# Redistribution Equilibria of Fluorine Derivatives of Group IV Elements. Part I. The Relative Affinity of Fluorine vs Chlorine for Silicon, Methylsilicon, Dimethylsilicon and Trimethylsilicon Moieties

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*The exchange of fluorine with chlorine atoms between pairs of silicon-based central moieties corresponding to the listing of the title has been investigated $^1H$ or $^{19}F$ NMR. The resulting equilibria have been described in terms of two sets of constants for the distribution of the halogens on each of the two central moieties, plus one "intersystem" constant which describes the relative affinity vs chlorine for the two competing centers. Redistribution always occurs at moderate temperatures, i.e. equilibrium with respect to the exchange of the halogens is reached before silicon–carbon bond scrambling occurs. At equilibrium the mixed fluorochloro species are generally present in lesser amounts than would be expected from random sorting of the substituents. There is a definite preference of fluorine for the silicon atom which bears the lesser number of alkyl groups.*

## Introduction

It is well known that the heat of formation of mixed species cannot be estimated from additive bond energies and that these bond energies vary as a function of increasing substitution of a given central atom by other substituents.[1] Yet the problem of interpreting and predicting such effects is still poorly documented and far from having received its solution.

One potent method for experimentally apprehending bond-energy *differences* involving various bonds to a given polyfunctional atom is to measure the redistribution equilibria of given pairs of substituents on a given central moiety.[2] Moreover, the redistribution between *two* distinct central moieties provides a way of quantitatively evaluating the relative affinities of a series of substituents for this pair of central moieties and is thus also related to the problem of bond-energy nonadditivity.

Although fluorine is an important substituent, both because of the variety of its derivatives and its unique position in the Periodical Table, redistribution involving bonds to fluorine has as yet received surprisingly little attention when compared to the redistribution of the other halogens, with other common substituents. Thus, for example, while redistribution reactions in silicon chemistry have been very extensively explored in recent years,[3] quantitative data for exchange involving fluorine on silicon are still limited to a few examples[4–6] which are insufficient to give a general and comprehensive picture of the redistribution behavior of fluorine. Moreover it appears that, prior to the work reported here, there has been no quantitative report on the exchange equilibria of fluorine vs other substituents between pairs of competing central moieties.

The purpose of the present series of papers is to provide quantitative data on the equilibrium distributions resulting from the exchange of fluorine vs other common substituents on typical central moieties based on group IV and V elements in order to classify both substituents and central moieties in "relative affinity series", thereby elucidating the controlling factors and providing a rationale for predicting new unknown equilibrium constants.

In the first paper, the exchange of fluorine vs chlorine atoms between the representative alkyl-substituted silicon moieties of the series $(CH_3)_nSi$, with n = 0 to 3, is reported. Chlorine has been chosen as a reference substituent since an extensive body of data is already available on the redistribution of Si–Cl bonds on these central moieties[7] which could then be used to predict additional sets of constants for fluorine exchanging systems.[8]

## Phenomenological Description[2,3,7]

It suffices, to evaluate the relative distribution of fluorine vs chlorine in the whole series of four centers $(CH_3)_nSi$ (n = 0 to 3) to examine separately the equilibrium distributions which result from the exchange

of the two halogens between three of the possible distinct pairs of central moieties. However, additionnal scrambling experiments were performed, both on one single central moiety and between other pairs of centers, in order to cross-check the results. Simultaneous competition of more than two centers at a time was also attempted but resulted in too complex mixtures and/or undetectably low proportions of some species.

The following short-form notation will be used throughout this series of papers for each system: {T/Z–Q/M} where T and Z are the pair of substituents presently under examination, and Q and M a pair of central moieties. For example {F/Cl–CH$_3$Si/(CH$_3$)$_2$Si} represents the scrambling of fluorine and chlorine atoms between the methyl and dimethylsilicon moieties. This notation has the advantage over previous ones not to suggest a dependence of the redistribution data on any given starting material as does for example, the notation (CH$_3$)$_2$SiF$_2$/CH$_3$SiCl$_3$ or (CH$_3$)$_2$SiCl$_2$/CH$_3$SiF$_3$.

