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Scrambling Equilibria of Pairs of Substituents Between the Dimethylsilicon and Methylgermanium Moieties

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Equilibrium constants were determined for the scrambling of the pairs of substituents Cl/Br, Cl/I, Br/I, Cl/OCH_3, Br/OCH_3, Cl/OC_6H_5, Cl/SCH_3 and Br/SCH_3 between the $(CH_3)_2Si$ and CH_3Ge moieties. Proton nuclear magnetic resonance was used to assay the mixtures at equilibrium. In the halogen/halogen exchanges, the lower atomic weight halogen at equilibrium prefers association with the dimethylsilicon moiety. In the halogen/oxygen bonded substituent exchanges, halogens favor attachment to methylgermanium. The opposite is found for the exchange of halogen/sulfur-bonded substituents.

Introduction

In the course of our studies of competition equilibria of pairs of exchangeable, monofunctional substituents between two kinds of polyfunctional central moieties, we have shown that generally at equilibrium, a pronounced preference of attachment exists for one of the central moieties.[1] In this paper, such competition (redistribution) equilibria between dimethylsilicon and methylgermanium as the central moieties are reported. These studies are closely related to earlier work[2–5] dealing with corresponding equilibria between other pairs of methylsubstituted moieties of silicon and germanium and represent part of a comprehensive investigation of all the equilibria between all the methylsubstituted moieties of silicon and germanium.

Experimental

Materials

Dimethyldichlorosilane was obtained from Peninsular ChemResearch, Inc., Gainesville, Fla. and distilled before use. Dimethyldibromosilane,[6] dimethyldi(methylthio)silane,[7] the methyltrihalogermanes,[8] methyltrimethoxygermane,[9] methyltriphenoxygermane,[10] and methyltri(methylthio)germane[5] were prepared by literature methods.

Data Acquisition

Sample preparation, equilibration, proton nuclear magnetic (nmr) measurements and calculation of weighted-average equilibrium constants and theoretical compositions were performed as reported previously.[2,4]

The pairs of reagents utilized to make up the sets of equilibrated samples are shown as subheadings in Table I which summarizes the equilibrium compositions studied. The proton nmr chemical shifts of the methylgroups of the species seen at equilibrium are listed in Table II. However, only the relative areas of the nmr peaks of the methylgroups attached directly to silicon or germanium were used for the quantitative determination of the respective molecular species at equilibrium. The experimental error of the relative area of each peak measured by electronic integration is about 1% of the total area of all methylgroups directly attached to silicon and germanium.

For the various combinations of the two neat reagents, the reaction conditions at which the equilibrium data were obtained are the following, with the approximate time to reach equilibrium at the same temperature being given in parentheses. System A: 192(46) h at 120° C; System B: 16(5) d at 120° C; System C: 109(64) h at 120° C; System D: 3(2) h at 120° C; System E: 3(1) d at room temperature (in benzene as solvent); System F: 3(1) d at room temperature (in benzene as solvent); System G: 9(5) h at 150° C; System H: 31(14) d at 120° C; System I: 24(16) d at 120° C.

The rates of equilibration involving transfer of exchangeable substituents from silicon to germanium and vice versa, as well as from silicon to silicon in samples which were held at elevated temperatures are quite slow at room temperature. Therefore, upon quenching these samples to room temperature and obtaining the nmr spectra subsequently at this temperature, these equilibria still correspond to the elevated temperature at which the samples were held. The equilibrations involving transfer of substituents from germanium to germanium are rapid at room temperature so that such equilibria will correspond to this temperature. Methylgroups directly attached to silicon or germanium under the present experimental conditions do not exchange.

