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# Competition Equilibria of Exchangeable Substituents Between Methylsilicon and Methylgermanium Moieties

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*Equilibria resulting from the exchange between methylsilicon and methylgermanium moieties of halogens (Cl, Br, or I) with either methoxyl, methylthio, or dimethylamino groups have been studied by proton nuclear magnetic resonance. Each set of experimental data was evaluated in terms of five independent equilibrium constants. Two of these describe the scrambling of pairs of substituents on the methylsilicon moiety, two similar ones describe the same process on the methylgermanium moiety, while an intersystem equilibrium constant relates the distribution of the pairs of substituents between the methylsilicon and methylgermanium moieties. For the various systems, the latter constant deviates over a wide range from the value corresponding to a random distribution.*

## Introduction

In an earlier paper[1] by these authors, it has been shown that pairs of exchangeable halogen substituents when scrambled between the trifunctional methylsilicon and methylgermanium moieties at equilibrium exhibit a definite preference of attachment to the silicon or germanium. These preferences have been expressed in terms of intersystem equilibrium constants. The study reported here represents an extension of this work to include scrambling equilibria between the methylsilicon and methylgermanium moieties of halogens (Cl, Br, or I) with either methoxyl, methylthio, or dimethylamino groups.

## Experimental Section

*Reagents.* Methyltrichlorosilane and methyltrimethoxysilane were purchased from Columbia Organic Chemicals, Inc., Columbia, S.C., and Anderson Chemical Co., Weston, Mich., respectively, and were fractionated before use. Methyltribromosilane,[1,2] methyltri(methylthio)silane,[3] and methyltris(dimethylamino)silane[4] were prepared according to methods of the literature. The methyltrihalogermanes were obtained by a modified version[5] of the Direct Synthesis[6] from germanium and methylhalide. Methyltrimethoxygermane was synthesized from methyltribromogermane, methanol, and triethylamine in benzene.

*Equilibrations and Measurements.* Sample preparation, equilibration, proton nuclear-magnetic-resonance (nmr) measurements and the calculations of weighted-average equilibrium constants were performed as previously reported.[1,7] The proton nmr chemical shifts of the methyl groups directly attached to both the silicon and the germanium atoms as well as of $OCH_3$, $SCH_3$, and $N(CH_3)_2$ groups in the equilibrated compounds are listed in Table I. Only the relative areas of the first kind of nmr peaks were used for the quantitative determination of the molecular species. The experimental error of the relative area of each peak measured is about 1% of the total methyl groups directly attached to silicon and germanium. Due to solvent effects, the shifts measured for benzene solutions differ considerably from those obtained for the neat liquids.

For the equilibrated mixtures made up of various proportions of the reagents $CH_3GeT_3$ and $CH_3SiZ_3$, where T and Z are different exchangeable substituents, the reaction conditions at which the data were obtained are the following, with the time for reaching equilibrium at the same temperature given in parentheses. For $Z = Cl$, $T = OCH_3$: 38 days at room temperature in benzene (11 days); for $Z = Br$, $T = OCH_3$: 10 days at room temperature in benzene (5 days); for $Z = SCH_3$, $T = Cl$: 160 hr at 120°, neat liquid, (141 hr); for $Z = SCH_3$, $T = Br$: 14 days at 120°, neat (136 hr); for $Z = SCH_3$, $T = I$: 10 days at 120°, neat (2 days); for $Z = N(CH_3)_2$, $T = Cl$: 136 hr at room temperature, neat (117 hr); $Z = N(CH_3)_2$, $T = Br$: 250 hr at room temperature, neat (145 hr); $Z = N(CH_3)_2$, $T = I$: 3 days at room temperature in benzene (5 hr). For the systems involving methylthio groups, the rate of exchange was sufficiently slow at room temperature so that samples which had been equilibrated at 120° and were quenched to room temperature still represented, upon immediate measurement, the equilibrium at 120°.

## Results and Conclusion

Scrambling equilibria involving the exchange of two kinds of monofunctional substituents, Z and T, between

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[1] K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, 5, 547 (1966).
[2] E. G. Rochow, *J. Am. Chem. Soc.*, 67, 963 (1945).
[3] K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, 5, 1254 (1966).
[4] H. Breederveld and H. I. Waterman, *Research London*, 5, 537 (1952).
[5] K. Moedritzer, *J. Organometal. Chem.*, 6, 282 (1966).
[6] E. G. Rochow, *J. Am. Chem. Soc.*, 69, 1729 (1947).
[7] J. R. Van Wazer, K. Moedritzer and L. C. D. Groenweghe, *J. Organometal. Chem.*, 5, 420 (1966).

**Table I.** Proton nmr chemical shifts observed in spectra of equilibrated samples in systems $CH_3GeT_3$ *vs.* $CH_3SiZ_3$ in ppm relative to internal tetramethylsilane[a]

