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Multicomponent Redistribution Equilibria Between Methylsilanes and Methylgermanes

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Redistribution equilibria of the substituents Cl, Br, and I (System I), and Cl, Br, I, and OC_6H_5 (System II) between the methylsilicon and methylgermanium moieties have been studied quantitatively by proton nuclear magnetic resonance spectroscopy. The experimental data have been evaluated in terms of a minimum-number set of 16 equilibrium constants for System I and 35 equilibrium constants for System II. These sets of constants in turn have been used to compute theoretical equilibrium distributions. As a result of preferential affinities of the redistributing substituents for either silicon or germanium, certain species do not appear at equilibrium in detectable amounts. For System I compounds with Si–Cl–, Ge–Br, and Ge–I bonds are strongly favored and for System II compounds with Si–Cl, Si–O, Ge–Br, and Ge–I bonds predominate.

Introduction

In previous communications from this laboratory dealing with multicomponent scrambling equilibria[1-5] the experimental techniques as well as the mathematical treatment of such systems has been developed. This paper deals with two such systems of advanced complexity. In one of these as many as forty different chemical species will have to be considered, experimentally as well as mathematically, as potential components of the equilibria.

Experimental Section

Reagents. Methyltrichlorosilane was purchased from Peninsular Chem. Research, Inc., Gainesville, Florida and redistilled before use. Methyltribromosilane,[6] methyltriphenoxysilane[7] and the methyltrihalogermanes[8] were prepared according to methods of the literature.

Sample Preparation and Data Acquisition. For System I of this communication equilibrated samples were prepared by sealing various proportions of the components CH_3SiCl_3, CH_3SiBr_3, CH_3GeCl_3, CH_3GeBr_3, and CH_3GeI_3 in 5 mm o.d. nuclear magnetic resonance (nmr) tubes under anhydrous conditions and holding these at 120° . Equilibrium was established within 56 hours at this temperature as evidenced by no further change with time of the nmr spectra of these samples. The quantitative measurements, however, were made after the samples had been held for 13 days at this temperature. Samples of System II, prepared from various proportions of CH_3SiCl_3, $CH_3Si(OC_6H_5)_3$, CH_3GeBr_3, and CH_3GeI_3, were studied in a similar manner. Equilibrium was reached after the samples were held for 62 days at 150° and the final equilibrium data were obtained after 84 days at this temperature. In the latter system a higher equilibration temperature had to be chosen on account of the slow equilibration rates involving $CH_3Si(OC_6H_5)_3$.

The mole fractions of the various compounds present at equilibrium were determined by quantitatively evaluating the proton nmr spectra (obtained on a Varian A-60 Spectrometer operating at a probe temperature of 33°) given by the methyl group of the various methylsilanes and methylgermanes participating in the equilibrium. The spectra were obtained after rapid quenching of the samples from the reaction temperature to the temperature of the nmr probe. From these data weighted-average equilibrium constants were calculated using previously reported procedures.[9] Also the computation of the equilibrium distributions in the multicomponent systems from the chosen equilibrium constants was done by computer using a program developed in this laboratory.[3]

Results

The exchange processes occurring in systems prepared by combining various species of the general type CH_3SiT_3 and CH_3GeZ_3 involve interchanges of the monofunctional, exchangeable substituents T and Z between the moieties CH_3Si and CH_3Ge. The reaction conditions were selected to permit interchanges involving Si–T, Si–Z, Ge–T, and Ge–Z bonds but not Si–C and Ge–C bonds. This leaves the methylsilicon and methylgermanium moieties intact and the different single-line nmr spectra of the resulting me-

(1) K. Moedritzer and J.R. Van Wazer, *Inorg. Chim. Acta*, 2, 111 (1968).
(2) *K. Moedritzer*, J.R. Van Wazer and R.E. Miller, *Inorg. Chem.*, 7, 1638 (1968).
(3) K. Moedritzer, L.C.D. Groenweghe and J.R. Van Wazer, *J. Phys. Chem.*, 72, 4380 (1968).
(4) K. Moedritzer and J.R. Van Wazer, *J. Chem. Soc.* (*A*), 1124 (1969).
(5) J.R. Van Wazer and S. Norval, *Inorg. Chem.*, 4, 1294 (1965).
(6) K. Moedritzer and J.R. Van Wazer, *Inorg. Chem.*, 5, 547 (1966).
(7) K. Moedritzer and J.R. Van Wazer, *J. Inorg. Nucl. Chem.*, 29, 1851 (1967).
(8) K. Moedritzer, *J. Organometal. Chem.*, 6, 282 (1966).
(9) L.C.D. Groenweghe, J.R. Van Wazer and A.W. Dickinson, *Anal. Chem.*, 36, 303 (1964).