TABLE I. Experimental and Calculated Equilibrium Concentrations (in mol. %) for the Exchange of Pairs of Substituents between the Moieties $CH_3Ge\leqq$ and $(CH_3)_2Si\lesssim$

A. System CH_3GeCl_3 *vs.* $(CH_3)_2SiBr_2$

R ≡ [Cl]/ ([Si] + [Ge])	*R'* ≡ [Si]/ ([Si] + [Ge])	CH_3GeBr_3	CH_3GeBr_2-Cl	CH_3GeBr-Cl_2	CH_3GeCl_3	$(CH_3)_2$-$SiBr_2$	$(CH_3)_2$-SiBrCl	$(CH_3)_2$-$SiCl_2$
2.404[a]	0.199[a]	0.6[b]	6.4	27.3	46.6	–	0.2	18.9
(2.388)[c]	(0.191)[c]	(0.5)[d]	(5.9)	(26.3)	(47.4)	(0.0)	(0.1)	(19.8)
2.157	0.281	1.5	11.4	29.3	30.8	–	0.1	26.9
(2.163)	(0.270)	(1.7)	(11.1)	(28.8)	(30.2)	(0.0)	(0.1)	(28.0)
1.698	0.434	8.7	21.1	20.5	7.9	–	0.6	41.2
(1.688)	(0.418)	(8.3)	(20.7)	(19.9)	(7.7)	(0.0)	(0.6)	(42.8)
1.379[e]	0.540	21.8	18.4	5.7	0.8	–	3.0	50.2
(1.356)	(0.532)	(21.4)	(18.0)	(5.8)	(0.8)	(0.0)	(2.1)	(51.9)
1.048	0.651	33.4	2.9	0.1	–	4.0	23.0	36.7
(0.995)	(0.637)	(32.7)	(2.1)	(0.1)	(0.0)	(3.2)	(21.2)	(40.7)
0.708	0.764	23.8	0.4	–	–	23.5	36.0	16.3
(0.690)	(0.758)	(23.2)	(0.4)	(0.0)	(0.0)	(22.9)	(36.5)	(17.0)
0.352	0.883	12.3	–	–	–	58.1	26.2	3.4
(0.330)	(0.877)	(11.7)	(0.1)	(0.0)	(0.0)	(57.0)	(27.4)	(3.9)

B. System CH_3GeBr_3 *vs.* $(CH_3)_2SiCl_2$

R ≡ [Cl]/ ([Si] + [Ge])	*R'* ≡ [Si]/ ([Si] + [Ge])	CH_3GeBr_3	CH_3GeBr_2-Cl	CH_2GeBr-Cl_2	CH_3GeCl_3	$(CH_3)_2$-$SiBr_2$	$(CH_3)_2$-$SiCl_2$	$(CH_3)_2$-$SiCl_2$
0.387[a]	0.193[a]	68.4[b]	9.9	0.5	–	0.1	7.7	12.5
(0.436)[c]	(0.203)[c]	(73.6)[d]	(6.8)	(0.2)	(0.0)	(0.7)	(6.0)	(12.7)
0.625	0.313	60.1	8.8	0.5	–	0.5	7.2	22.9
(0.628)	(0.306)	(60.4)	(8.0)	(0.4)	(0.0)	(0.6)	(7.6)	(23.0)
0.829	0.415	50.8	8.0	0.5	–	0.4	7.3	33.0
(0.823)	(0.407)	(49.6)	(8.3)	(0.5)	(0.0)	(0.5)	(8.5)	(32.5)
1.060[e]	0.530	39.6	8.0	0.6	–	0.4	8.3	43.1
(1.037)	(0.518)	(38.1)	(8.2)	(0.7)	(0.0)	(0.4)	(8.8)	(43.7)
1.306	0.653	27.4	7.4	0.9	–	0.5	8.0	55.9
(1.290)	(0.644)	(26.3)	(7.5)	(0.8)	(0.0)	(0.3)	(8.6)	(56.3)
1.530	0.765	17.5	6.3	0.9	–	0.3	7.6	67.3
(1.503)	(0.752)	(16.3)	(6.2)	(0.9)	(0.1)	(0.2)	(7.8)	(68.5)
1.767	0.884	7.5	4.3	0.9	–	0.2	6.6	80.4
(1.735)	(0.872)	(6.6)	(4.0)	(0.9)	(0.1)	(0.1)	(6.0)	(82.3)