| | | Compounds | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Z | T | $CH_3GeZ_3$ | $CH_3GeZ_2T$ | $CH_3GeZT_2$ | $CH_3GeT_3$ | $CH_3SiZ_3$ | $CH_3SiZ_2T$ | $CH_3SiZT_2$ | $CH_3SiT_3$ |
| Cl[b] | $OCH_3$ | **-0.833** | **-0.692** | **-0.513** | —[c] | **-0.692** | **-0.508** | **-0.267** | **-0.050** |
| | | | -3.475 | -3.483 | — | — | -3.380 | -3.355 | -3.330 |
| Br[b] | $OCH_3$ | **-1.258** | **-0.925** | **-0.592** | **-0.300** | **-0.950** | **-0.558** | **-0.158** | **-0.058** |
| | | | -3.458 | -3.508 | -3.550 | — | -3.468 | -3.433 | -3.408 |
| Cl | $SCH_3$ | **-1.617** | **-1.383** | **-1.150** | **-0.917** | **-1.083** | **-0.942** | **-0.783** | **-0.650** |
| | | | -2.250 | -2.150 | -2.058 | — | -2.133 | -2.050 | -1.983 |
| Br | $SCH_3$ | **-2.075** | **-1.700** | **-1.333** | **-0.967** | **-1.555** | **-1.267** | **-0.983** | **-0.683** |
| | | | -2.292 | -2.183 | -2.083 | — | -2.183 | -2.083 | -2.033 |
| I | $SCH_3$ | **-2.879** | **-2.283** | **-1.583** | **-0.787** | —[c] | **-1.817** | **-1.242** | **-0.717** |
| | | | -2.253 | -2.213 | -2.090 | — | -2.250 | -2.220 | -2.200 |
| Cl[d] | $N(CH_3)_2$ | **-1.652** | **-1.200** | **-0.767** | **-0.325** | —[c] | **-0.767** | **-0.350** | **-0.017** |
| | | | -2.645 | -2.559 | -2.498 | — | -2.583 | -2.486 | -2.426 |
| Br | $N(CH_3)_2$ | **-2.067** | **-1.396** | —[c] | —[c] | —[c] | —[c] | **-0.479** | **+0.029** |
| | | | -2.600 | — | — | — | — | -2.496 | -2.429 |
| I[b] | $N(CH_3)_2$ | **-2.254** | **-1.446** | —[c] | —[c] | —[c] | —[c] | **-0.582** | **-0.053** |
| | | | -2.195 | — | — | — | — | -2.319 | -2.427 |

[a] Tetramethylsilane was added to the samples after equilibrium had been reached. The values in boldface type represent $CH_3$ groups attached to either the Si or Ge, whereas the other values are the shifts of the corresponding $CH_3$ groups bonded to either the O, S or N atoms of the exchangeable substituents. The data were obtained in the neat liquids if not stated otherwise. [b] In benzene 5:1. [c] Not observed. [d] After equilibration, the samples were diluted with 5 parts of $CCl_4$ and tetramethylsilane was added.

two polyfunctional central moieties are expressed most conveniently in terms of intersystem equilibrium constants, $K_I$, which in the present case are derived from the following reaction:

$$CH_3SiZ_3+CH_3GeT_3 \rightleftarrows CH_3SiT_3+CH_3GeZ_3 \quad (1)$$

In addition to equation (1), two equilibrium equations are required to account for the scrambling of the Z and T substituents on the methylsilicon and two more for the scrambling on the methylgermanium moiety. The constants, $K_{(Si)_1}$ and $K_{(Si)_2}$, for the equilibria in the silicon system have been based on the reactions of equations (2) and (3).

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

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

The corresponding constants $K_{(Ge)_1}$ and $K_{(Ge)_2}$ for the germanium system are based on the reactions of equations (4) and (5).

$$2CH_3GeZ_2T \rightleftarrows CH_3GeZ_3+CH_3GeZT_2 \quad (4)$$

$$2CH_3GeZT_2 \rightleftarrows CH_3GeT_3+CH_3GeZ_2T \quad (5)$$

Values for the intersystem equilibrium constants for the mixtures studied are presented in Table II along with the pertinent constants $K_{(Si)_i}$ and $K_{(Ge)_i}$, i = 1 or 2. Also listed in Table II, in brackets, are values for the latter sets of constants obtained from studies of scrambling of the same pair of substituents on either the methylsilicon or methylgermanium moiety taken by itself.[8-10] It is seen that the values of these constants obtained from the two different types of experiments generally agree quite well. In all of the cases discussed herein, the values of these constants are smaller than the random value, $K_{1(rand)} = K_{2(rand)} = 0.333$.

Some of the intersystem constants $K_I$ in Table II deviate by many orders of magnitude from the value corresponding to random sorting of the substituents between the two central moieties, $K_{I(rand)} = 1.00$. For the substituents being a halogen and the methoxyl group, the $OCH_3$ at equilibrium is preferentially attached to the silicon and the halogen to germanium. When starting with a mixture of $CH_3Si(OCH_3)_3$ and $CH_3GeX_3$ (X = halogen) instead of $CH_3SiX_3$ and $CH_3Ge(OCH_3)_3$, no appreciable reaction is observed since the system is at the equilibrium state or very close to it – with the $OCH_3$ already being attached to silicon and the halogen to germanium. For the reverse situation, however, as many $OCH_3$ groups are transferred in a rapidly occurring exothermic reaction from $CH_3Ge$ as there are halogens available on $CH_3Si$ to be exchanged, depending, of course, on the relative molar amounts of the two reagents. This tendency increases when going from chlorine to bromine.

In the systems involving the exchange of methylthio groups with halogens, the values of $K_I$ become larger, in the order $Cl<Br<I$. This means that, for the substituents $SCH_3$ and Cl at equilibrium, the methylthio group prefers to be linked to germanium with the chlorine on the silicon ($K_I \sim 10^{-7}$). For the pairs of substituents $SCH_3$ and Br, this situation is reversed, with the methylthio group preferring at equilibrium to associate with the methylsilicon moiety. However, the effect is relatively small, since the intersystem equilibrium constant in this case is quite close to the random value, $K_{I(rand)} = 1.00$. For the substituents $SCH_3$ and I, the preference seen for the bromine system is greatly enhanced ($K_I \sim 10^{+4}$).