Table I. Equilibrium Constants[a] as Calculated from the Experimental Data.

		SYSTEM I[b]		SYSTEM II[c]		Literature Values[d]	
		$Q = CH_3Si$	$Q = CH_3Ge$	$Q = CH_3Si$	$Q = CH_3Ge$	$Q = CH_3Si$	$Q = CH_3Ge$
K_1	$:[QCl_3][QBr_2Cl]/[QBrCl_2]^2$	0.37 ± 0.02	(0.42)[e]	0.39 ± 0.14	(0.42)[e]	0.40 ± 0.02 (120°)[e]	0.42 ± 0.03 (35°)[e]
K_2	$:[QBr_3][QBrCl_2]/[QBr_2Cl]^2$	0.41 ± 0.07	0.42 ± 0.12	(0.43)[e]	0.40 ± 0.11	0.43 ± 0.02 (120°)[e]	0.41 ± 0.03 (35°)[e]
K_3	$:[QCl_3][QClI_2]/[QCl_2I]^2$	(0.333)[f]	(0.79)[e]	(0.333)[f]	(0.79)[e]	0.29 ± 0.03 (460°)[l]	0.79 ± 0.07 (35°)[e]
K_4	$:[QI_3][QCl_2I]/[QClI_2]^2$	(0.333)[f]	0.51 ± 0.41	(0.333)[f]	0.79 ± 0.64	0.45 ± 0.05 (460°)[l]	0.72 ± 0.06 (35°)[e]
K_5	$:[QBr_3][QBrI_2]/[QBr_2I]^2$	(0.333)[f]	0.39 ± 0.02	(0.333)[f]	0.42 ± 0.02	--[k]	0.42 ± 0.03 (35°)[e]
K_6	$:[QI_3][QBr_2I]/[QBrI_2]^2$	(0.333)[f]	0.43 ± 0.02	(0.333)[f]	0.42 ± 0.03	--[k]	0.44 ± 0.03 (35°)[e]
K_7	$:[QCl_3][QCl(OPh)_2]/[QCl_2(OPh)]^2$	--	--	0.22 ± 0.01	(0.16)[g]	0.22 ± 0.04 (150°)[h]	--[k]
K_8	$:[Q(OPh)_3][QCl_2(OPh)]/[QCl(OPh)_2]^2$	--	--	0.19 ± 0.04	(0.05)[g]	0.18 ± 0.04 (150°)[h]	--[k]
K_9	$:[QBr_3][QBr(OPh)_2]/[QBr_2(OPh)]^2$	--	--	(0.38)[h]	(0.19)[g]	0.38 ± 0.02 (150°)[h]	--[k]
K_{10}	$:[Q(OPh)_3][QBr_2(OPh)]/[QBr(OPh)_2]^2$	--	--	0.17 ± 0.19	(0.26)[g]	0.28 ± 0.02 (150°)[h]	--[k]
K_{11}	$:[QI_3][QI(OPh)_2]/[QI_2(OPh)]^2$	--	--	(0.333)[f]	(1.7)[g]	--[k]	--[k]
K_{12}	$:[Q(OPh)_3][QI_2(OPh)]/[QI(OPh)_2]^2$	--	--	(0.333)[f]	(0.30)[g]	--[k]	--[k]
K_{13}	$:[QBr_2Cl][QClI_2]/[QBrClI]^2$	(0.25)[f]	0.32 ± 0.08	(0.250)[f]	0.33 ± 0.08	--[k]	0.33 ± 0.02 (35°)[j]
K_{14}	$:[QBr_2Cl][QCl(OPh)_2]/[QBrCl(OPh)]^2$	--	--	0.30 ± 0.12	(0.28)[g]	--[k]	0.16 ± 0.02 (35°)[j]
K_{15}	$:[QClI_2][QCl(OPh)_2]/[QClI(OPh)]^2$	--	--	(0.250)[f]	(0.80)[g]	--[k]	0.55 ± 0.08 (35°)[j]
K_{16}	$:[QBrI_2][QBr(OPh)_2]/[QBrI(OPh)]^2$	--	--	(0.250)[f]	(0.35)[g]	--[k]	0.55 ± 0.08 (35°)[j]
K_I	$:[MeSiCl_3][MeGeI_3]/\{[MeSiI_3][MeGeCl_3]\}$	$(6.67 \times 10^{+11})$[e]		$(6.7 \times 10^{+11})$[e]		$(6.7 \pm 3.1)10^{+11}$ (120°)[e]	
K_{II}	$:[MeSiCl_3][MeGe(OPh)_3]/\{[MeSi(OPh)_3][MeGeCl_3]\}$	--		(1×10^{-12})[i]		$(1 \pm 0.9)10^{-12}$ (150°)[i]	
K_{III}	$:[MeSiCl_3][MeGeBr_3]/\{[MeSiBr_3][MeGeCl_3]\}$	$(1.03 \times 10^{+5})$[e]		$(1.0 \times 10^{+5})$[e]		$(1.0 \pm 0.4)10^{+5}$ (120°)[e]	