The most generally adopted format for the constants consists,[7] first of the set of $\nu$–1 and $\mu$–1 constants which represent respectively the scrambling of the two substituents on centers Q and M taken separately

$$K_i(Q) = [QF_{i-1}Cl_{\nu-i+1}][QF_{i+1}Cl_{\nu-i-1}]/ [QF_iCl_{\nu-i}]^2 \quad (1)$$

where brackets denote concentrations, and secondly of

$$K_i(M) = [MF_{i-1}Cl_{\mu-i+1}][MF_{i+1}Cl_{\mu-i-1}]/ [MF_iCl_{\mu-i}]^2 \quad (2)$$

plus one constant which is chosen so as to relate both single-center based systems,

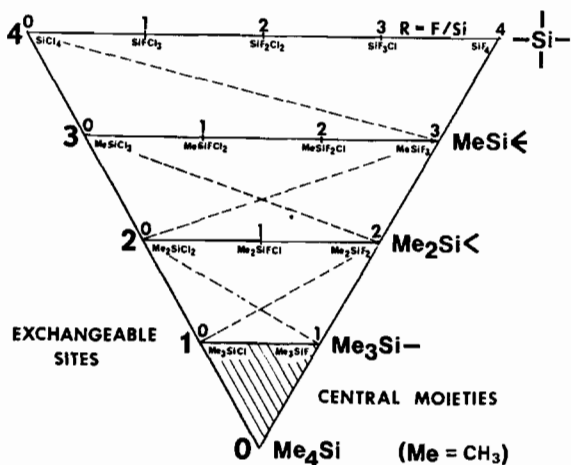$$K_1(Q/M) = [QCl_\nu]^\mu [MF_\mu]^\nu / [QF_\nu]^\mu [MCl_\mu]^\nu \quad (3)$$



Figure 1. Complete composition domain for the exchange of fluorine vs chlorine between the silicon, methylsilicon, dimethylsilicon and trimethylsilicon moieties.
The broken lines represent the two component mixtures which were investigated.

The complete composition domain covered in the present study is represented on Figure 1. Any given overall composition will be described by a set of two parameters, $R$ and $R'$, which were chosen as follows:

$$R = [F]/[Q] + [M] \qquad R' = [Q]/[Q] + [M]$$

Provided that the necessary starting materials were accessible we explored two diagonal cuts through the composition domain of each system. This is desirable for checking the invariance of the equilibrium constants and the validity of the usual assumption that concentrations rather than activities suffice to give a coherent description of the equilibrated scrambling phenomenon.

## Experimental

### Reagents
The silicon chlorides were carefully redistilled commercial products. The fluorides were obtained by the action of zinc difluoride[9] on the corresponding chlorides and the purity of the products was checked by nuclear magnetic resonance. All components were handled under dry nitrogen.

### Sample Preparation and Equilibration
The appropriate starting materials were distilled into NMR tubes and mixed in the chosen proportions in 5 mm O.D. NMR tubes and an equal volume of dry benzene or carbon tetrachloride was added. Neat liquids and thick-walled tubes were used when silicon tetrafluoride was expected to form, and medium thick-walled tubes when methylsilicon trifluoride was the most volatile species present in appreciable amounts. The sample tubes were filled so as to limit the vapor phase to its smallest possible volume. Great care was given to the sealing of the tubes: the portion of tube to be sealed must be kept clean from traces of fluoro–silicon compounds.

Equilibration was achieved by maintaining the sealed sample tubes for a sufficiently long period of time at 120° C. The time required for reaching equilibrium was estimated on the basis of test runs after various time intervals, and at several composition ratios, until the NMR spectra did not exhibit any further change. The reported equilibrium data generally correspond to much longer periods of heating.