Highly nonrandom intersystem equilibrium constants corresponding to a preference of the halogens for the $CH_3Ge$ moiety were also observed for the scrambling of dimethylamino groups with halogens. The constants

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

(9) K. Moedritzer and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, *29*, 1571, 1851 (1967).

(10) K. Moedritzer and J. R. Van Wazer, *Makromol. Chem.*, *104*, 148 (1967).

**Table II.** Equilibrium constants[a] for $CH_3GeT_3$ *vs.* $CH_3SiZ_3$ systems at room temperature

| Z | T | $K_{(Si)1}=\frac{[MeSiZ_3][MeSiZT_2]}{[MeSiZ_2T]^2}$ | $K_{(Si)2}=\frac{[MeSiZ_2T][MeSiT_3]}{[MeSiZT_2]^2}$ | $K_{(Ge)1}=\frac{[MeGeZ_3][MeSiZT_2]}{[MeGeZ_2T]^2}$ | $K_{(Ge)2}=\frac{[MeGeZ_2T][MeGeT_3]}{[MeGeZT_2]^2}$ | $K_1=\frac{[CH_3SiT_3][CH_3GeZ_3]}{[CH_3SiZ_3][CH_3GeT_3]}$ |
|---|---|---|---|---|---|---|
| Cl [b] | $OCH_3$ | $(8.4\pm1.1)\times10^{-3}$<br>$[(4.2\pm0.2)\times10^{-2}]$ [d] | $(6.7\pm2.3)\times10^{-3}$<br>$[(1.8\pm0.1)\times10^{-2}]$ [d] | $(1.7\pm0.2)\times10^{-2}$<br>$[(1.3\pm0.2)\times10^{-2}]$ [e] | — [c]<br>$[(2.1\pm0.2)\times10^{-2}]$ [e] | $(1\pm10)\times10^{14}$ |
| Br [b] | $OCH_3$ | $(1.9\pm0.2)\times10^{-2}$<br>$[(5.8\pm0.3)\times10^{-2}]$ [f] | — [c]<br>$[(1.3\pm0.1)\times10^{-2}]$ [f] | $(2.1\pm0.3)\times10^{-2}$<br>$[(2.1\pm0.8)\times10^{-2}]$ [e] | $(3.5\pm0.4)\times10^{-2}$<br>$[(4.0\pm1.4)\times10^{-2}]$ [e] | $(1\pm10)\times10^{20}$ |
| Cl [g] | $SCH_3$ | $(9.3\pm0.6)\times10^{-2}$<br>$[(1.6\pm0.9)\times10^{-1}]$ [h] | $(1.4\pm0.1)\times10^{-1}$<br>$[(1.2\pm0.6)\times10^{-1}]$ [h] | $(3.4\pm0.7)\times10^{-2}$<br>$[(4.8\pm0.6)\times10^{-2}]$ [e] | $(2.8\pm0.4)\times10^{-2}$<br>$[(4.0\pm0.6)\times10^{-2}]$ [e] | $(1.4\pm0.5)\times10^{-7}$ |
| Br [g] | $SCH_3$ | $(2.0\pm0.2)\times10^{-2}$<br>$[(8.6\pm0.5)\times10^{-2}]$ [h] | $(1.2\pm0.5)\times10^{-2}$<br>$[(4.1\pm0.3)\times10^{-2}]$ [h] | $(5.7\pm0.7)\times10^{-2}$<br>$[(3.1\pm0.7)\times10^{-2}]$ [e] | $(3.6\pm0.3)\times10^{-2}$<br>$[(3.2\pm0.8)\times10^{-2}]$ [e] | $6.3\pm1.6$ |
| I [g] | $SCH_3$ | — [c]<br>— | $(3.7\pm0.3)\times10^{-2}$<br>— | $(2.9\pm0.3)\times10^{-2}$<br>$[(4.3\pm0.6)\times10^{-2}]$ [e] | $(6.5\pm1.1)\times10^{-2}$<br>$[(3.3\pm0.5)\times10^{-2}]$ [e] | $(9.1\pm4.1)\times10^{3}$ |
| Cl | $N(CH_3)_2$ | $1\times10^{-4}$<br>$[(5\pm7)\times10^{-4}]$ [d] | $1\times10^{-4}$<br>$[(5\pm6)\times10^{-4}]$ [d] | $1\times10^{-4}$<br>— | $1\times10^{-4}$<br>— | $(3.4\pm2.9)\times10^{12}$ |
| Br | $N(CH_3)_2$ | $1\times10^{-4}$<br>$[(1.4\pm0.9)\times10^{-4}]$ [h] | $1\times10^{-4}$<br>$[(1.6\pm6)\times10^{-4}]$ [h] | $1\times10^{-4}$<br>— | $1\times10^{-4}$<br>— | $(4.0\pm1.8)\times10^{20}$ |
| I [b] | $N(CH_3)_2$ | $1\times10^{-4}$<br>— | $1\times10^{-4}$<br>— | $1\times10^{-4}$<br>— | $1\times10^{-4}$<br>— | $(4.2\pm8.6)\times10^{20}$ |
| Ideal Randomness | | 0.333 | 0.333 | 0.333 | 0.333 | 1.00 |

[a] The equilibrium constants in square brackets were obtained in separate studies of the appropriate system: $CH_3SiZ_3$ *vs.* $CH_3SiT_3$ or $CH_3GeZ_3$ *vs.* $CH_3GeT_3$. [b] In 5 volumes of benzene as solvent. [c] Equilibrium constants could not be determined owing to the presence of an insufficient number of species at equilibrium. [d] Ref. 8. [e] Ref. 9. [f] Ref. 10. [g] Equilibrium constants correspond to 120°C. [h] Unpublished data.

