072	3.6 (2)	−4.000	3.7 (10)
$(CH_3)_2SiCl_2$ *vs.* $(CH_3)_3SiH$[c]	$(CH_3)_2SiCl_2$	−0.740			
	$(CH_3)_2SiClH$	−0.460	3.1 (2)	−4.858	3.2 (7)
	$(CH_3)_2SiH_2$	−0.125	4.2 (3)	−3.792	4.2 (7)
	$(CH_3)_3SiCl$	−0.392			
	$(CH_3)_3SiH$	−0.070	3.7 (2)	−3.992	3.6 (10)
CH_3SiCl_3 *vs.* CH_3SiH_3[d]	CH_3SiCl_3	−1.067			
	CH_3SiCl_2H	−0.812	2.3 (2)	−5.500	2.3 (4)
	CH_3SiClH_2	−0.550	3.6 (3)	−4.683	3.5 (4)
	CH_3SiH_3	−0.138	4.6 (4)	−3.500	4.7 (4)
$(CH_3)_2SiCl_2$ *vs.* $(CH_3)_2SiH_2$[b]	$(CH_3)_2SiCl_2$	−0.758			
	$(CH_3)_2SiClH$	−0.478	3.1 (2)	−4.875	3.2 (7)
	$(CH_3)_2SiH_2$	−0.142	4.2 (3)	−3.808	4.2 (7)

[a] Multiplicity (in parentheses) of the CH_3 proton spectra. [b] Referenced against internal $(CH_3)_2SiCl_2 = -0.758$ ppm. [c] Referenced against internal $(CH_3)_3SiCl = -0.392$ ppm. [d] Referenced against internal $CH_3SiCl_3 = -1.067$ ppm.

The equilibrations, the measurement of the relative concentrations of the species at equilibrium by proton NMR, and the calculations of equilibrium constants were performed as reported previously[3–9]. Generally the rates of equilibration in the systems studied here were quite slow at room temperature. Therefore, by rapidly quenching the samples which had been held at 100° and obtaining the NMR spectra immediately afterwards, the measured equilibria were forced to correspond to 100°. The shifts of the observed proton NMR resonances in the samples at equilibrium are presented in Table 1. Only the resonances of the methyl groups were used for the quantitative evaluation of the spectra. Although in some of the samples methyl multiplets resulting from spin-spin splitting with silanic hydrogen overlapped to some extent, generally at least one of the multiplet peaks was well resolved and thus could be integrated quite accurately. Since the individual peaks of a multiplet always appear in constant area ratios, the mole fractions of two compounds showing overlapping multiplets may be calculated.

RESULTS AND CONCLUSIONS

By pairing one of the three methylchlorosilanes, $(CH_3)_iSiCl_{4-i}$, with one of the three methylsilanes, $(CH_3)_jSiH_{4-j}$, where i and j independently have a value of 1, 2, or 3, a series of eight different chemically meaningful substituent-exchange combinations of reagents may be realized. Three of these, however, represent combinations which are complementary to three others and do not constitute new systems as far as redistribution equilibria are concerned. These are the systems CH_3SiCl_3 *vs.* $(CH_3)_2SiH_2$ and CH_3SiH_3 *vs.* $(CH_3)_2SiCl_2$; CH_3SiCl_3 *vs.* $(CH_3)_3SiH$ and CH_3SiH_3 *vs.* $(CH_3)_3SiCl$; and $(CH_3)_2SiCl_2$ *vs.* $(CH_3)_3SiH$ and $(CH_3)_2SiH_2$ *vs.* $(CH_3)_3SiCl$. This leaves five meaningfully different systems in which redistribution equilibria were to be determined.

TABLE 2

EQUILIBRIUM CONSTANTS FOR THE EXCHANGE OF SILANIC HYDROGEN WITH CHLORINE ON MOIETIES OF METHYLSILICON AT 100°

A. System CH_3SiCl_3 *vs.* $(CH_3)_2SiH_2$

$K_1 = [Me_2SiCl_2]\cdot[Me_2SiH_2]/[Me_2SiClH]^2 = (9.0 \pm 0.8) \times 10^{-2}$