### NMR Measurements and Data Reduction
Proton and fluorine NMR spectra were carried out at room temperature on Jeol Model C–60 HL or Varian Model A–60 spectrometers. The samples were quenched in order to insure freezing of the equilibrium. Since the exchange rates are exceed-

ingly slow at room temperature, the data correspond truly to equilibrium distributions at 120°. A typical $^1H$ NMR spectra is shown in Figure 2 for an equilibrated sample of the system {F/Cl–$CH_3Si$/$(CH_3)_2Si$}, and clearly demonstrates the occurrence of the redistribution phenomenon. Signal assignment was greatly simplified by the characteristic $^1H$–$^{19}F$ spin coupling patterns. The peaks for mixed species were further identified on the basis of the nearly linear increase of both $^1H$ and $^{19}F$ chemical shifts with increasing substitution along a given series. Verification of the signal assignments was obtained from material balance constancy throughout the scrambling experiments. Typical chemical shifts and spin coupling constants, as they were
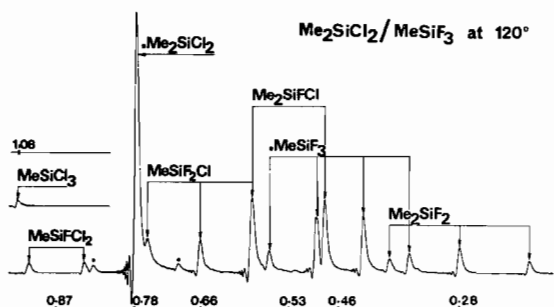
measured in equilibrated mixtures, are given in Table I. Peak areas were estimated by cutting out and weighing of Xerox copies (at least two copies each of two spectra per sample) of the expanded spectra. Calculation of the equilibrium constants and standard errors was achieved according to the principles and statistical data reduction processes laid down by Van Wazer and co-workers.[7]



Figure 2. Typical $^1H$ NMR spectra as measured on a sample from system {F/Cl–$CH_3Si$/$(CH_3)_2Si$}, for R = 0.75 and R' = 0.85, equilibrated at 120° C.

TABLE I. $^1H$ and $^{19}F$ NMR Data[a]

| Compounds | $^1H$ | $^{19}F$ | $J_{H-F}$ |
|---|---|---|---|
| $SiF_4$ | – | 163 | – |
| $SiF_3Cl$ | – | 135 | – |
| $SiF_2Cl_2$ | – | 112 | – |
| $SiFCl_3$ | – | 94 | – |
| $CH_3SiF_3$ | 0.47 | 134 | 4.1 |
| $CH_3SiF_2Cl$ | 0.66 | 119 | 4.6 |
| $CH_3SiFCl_2$ | 0.87 | 109 | 4.9 |
| $CH_3SiCl_3$ | 1.00 | – | – |
| $(CH_3)_2SiF_2$ | 0.29 | 131 | 6.1 |
| $(CH_3)_2SiFCl$ | 0.53 | 130 | 6.3 |
| $(CH_3)_2SiCl_2$ | 0.75 | – | – |
| $(CH_3)_3SiF$ | 0.20 | 155 | 7.1 |
| $(CH_3)_3SiCl$ | 0.39 | – | – |

[a] As measured on typical samples mixtures.

TABLE II. Equilibrium Constants Evaluated for Systems {F/Cl–$(CH_3)_nSi$/$(CH_3)_n$ Si} (n = n' ranging from 0 to 4).