[a] Weighted average values and their standard error; values listed in parentheses are either estimated or literature data. These, together with the experimental values obtained directly in these systems, were used for the calculation of the theoretical concentrations of Tables II and III. [b] Exchange of Cl, Br and I between CH_3Si and CH_3Ge at 120°. [c] Exchange of Cl, Br, I and OC_6H_5 between CH_3Si and CH_3Ge at 150° (Ph = C_6H_5). [d] These represent data obtained from the simplest possible system for a particular equilibrium constant. [e] Ref. 6. [f] Estimated. [g] Ref. 1. [h] Ref. 7. [i] Unpublished data. [j] Ref. 2. [k] Data not available. [l] G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, 73, 5804 (1951).

thylsilane and methylgermane derivatives may be utilized to study the equilibria as well as the kinetics of such systems in a quantitative manner.

Equilibrium Constants. Systems of the above type, like any other system at equilibrium, may be described mathematically in terms of sets of equilibrium constants. These may be chosen in many different ways, however, in agreement with previous practice,[1-5] the sets described below will be used.

For each pair of exchanging monofunctional substituents on a given trifunctional central moiety, Q, such as methylsilicon or methylgermanium, a pair of equilibrium constants, K_a and K_b, is required which are derived from the equations shown below.

$$2QTZ_2 \leftrightarrows QT_2Z + QZ_3 \tag{1}$$

$$K_a = [QT_2Z][QZ_3]/[QTZ_2]^2 \tag{2}$$

$$2QT_2Z \leftrightarrows QT_3 + QTZ_2 \tag{3}$$

$$K_b = [QT_3][QTZ_2]//[QT_2Z]^2 \tag{4}$$

In addition, in the presence of three or more different kinds of monofunctional substituents one equilibrium constant is required for each possible combination of any three different substituents. Denoting with X a third monofunctional, exchangeable substituent, in addition to T and Z, the following type of general equilibrium equation and equilibrium constant is to be considered.

$$2KTXZ \leftrightarrows QT_2X + QXZ_2 \tag{5}$$

$$K_c = [QT_2X][QXZ_2]/[QTXZ]^2 \tag{6}$$

Furthermore, when two different kinds of trifunctional central moieties, Q and M, are present, one additional equilibrium constant for each pair of monofunctional substituents may be written. This constant (intersystem constant), in general form, is derived from the equilibrium reaction given below.

$$QT_3 + MZ_3 \leftrightarrows QZ_3 + MT_3 \tag{7}$$

$$K_d = [QZ_3][MT_3]/\{[QT_3][MZ_3]\} \tag{8}$$

The number of constants of the above type that one may write is equal to the number of possible, different pairings of two exchangeable substituents each, but not all of these constants are independent ones.

System I. The components of this system are the three exchangeable, monofunctional substituents Cl, Br, I, and the two trifunctional central moieties CH_3Si and CH_3Ge. In agreement with the above and the previously reported rational,[1-5] there is required a set of three pairs of equilibrium constants of the type of K_a and K_b, defined by Eq. (2) and (4), for each of the two central moieties. These are shown in a more specific form in Table I as K_1 through K_6. Since two kinds of central moieties will have to be considered here, a total of twelve such constants will result.

In the present case only one compound may be realized for each of the two central moieties which has three different exchangeable, monofunctional substituents. Thus two constants of the type of K_c defined by Eq. (6) may be written. These are expressed in a more specific form as K_{13} in Table I.

Considering now the constants governing the distribution of the exchangeable substituents between the two central moieties, there are three possible pairings of the three different substituents Cl, Br, and I: Cl/Br, Cl/I, and Br/I. These will give three constants of the form of K_d, defined by Eq. (8), or, more

Table II. Equilibrium Data (in Mole Percent) for the System Involving Exchange of Cl, Br and I between CH_3Si and CH_3Ge at 120° (System I).