**Table III.** Equilibrium data in mole per cent in the systems $CH_3GeT_3$ *vs.* $CH_3SiZ_3$

(A) System $CH_3Ge(OCH_3)_3$ *vs.* $CH_3SiCl_3$

| $R\equiv Cl/(Si+Ge)$ | $R'\equiv Si/(Si+Ge)$ | $CH_3GeCl_3$ | $CH_3GeCl_2$-$(OCH_3)$ | $CH_3GeCl$-$(OCH_3)_2$ | $CH_3Ge$-$(OCH_3)_3$ | $CH_3SiCl_3$ | $CH_3SiCl_2$-$(OCH_3)$ | $CH_3SiCl$-$(OCH_3)_2$ | $CH_3Si$-$(OCH_3)_3$ |
|---|---|---|---|---|---|---|---|---|---|
| 1.141 [a] | 0.380 [a] | 3.5 [b] | 46.7 | 12.7 | — | — | — | 1.1 | 36.3 |
| (1.177) [c] | (0.374) [c] | (2.8) [d] | (46.2) | (12.9) | (0.1) | (0.0) | (0.0) | (0.4) | (37.7) |
| 1.268 | 0.423 | 14.4 | 42.7 | 1.3 | — | — | — | — | 41.6 |
| (1.299) | (0.416) | (12.0) | (43.1) | (2.6) | (0.0) | (0.0) | (0.0) | (1.8) | (40.4) |
| 1.751 | 0.584 | 43.6 | — | — | — | — | 1.5 | 45.5 | 9.3 |
| (1.793) | (0.563) | (40.4) | (1.2) | (0.0) | (0.0) | (0.0) | (1.8) | (47.8) | (8.8) |
| 2.230 | 0.744 | 26.2 | 0.7 | — | — | 4.3 | 61.5 | 7.4 | — |
| (2.233) | (0.732) | (25.6) | (0.0) | (0.0) | (0.0) | (4.6) | (62.6) | (7.2) | (0.0) |
| 2.386 | 0.795 | 19.9 | — | — | — | 19.1 | 59.4 | 1.6 | — |
| (2.374) | (0.801) | (20.5) | (0.0) | (0.0) | (0.0) | (19.6) | (58.5) | (1.5) | (0.0) |

(B) System $CH_3Ge(OCH_3)_3$ *vs.* $CH_3SiBr_3$

| $R\equiv Br/(Si+Ge)$ | $R'\equiv Si/(Si+Ge)$ | $CH_3GeBr_3$ | $CH_3GeBr_2$-$(OCH_3)$ | $CH_3GeBr$-$(OCH_3)_2$ | $CH_3Ge$-$(OCH_3)_3$ | $CH_3SiBr_3$ | $CH_3SiBr_2$-$(OCH_3)$ | $CH_3SiBr$-$(OCH_3)_2$ | $CH_3Si$-$(OCH_3)_3$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.612 [a] | 0.204 [a] | — [b] | 4.3 | 53.6 | 23.3 | — | — | — | 18.9 |
| (0.622) [c] | (0.189) [c] | (0.0) [d] | (4.2) | (52.7) | (22.7) | (0.0) | (0.0) | (0.0) | (20.4) |
| 1.206 | 0.402 | 10.6 | 44.2 | 3.8 | — | — | — | — | 41.5 |
| (1.240) | (0.415) | (7.3) | (46.3) | (6.2) | (0.0) | (0.0) | (0.0) | (0.0) | (40.2) |
| 1.367 | 0.456 | 27.7 | 26.3 | — | — | — | — | — | 46.1 |
| (1.357) | (0.461) | (28.3) | (25.7) | (0.5) | (0.0) | (0.0) | (0.0) | (0.0) | (45.5) |
| 2.324 | 0.775 | 22.3 | — | — | — | 15.5 | 58.0 | 4.2 | — |
| (2.336) | (0.777) | (22.5) | (0.0) | (0.0) | (0.0) | (14.4) | (58.5) | (4.5) | (0.0) |
| 2.576 | 0.859 | 14.6 | — | — | — | 44.6 | 40.2 | 0.7 | — |
| (2.587) | (0.855) | (14.1) | (0.0) | (0.0) | (0.0) | (44.2) | (40.9) | (0.7) | (0.0) |