$K_2 = [MeSiCl_3]\cdot[MeSiClH_2]/[MeSiCl_2H]^2 = (6.2 \pm 0.9) \times 10^{-2}$

$K_3 = [MeSiCl_2H]\cdot[MeSiH_2]/[MeSiClH_2]^2 = 0.30 \pm 0.04$

$K_{I,A} = [MeSiCl_3]^2\cdot[Me_2SiH_2]^3/\{[MeSiH_3]^2\cdot[Me_2SiCl_2]^3\} = (1.0 \pm 0.6) \times 10^{-7}$

B. System CH_3SiCl_3 *vs.* $(CH_3)_3SiH$

$K_2 = [MeSiCl_3]\cdot[MeSiClH_2]/[MeSiCl_2H]^2 = (5.8 \pm 0.8) \times 10^{-2}$

$K_3 = [MeSiCl_2H]\cdot[MeSiH_3]/[MeSiClH_2]^2 = 0.25 \pm 0.21$

$K_{I,B} = [MeSiCl_3]\cdot[Me_3SiH]^3/\{[MeSiH_3]\cdot[Me_3SiCl]^3\} = (1.0 \pm 0.9) \times 10^{-8}$

C. System $(CH_3)_2SiCl_2$ *vs.* $(CH_3)_3SiH$

$K_1 = [Me_2SiCl_2]\cdot[Me_2SiH_2]/[Me_2SiClH]^2 = (1.0 \pm 0.1) \times 10^{-1}$

$K_{I,C} = [Me_2SiCl_2]\cdot[Me_3SiH]^2/\{[Me_2SiH_2]\cdot[Me_3SiCl]^2\} = (5.6 \pm 3.4) \times 10^{-3}$

D. System CH_3SiCl_3 *vs.* CH_3SiH_3

$K_2 = [MeSiCl_3]\cdot[MeSiClH_2]/[MeSiCl_2H]^2 = (4.1 \pm 0.6) \times 10^{-2}$

$K_3 = [MeSiCl_2H]\cdot[MeSiH_3]/[MeSiClH_2]^2 = 0.48 \pm 0.05$

E. System $(CH_3)_2SiCl_2$ *vs.* $(CH_3)_2SiH_2$

$K_1 = [Me_2SiCl_2]\cdot[Me_2SiH_2]/[Me_2SiClH]^2 = (9.8 \pm 0.7) \times 10^{-2}$

The simplest such case involves the exchange of hydrogen and chlorine on the dimethylsilicon moiety as represented by the equilibrium equation given below:

$$2\,(CH_3)_2SiClH \rightleftarrows (CH_3)_2SiCl_2+(CH_3)_2SiH_2 \qquad (1)$$

Evaluation of the experimental data shows that the equilibrium constant K_1 (see system E in Table 2) for eqn. (1) is considerably smaller than the random value, $K_{rand}=0.25$. This indicates a greater-than-statistical preference at equilibrium for the mixed species, $(CH_3)_2SiClH$, with respect to the other two participating compounds.

The second system involving exchange of hydrogen and chlorine on a single kind of moiety of silicon deals with the equilibria of these substituents on the methylsilicon moiety. In this case, two equations are required to describe the resulting equilibria, and these may be the following:

$$2\,CH_3SiCl_2H \rightleftarrows CH_3SiCl_3+CH_3SiClH_2 \qquad (2)$$

$$2\,CH_3SiClH_2 \rightleftarrows CH_3SiCl_2H+CH_3SiH_3 \qquad (3)$$

Values for the equilibrium constants K_2 and K_3 corresponding to eqns. (2) and (3) were obtained from the experimental data and are shown in Table 2 as system D. The constant K_2 is smaller than the random value by a factor of 10 thus favoring at equilibrium the formation of the species CH_3SiCl_2H. On the other hand, the constant K_3 is quite close to the random value, $K_{rand}=0.333$. These two constants are to be compared with values of the same type of constant for the analogous phenyl system[10], with C_6H_5 instead of CH_3 in eqns. (2) and (3). For this system, $K_2=(6.2\pm0.1)\times10^{-2}$ and $K_3=0.38\pm0.01$ which is in surprisingly good agreement with the related constants for the methyl derivatives in Table 2. The conclusion to be drawn is that, as far as the hydrogen/chlorine exchange equilibrium is concerned, it does not appear to make a great deal of difference whether the central moiety is methylsilicon or phenylsilicon. Significant differences, however, may be expected in the rates of equilibration.