| Systems {F/Cl–Q/M} | | System Constants[a] | | | | | | Intersystem Constants[a] |
|---|---|---|---|---|---|---|---|---|
| Q | M | $K_1(Si)$ | $K_2(Si)$ | $K_3(Si)$ | $K_1(CH_3Si)$ | $K_2(CH_3Si)$ | $K_1(CH_3)_2Si$ | $K_I(Q/M)$ |
| Si | $CH_3Si$ | 0.37 ±0.04 | 0.79 ±0.09 | 0.42 ±0.05 | 1.03 ±0.10 | 0.90 ±0.08 | | $(1.1 ± 0.6) \times 10^2$ |
| $CH_3Si$ | $(CH_3)_2Si$ | | | | 0.84 ±0.17 | 0.66 ±0.17 | 0.88 ±0.07 | $(1.4 ± 0.9) \times 10^4$ |
| $CH_3Si$ | $(CH_3)_3Si$ | | | | – | – | | $(1.2 ± 0.6) \times 10^5$ |
| $(CH_3)_2Si$ | $(CH_3)_3Si$ | | | | | | 0.91 ±0.10 | $(1.1 ± 0.2) \times 10^2$ |
| $CH_3Si$ | | | | | 0.80 ±0.09 | 0.83 ±0.10 | | |
| $(CH_3)_2Si$ | | | | | | | 0.87 ±0.06 | |
| Ideal Randomness | | 0.38 | 0.45 | 0.38 | 0.33 | 0.33 | 0.25 | 1.0 |

[a] $K_i$ from equation 1 or 2, $K_I$ from equation 3.

TABLE III. Experimental Equilibrium Data in Mole Percent for System $\{F/Cl–Si/CH_3Si\}$ at 120° C.

| $R =$ F/Si | $R' =$ >Si</Si | $SiF_4$ | $SiF_3Cl$ | $SiF_2Cl_2$ | $SiFCl_3$ | $SiCl_4$ | $CH_3SiF_3$ | $CH_3SiF_2Cl$ | $CH_3SiFCl_2$ | $CH_3SiCl_3$ | $K_1(Si)$ $K_2(Si)$ $K_3(Si)$ | $K_1(CH_3Si)$ $K_2(CH_3Si)$ | $K_1(4/3)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.95[a] | 0.50[a] | 1.7[a] | 7.1 | 10.8 | 16.9 | 13.3 | 1.7 | 5.1 | 13.5 | 29.7 | 0.36 1.03 0.50 | 0.88 0.83 | $2.1 \times 10^2$ |
| 1.13 | 0.42 | 2.6 | 8.6 | 10.0 | 13.9 | 7.2 | 4.1 | 7.4 | 15.5 | 30.8 | 0.35 1.19 0.37 | 1.16 0.95 | $1.5 \times 10^2$ |
| 1.25 | 0.55 | 3.9 | 9.8 | 15.9 | 15.7 | 9.3 | 3.1 | 5.8 | 11.8 | 24.7 | 0.65 0.61 0.60 | 1.09 1.03 | $2.7 \times 10^2$ |
| 1.27 | 0.34 | 2.7 | 8.6 | 10.1 | 9.2 | 3.1 | 6.9 | 11.1 | 18.3 | 30.1 | 0.37 0.78 0.37 | 1.03 1.00 | $2.4 \times 10^2$ |
| 1.63 | 0.36 | 4.4 | 8.9 | 6.7 | 4.8 | 1.4 | 15.4 | 17.0 | 20.0 | 21.4 | 0.41 0.95 0.40 | 1.07 0.91 | $1.4 \times 10^2$ |
| 1.95 | 0.40 | 6.3 | 14.9 | 11.2 | 6.4 | –[b] | 16.1 | 16.2 | 15.5 | 12.3 | 0.32 0.76 – | 0.95 0.83 | $0.7 \times 10^2$ |
| 2.60 | 0.16 | 7.2 | 6.2 | 2.1 | – | – | 53.4 | 19.8 | 8.3 | 2.9 | 0.39 – – | 1.13 0.84 | $1.2 \times 10^2$ |

[a] From the NMR data. [b] The corresponding undetected concentrations were calculated from $K_1(Si)$, $K_2(Si)$ and $K_3(Si)$ of Table II.