C. System CH_3GeI_3 *vs.* $(CH_3)_2SiCl_2$

R ≡ [I]/ ([Si] + [Ge])	*R'* ≡ [Si]/ ([Si] + [Ge])	CH_3GeI_3	CH_3GeClI_2	CH_3GeCl_2I	CH_3GeCl_3	$(CH_3)_2SiI_2$	$(CH_3)_2$-SiClI	$(CH_3)_2$-$SiCl_2$
2.146[a]	0.285[a]	69.3[b]	1.8	–	–	–	1.9	27.0
(2.134)[c]	(0.289)[c]	(70.7)[d]	(0.9)	(0.0)	(0.0)	(0.0)	(0.9)	(27.6)
1.539[e]	0.487	50.8	1.8	–	–	–	1.9	45.6
(1.579)	(0.475)	(50.3)	(1.0)	(0.0)	(0.0)	(0.0)	(1.0)	(47.7)
1.281	0.573	43.1	1.2	–	–	–	1.2	54.5
(1.329)	(0.557)	(41.7)	(0.9)	(0.0)	(0.0)	(0.0)	(1.0)	(56.3)
0.614	0.795	21.1	0.5	–	–	–	0.5	77.8
(0.648)	(0.783)	(19.7)	(0.8)	(0.0)	(0.0)	(0.0)	(0.8)	(78.7)
0.290	0.904	10.4	0.5	–	–	–	0.6	88.4
(0.328)	(0.890)	(9.1)	(0.5)	(0.0)	(0.0)	(0.0)	(0.6)	(89.8)

D. System CH_3GeI_3 *vs.* $(CH_3)_2SiBr_2$

$R \equiv [I]/([Si]+[Ge])$	$R' \equiv [Si]/([Si]+[Ge])$	CH_3GeI_3	CH_3GeBrI_2	CH_3GeBr_2I	CH_3GeBr_3	$(CH_3)_2SiI_2$	$(CH_3)_2$-SiBrI	$(CH_3)_2$-$SiBr_2$
2.425[a]	0.192[a]	75.0[b]	7.1	0.1	–	0.7	4.7	12.4
(2.454)[c]	(0.178)[c]	(73.7)[d]	(6.9)	(0.2)	(0.0)	(1.0)	(5.4)	(12.8)
1.986	0.338	58.3	9.1	0.8	–	0.6	6.2	25.0
(2.013)	(0.318)	(57.6)	(8.1)	(0.4)	(0.0)	(0.9)	(7.3)	(25.7)
1.507[e]	0.498	40.6	8.6	0.8	–	0.7	7.6	41.6
(1.488)	(0.499)	(41.3)	(8.2)	(0.6)	(0.0)	(0.7)	(8.2)	(40.9)
1.036	0.655	26.5	9.0	1.3	–	0.6	8.6	54.0
(1.086)	(0.632)	(26.3)	(7.4)	(0.8)	(0.0)	(0.5)	(8.1)	(56.9)
0.505	0.832	10.1	5.9	1.0	–	0.1	7.1	75.9
(0.504)	(0.831)	(10.8)	(5.0)	(0.9)	(0.1)	(0.2)	(6.5)	(76.4)

E. System $CH_3Ge(OCH_3)_3$ *vs.* $(CH_3)_2SiCl_2$

$R \equiv [Cl]/([Si]+[Ge])$	$R' \equiv [Si]/([Si]+[Ge])$	CH_3GeCl_3	CH_3GeCl_2-(OCH_3)	CH_3GeCl-$(OCH_3)_2$	CH_3Ge-$(OCH_3)_3$	$(CH_3)_2SiCl_2$	$(CH_3)_2SiCl$-(OCH_3)	$(CH_3)_2Si$-$(OCH_3)_2$
0.448[a]	0.224[a]	–[b]	1.3	44.5	32.3	–	–	22.0
(0.471)[c]	(0.220)[c]	(0.0)[d]	(1.0)	(42.7)	(33.9)	(0.0)	(0.0)	(22.4)
0.683	0.341	–	9.9	50.1	4.7	–	–	35.3
(0.699)	(0.353)	(0.0)	(8.3)	(51.6)	(6.0)	(0.0)	(0.0)	(34.1)
1.115[e]	0.557	23.1	22.1	–	–	–	–	54.8
(1.135)	(0.548)	(22.7)	(21.3)	(0.3)	(0.0)	(0.0)	(0.5)	(55.2)
1.434	0.717	29.4	–	–	–	1.2	55.1	14.3
(1.457)	(0.706)	(28.2)	(0.1)	(0.0)	(0.0)	(1.2)	(56.1)	(14.4)
1.715	0.857	14.6	–	–	–	40.3	44.8	0.3
(1.689)	(0.854)	(14.3)	(0.0)	(0.0)	(0.0)	(43.3)	(42.4)	(0.2)