Peak No.	Chem. Shift[a] (ppm)	Assignment	Experiment Number					
			1	2	3	4	5	6
(1)	2.766	CH_3GeI_3	3.9[b] (3.9)[c]	3.6 (3.6)	2.8 (3.0)	1.5 (1.5)	17.0 (16.9)	2.3 (2.5)
(2)	2.488	CH_3GeBrI_2	11.5 (11.4)	12.4 (12.9)	9.0 (9.0)	7.6 (7.7)	21.2 (20.7)	8.2 (8.2)
	--	CH_3SiI_3	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.0)
(3)	2.310	CH_3GeClI_2	1.9 (1.8)	0.4 (0.3)	0.6 (0.7)	1.2 (1.2)	3.4 (3.3)	0.4 (0.4)
(4)	2.248	CH_3GeBr_2I	14.4 (14.4)	20.2 (19.8)	12.1 (11.7)	17.0 (17.2)	11.1 (10.8)	11.9 (11.6)
	--	CH_3SiBrI_2	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.0)
(5)	2.083	$CH_3GeClBrI$	4.5 (4.5)	1.0 (0.9)	1.7 (1.8)	5.7 (5.4)	3.8 (3.5)	1.2 (1.2)
	--	CH_3SiClI_2	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.0)
(6)	2.037	CH_3GeBr_3	7.0 (7.1)	12.7 (11.9)	6.1 (5.9)	15.4 (17.2)	2.4 (2.2)	6.7 (6.4)
(7)	1.936	CH_3GeCl_2I	0.4 (0.4)	-- (0.0)	-- (0.1)	0.7 (0.5)	0.3 (0.3)	-- (0.0)
(8)	1.900	CH_3GeBr_2Cl	3.6 (3.7)	0.8 (0.9)	1.5 (1.6)	8.0 (8.0)	1.6 (1.2)	1.2 (1.1)
	--	CH_3SiBr_2I	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.0)
	--	$CH_3SiBrClI$	-- (0.0)	-- (0.1)	-- (0.0)	-- (0.0)	-- (0.0)	-- (0.1)
(9)	1.760	$CH_3GeBrCl_2$	0.9 (0.8)	-- (0.0)	-- (0.2)	1.8 (1.8)	0.3 (0.3)	-- (0.1)
	--	CH_3GeCl_3	-- (0.1)	-- (0.0)	-- (0.0)	-- (0.2)	-- (0.0)	-- (0.0)
(10)	1.555	CH_3SiBr_3	-- (0.0)	3.2 (3.5)	0.3 (0.3)	-- (0.0)	-- (0.0)	0.7 (0.9)
	--	CH_3SiCl_2I	-- (0.1)	-- (0.1)	-- (0.1)	-- (0.0)	-- (0.1)	-- (0.1)
(11)	1.400	CH_3SiBr_2Cl	0.9 (1.0)	12.6 (13.4)	3.7 (3.8)	0.7 (0.8)	0.6 (0.7)	7.7 (7.7)
(12)	1.247	$CH_3SiBrCl_2$	9.5 (10.4)	20.7 (20.7)	20.8 (20.6)	7.6 (8.1)	6.9 (7.8)	25.7 (26.3)
(13)	1.105	CH_3SiCl_3	41.5 (40.6)	12.3 (11.9)	41.6 (41.2)	32.8 (32.4)	31.5 (32.0)	34.0 (33.4)
Composition Parameter:		$\underline{R}_1 \equiv [Cl]/([Ge]+[Si])$	1.562[d] (1.570)[e]	0.929 (0.931)	1.735 (1.739)	1.341 (1.342)	1.220 (1.189)	1.638 (1.639)
		$\underline{R}_2 \equiv [Br]/([Ge]+[Si])$	0.866[d] (0.852)[e]	1.491 (1.490)	0.843 (0.853)	1.206 (1.203)	0.645 (0.660)	0.986 (0.989)
		$\underline{R}_3 \equiv [I]/([Ge]+[Si])$	0.573[d] (0.578)[e]	0.579 (0.576)	0.422 (0.414)	0.453 (0.455)	1.135 (1.154)	0.377 (0.372)
		$\underline{R}_I \equiv [Ge]/([Ge]+[Si])$	0.480[d] (0.481)[e]	0.503 (0.511)	0.339 (0.338)	0.586 (0.589)	0.593 (0.611)	0.315 (0.319)

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[a] TMS = 0 with downfield shifts positive; measured in the neat liquid sample of experiment No. 4 of this table with TMS as internal standard. [b] From the nmr data in mole percent. [c] Calculated from the equilibrium constants of System I in Table I for the *R* values as calculated from the ingredients. [d] From the ingredients of the mixture as defined. [e] From the nmr data as defined.

specifically, in K_I for Cl/I, K_{III} for Cl/Br, both shown in Table I, and K_{IV} for Br/I listed below (Me=CH_3).

$$K_{IV}=[MeSiBr_3][MeGeI_3]]/\{[MeSiI_3][MeGeBr_3]\} \qquad (9)$$

In view of the relationship

$$K_{IV}=K_I/K_{III} \qquad (10)$$

one of these three constants is redundant and, therefore, K_{IV} has been omitted from the Table since two constants of the type of K_d are sufficient for inclusion in the minimum-number set of 16 constants. Such a set is required for the complete mathematical description of all equilibria in this system involving the 20 participating chemically different species.