(C) System $CH_3GeCl_3$ *vs.* $CH_3Si(SCH_3)_3$

| $R\equiv Cl/(Si+Ge)$ | $R'\equiv Si/(Si+Ge)$ | $CH_3GeCl_3$ | $CH_3GeCl_2$-$(SCH_3)$ | $CH_3GeCl$-$(SCH_3)_2$ | $CH_3Ge$-$(SCH_3)_3$ | $CH_3SiCl_3$ | $CH_3SiCl_2$-$(SCH_3)$ | $CH_3SiCl$-$(SCH_3)_2$ | $CH_3Si$-$(SCH_3)_3$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.542 [a] | 0.819 [a] | — [b] | — | 0.8 | 16.9 | — | 7.0 | 40.0 | 35.4 |
| (0.547) [c] | (0.824) [c] | (0.0) [d] | (0.0) | (0.9) | (17.2) | (0.1) | (6.5) | (40.0) | (35.5) |
| 1.045 | 0.652 | — | — | 9.1 | 23.9 | 3.3 | 29.2 | 30.7 | 3.9 |
| (1.079) | (0.671) | (0.0) | (0.1) | (8.6) | (26.2) | (2.7) | (29.3) | (29.1) | (4.1) |
| 1.272 | 0.576 | — | 0.9 | 19.1 | 23.2 | 9.9 | 35.3 | 10.7 | 1.0 |
| (1.317) | (0.569) | (0.0) | (0.4) | (18.7) | (23.2) | (8.0) | (34.8) | (14.0) | (0.8) |
| 1.523 | 0.492 | — | 2.2 | 34.1 | 14.1 | 20.3 | 24.8 | 4.1 | 0.4 |
| (1.531) | (0.496) | (0.0) | (2.3) | (34.3) | (14.2) | (18.6) | (26.9) | (3.6) | (0.1) |
| 1.822 | 0.393 | — | 16.4 | 41.8 | 3.0 | 29.7 | 8.6 | 0.6 | — |
| (1.813) | (0.389) | (0.2) | (15.2) | (42.1) | (3.2) | (30.8) | (8.3) | (0.2) | (0.0) |
| 2.032 | 0.323 | 1.8 | 39.6 | 27.6 | 0.4 | 28.5 | 2.2 | — | — |
| (2.020) | (0.307) | (1.8) | (37.8) | (27.6) | (0.6) | (30.1) | (2.1) | (0.0) | (0.0) |
| 2.531 | 0.185 | 40.0 | 43.2 | 1.8 | — | 15.0 | — | — | — |
| (2.532) | (0.150) | (36.4) | (43.3) | (1.8) | (0.0) | (18.5) | (0.1) | (0.0) | (0.0) |

(D) System $CH_3GeBr_3$ *vs.* $CH_3Si(SCH_3)_3$

| $R \equiv Br/(Si+Ge)$ | $R' \equiv Si/(Si+Ge)$ | $CH_3GeBr_3$ | $CH_3GeBr_2\text{-}(SCH_3)$ | $CH_3GeBr\text{-}(SCH_3)_2$ | $CH_3Ge\text{-}(SCH_3)_3$ | $CH_3SiBr_3$ | $CH_3SiBr_2\text{-}(SCH_3)$ | $CH_3SiBr\text{-}(SCH_3)_2$ | $CH_3Si\text{-}(SCH_3)_3$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.355 [a] | 0.882 [a] | — [b] | 1.4 | 6.1 | 4.8 | — | 0.5 | 30.2 | 57.0 |
| (0.401) [c] | (0.877) [c] | (0.0) [d] | (0.2) | (8.1) | (3.5) | (0.0) | (0.4) | (26.2) | (61.6) |
| 0.699 | 0.767 | 0.5 | 1.9 | 18.9 | 4.1 | — | 2.1 | 44.0 | 28.5 |
| (0.724) | (0.746) | (0.0) | (1.7) | (19.0) | (2.6) | (0.0) | (2.1) | (43.2) | (31.4) |
| 1.106 | 0.632 | — | 10.8 | 27.3 | — | 0.2 | 9.5 | 44.6 | 7.6 |
| (1.131) | (0.619) | (0.1) | (9.8) | (26.1) | (0.9) | (0.1) | (9.3) | (45.7) | (8.0) |
| 1.444 | 0.519 | 2.1 | 24.0 | 22.8 | — | 0.8 | 20.1 | 28.5 | 1.8 |
| (1.482) | (0.512) | (0.6) | (25.2) | (22.2) | (0.2) | (0.7) | (18.8) | (30.6) | (1.8) |
| 1.825 | 0.392 | 3.3 | 45.6 | 11.6 | — | 3.2 | 25.3 | 10.7 | 0.3 |
| (1.836) | (0.395) | (3.5) | (45.5) | (11.8) | (0.0) | (2.9) | (24.4) | (11.6) | (0.2) |
| 2.134 | 0.288 | 13.9 | 54.0 | 4.0 | — | 7.8 | 17.7 | 2.5 | 0.2 |
| (2.150) | (0.282) | (13.2) | (53.7) | (4.3) | (0.0) | (7.2) | (18.8) | (2.8) | (0.0) |
| 2.367 | 0.211 | 29.6 | 46.8 | 1.8 | — | 10.4 | 10.5 | 0.9 | — |
| (2.373) | (0.218) | (29.0) | (48.3) | (1.6) | (0.0) | (9.9) | (10.6) | (0.6) | (0.0) |