F. System $CH_3Ge(OCH_3)_3$ *vs.* $(CH_3)_2SiBr_2$

$R \equiv [Br]/([Si]+[Ge])$	$R' \equiv [Si]/([Si]+[Ge])$	CH_3GeBr_3	CH_3GeBr_2-(OCH_3)	CH_3GeBr-$(OCH_3)_2$	CH_3Ge-$(OCH_3)_3$	$(CH_3)_2$-$SiBr_2$	$(CH_3)_2SiBr$-(OCH_3)	CH_3Ge-$(OCH_3)_2$
0.326[a]	0.163[a]	–[b]	–	32.1	50.2	–	–	17.7
(0.321)[c]	(0.177)[c]	(0.0)[d]	(0.6)	(31.5)	(51.7)	(0.0)	(0.0)	(16.3)
0.750	0.375	–	18.3	40.6	3.0	–	–	38.1
(0.772)	(0.381)	(0.1)	(15.7)	(43.2)	(3.5)	(0.0)	(0.0)	(37.5)
0.970[e]	0.485	4.3	40.9	8.3	–	–	–	46.5
(1.030)	(0.465)	(3.4)	(38.6)	(9.4)	(0.1)	(0.0)	(0.2)	(48.3)
1.691	0.846	16.6	–	–	–	40.5	42.4	0.5
(1.732)	(0.834)	(15.4)	(0.0)	(0.0)	(0.0)	(38.9)	(45.0)	(0.7)

G. System $CH_3Ge(OC_6H_5)_3$ *vs.* $(CH_3)_2SiCl_2$

$R \equiv [Cl]/([Si]+[Ge])$	$R' \equiv [Si]/([Si]+[Ge])$	CH_3GeCl_3	CH_3GeCl_2-(OC_6H_5)	CH_3GeCl-$(OC_6H_5)_2$	CH_3Ge-$(OC_6H_5)_3$	$(CH_3)_2SiCl_2$	$(CH_3)_2SiCl$-(OC_6H_5)	$(CH_3)_2Si$-$(OC_6H_5)_2$
1.848[a]	0.916[a]	8.4[b]	–	–	–	68.8	22.0	0.8
(1.853)[c]	(0.927)[c]	(7.3)[d]	(0.0)	(0.0)	(0.0)	(71.5)	(20.3)	(0.8)
1.655	0.817	18.3	–	–	–	35.9	38.8	7.0
(1.654)	(0.827)	(17.3)	(0.0)	(0.0)	(0.0)	(37.0)	(39.5)	(6.2)
1.393	0.687	31.3	–	–	–	5.3	34.8	28.6
(1.392)	(0.696)	(30.2)	(0.2)	(0.0)	(0.0)	(6.5)	(35.2)	(27.9)
1.042[e]	0.541	17.4	23.9	4.2	0.4	–	–	54.1
(1.062)	(0.531)	(17.1)	(24.9)	(4.7)	(0.2)	(0.0)	(0.3)	(52.8)
0.580	0.262	0.9	9.6	36.1	27.1	–	–	26.2
(0.553)	(0.276)	(0.3)	(9.4)	(35.6)	(27.1)	(0.0)	(0.0)	(27.6)