TABLE IV. Experimental and Calculated Data in Mole Percent for the System $\{F/Cl\text{–}CH_3Si\}$ at $120°$ C.

| $R =$ [F]/[Si] | $CH_3SiF_3$ | $CH_3SiF_2Cl$ | $CH_3SiFCl_2$ | $CH_3SiCl_3$ | $K_1(CH_3Si)$ | $K_2(CH_3Si)$ |
|---|---|---|---|---|---|---|
| 0.90[a] [0.87][b] | 8.0[a] (8.2)[c] | 17.6 (17.0) | 30.5 (31.2) | 43.9 (44.6) | 0.88 | 0.78 |
| 1.78 [1.75] | 31.1 (31.4) | 30.3 (30.4) | 24.2 (23.3) | 14.3 (14.9) | 0.82 | 0.74 |
| 2.23 [2.28] | 49.3 (49.3) | 30.5 (30.2) | 14.1 (14.6) | 6.2 (5.9) | 0.75 | 0.95 |
| 2.60 [2.63] | 69.1 (69.0) | 23.4 (23.4) | 6.0 (6.3) | 1.6 (1.4) | 0.76 | 1.02 |
| 2.70 [2.74] | 76.0 (75.3) | 18.8 (19.8) | 4.1 (4.1) | 1.1 (0.7) | 0.87 | 1.24 |

[a] From the NMR data. [b] From the weights of the ingredients. [c] Values calculated from the equilibrium constants $K_1(CH_3Si)$ = 0.80 and $K_2(CH_3Si)$ = 0.83.

TABLE V. Experimental and Calculated Equilibrium Data in Mole Percent for System $\{F/Cl\text{–}CH_3Si/(CH_3)_2Si\}$ at $120°$ C.

| $R =$ [F]/[Si] | $R' =$ [CH_3Si] /[Si] | $CH_3SiF_3$ | $CH_3SiF_2$ Cl | $CH_3SiF$ Cl_2 | $CH_3Si$ Cl_3 | $(CH_3)_2$ SiF_2 | $(CH_3)_2$ SiFCl | $(CH_3)_2$ SiCl_2 | $K_1$ $(CH_3)_2$ Si | $K_1$ $(CH_3Si)$ $K_2$ $(CH_3Si)$ | $K_1(3/2)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *0.89[a] [1.01][b] | 0.22[a] [0.49] | 13.3[a] (12.8)[c] | 5.6 (5.9) | 2.1 (2.3) | 0.6 (0.6) | 8.1 (7.9) | 19.8 (20.8) | 50.2 (49.6) | 1.04 | 0.89 0.76 | $1.1 \times 10^5$ |
| 1.02 [1.12] | 0.39 [0.44] | 15.6 (17.3) | 11.7 (12.2) | 7.6 (7.1) | 4.5 (2.9) | 4.1 (3.1) | 15.8 (12.4) | 40.7 (45.0) | 0.67 | 0.86 0.90 | $0.1 \times 10^5$ |
| 1.27 [1.33] | 0.29 [0.33] | 20.1 (21.0) | 7.0 (6.2) | 1.6 (1.5) | 0.3 (0.3) | 14.1 (13.6) | 22.8 (22.8) | 34.1 (34.6) | 0.93 | 0.65 0.82 | $0.6 \times 10^5$ |
| **0.74 [0.77] | 0.26 [0.25] | 11.6 (10.6) | 8.1 (8.0) | 4.7 (5.0) | 1.3 (2.2) | 4.0 (3.4) | 13.9 (14.6) | 56.5 (56.3) | 1.16 | 0.83 0.49 | $2.2 \times 10^5$ |
| 1.51 [1.71] | 0.50 [0.57] | 31.7 (31.5) | 12.7 (13.1) | 4.9 (4.6) | 1.0 (1.1) | 5.5 (5.9) | 14.7 (13.9) | 29.5 (29.9) | 0.75 | 0.96 0.53 | $1.5 \times 10^5$ |

* Samples prepared from $(CH_3)_2SiF_2$ and $CH_3SiCl_3$. ** Samples prepared from $CH_3SiF_3$ and $(CH_3)_2SiCl_2$. [a] From the NMR data. [b] From the ingredients. [c] Values in parentheses are calculated from the averaged equilibrium constants $K(CH_3)_2Si$ = 0.88, $K_1(CH_3Si)$ = 0.84, $K_2(CH_3Si)$ = 0.66, and $K_1(3/2)$ = $1.4 \times 10^4$.