(E) System $CH_3GeI_3$ *vs.* $CH_3Si(SCH_3)_3$

| $R \equiv I/(Si+Ge)$ | $R' \equiv Si/(Si+Ge)$ | $CH_3GeI_3$ | $CH_3GeI_2\text{-}(SCH_3)$ | $CH_3GeI\text{-}(SCH_3)_2$ | $CH_3Ge\text{-}(SCH_3)_3$ | $CH_3SiI_3$ | $CH_3SiI_2\text{-}(SCH_3)$ | $CH_3SiI\text{-}(SCH_3)_2$ | $CH_3Si\text{-}(SCH_3)_3$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.359 [a] | 0.880 [a] | 0.7 [b] | 7.3 | 6.6 | 2.9 | — | 0.7 | 21.9 | 59.9 |
| (0.466) [c] | (0.825) [c] | (0.2) [d] | (4.8) | (4.4) | (2.6) | (0.0) | (0.2) | (20.9) | (66.9) |
| 0.730 | 0.757 | 1.9 | 19.4 | 6.3 | 3.1 | — | 0.9 | 28.2 | 40.3 |
| (0.800) | (0.694) | (1.1) | (15.4) | (6.2) | (1.6) | (0.0) | (0.8) | (31.0) | (43.8) |
| 1.094 | 0.635 | 4.7 | 29.1 | 4.6 | 2.4 | — | 2.4 | 33.7 | 23.3 |
| (1.154) | (0.594) | (3.8) | (26.5) | (5.4) | (0.7) | (0.0) | (1.9) | (35.9) | (25.8) |
| 1.443 | 0.519 | 10.8 | 35.3 | 3.5 | 1.3 | — | 3.3 | 33.7 | 12.2 |
| (1.468) | (0.492) | (9.6) | (34.6) | (3.6) | (0.2) | (0.0) | (3.6) | (35.4) | (12.9) |
| 1.814 | 0.396 | 23.6 | 34.3 | 1.8 | 0.8 | — | 5.3 | 28.6 | 5.6 |
| (1.804) | (0.395) | (21.6) | (34.9) | (1.8) | (0.1) | (0.0) | (6.1) | (28.5) | (4.9) |
| 2.136 | 0.288 | 39.2 | 30.1 | 0.8 | 0.6 | — | 6.8 | 20.4 | 2.1 |
| (2.126) | (0.293) | (37.0) | (33.3) | (0.9) | (0.0) | (0.1) | (7.8) | (19.2) | (1.7) |
| 2.535 | 0.155 | 59.2 | 24.3 | 0.9 | — | — | 5.9 | 9.5 | 0.3 |
| (2.484) | (0.157) | (61.5) | (22.7) | (0.2) | (0.0) | (0.3) | (7.4) | (7.5) | (0.3) |

(F) System $CH_3GeCl_3$ *vs.* $CH_3Si[N(CH_3)_2]_3$

| $R \equiv Cl/(Si+Ge)$ | $R' \equiv Si/(Si+Ge)$ | $CH_3GeCl_3$ | $CH_3GeCl_2\text{-}[N(CH_3)_2]$ | $CH_3GeCl\text{-}[N(CH_3)_2]_2$ | $CH_3Ge\text{-}[N(CH_3)_2]_3$ | $CH_3SiCl_3$ | $CH_3SiCl_2\text{-}[N(CH_3)_2]$ | $CH_3SiCl\text{-}[N(CH_3)_2]_2$ | $CH_3Si\text{-}[N(CH_3)_2]_3$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.543 [a] | 0.819 [a] | — [b] | 9.6 | 6.0 | 1.0 | — | 0.4 | 25.2 | 57.8 |
| (0.522) [c] | (0.834) [c] | (0.0) [d] | (9.3) | (8.8) | (0.0) | (0.0) | (0.0) | (26.9) | (55.0) |
| 0.813 | 0.729 | — | 19.1 | 6.3 | 1.4 | — | 0.4 | 34.3 | 38.5 |
| (0.796) | (0.732) | (0.0) | (18.3) | (8.8) | (0.0) | (0.0) | (0.0) | (35.9) | (37.0) |
| 0.938 | 0.646 | — | 29.0 | 5.0 | 1.1 | — | 0.2 | 41.7 | 23.1 |
| (1.105) | (0.650) | (0.0) | (24.8) | (10.6) | (0.0) | (0.0) | (0.0) | (33.5) | (31.0) |
| 1.213 | 0.556 | — | 42.1 | 0.9 | 1.2 | — | 0.9 | 47.0 | 7.9 |
| (1.339) | (0.558) | (0.0) | (37.3) | (7.0) | (0.0) | (0.0) | (0.0) | (39.6) | (16.1) |
| 1.540 | 0.487 | — | 51.2 | — | 0.3 | — | 0.9 | 47.4 | 0.3 |
| (1.516) | (0.486) | (2.1) | (49.1) | (0.1) | (0.0) | (0.0) | (0.9) | (47.5) | (0.2) |
| 1.821 | 0.386 | 16.9 | 46.5 | — | — | — | 4.6 | 32.0 | — |
| (1.849) | (0.366) | (15.5) | (45.9) | (0.0) | (0.0) | (0.0) | (5.2) | (33.3) | (0.0) |
| 2.081 | 0.306 | 32.0 | 40.6 | — | — | — | 7.3 | 20.1 | — |
| (2.119) | (0.274) | (30.6) | (38.8) | (0.0) | (0.0) | (0.0) | (8.2) | (22.4) | (0.0) |
| 2.310 | 0.230 | 48.0 | 30.3 | — | — | — | 8.6 | 11.2 | — |
| (2.330) | (0.198) | (44.9) | (32.0) | (0.0) | (0.0) | (0.0) | (9.1) | (13.9) | (0.0) |
| 2.555 | 0.148 | 62.9 | 23.3 | — | — | — | 7.7 | 6.2 | — |
| (2.569) | (0.139) | (62.1) | (23.1) | (0.0) | (0.0) | (0.0) | (8.2) | (6.6) | (0.0) |