The experimental equilibrium data in Table II as obtained from the nmr spectra show that not all of the twenty species expected to be seen at equilibrium are present in detectable amounts. Species which are present in very small amounts or, for practical purposes, not present at all are the following: CH_3SiI_3, CH_3SiBrI_2, CH_3SiClI_2, CH_3SiBr_2I, CH_3SiCl_2I, and $CH_3SiBrClI$; CH_3GeCl_3, $CH_3GeBrCl_2$ and CH_3GeCl_2I. Therefore, not all of the 16 equilibrium constants discussed above could be determined from the data. The data, however, permitted the calculation of K_1^{Si} and K_2^{Si} for the silicon-based species and K_2^{Ge}, K_4^{Ge}, K_5^{Ge}, K_6^{Ge}, and K_{13}^{Ge} for the germanium-based species. It is seen in Table I that the values of these constants agree quite well with values determined in the simplest possible systems reported previously.

For the computation of the theoretical distribution of species (values shown in parenthese in Table II) from the set of 16 equilibrium constants and the composition parameters of Table II it was, therefore, necessary to use values for the missing constants which were adopted from other studies or which were estimated. These values are shown in parentheses in Table I. The estimated values (K_3^{Si}, K_4^{Si}, K_5^{Si}, K_6^{Si}, and K_{13}^{Si}) are based on the assumption that halogen-halogen exchanges to a first order approximation generally are random processes[10] and, therefore, it is reasonable to assign the random value to these constants. Remarkable good agreement is seen in Table II between experimental and calculated equilibrium concentrations which indicates that the procedure used is quite reliable.

The conspicuous absence of certain speciese at equilibrium is governed by the extremely large values of K_I and K_{III} which at equilibrium favor the existence of compounds with Ge–I, Ge–Br, and Si–Cl bonds at the expense of species having Ge–Cl, Si–I, and Si–Br bonds. The influence of the constants of the type of K_a, K_b, and K_c, which all have values close to the ideal random case (for K_a and K_b, $K_{rand}=0.333$; for K_c, $K_{rand}=0.25$) on the other hand, is relatively minor.

System II. The incorporation of one additional kind of monofunctional, exchangeable substituent, the phenoxy group, into the equilibria of System I doubles the number of species in System II expected as a result of exchange processes. A total of 40 different species is to be considered and the equilibrium concentration of each of these is governed by a minimum-number set of 35 equilibrium constants. With the four monofunctional substituents being Cl, Br, I, and OPh, Ph=C_6H_5, and the trifunctional central moiety Q being either CH_3Si or CH_3Ge, the following 20 compounds each for Q=CH_3Si or CH_3Ge are potential participants of the equilibria.

QT_3,(QZ_3)	QT_2Z	QTZ_2	QTXZ
QCl_3	QBr_2Cl	$QBrCl_2$	QBrClI
QBr_3	QCl_2I	$QClI_2$	QBrCl(OPh)
QI_3	QBr_2I	$QBrI_2$	QClI(OPh)
$Q(OPh)_3$	$QCl_2(OPh)$	$QCl(OPh)_2$	QBrI(OPh)
	$QBr_2(OPh)$	$QBr(OPP)_2$	
	$QI_2(OPh)$	$QI(OPh)_2$	

As was done above for System I, it can be shown that for System II a set of six pairs of constants of the type of K_a and K_b, defined by Eqs. (2) and (3), for each one of the two central moieties will be effective. This total of 24 equilibrium constants expressed in a more detailed form is presented as K_1 through K_{12} in Table I.

The four species having each three different exchangeable substituents require four constants of the type of K_c, defined by Eq. (6), for each one of the two central moieties. These are shown in Table I as K_{13} through K_{16} representing a total of 8 equilibrium constants.