## Results

At $120°$ redistribution of fluorine and chlorine atoms was observed to occur in all of the 28 sample mixtures which were prepared for this study. No exchange involving methyl groups was detected at that temperature or even when a sample from the system $\{F/Cl\text{–}CH_3Si/(CH_3)_2Si]$ was heated for 15 months at $150°$. The time required to reach equilibrium depends to a large extent on the central moieties, starting materials, and overall compositions. No side reactions or attack of the fluorine compounds on the glasses tubes nor interaction or influence of the solvent (carbon tetrachloride or benzene) on the equilibrium distributions were noticed.

Averaged values of the equilibrium constants, corresponding to equations 1 to 3, are collected in Table II. The underlying experimental equilibrium distributions are given for the individual systems

TABLE VI. Experimental and Calculated Equilibrium Data in Mole Percent in the System {F/Cl–(CH$_3$)$_2$Si/(CH$_3$)$_3$Si} at 120° C.

| $R =$ [F]/[Si] | $R' =$ [(CH$_3$)$_2$Si]/ [Si] | (CH$_3$)$_2$SiF$_2$ | (CH$_3$)$_2$SiFCl | (CH$_3$)$_2$SiCl$_2$ | (CH$_3$)$_3$SiF | (CH$_3$)$_3$SiCl | $K_1$ (CH$_3$)$_2$Si) | $K_1$(2/1) |
|---|---|---|---|---|---|---|---|---|
| *0.59[a] [0.55][b] | 0.29[a] [0.28][b] | 18.6[a] (18.7)[c] | 7.1 (7.3) | 3.0 (2.7) | 14.2 (13.9) | 57.0 (57.4) | 1.10 | 99 |
| 0.92 [0.91] | 0.46 [0.46] | 34.7 (34.1) | 8.7 (9.2) | 2.4 (2.4) | 13.4 (14.1) | 40.9 (40.2) | 1.08 | 137 |
| 1.34 [1.29] | 0.66 [0.64] | 56.1 (56.3) | 9.0 (8.7) | 1.2 (1.3) | 13.0 (12.8) | 20.7 (20.9) | 0.83 | 116 |
| **0.49 [0.49] | 0.51 [0.51] | 14.2 (14.2) | 17.1 (17.1) | 19.7 (19.8) | 3.5 (3.6) | 45.5 (45.4) | 0.95 | 121 |
| 0.54 [0.50] | 0.56 [0.51] | 15.4 (15.8) | 19.6 (18.7) | 20.7 (21.2) | 3.3 (3.3) | 41.1 (41.0) | 0.83 | 118 |
| 0.73 [0.71] | 0.29 [0.29] | 22.7 (22.8) | 4.9 (4.9) | 1.1 (1.0) | 22.2 (22.0) | 49.1 (49.4) | 1.02 | 103 |

* Samples prepared from (CH$_3$)$_2$SiF$_2$ and (CH$_3$)$_3$SiCl. ** Samples prepared from (CH$_3$)$_2$SiCl$_2$ and (CH$_3$)$_3$SiF.
[a] From the NMR data. [b] From the ingredients. [c] Values in parentheses are calculated from the equilibrium constants $K_1$(CH$_3$)$_2$Si = 0.91 and $K_1$(2/1) = (1.1) × 10$^2$.

TABLE VII. Experimental and Calculated Data in Mole Percent for the System {F/Cl–CH$_3$Si/(CH$_3$)$_3$Si} at 120° C.