H. System $CH_3Ge(SCH_3)_3$ *vs.* $(CH_3)_2SiCl_2$

$R \equiv [Cl]/([Si]+[Ge])$	$R' \equiv [Si]/([Si]+[Ge])$	CH_3GeCl_3	CH_3GeCl_2-(SCH_3)	CH_3GeCl-$(SCH_3)_2$	CH_3Ge-$(SCH_3)_3$	$(CH_3)_2SiCl_2$	$(CH_3)_2SiCl$-(SCH_3)	$(CH_3)_2Si$-$(SCH_3)_2$
0.477[a]	0.238[a]	–[b]	0.6	12.9	65.6	12.6	7.5	0.8
(0.468)[c]	(0.209)[c]	(0.0)[d]	(0.1)	(11.8)	(64.3)	(13.5)	(8.8)	(1.6)
0.889	0.445	–	0.4	14.0	42.5	31.5	10.7	1.0
(0.885)	(0.432)	(0.0)	(0.2)	(13.6)	(41.7)	(31.6)	(11.6)	(1.2)
1.215	0.608	–	0.2	14.1	26.0	48.1	10.3	1.3
(1.210)	(0.597)	(0.0)	(0.3)	(12.8)	(26.1)	(48.2)	(11.8)	(0.8)
1.510[e]	0.755	–	0.2	11.5	14.1	64.9	8.5	0.8
(1.502)	(0.742)	(0.0)	(0.4)	(10.4)	(13.7)	(64.8)	(10.2)	(0.5)
1.770	0.885	–	0.6	6.9	5.5	80.6	5.6	0.8
(1.749)	(0.870)	(0.0)	(0.4)	(6.4)	(4.6)	(81.4)	(7.0)	(0.2)

I. System CH_3GeBr_3 *vs.* $(CH_3)_2Si(SCH_3)_2$

$R \equiv [Br]/([Si]+[Ge])$	$R' \equiv [Si]/([Si]+[Ge])$	CH_3GeBr_3	CH_3GeBr_2-(SCH_3)	CH_3GeBr-$(SCH_3)_2$	CH_3Ge-$(SCH_3)_3$	$(CH_3)_2SiBr_2$	$(CH_3)_2SiBr$-(SCH_3)	$(CH_3)_2Si$-$(SCH_3)_2$
2.456[a]	0.181[a]	48.8[b]	33.7	0.6	–	16.8	0.2	–
(2.482)[c]	(0.170)[c]	(46.4)[d]	(34.8)	(0.6)	(0.0)	(17.9)	(0.2)	(0.0)
2.125	0.292	19.4	50.5	2.7	–	26.1	1.2	–
(2.153)	(0.273)	(17.2)	(50.0)	(3.6)	(0.0)	(28.1)	(1.1)	(0.0)
1.801	0.400	3.9	43.9	14.3	0.2	31.5	6.2	–
(1.830)	(0.377)	(2.8)	(41.6)	(15.5)	(0.2)	(33.2)	(6.7)	(0.1)
1.450[e]	0.517	–	19.4	28.1	1.2	28.5	22.0	0.9
(1.459)	(0.514)	(0.3)	(18.6)	(28.0)	(1.4)	(28.0)	(22.7)	(0.9)
1.093	0.636	–	5.8	27.9	4.5	15.5	41.3	5.1
(1.118)	(0.619)	(0.0)	(5.0)	(26.7)	(4.8)	(14.9)	(42.8)	(5.9)
0.712	0.763	–	0.8	14.9	9.9	4.6	46.8	23.0
(0.725)	(0.744)	(0.0)	(0.7)	(13.8)	(9.3)	(4.4)	(47.4)	(24.5)
0.351	0.883	–	–	4.0	9.4	1.0	29.9	55.8
(0.367)	(0.859)	(0.0)	(0.0)	(3.3)	(8.3)	(0.8)	(30.1)	(57.5)

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[a] From the ingredients of the mixture as defined. [b] From the nmr data in mol.%. [c] Calculated from the nmr data as defined. [d] Calculated from the equilibrium constants. [e] Compositions in which chemical shifts were determined after equilibration.

TABLE 11. Proton Nuclear Magnetic Resonance Chemical Shifts δ of Methylgroups (TMS = 0) Determined in the Equilibrated Mixtures of Table I Marked with the Superscript e.

System	T	Z	Me_2SiT_2	Me_2SiTZ	Me_2SiZ_2	$MeGeT_3$	$MeGeT_2Z$	$MeGeTZ_2$	$MeGeZ_3$
A	Cl	Br	0.75	0.89	1.05[a]	1.60	1.73	1.87	2.00
B	Cl	Br	0.76	0.90	1.05	–[b]	1.72	1.85	1.99
C	Cl	I	0.75	1.11	–[b]	–[b]	–[b]	2.39	2.77
D	Br	I	1.10	1.33	1.73	–[b]	2.29	2.53	2.80
E[c]	Cl	OCH_3	0.54[a]	0.31[a]	0.04	1.15	0.92	0.69[a]	0.37[a]
				(3.37)	(3.37)		(3.56)	(3.53)	(3.51)
F[c]	Br	OCH_3	1.13[a]	0.61[a]	0.04	2.05	1.54	1.03	0.58[a]
					(3.40)		(3.60)	(3.58)	(3.56)
G	Cl	OC_6H_5	0.51[a]	0.38[a]	0.22	1.13	1.02	0.87	0.62
H[d]	Cl	SCH_3	0.82	0.68	0.50	–[b]	1.50	1.26	1.02
				(2.14)	(–)[e]		(–)[e]	(2.29)	(2.19)
I[d]	Br	SCH_3	1.08	0.79	0.48	1.92[a]	1.70	1.34	0.94
				(2.03)	(1.97)		(2.31)	(2.18)	(2.09)