(G) System $CH_3GeBr_3$ *vs.* $CH_3Si[N(CH_3)_3]_3$

| $R \equiv Br/(Si+Ge)$ | $R' \equiv Si/(Si+Ge)$ | $CH_3GeBr_3$ | $CH_3GeBr_2\text{-}[N(CH_3)_2]$ | $CH_3GeBr\text{-}[N(CH_3)_2]_2$ | $CH_3Ge\text{-}[N(CH_3)_2]_3$ | $CH_3SiBr_3$ | $CH_3SiBr_2\text{-}[N(CH_3)_2]$ | $CH_3SiBr\text{-}[N(CH_3)_2]_2$ | $CH_3Si\text{-}[N(CH_3)_2]_3$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.841 [a] | 0.720 [a] | 2.6 [b] | 27.5 | — | — | — | — | 25.8 | 44.2 |
| (0.886) [c] | (0.700) [c] | (1.2) [d] | (26.8) | (0.1) | (0.0) | (0.0) | (0.0) | (26.9) | (45.1) |
| 1.157 | 0.614 | 3.6 | 35.7 | — | — | — | — | 34.9 | 25.8 |
| (1.171) | (0.607) | (3.6) | (34.9) | (0.0) | (0.0) | (0.0) | (0.0) | (35.0) | (26.4) |
| 1.375 | 0.542 | 6.3 | 40.3 | — | — | — | — | 37.7 | 15.7 |
| (1.372) | (0.534) | (7.3) | (38.5) | (0.0) | (0.0) | (0.0) | (0.0) | (38.5) | (15.7) |
| 1.567 | 0.478 | 12.9 | 40.2 | — | — | — | — | 39.7 | 7.2 |
| (1.588) | (0.469) | (13.3) | (38.9) | (0.0) | (0.0) | (0.0) | (0.0) | (38.9) | (8.8) |
| 2.063 | 0.313 | 40.0 | 30.2 | — | — | — | — | 28.5 | 1.4 |
| (2.089) | (0.299) | (39.2) | (29.6) | (0.0) | (0.0) | (0.0) | (0.1) | (29.5) | (1.7) |
| 2.351 | 0.216 | 58.7 | 21.1 | — | — | — | — | 19.5 | 0.7 |
| (2.378) | (0.202) | (57.3) | (21.1) | (0.0) | (0.0) | (0.0) | (0.1) | (21.0) | (0.6) |
| 2.621 | 0.126 | 76.2 | 12.5 | — | — | — | — | 11.3 | — |
| (2.649) | (0.113) | (74.8) | (12.6) | (0.0) | (0.0) | (0.0) | (0.1) | (12.4) | (0.2) |

(H) System $CH_3GeI_3$ *vs.* $CH_3Si[N(CH_3)_2]_3$

| $R \equiv I/(Si+Ge)$ | $R' \equiv Si/(Si+Ge)$ | $CH_3GeI_3$ | $CH_3GeI_2$-$[N(CH_3)_2]$ | $CH_3GeI$-$[N(CH_3)_2]_2$ | $CH_3Ge$-$[N(CH_3)_2]_3$ | $CH_3SiI_3$ | $CH_3SiI_2$-$[N(CH_3)_2]$ | $CH_3SiI$-$[N(CH_3)_2]_2$ | $CH_3Si$-$[N(CH_3)_2]_3$ |
|---|---|---|---|---|---|---|---|---|---|
| 2.557 [a] | 0.148 [a] | 79.8 [b] | 4.7 | — | — | — | — | 4.2 | 11.4 |
| (2.530) [c] | (0.156) [c] | (81.0) [d] | (4.3) | (0.0) | (0.0) | (0.0) | (0.0) | (4.3) | (10.5) |
| 2.320 | 0.227 | 72.8 | 5.6 | — | — | — | — | 4.3 | 17.3 |
| (2.339) | (0.216) | (72.1) | (5.2) | (0.0) | (0.0) | (0.0) | (0.0) | (5.2) | (17.4) |
| 2.063 | 0.313 | 63.3 | 5.9 | — | — | — | — | 5.9 | 24.9 |
| (2.076) | (0.308) | (62.9) | (5.9) | (0.0) | (0.0) | (0.0) | (0.0) | (5.9) | (25.4) |
| 1.878 | 0.374 | 56.3 | 7.9 | — | — | — | — | 5.6 | 30.2 |
| (1.903) | (0.358) | (56.4) | (6.2) | (0.0) | (0.0) | (0.0) | (0.0) | (6.2) | (31.2) |
| 1.593 | 0.469 | 44.8 | 8.7 | — | — | — | — | 5.8 | 40.7 |
| (1.576) | (0.465) | (46.7) | (6.4) | (0.0) | (0.0) | (0.0) | (0.0) | (6.4) | (40.7) |

[a] Determined from the ingredients. [b] Values from the experimental nmr data. [c] Values in parentheses are calculated from the nmr data. [d] Values in parentheses are calculated from the equilibrium constants $K_{(Si)_1}$, $K_{(Si)_2}$, $K_{(Ge)_1}$, $K_{(Ge)_2}$, and $K_I$.

again increase in the order $Cl < Br < I$ but are always large numbers.

The sets of five constants for each system in Table II were used to calculate the theoretical distribution of molecules at equilibrium for the composition for which the experimental nmr data were obtained. The good agreement of the experimental mole-percentage values in Table III with the corresponding calculated ones (listed in parentheses) shows that the invariant equilibrium constants of Table II adequately represent the equilibria in systems of this kind without use of activity coefficients.