| $R =$ [F]/[Si] | $R' =$ [CH$_3$Si] /[Si] | CH$_3$SiF$_3$ | CH$_3$SiF$_2$Cl | CH$_3$SiFCl$_2$ | CH$_3$SiCl$_3$ | (CH$_3$)$_3$SiF | (CH$_3$)$_3$SiCl | $K_1$CH$_3$Si $K_2$CH$_3$Si | $K_1$(3/1) |
|---|---|---|---|---|---|---|---|---|---|
| *0.75[a] [0.82][b] | 0.25[a] [0.27][b] | 20.1[a] (19.8)[c] | 5.3 (4.3) | –[d] (0.8) | – (0.1) | 3.8 (6.1) | 70.8 (68.9) | – – | 1.3 × 10$^5$ |
| 1.44 [1.51] | 0.49 [0.50] | 44.7 (41.6) | 3.8 (6.1) | – (0.7) | – (0.1) | 2.1 (6.0) | 49.3 (45.5) | – – | 7.5 × 10$^5$ |
| 1.48 [1.59] | 0.52 [0.53] | 39.5 (41.6) | 11.1 (8.8) | 1.4 (1.5) | – (0.2) | 5.7 (4.0) | 42.3 (43.9) | 0.46 – | 1.1 × 10$^5$ |
| 2.02 [2.09] | 0.68 [0.70] | 63.3 (61.5) | 4.4 (6.0) | – (0.5) | – (0.0) | 3.5 (5.3) | 28.7 (26.7) | – – | 1.0 × 10$^5$ |
| ** 0.47 [0.48] | 0.54 [0.52] | 4.0 (4.2) | 9.2 (9.0) | 15.7 (15.7) | 24.5 (24.6) | 0.4 (0.4) | 46.1 (46.1) | 0.75 0.91 | 2.4 × 10$^5$ |

* Samples prepared from (CH$_3$)$_3$SiCl and CH$_3$SiF$_3$. ** Samples prepared from (CH$_3$)$_3$SiF and CH$_3$SiCl$_3$. [a] From the NMR data.
[b] From the weights of the ingredients. [c] Values calculated from the equilibrium constants $K_1$CH$_3$Si = 0.80, $K_2$CH$_3$Si = 0.83, and $K_1$(1/3) = 1.2 × 10$^5$. [d] The corresponding undetected concentrations were calculated from $K_1$CH$_3$Si and $K_2$CH$_3$Si of Table IV.

in Tables III to VII, where they are compared with the molecular distributions calculated from the corresponding sets of equilibrium constants of Table II.

*Systems {F/Cl–Si/CH$_3$Si} and {F/Cl–CH$_3$Si}*

When system {F/Cl–Si/CH$_3$Si} is considered, a total of nine distinct molecular species participate in the redistribution equilibria (Table III). They are

determined by a set of six independent constants (Table II). Seven sample mixtures were prepared from silicon tetrachloride and methylsilicon trifluoride. Equilibrium was reached after *ca.* 12 months at 120° C. This time is considerably reduced (to less than 1 month) when trace amounts of pyridine are added to the sample mixtures. Both $^1$H and $^{19}$F NMR were employed for quantitatively analyzing the equilibrated mixtures. The accuracy of the measurements is relatively poor for this particular system because of the use of thick-walled NMR tubes, the complexity of the sample mixtures, and the fact that one of the constituents, $SiCl_4$, can only be estimated by difference from the material balance. Because of this we undertook a separate study (Table IV) of the single-center based system {F/Cl–CH$_3$Si}. This study was of further use in the analysis of the system {F/Cl–CH$_3$Si/(CH$_3$)$_2$Si}, where considerable peak overlap was encountered.

### System {F/Cl–CH$_3$Si/(CH$_3$)$_2$Si} and {F/Cl–(CH$_3$)$_2$Si/(CH$_3$)$_3$Si}

Seven distinct species result from the scrambling of fluorine vs chlorine between methyl and dimethylsilicon moieties (Table V). From this case on, equilibrium was approached from both sides, i.e. by examining samples the composition of which were taken on both diagonals of the composition domain. Good agreement was found for the constants $K_i$(CH$_3$Si) with those estimated from the above studies. Sample mixtures prepared from both pairs of end members were also used to investigate the system {F/Cl–(CH$_3$)$_2$Si/(CH$_3$)$_3$Si}. Equilibrium data are reported in Table VI. For this system a set of experiments was also run at three temperatures (80, 120 and 150° C). It was found that the enthalpy of formation of the mixed species (CH$_3$)$_2$SiFCl, as estimated in van't Hoff's approximation, agrees well with the value which could be evaluated on the assumption that there are no significant changes in the exchange entropy between random and nonrandom sorting.