The systems discussed subsequently are characterized by the additional feature that the exchanging substituents hydrogen and chlorine redistribute between two kinds of silicon moieties. If the two central moieties are methylsilicon and dimethylsilicon, equilibrium in terms of exchange of hydrogen and chlorine is attained not only with respect to the distribution of these two substituents on the dimethyl or methylsilicon moieties according to eqns. (1)–(3) but also between these two central moieties. In other words, in addition to the equilibria represented by eqns. (1)–(3), another equilibrium, such as the one shown in eqn. (4), has to be considered also.

$$2\,CH_3SiH_3+3\,(CH_3)_2SiCl_2 \rightleftarrows 2\,CH_3SiCl_3+3\,(CH_3)_2SiH_2 \qquad (4)$$

The latter expresses the relative distribution of exchangeable chlorine and hydrogen atoms between the methylsilicon and dimethylsilicon moieties. Therefore, the equilibria in this system are determined by the constants K_1, K_2, and K_3 corresponding to equations (1)–(3) as well as an intersystem constant $K_{I,A}$ corresponding to eqn. (4). As shown in Table 2, the equilibrium constants K_1, K_2, and K_3 determined in this system (system A) agree very well with the values for these constants determined in systems D and E. The very small value of the intersystem constant $K_{I,A}$ indicates that at equilibrium, the silanic hydrogen atoms favor the methylsilicon moiety with the chlorine atoms preferring the dimethylsilicon moiety. If the distribution were random, the value of this constant would be 1.00.

The distribution of these two exchangeable substituents between methylsilicon and trimethylsilicon may be treated analogously. Thus, in addition to the equilibria on the methylsilicon moiety represented by eqns. (2) and (3), the distribution of the two substituents with respect to the two central moieties is determined by an inter-system equilibrium given by eqn. (5). Again the values of the constants K_2 and K_3

$$CH_3SiH_3 + 3(CH_3)_3SiCl \rightleftarrows CH_3SiCl_3 + 3(CH_3)_3SiH \qquad (5)$$

TABLE 3

EQUILIBRIUM DATA (in mole %) FOR THE EXCHANGE OF SILANIC HYDROGEN WITH CHLORINE ATOMS BETWEEN MOIETIES OF METHYLSILICON AT 100° (WITH TETRABUTYLAMMONIUM CHLORIDE AS CATALYST)

A. System[a] CH_3SiCl_3 *vs.* $(CH_3)_2SiH_2$

$R \equiv$ Cl/Si	$R' \equiv$ MeSi/Si	$MeSiCl_3$	$MeSiCl_2H$	$MeSiClH_2$	$MeSiH_3$	Me_2SiCl_2	Me_2SiClH	Me_2SiH_2
0.584[b]	0.195[b]	[c]		3.7	15.5	5.5	44.2	31.1
(0.589)[d]	(0.192)[d]	(0.0)[e]	(0.1)	(3.0)	(16.4)	(5.6)	(43.9)	(31.0)
0.876	0.292		1.4	7.2	19.0	15.8	45.3	11.4
(0.869)	(0.276)	(0.0)	(1.2)	(9.5)	(18.4)	(15.8)	(44.0)	(11.0)
1.113	0.371		6.2	16.6	14.5	23.5	33.7	5.4
(1.097)	(0.373)	(0.1)	(4.7)	(17.0)	(15.3)	(25.6)	(33.4)	(3.9)
1.499	0.500	0.7	21.6	20.9	8.1	33.3	15.4	
(1.482)	(0.513)	(1.1)	(19.8)	(22.7)	(6.5)	(35.0)	(14.5)	(0.5)
2.020	0.673	14.6	45.7	9.1		27.1	3.6	
(2.021)	(0.694)	(13.9)	(44.2)	(8.8)	(0.4)	(30.5)	(2.2)	(0.0)

B. System[f] CH_3SiCl_3 *vs.* $(CH_3)_3SiH$

$R \equiv$ Cl/Si	$R' \equiv$ MeSi/Si	$MeSiCl_3$	$MeSiCl_2H$	$MeSiClH_2$	$MeSiH_3$	Me_3SiCl	Me_3SiH
0.582[b]	0.194[b]	[c]			18.8	57.6	23.6
(0.576)[d]	(0.188)[d]	(0.0)[e]	(0.0)	(0.7)	(18.7)	(57.5)	(23.1)
1.326	0.445	4.0	28.0	11.5	1.3	55.2	
(1.347)	(0.448)	(2.7)	(28.5)	(12.0)	(1.3)	(55.4)	(0.1)
1.519	0.507	10.2	34.6	6.9		48.0	0.3
(1.547)	(0.517)	(8.1)	(35.9)	(6.3)	(0.2)	(49.3)	(0.0)
1.690	0.563	20.4	36.0	3.7		40.0	
(1.769)	(0.601)	(16.2)	(36.7)	(3.3)	(0.1)	(43.7)	(0.0)
1.965	0.655	36.6	30.4	1.1		32.0	
(2.030)	(0.681)	(32.3)	(31.9)	(1.3)	(0.0)	(34.5)	(0.0)