In some of the systems in Table II, all of the required five equilibrium constants could not be calculated from the experimental data due to an insufficient number of species detected at equilibrium. In these instances, *e.g.* $K_{(Ge)_2}$ for Z = Cl and T = $OCH_3$ and $K_{(Si)_1}$ for Z = Br and T = $OCH_3$, the corresponding equilibrium constants listed in brackets in Table II were used for the computation of the calculated values listed in parentheses in Table III. In another case, $K_{(Si)_1}$ for Z = I and T = $SCH_3$, the constant could neither be determined from the experimental data nor was it available from separate studies of the exchange of iodine with methylthio groups on methylsilicon. Here good agreement between experimental and calculated data was obtained by assuming $K_{(Si)_1} = K_{(Si)_2}$. Due to the known extremely nonrandom character of the exchange of halogens with dimethylamino groups on either the $CH_3Si$ or $CH_3Ge$ moieties taken separately and the insufficient number of species seen at equilibrium in the systems $CH_3GeX_3$ *vs.* $CH_3Si[N(CH_3)_2]_2$ where X = halogen, the constants $K_{(Si)_1}$, $K_{(Si)_2}$, $K_{(Ge)_1}$, and $K_{(Ge)_2}$ were uniformly assumed to have the value $1 \times 10^{-4}$. This appears justified since it is not significant with regard to the equilibrium distribution if these constants vary between the values of *ca.* $10^{-4}$ and $10^{-\infty}$

## Conclusion

The results obtained in this study showing a differing affinity of pairs of substituents at equilibrium to competing pairs of central moieties are in rather close agreement with related work[7] describing the equilibria in the systems $(CH_3)_2GeT_2$ *vs.* $(CH_3)_2SiZ_2$. In the case of either mono- or dimethyl substitution of the silicon and germanium, the halogends when competing with methoxyl groups preferentially attach to the germanium. Likewise in both cases, there is parallel behavior for exchange of halogens with methylthio groups. This means that the relative affinity of silicon *vs.* germanium for a given exchangeable substituent is, to a first approximation, independent of the other substituents on these atoms. Thus, knowledge

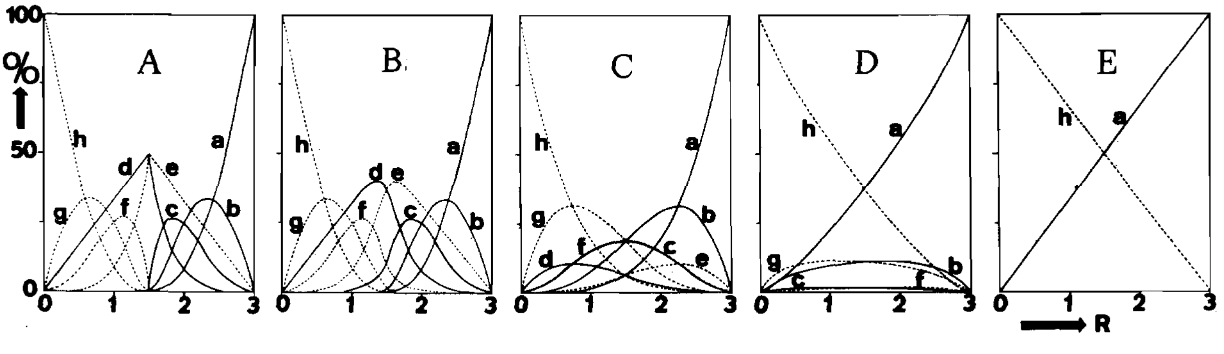

Figure 1. Calculated equilibrium curves for the redistribution of the monofunctional exchangeable substituents Z and T between two kinds of trifunctional central moieties Q and M in systems $QZ_3$ *vs.* $MT_3$ for various values of the intersystem constant $K_I = [QZ_3][MT_3]/\{[QT_3][MZ_3]\}$ as a function of $R = [T]/([Q]+[M])$ and $R' = [M]/([Q]+[M]) = R/3$. The constants $K_{(Q)_1}$, $K_{(Q)_2}$, $K_{(M)_1}$, and $K_{(M)_2}$ are assumed to have the random value = 0.333. The values of $K_I$ are A, $10^{-20}$; B, $10^{-6}$; C, 1.00 (ideal randomness); D, $10^{+6}$; and E, $10^{+20}$. The curves in each graph represent the following species: a = $MT_3$, b = $MT_2Z$, c = $MTZ_2$, d = $MZ_3$, e = $QT_3$, f = $QT_2Z$, g = $QTZ_2$, and h = $QZ_3$.

of the relative affinities can be obtained from the exchange of two kinds of substituents between moieties having all but one potentially exchangeable site blocked off by nonexchangeable groups, such as methyl. In view of this, we have embarked on a program in which various pairs of substituents are exchanged between two monofunctional moieties such as $(CH_3)_3Si-$, $(CH_3)_2P(O)-$, $(CH_3)_3C-$, and $(CH_3)_2As-$. Obviously fewer experimental points (*e.g.* see Table III) and much simpler calculations are involved in this new program than in the studies reported here – studies which must necessarily have preceded the simpler work in order to justify its general applicability.

The systems discussed in this paper are a special case of the general equilibria resulting from scrambling of two kinds of monofunctional exchangeable substituents between two kinds of polyfunctional central moieties. Although the general principles are the same, the distribution of molecular species as a function of the ratio of reagents differs considerably with variation in the number of exchangeable sites on the central moieties. Therefore, a series of computer-calculated graphs are shown in Figure 1 for a pair of trifunctional central moieties – a case which is exemplified by the experimental data of this paper. In these graphs, the intersystem constants vary from very small to very large values while the other four constants required for the complete description of the system are maintained at the random value. Somewhat different graphs will result, of course, when these four constants differ from the random value. The graphs of Figure 1 should be compared with similar graphs for both central moieties being difunctional[7] and for one being trifunctional and the other monofunctional.[3]

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