### System {F/Cl–CH$_3$Si/(CH$_3$)$_3$Si}

This system (Table VII) was investigated to check the consistency of the experimental equilibrium constants. The intersystem constant may indeed be evaluated from the constants determined above according to

$$K_I(CH_3Si/(CH_3)_3Si) =$$

$$\sqrt{K_I(CH_3Si/(CH_3)_2Si)^3 \; K_I((CH_3)_2Si/(CH_3)_3Si)}$$

$$= 1.6 \times 10^5$$

The concordance of the directly measured value (1.2 × 10$^5$) is rather gratifying. Further agreement is found for constants $K_i$(CH$_3$Si) with the *three* above determined sets of values.

## Discussion

Inspection of Table II leads to the following generalisations and conclusions: the system constants, which represent the equilibrium distributions of fluorine and chlorine on a single center, have values which are generally higher than those expected from random sorting. This means that the mixed species are less abundant in the equilibrated mixtures than would be expected from a thermoneutral[1,2] reaction, and is in contrast with the close-to-random distributions which were always observed for the sorting of chlorine vs bromine on a wide range of centers.[3]

The intersystem constants, as they are expressed here in the format of equation 3, are all significantly larger than their random value ($K_I = 1.00$). This means that fluorine exhibits a definite preference for the central moieties in which the silicon bears the lesser number of methyl groups. A parallel trend has been observed when chlorine was exchanged with bromine on the same series of centers, while the reverse trend was observed when chlorine was exchanged with methoxy, dimethylamino or thioalkyl groups.[7] However, when compared with the chlorine vs bromine exchange, the case of the fluorine vs chlorine exchange is characterized by much slower reactions and by an increase of two orders of magnitude in the values of the equilibrium constants.

These general trends: strong preferential affinity of fluorine for the least alkylated silicon, and unfavored mixed fluoro-chloro species, are illustrated by Figure 3 in which the observed equilibrium distributions are compared to random distributions for two diagonal cuts through the composition domain of Figure 1 for system {F/Cl–CH$_3$Si/(CH$_3$)$_2$Si}.

It is now widely admitted, if not fully established, that substitution of silicon by the strongly electron-withdrawing fluorine atom causes substantial d-orbital contraction and subsequent decrease in their energy, which makes them more available for both $\sigma$ and $\pi$ bonding.[10] This effect is expected to be much less pronounced with chlorine and bromine, and could account for the difference in magnitude which is found when the intersystem constants in Table II are compared with those obtained when chlorine is exchanged with bromine.[3] However, other factors, such as bond polarity differences and through space interactions between geminal fluorine atoms may also plausibly contribute to the observed differences in behavior between the three halogens. Furthermore, the influence of the number of methyl groups bonded to silicon is difficult to assess. It seems impossible at the moment to decide whether increasing methyl substitution acts primarily through some electronic − inductive or hyperconjugative − effect, or merely by blocking one more site for fluorine substitution, or by changing the symmetry at the silicon atom which in turn will affect the extent of

π-bonding. Steric hindrance is not expected to be a predominant factor since it would act in such a way as to destabilize species such as $(CH_3)_3SiCl$ in favor of $(CH_3)_3SiF$, which is not observed.

Thus, the problem of relating the measured equilibrium distributions to changes in electronic structure along a substitution series appears to be very intricate. On the whole, there must be a subtle balance between all these factors which leads to the adoption of the most stable possible electronic repartition. Unfortunately, there are presently no data available which would help estimate, on a theoretical basis, the magnitude or relative importance of the various contributions. At the present time, only the experimental measurement of well chosen equilibrium constants may be of some use, through the establishment of empirical rules, in rendering the *a priori* prediction of equilibrium constants possible.

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