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[a] Data obtained by extrapolation from sample other than designated by superscript e in Table I. [b] Not observed at equilibrium. [c] OCH_3 resonances in parentheses; shifts in benzene as solvent. [d] SCH_3 resonances in parentheses. [e] Not resolved.

Results and Discussion

As shown in previous studies[1] from this laboratory, a minimum of four equilibrium equations is required to completely describe the scrambling of two kinds of monofunctional substituents T and Z between the difunctional dimethylsilicon moiety and the trifunctional methylgermanium moiety. The equilibrium constants representing these scrambling equilibria are shown below (Me = CH_3).

$$K_a = [Me_2SiT_2][Me_2SiZ_2]/[Me_2SiTZ]^2 \qquad (1)$$

$$K_b = [MeGeT_3][MeGeTZ_2]/[MeGeT_2Z]^2 \qquad (2)$$

$$K_c = [MeGeZ_3][MeGeT_2Z]/[MeGeTZ_2]^2 \qquad (3)$$

$$K_I = [Me_2SiT_2]^3[MeGeZ_3]^2/\{[Me_2SiZ_2]^3[MeGeT_3]^2\} \qquad (4)$$

The constant of eq (4) is the one of particular interest here since it describes the distribution of T and Z between the two kinds of central moieties. The equilibria of the two "subsystems" involving the exchange of the two substituents T and Z on $(CH_3)_2Si$ as described by K_a and on CH_3Ge as determined by K_b and K_c are necessary for a complete mathematical description of these systems.

The values of K_a, K_b and K_c for the various systems listed in Table III agree quite well with values of the same constants obtained previously in separate studies[1] of the equilibria in the systems $(CH_3)_2SiT_2$ *vs.* $(CH_3)_2SiZ_2$ and CH_3GeT_3 *vs.* CH_3GeZ_3, respectively. Confirming the results of these latter studies, the subsystem equilibrium constants in Table III involving exchange of halogens with halogens in all instances are close to the ideal random case. Similarly, equilibria dealing with the interchange of halogens with OCH_3, OC_6H_5 and SCH_3 groups, respectively, in agreement with the above-mentioned earlier studies, deviate from randomness in the direction of favoring the mixed species. In a few instances in the systems of Table III, these constants could not be determined from the data of Table I due to the absence at equilibrium of at least one of the components required for the calculation of the respective equilibrium constants. In these situations, literature values for these constants (listed in parentheses in Table III) were used to calculate the theoretical equilibrium distributions listed in parentheses in Table I. These calculations have been done generally for the compositions for which experimental data were obtained using the constants of eqs (1)–(4) for the respective systems. Good agreement between experimental and theoretical values is observed.

All of the intersystem constants K_I in Table III were found to deviate considerably from the random value of 1.00. Deviation from randomness of K_I means that at equilibrium there is a preference of attachment of the monofunctional substituents to one of the central

TABLE III. Equilibrium Constants[a] for Substituent Exchange Between Dimethylsilicon and Methylgermanium Moieties at 120° C.