As intersystem constants we may consider 6 constants describing the distribution of the six pairs of substituents Cl/Br, Cl/I, Cl/OPh, Br/I, Br/OPh, and I/OPh between the two central moieties. It turns out that only three of these are independent, the three others may be derived from the independent ones. These independent constants of the general form of K_d, defined by Eq. (8), are shown in Table I as K_I, K_{II}, and K_{III}. The remaining three intersystem constants, the dependent ones, are K_{IV} of Eq. (9) which may be derived from K_I and K_{III} by using Eq. (10 and K_V and K_{VI} listed below.

$$K_V=[MeSiBr_3][MeGe(OPh)_3]\}[MeSi(OPh)_3][MeGeBr_3]\} =K_{II}/K_{III} \qquad (11)$$

$$K_{VI}=[MeSiI_3][MeGe(OPh)_3]/\{[MeSi(OPh)_3][MeGeI_3]\} =K_{II}/K_I \qquad (12)$$

The experimental equilibrium data shown in Table III indicate again that not all of the expected species are present in detectable amounts. There are twenty species out of the forty species expected, which in the nmr spectra of experiments 1 to 5 of Table III do not show at all and four species which appear in all of the five experiments in equilibrium concentrations which are less than 1 mole percent. The species not seen at equilibrium are $MeSiI_3$, $MeSiI_2(OPh)$, $MeSiClI_2$, $MeSiBrI_2$, $MeSiCl_2I$, $MeSiBr_2I$, $MeSiI(OPh)_2$, MeSiBrClI, MeSiClI(OPh), and MeSiBrI(OPh) for the silicon-based species and $MeGe(OPh)_3$, $MeGeCl(OPh)_2$, $MeGeBr(OPh)_2$, $MeGeI(OPh)_2$, $MeGeCl_2(OPh)$, $MeGeBr_2(OPh)$, $MeGeI_2(OPh)$, MeGeBrCl(OPh), MeGeClI(OPh), and MeGeBrI(OPh) for the germanium-based species. Those appearing in equilibrium concentrations of less than 1 mole percent are $MeSiBr_3$, $MeSiBr_2(OPh)$, $MeGeCl_3$, and $MeGeCl_2I$.

This situation on one hand is quite fortunate since it would have been extremely difficult, if not impossible, to resolve all 40 nmr signals in the rather narrow range of ca. 0.4 to 2.5 ppm; on the other hand, it allowed, as shown in Table I, the calculation from the data of Table III of only five equilibrium con-

Table III. Equilibrium Data (in Mole Per Cent) for the System Involving Exchange of Cl, Br, I, and OC_6H_5 between CH_3Si and CH_3Ge at 150° (System II).

Peak Number	Chem. Shift (ppm)[a]	Assignment[b]	Experiment Number				
			1	2	3	4	5
(1)	2.532	CH_3GeI_3	4.0^{c} (4.6)^{d}	2.3 (2.5)	1.3 (1.3)	6.2 (6.4)	1.3 (1.3)
(2)	2.248	CH_3GeBrI_2	13.1 (14.2)	7.8 (8.0)	6.4 (7.0)	18.3 (18.9)	7.8 (7.9)
(3)	2.064	CH_3GeClI_2	1.3 (1.2)	1.1 (1.0)	0.8 (0.6)	1.5 (1.1)	0.6 (0.4)
(4)	1.992	CH_3GeBr_2I	17.6 (18.1)	10.8 (11.0)	15.7 (16.1)	22 9 (23.4)	19.6 (19.7)
(5)	1.825	$CH_3GeBrClI$	3.9 (3.8)	3.8 (3.3)	3.9 (3.4)	4.2 (3.5)	3.5 (2.7)
(6)	1.768	CH_3GeBr_3	10.4 (9.7)	6.2 (6.3)	15.6 (15.5)	11.8 (12.1)	20.5 (20.4)
(7)	1.664	CH_3GeCl_2I	0.3 (0.2)	0.4 (0.3)	0.4 (0.2)	0.3 (0.2)	0.2 (0.1)
(8)	1.617	CH_3GeBr_2Cl	4.2 (3.9)	3.9 (3.6)	6.8 (6.3)	3.9 (3.5)	6.1 (5.5)
(9)	1.471	$CH_3GeBrCl_2$	0.7 (0.6)	0.9 (0.8)	1.3 (1.0)	0.4 (0.4)	0.8 (0.6)
(10)	1.338	CH_3GeCl_3	-- (0.0)	0.1 (0.1)	-- (0.1)	0.2 (0.0)	-- (0.0)
(11)	1.314	CH_3SiBr_3	-- (0.0)	-- (0.0)	0.4 (0.1)	-- (0.0)	-- (0.0)
(12)	1.197	CH_3SiBr_2Cl	0.5 (0.6)	0.3 (0.4)	1.2 (0.9)	0.8 (0.5)	0.3 (0.3)
(13)	1.046	$CH_3SiBrCl_2$	4.4 (4.2)	4.4 (3.9)	6.5 (6.4)	2.9 (2.8)	1.7 (1.4)
(14)	0.992	$CH_3SiBr_2(OC_6H_5)$	0.2 (0.3)	0.6 (0.2)	0.3 (0.2)	0.3 (0.3)	0.3 (0.4)
(15)	0.911	CH_3SiCl_3	13.5 (11.8)	14.8 (15.7)	16.4 (18.1)	5.2 (5.6)	2.4 (2.6)
(16)	0.800	$CH_3SiBrCl(OC_6H_5)$	3.1 (3.9)	4.4 (4.3)	3.4 (3.6)	3.5 (3.6)	4.3 (4.4)
(17)	0.788	$CH_3SiCl_2(OC_6H_5)$	16.5 (16.7)	26.8 (26.9)	15.5 (15.8)	11.1 (11.3)	11.8 (12.8)
(18)	0.731	$CH_3SiBr(OC_6H_5)_2$	0.4 (0.7)	0.7 (0.9)	0.2 (0.4)	1.0 (0.9)	2.5 (2.7)
(19)	0.603	$CH_3SiCl(OC_6H_5)_2$	5.5 (5.2)	9.9 (10.2)	3.9 (3.1)	5.2 (5.0)	13.3 (13.8)
(20)	0.388	$CH_3Si(OC_6H_5)_3$	0.4 (0.3)	0.6 (0.7)	0.1 (0.1)	0.5 (0.4)	2.9 (2.9)
Composition Parameter		$\underline{R}_1 \equiv [Cl]/([Ge]+[Si])$	0.977^{e} (1.028)^{f}	1.338 (1.331)	1.193 (1.166)	0.634 (0.647)	0.648 (0.643)
		$\underline{R}_2 \equiv [Br]/([Ge]+[Si])$	1.020^{e} (1.018)^{f}	0.704 (0.718)	1.152 (1.177)	1.219 (1.215)	1.329 (1.347)
		$\underline{R}_3 \equiv [I]/([Ge]+[Si])$	0.667^{e} (0.626)^{f}	0.399 (0.397)	0.386 (0.383)	0.864 (0.856)	0.432 (0.440)
		$\underline{R}_4 \equiv [(OPh)]/([Ge]+[Si])$	0.336^{e} (0.328)^{f}	0.559 (0.548)	0.270 (0.277)	0.283 (0.288)	0.591 (0.567)
		$\underline{R}_I \equiv [Si]/([Ge]+[Si]$	0.438^{e} (0.445)^{f}	0.632 (0.625)	0.487 (0.479)	0.306 (0.305)	0.413 (0.395)