C. System[g] $(CH_3)_2SiCl_2$ *vs.* $(CH_3)_3SiH$

$R \equiv$ Cl/Si	$R' \equiv Me_2$Si/Si	Me_2SiCl_2	Me_2SiClH	Me_2SiH_2	Me_3SiCl	Me_3SiH
0.499[b]	0.250[b]	0.5[c]	7.0	19.8	41.8	31.0
(0.498)[d]	(0.273)[d]	(0.2)[e]	(6.1)	(18.7)	(43.4)	(31.6)
1.080	0.540	16.6	33.0	6.0	42.6	1.9
(1.088)	(0.556)	(16.2)	(31.6)	(6.2)	(44.0)	(2.0)
1.162	0.581	21.9	29.6	5.7	41.0	1.9
(1.144)	(0.572)	(22.1)	(31.5)	(4.5)	(40.5)	(1.4)
1.247	0.623	29.1	29.9	3.7	36.2	1.1
(1.243)	(0.627)	(28.8)	(30.3)	(3.2)	(36.8)	(0.9)
1.490	0.745	52.0	20.6	1.4	24.9	1.2
(1.495)	(0.740)	(50.3)	(23.1)	(1.1)	(25.2)	(0.3)

(continued on next page)

TABLE 3 (*continued*)

D. System[h] CH_3SiCl_3 *vs.* CH_3SiH_3

R≡H/Si	$MeSiCl_3$	$MeSiCl_2H$	$MeSiClH_2$	$MeSiH_3$
1.000 [b]	13.0 [c]	71.5	13.8	1.6
(1.041)[d]	(15.4)[e]	(70.3)	(13.1)	(1.2)
1.179	10.1	63.2	22.3	4.5
(1.211)	(8.9)	(67.2)	(20.8)	(3.0)
1.599	2.7	48.5	35.5	13.4
(1.596)	(2.6)	(48.0)	(36.3)	(13.1)
1.730	2.2	37.9	40.5	19.4
(1.770)	(1.8)	(41.2)	(39.2)	(17.7)
2.591		5.3	26.5	68.2
(2.629)	(0.1)	(6.0)	(28.7)	(65.2)

E. System[i] $(CH_3)_2SiCl_2$ *vs.* $(CH_3)_2SiH_2$

R≡H/Si	Me_2SiCl_2	Me_2SiClH	Me_2SiH_2
0.674 [b]	39.5	53.1	7.4
(0.679)[d]	(39.6)[e]	(53.4)	(7.0)
0.840	26.2	60.7	13.1
(0.869)	(28.2)	(59.5)	(12.3)
1.165	11.5	60.2	28.3
(1.168)	(12.1)	(59.4)	(28.5)
1.285	9.1	52.2	38.7
(1.296)	(8.1)	(55.2)	(36.6)
1.559	2.2	38.6	59.2
(1.570)	(2.5)	(39.0)	(58.5)

[a] Equilibrium reached in less than 23 h at 100°. Data correspond to 44 h at this temperature. [b] From the ingredients. [c] Experimental NMR data. [d] Calculated from the NMR data. [e] Calculated from the equilibrium constants in Table 2. [f] Equilibrium reached in less than 28 h at 100°. Data correspond to 46 h at this temperature. [g] Equilibrium reached in less than 128 h at 100°. Data correspond to 150 h at this temperature. [h] Equilibrium reached in less than 23 h at 100°. Data correspond to 42 h at this temperature. [i] Equilibrium reached in less than 23 h at 100°. Data correspond to 44 h at this temperature.

determined in this system (system B in Table 2) agree well with the values of these constants determined independently in system D. The intersystem constant $K_{I,B}$ corresponding to the equilibrium of eqn. (5) is very small here also, indicating preference at equilibrium of the silanic hydrogens for the methylsilicon moiety.