System	T	Z	K_a	K_b	K_c	K_I	K_I converted to 120° C
A	Cl	Br	0.29 ± 0.07	0.40 ± 0.01	0.39 ± 0.03	$(6.9 \pm 3.5) \times 10^{12}$	
B	Cl	Br	0.23 ± 0.05	–[d] (0.39)	0.39 ± 0.02	$(3.2 \pm 1.1) \times 10^{12}$	
C	Cl	I	–[d] (0.25)	–[d] (0.79)	–[d] (0.72)	1×10^{23}	
D	Br	I	0.42 ± 0.06	–[d] (0.42)	0.38 ± 0.01	$(9.6 \pm 4.0) \times 10^{11}$	
E[b]	Cl	OCH_3	$(5.5 \pm 0.2) \times 10^{-3}$	$(1.9 \pm 0.2) \times 10^{-2}$	–[d] (1.3 ± 10^{-2})	1×10^{-30}	1×10^{-23}
F[b]	Br	OCH_3	1.3×10^{-2}	2.1×10^{-2}	2.9×10^{-2}	1×10^{-23}	4×10^{-18}
G[c]	Cl	OC_6H_5	0.15 ± 0.09	0.13 ± 0.02	0.20 ± 0.01	1×10^{-20}	3×10^{-22}
H	Cl	SCH_3	0.29 ± 0.08	–[d] (4.8×10^{-2})	$(4.9 \pm 0.1) \times 10^{-2}$	$(1.2 \pm 0.7) \times 10^{15}$	
I	Br	SCH_3	$(4.8 \pm 0.3) \times 10^{-2}$	$(2.5 \pm 0.3) \times 10^{-2}$	$(3.3 \pm 0.4) \times 10^{-2}$	$(6.8 \pm 4.) \times 10^5$	
Ideal Randomness			0.25	0.33	0.33	1.00	

[a] The equilibrium constants K_a, K_b, K_c and K_I are defined by eqs (1), (2), (3) and (4) in the text. [b] At room temperature. [c] At 150° C. [d] The constant could not be calculated due to the absence at equilibrium of at least one of the necessary components. The theoretical equilibrium concentrations in Table I were calculated using the constant given underneath in parentheses. The latter are values of the literature: System B: K_b, ref. 2, System C: K_a = 0.25 (random value); K_b, ref. 2; K_c, ref. 2. System D: K_b, ref. 2. System E: K_c, ref. 9. System H: K_b, ref. 9.

moeties. If this constant is larger than 1.00, the substituent T in Table III at equilibrium is preferentially associated with the dimethylsilicon moiety. For values of K_{I} being smaller than 1.00, the reverse situation is to be found.

For the systems E, F and G, the intersystem constant K_{I} was determined at temperatures other than that of 120° C, the temperature where the remainder of the constants were measured. The exchange of halogens with OCH_3 groups (Systems E and F) proceeded quite rapidly at room temperature, with the equilibrium data corresponding to this temperature. In System G (exchange of Cl with OC_6H_5 groups), the rates of equilibration were too slow at 120° C; the equilibrium data, therefore, were obtained at 150° C. In order to be able to compare all K_{I} values with each other, the constants of the above three systems were converted to 120° C on the basis that the entire ΔS of the reaction equation is attributed to scrambling. These converted constants are also incorporated into Table III.

For the halogen–halogen exchanges, the K_{I} values are > 1.00 indicating greater affinity at equilibrium of silicon to the halogen of lower atomic weight. In the equilibria of halogens with oxygen-bonded substituents, the intersystem equilibrium constants are < 1.00 which means that at equilibrium, the silicon moiety favors the latter substituents. The equilibria of halogens with sulfur-bonded substituents favor the association of silicon with the halogens. A similar, general over-all trend in the intersystem equilibrium constants was observed earlier in the systems[2–5] $(CH_3)_2SiT_2$ *vs.* $(CH_3)_2GeZ_2$ and CH_3SiT_3 *vs.* CH_3GeZ_3 and may be rationalized in terms of bond energies[11] of the bonds involved in the exchange processes. Averaged values are (in kcal): Si–O, 106.3; Ge–O, 85; Si–Cl, 97.2; Ge–Cl, 81; Si–Br, 75.6; Ge–Br, 66; Si–I, 56; Ge–I, 51 (no data were available for Si–S and Ge–S). Considering these bond energy data, it is clearly seen that *e.g.* for the substituent pair Cl/Br, an energy maximum is attained for the combinations Si–Cl and Ge–Br rather than for Si–Br and Ge–Cl. Similar reasoning applies to the other pairs of substituents.

In Table III, two intersystem constants are listed for the exchange of Cl with Br. One was obtained in equilibrated mixtures prepared from the two components $(CH_3)_2SiBr_2 + CH_3GeCl_3$ (System A) and the other from the components $(CH_3)_2SiCl_2 + CH_3GeBr_3$ (System B). Both of the thus obtained constants, as expected, agree well with each other.