[a] TMS=0 with downfield shifts positive; measured in the neat liquid sample of experiment No. 2 of this table with TMS as internal standard. [b] Species for which no nmr peak was seen are not shown. [c] From the nmr data in mole per cent. [d] Calculated from the equilibrium constants of System II of Table I for the *R* values as calculated from the ingredients. [e] From the ingredients of the mixture as defined [f] From the nmr data as defined.

stants for the silicon system, K_1^{Si}, K_7^{Si}, K_8^{Si}, K_{10}^{Si}, and K_{14}^{Si}, and also five equilibrium constants for the germanium-based system, K_2^{Ge}, K_4^{Ge}, K_5^{Ge}, K_6^{Ge}, and K_{13}^{Ge}. None of the intersystem constants could be calculated from the experimental data of Table III. The values of the above ten constants calculated directly agree quite well with values for these constants reported previously in studies of systems consisting of a minimum number of components. The latter are also shown in Table I.

In order to be able to compute the theoretical distribution of species at equilibrium (values shown in parentheses in Table III) from the minimum number set of 35 equilibrium constants, values for the additionally required 25 equilibrium constants were either estimated or taken from previous studies. The values of the latter type of constants are listed in parentheses in Table I. As mentioned above for System I, also here the estimated values describing the halogen-halogen exchanges (K_3^{Si}, K_4^{Si}, K_5^{Si}, K_6^{Si}, and K_{13}^{Si}) correspond to the random values of these types of constants and were chosen on the basis that to a first order approximation halogen-halogen exchanges generally follow random statistics.[10] The other estimated constants (K_{11}^{Si}, K_{12}^{Si}, K_{15}^{Si}, and K_{16}^{Si}) involving exchange of halogens with OPh groups were also assumed to represent processes which, in a first order approximation, approach random statistics. This assumption, of course is less accurate than the one made for the halogen-halogen exchanges, however, the few data available on halogen-phenoxy exchanges on silicon[7] confirm that these do not deviate by a lot from the random values. Again, good agreement is seen between experimental and calculated equilibrium concentrations in spite of the estimation of some of the required equilibrium constants.