Similarly, in the system involving dimethylsilicon and trimethylsilicon as central moieties, exchange equilibria are established corresponding to equations (1) and (6), with the latter describing the distribution of the two exchangeable substituents between the two central moieties. Table 2 shows (system C) the values of the constant K_1 corresponding to eqn. (1) and an intersystem constant $K_{I,C}$ corresponding to equation (6). Good agreement is seen again for the values of K_1

$$(CH_3)_2SiH_2+2\,(CH_3)_3SiCl \rightleftharpoons (CH_3)_2SiCl_2+2\,(CH_3)_3SiH \qquad (6)$$

as determined in systems C and E. Also in this case, the intersystem constant $K_{I,C}$ is quite small, with the equilibrium situation being characterized by the preference of the silanic hydrogens for the moiety of silicon bearing the lesser number of methyl groups.

The experimental data expressed in mole percent of each compound in the equilibrated mixtures are summarized in Table 3 where they are compared with values computed[8,9] for the same respective over-all compositions (expressed in terms of the composition parameters R and R') using the constants of Table 2. Good agreement between these values is generally observed.

DISCUSSION

In agreement with Ref. 1, the three intersystem constants of the systems A, B, and C in Table 2 show in quantitative terms that at equilibrium silanic hydrogen is preferentially attached to the moiety of silicon bearing the lesser number of methyl groups[1]. Accordingly, the chlorine atoms show a preference for the silicon moiety having the larger number of methyl groups. This means that at equilibrium the combination of products in which hydrogen (chlorine) atoms accumulate on the silicon atoms bearing the lesser (greater) number of methyl groups will be favored. A similar trend, exhibited in varying degree has been observed earlier[4–6] for the scrambling equilibria on these moieties of halogens with other substituents; *e.g.* $N(CH_3)_2$, OCH_3, and SCH_3. In these latter cases, halogen atoms at equilibrium also are preferentially associated with the silicon moiety bearing the larger number of methyl groups.

In describing systems of the type discussed in this paper, we have chosen equilibrium constants of the form given in Table 2. There are of course many other meaningful equilibrium equations one may write for which constants may be determined. We therefore have used the experimental equilibrium data in Table 3 to calculate a number of additional equilibrium constants which are shown in Table 4. Constants K_4 through K_{12} represent the experimental system A of Table 3; while K_{13} through K_{17} describe system B; and K_{18} and K_{19} system C. These constants and their standard deviations were calculated in the same fashion[9] as the ones listed in Table 2. Alternatively they may also be obtained from the set of equilibrium constants of Table 2 (K_1 through K_3, $K_{I,A}$, $K_{I,B}$, and $K_{I,C}$).

It should be noted in Table 4 that the relative experimental errors* for the constants K_4 through K_{17} calculated from the equilibrium constants of Table 2 are considerably smaller than the relative errors for these same constants as calculated directly from experimental data. This lesser error explains why data from our laboratory for exchange on a given central moiety are always expressed in terms of the equilibria resulting from exchanging the two distinguishable substituents between a pair of like molecules, since the set of three molecules thus involved in calculating the equilibrium constants [*e.g.*, see eqns. (1) through (3)] are always simultaneously present in comparable amounts. Similarly, the intersystem constant, K_I, is calculated[8] from a previous evaluation of constants of the form of K_1 through K_3 and hence also have relatively small errors.

The minimum number of equilibrium constants needed to describe the over-all system in which silanic hydrogen and chlorine atoms are scrambled between all of the mono-, di-, and trimethylsilicon moieties is five. There is one constant in Table 2 which is not independent, since only two rather than three intersystem constants are needed. Thus, $K_{I,C} = \sqrt[3]{K_{I,B}^2/K_{I,A}}$. The form for the equilibrium constants of Table 2 is also advantageous for determining immediately which constants are independent. Note that, if there are n different "systems" in each of which two kinds of substituents are scrambled on a given central moiety, there need only be $n-1$ intersystem constants to define the over-all equilibria. A set of five independent equilibrium constants may be garnered from Table 4 in a number of ways. For example, one may choose a set of four different relationships from equations (1)–(12) plus one from eqns. (13)–(19).