With the experimentally determined constants K_{I}, converted to 120° C where necessary, we may now estimate additional equilibrium constants for systems which were not studied experimentally, by simple stoichiometric considerations. These new intersystem equilibrium constants were derived from the ones in Table III and are summarized in Table IV along with the ratios of the experimentally derived ones from which the new constants were obtained. These indirectly determined constants show that in three instances, I/OCH_3, I/SCH_3 and OCH_3/SCH_3, the same constants could be determined from two independent sources. However, only in the first two cases, the agreement between the two values of each constant from different sources is satisfactory. An unexplained discrepancy is seen for the third case, although both constants indicate nonrandomness favoring Si–O and Ge–S bonds at equilibrium. The new constants follow the general trends established by the constants of Table III. It is interesting to note that compared to the equilibria in the systems H (Cl/SCH_3) and I (Br/SCH_3), the estimated constant for the exchange of I/SCH_3 is smaller than 1.00, indicating preference at equilibrium of Si–S and Ge–I bonds. From these findings, it may be concluded that the bond energy of the Si–S bond lies between those of the Si–Br and Si–I bonds and that of the Ge–S bond between those of the Ge–Br and Ge–I bonds.

TABLE IV. Intersystem Equilibrium Constants[a] at 120° C as Estimated from the Corresponding Experimental Constants of Table III.

T	Z	K_{I}
I	OCH_3	$K_E/K_{\overline{AB}} = 8 \times 10^{-31}$ $K_F/K_D = 4 \times 10^{-30}$
Br	OPh	$K_G/K_{\overline{AB}} = 6 \times 10^{-35}$
I	OPh	$K_G/K_C = 3 \times 10^{-45}$
OCH_3	OPh	$K_G/K_E = 30$
I	SCH_3	$K_H/K_C = 1 \times 10^{-8}$ $K_I/K_D = 7 \times 10^{-7}$
OCH_3	SCH_3	$K_H/K_E = 1 \times 10^{38}$ $K_I/K_F = 2 \times 10^{23}$
OPh	SCH_3	$K_H/K_G = 4 \times 10^{36}$

[a] K_{I} is defined by eq (4); according to the notation used K_E signifies the intersystem constant as defined by eq (4) for the system E (Table III). $K_{\overline{AB}}$ indicates the average of K_{I} of system A and K_{I} of system B.

It is noteworthy to point out that some of the constants of Table III [for the substituent pairs Cl/I, Cl/Br and $Cl/(OC_6H_5)$] were employed previously[12] to calculate the theoretical distributions of components at equilibrium in multicomponent scrambling equilibria involving Me_2Si and MeGe as the central moieties and Cl, Br, I and OC_6H_5 as the exchanging substituents.

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References

1 K. Moedritzer, *Adv. Organometal. Chem., 6,* 171 (1968).

2 K. Moedritzer and J. R. Van Wazer, *Inorg. Chem., 5,* 547 (1966).

3 K. Moedritzer and J. R. Van Wazer, *J. Inorg. Nucl. Chem., 28,* 957 (1966).

4 J. R. Van Wazer, K. Moedritzer and L. C. D. Groenweghe, *J. Organometal. Chem., 5,* 420 (1966).

5 K. Moedritzer and J. R. Van Wazer, *Inorg. Chim. Acta, 1,* 407 (1967).

6 K. Moedritzer and J.R. Van Wazer, *J. Organometal. Chem., 6,* 242 (1966).

7 K. Moedritzer, J.R. Van Wazer and C.H. Dungan, *J. Phys. Chem., 42,* 2478 (1965).

8 K. Moedritzer, *J. Organometal. Chem., 6,* 282 (1966).

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

10 K. Moedritzer, J.R. Van Wazer and R.E. Miller, *Inorg. Chem., 7,* 1638 (1968).

11 E. A. V. Ebsworth, "Organometallic Compounds of the Group IV Elements", A.G. MacDiarmid, Ed., Vol. 1, Chapter 1, Dekker, New York, N.Y., 1968.

12 K. Moedritzer, *Z. Naturforsch., 26b,* 517 (1971).