Examining the pattern in the types of species not detectable at equilibrium, it turns out that the ten silicon-based species not seen consist of all the ones containing one or more iodine substituents, whereas the ten germanium-based species not seen at equilibrium represent all the ones containing one or more OPh substituents. Considering the values of the three independent intersystem constants K_{I}, K_{II}, and K_{III} in Table I and those of the three dependent intersystem constants calculated from the independent ones using Eqs. (10), 11), and (12). $K_{IV}=6.7\times10^{+6}$, $K_{V}=10^{-17}$ and $K_{VI}=1.5\times10^{-24}$, it appears that the overall equilibrium is governed mainly by the intersystem constant deviating the most from the ideal random value ($K_{rand} = 100$). That constant is K_{VI} describing the distribution of the substituents I and OPh between MeSi and MeGe. The extremely small value of this constant indicates that for all practical purposes the equilibrium of the equation below based on K_{VI},

$$\mathrm{MeSi(OPh)_3 + MeGeI_3 \rightleftarrows MeSiI_3 + MeGe(OPh)_3} \qquad (13)$$

exclusively favors the left side of Equation (13). Similarly, it may be shown for any other species containing the substituents I and OPh by calculation of the pertinent equilibrium constant from the minimum-number set of 35 constants, that any compound having one or more Si–I bonds or one or more Ge–OPh bonds is thermodynamically unstable in this system and will readily rearrange exchanging substituents to the thermodynamically stable arrangement of Si–OPh and Ge–I bonds.

The intersystem constant with the second largest deviation from randomness is K_{V}. This constant is based on the equation below

$$\mathrm{MeSi(OPh)_3 + MeGeBr_3 \rightleftarrows MeSiBr_3 + MeGe(OPh)_3} \qquad (14)$$

indicating that the components of the left hand side of Eq. (14) are favored at equilibrium. As a consequence, the equilibrium concentration of the species $MeSiBr_3$, $MeSiBr_2(OPh)$, and $MeSiBr_2Cl$ is quite small in the samples of Table III. The combined influence of these two constants as well as the other intersystem constants, the influence of the latter on the overall equilibrium is less drastic, results in an overall distribution of substituents favoring at equilibrium compounds having Si–Cl, Si–(OPh), Ge–Br and Ge–I bonds. The effect of the constants of the type of K_a, K_b, and K_c, which all are random or close to random, upon the distribution is less significant.

Equilibrium Temperature. In System I as well as in System II the equilibrium constants of the form of K_a, K_b, and K_c for the germanium based species correspond to 33°, the temperature of the nmr probe, on account of rapid exchange of substituents bonded to germanium with other such substituents. A high temperature nmr study of the composition of experiment 2 of System II in Table III shows increasing line broadening of the nmr signals corresponding to germanium-based species with increasing temperature. It is estimated that the average life time of a germanium species at 100-150° is of the order of 1 second, and at room temperature of the order of 3 to 10 seconds. Exchange reactions involving silicon-based compounds generally are quite slow in this temperature range, thus the constants of the type K_a, K_b, and K_c for the silicon-based systems correspond to the temperature at which the samples were equilibrated since rapid quenching will freeze the equilibrium corresponding to this temperature. As a matter of fact, in the equilibria involving OPh groups on silicon the exchange rates of this substituent are so slow at 120° that for the system where OPh substituents were participating, the higher equilibration temperature of 150° had to be chosen in order to attain reasonable reaction rates. The equilibria of the intersystem constant also correspond to the equilibration temperature, since, as has been shown previously,[6] the transfer of substituents from silicon to germanium and vice versa is relatively slow at room temperature, so that rapid quenching of the samples and immediate recording of the nmr spectra will represent the equilibrium situation at or near the equilibration temperature.

Bond Energy Considerations. The unusual distribution of components at equilibrium as found in the systems discussed in this paper may be rationalized in terms of bond energies and/or (p–d)π bond effects. In a dynamic equilibrium, such as the one described above, where substituents freely exchange places, the bonds formed preferentially will be those having the

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(10) K. Moedritzer, « Organometallic Reactions », (E.I. Becker and M. Tsutsui, ed.), 2, 1 (1971).

highest bond energy. Considering the single bond energies[11] of the Si–A and Ge–A bond (A=Cl, Br, I, and O), the two largest values are those of the Si–O (112 kcal) and Si–Cl (93 kcal) bond, thus tying up the substituents OPh and Cl with silicon atoms and forcing Br and I to form bonds to germanium. It has been argued that the difference in bond energies between corresponding bonds to silicon or germanium are due to π interactions which are stronger for silicon than for germanium. Therefore, the stronger π donors O and Cl will preferentially associate with silicon as the stronger π acceptor. It is believed that systematic studies of this type and careful evaluation of suitable equilibria will contribute towards the elucidation of differential π bonding effects in organometallic systems.

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(11) E.A.V. Ebsworth, « Organometallic Compounds of the Group IV Elements » (A.G. MacDiarmid, ed.), Marcel Dekker, Inc., New York, N. Y., 1968, p. 1.