Constants similar to the ones listed in Table 4 have been determined for the equilibria involving phenylmethylhalosilanes[10], *e.g.* ($Ph = C_6H_5$, $Me = CH_3$), $K_a =$

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* The calculations of standard deviations from those of the constants of Table 2 have been performed according to eqn. (24) in ref. 9.

TABLE 4

ADDITIONAL EXPERIMENTAL AND CALCULATED EQUILIBRIUM CONSTANTS FOR THE HYDROGEN-CHLORINE EXCHANGE ON VARIOUS METHYLSILICON MOIETIES

		From experimental data[a]	Calculated from the constants of Table 2	
K_4	$= [\mathrm{MeSiH_3}]\cdot[\mathrm{Me_2SiCl_2}]/\{[\mathrm{MeSiClH_2}]\cdot[\mathrm{Me_2SiClH}]\}$	$= 0.61 \pm 0.30$	$\sqrt[6]{K_1^3\cdot K_2^2\cdot K_3^4/K_{1,A}}$	$= 0.78 \pm 0.11$
K_5	$= [\mathrm{MeSiH_3}]\cdot[\mathrm{Me_2SiClH}]/\{[\mathrm{MeSiClH_2}]\cdot[\mathrm{Me_2SiH_2}]\}$	$= 7.30 \pm 2.78$	$\sqrt[6]{K_2^2\cdot K_3^4/(K_1^3\cdot K_{1,A})}$	$= 8.68 \pm 1.29$
K_6	$= [\mathrm{MeSiClH_2}]\cdot[\mathrm{Me_2SiCl_2}]/\{[\mathrm{MeSiCl_2H}]\cdot[\mathrm{Me_2SiClH}]\}$	$= 1.81 \pm 0.24$	$\sqrt[6]{K_1^3\cdot K_2^2/(K_3^2\cdot K_{1,A})}$	$= 2.60 \pm 0.33$
K_7	$= [\mathrm{MeSiClH_2}]\cdot[\mathrm{Me_2SiClH}]/\{[\mathrm{MeSiCl_2H}]\cdot[\mathrm{Me_2SiH_2}]\}.$	$= 22.3 \pm 6.7$	$\sqrt[6]{K_2^2/(K_1^3\cdot K_3^2\cdot K_{1,A})}$	$= 42.5 \pm 5.4$
K_8	$= [\mathrm{MeSiClH_2}]\cdot[\mathrm{Me_2SiClH}]/\{[\mathrm{MeSiH_3}]\cdot[\mathrm{Me_2SiCl_2}]\}$	$= 8.2 \pm 10.8$	$\sqrt[6]{K_{1,A}/(K_1^3\cdot K_2^2\cdot K_3^4)}$	$= 1.28 \pm 0.19$
K_9	$= [\mathrm{MeSiCl_2H}]\cdot[\mathrm{Me_2SiCl_2}]/\{[\mathrm{MeSiCl_3}]\cdot[\mathrm{Me_2SiClH}]\}$	$= 38.8 \pm 21.4$	$\sqrt[6]{K_1^3/(K_2^4\cdot K_3^2\cdot K_{1,A})}$	$= 42.0 \pm 6.4$
K_{10}	$= [\mathrm{MeSiCl_2H}]\cdot[\mathrm{Me_2SiClH}]/\{[\mathrm{MeSiCl_3}]\cdot[\mathrm{Me_2SiH_2}]\}$	$= (5.08 \pm 3.40)\times 10^2$	$1/\sqrt[6]{K_1^3\cdot K_2^4\cdot K_3^2\cdot K_{1,A}}$	$= (4.67 \pm 0.71)\times 10^2$
K_{11}	$= [\mathrm{MeSiH_3}]\cdot[\mathrm{Me_2SiCl_2}]/\{[\mathrm{MeSiCl_2H}]\cdot[\mathrm{Me_2SiH_2}]\}$	$= 18.7 \pm 7.7$	$\sqrt[3]{K_2^2\cdot K_3/K_{1,A}}$	$= 22.6 \pm 5.1$
K_{12}	$= [\mathrm{MeSiClH_2}]\cdot[\mathrm{Me_2SiCl_2}]/\{[\mathrm{MeSiCl_3}]\cdot[\mathrm{Me_2SiH_2}]\}$	$= (1.21 \pm 0.60)\times 10^3$	$1/\sqrt[3]{K_2\cdot K_3^2\cdot K_{1,A}}$	$= (1.21 \pm 0.3)\times 10^3$
K_{13}	$= [\mathrm{MeSiH_3}]\cdot[\mathrm{Me_3SiCl}]/\{[\mathrm{MeSiClH_2}]\cdot[\mathrm{Me_3SiH}]\}$	$= 60.8 \pm 41.5$	$\sqrt[3]{K_2\cdot K_3^2/K_{1,B}}$	$= 71.3 \pm 45.4$
K_{14}	$= [\mathrm{MeSiClH_2}]\cdot[\mathrm{Me_3SiCl}]/\{[\mathrm{MeSiCl_2H}]\cdot[\mathrm{Me_3SiH}]\}$	$= (3.69 \pm 6.62)\times 10^2$	$\sqrt[3]{K_2/(K_{1,B}\cdot K_3)}$	$= (2.85 \pm 1.18)\times 10^2$
K_{15}	$= [\mathrm{MeSiCl_2H}]\cdot[\mathrm{Me_3SiCl}]/\{[\mathrm{MeSiCl_3}]\cdot[\mathrm{Me_3SiH}]\}$	$= (3.81 \pm 3.26)\times 10^3$	$1/\sqrt[3]{K_{1,B}\cdot K_2^2\cdot K_3}$	$= (4.92 \pm 2.07)\times 10^3$
K_{16}	$= [\mathrm{MeSiH_3}]\cdot[\mathrm{Me_3SiCl}]^2/\{\mathrm{MeSiCl_2H}]\cdot[\mathrm{Me_3SiH}]^2\}$	$= (6.68 \pm 5.79)\times 10^3$	$\sqrt[3]{K_2^2\cdot K_3/K_{1,B}{}^2}$	$= (2.03 \pm 1.36)\times 10^4$
K_{17}	$= [\mathrm{MeSiCl_3}]\cdot[\mathrm{Me_3SiH}]^2/\{[\mathrm{MeSiClH_2}]\cdot[\mathrm{Me_3SiCl}]^2\}$	$= (1.64 \pm 2.76)\times 10^{-5}$	$\sqrt[3]{K_2\cdot K_3^2\cdot K_{1,B}{}^2}$	$= (7.13 \pm 5.86)\times 10^{-7}$
K_{18}	$= [\mathrm{Me_2SiH_2}]\cdot[\mathrm{Me_3SiCl}]/\{[\mathrm{Me_2SiClH}]\cdot[\mathrm{Me_3SiH}]\}$	$= 3.51 \pm 1.18$	$\sqrt[2]{K_1/K_{1,C}}$	$= 4.23 \pm 0.46$
K_{19}	$= [\mathrm{Me_2SiClH}]\cdot[\mathrm{Me_3SiCl}]/\{[\mathrm{Me_2SiCl_2}]\cdot[\mathrm{Me_3SiH}]\}$	$= 26.9 \pm 14.0$	$1/\sqrt[2]{K_{1,C}\cdot K_1}$	$= 42.3 \pm 4.6$

[a] For K_4 to K_{12}, the equilibrium constants of System A in Table 2 were used; for K_{13} to K_{17}, the constants of System B; and for K_{18} and K_{19}, the constants of system C.

$[\mathrm{PhMe_2SiCl}]\cdot[\mathrm{PhMeSiClH}]/\{[\mathrm{PhMe_2SiH}]\cdot[\mathrm{PhMeSiCl_2}]\} = 29.6 \pm 0.6$, and $K_b = [\mathrm{PhMe_2SiCl}]\cdot[\mathrm{PhMeSiH_2}]/\{[\mathrm{PhMe_2SiH}]\cdot[\mathrm{PhMeSiClH}]\} = 3.6 \pm 0.2$. Disregarding the difference between the phenyl and methyl groups, constant K_a is related to K_{19} and constant K_b to K_{18} in Table 4. The good agreements of the related equilibrium constants of the phenylmethyl system with those of the all-methyl system in Table 4 shows again that to a first-order approximation, the equilibria in these systems are determined by the number of Si–C bonds per molecule rather than by the nature of the carbon-bonded nonexchanging substituents.

The above generalizations are significant for synthetic purposes. In agreement with the quantitative findings in this and other laboratories[1,2,10], it has been reported in the literature[11–14] that alkyltrichlorosilanes and dialkyldichlorosilanes are converted in high yields to the corresponding alkylsilanes by transhydrogenation with triethylsilane.

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