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Equilibria Involving Scrambling of Three or Four Different Substituents on Methylgermanium

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Substituent exchange in the systems (A) CH_3GeCl_3–CH_3GeBr_3–CH_3GeI_3 and (B) CH_3GeCl_3–CH_3GeBr_3–CH_3GeI_3–$CH_3Ge(OC_6H_5)_3$ results in equilibria with, respectively, 10 and 20 different compounds participating. Proton nuclear magnetic resonance spectra of the equilibrated samples were evaluated in terms of sets of equilibrium constants, all of which had values which did uot deviate greatly from the random case. Utilizing a computer program, the resulting sets of equilibrium constants were employed to calculate the concentrations of the different species for the various stoichiometries studied.

Although several studies have appeared in the literature describing the exchange of more than two different kinds of substituents on a central moiety,[1-6] only two of these papers[2,6] present an interpretation of the experimental data in terms of a minimum-number set of necessary equilibrium constants. Even in these cases, the constants were not used to back-calculate the various molecular concentrations, which could then be compared with the observed concentrations in order to demonstrate that the reported equilibrium constants truly represented the experimental data.

Except for substituents bonded by carbon atoms, redistribution reactions on germanium as the polyfunctional exchangeable site generally proceed quite readily at moderate temperatures. Therefore, one can study exchange reactions on "methylgermanium" and "dimethylgermanium" moieties with these remaining intact *per se* while the redistribution of the other substituents (such as halogens and oxygen-, sulfur-, or nitrogen-bonded groups) proceeds to an equilibrium state at or slightly above room temperature.[7,8] This facile exchange of substituents on germanium prompted us to pick systems based on methylgermanium as suitable examples for the quantitative investigation of multicomponent-scrambling equilibria.

Experimental Part

Materials.—The methyltrihalogermanes were prepared as reported in the literature.[9] Methyltriphenoxygermane was synthesized from methyltribromogermane, phenol, and triethylamine in benzene, bp 168° (0.45 mm).

Equilibration, Measurements, and Data Reduction.—The reaction mixtures were prepared by sealing various proportions of the three (system A) or four (system B) end-member methylgermanium compounds in 5-mm o.d. nuclear magnetic resonance (nmr) tubes and holding these at room temperature. Generally within less than 4 days at this temperature, equilibrium was achieved; however, the quantitative measurements were made only after the samples had been held for 8 days at room temperature. The proton nmr spectra were obtained on a Varian A-60 spectrometer, using the electronic integrator for the determination of peak areas. In cases where several peaks were very close together (*i.e.*, the valley between two peaks did not reach the base line), areas were determined with a Du Pont Model 310 curve resolver.

Nmr chemical shifts of the protons in the methyl groups of the various methylgermanium derivatives seen at equilibrium are listed in the respective tables summarizing the experimental data. Computer programs for the IBM 7044 were used to calculate (1) weighted-average equilibrium constants,[10] (2) their standard errors, and (3) the theoretical equilibrium compositions[11] from the equilibrium constants.

Results and Conclusions

Equilibria.—Redistribution equilibria between two kinds of exchangeable substituents on a trifunctional central moiety are relatively simple to treat experimentally as well as mathematically. In each such equilibrium, there are participating four different species, whose concentrations are determined by two equilibrium constants.[12] The situation is somewhat more complex when there are three different kinds of substituents exchanging on one kind of trifunctional moiety. As shown by the left triangular face of the tetrahedron in Figure 1 representing the system CH_3GeCl_3–CH_3GeBr_3–CH_3GeI_3 (system A), there are to be considered at equilibrium the three methylgermanes having all like substituents and the six species containing two kinds of substituents as well as one species (located in the center of the triangular face) having all three substituents.

The equilibria in this system are described by six constants, each derived from the general equilibrium reactions

$$2CH_3GeZ_2T \rightleftharpoons CH_3GeZ_3 + CH_3GeZT_2 \qquad (1)$$

$$2CH_3GeZT_2 \rightleftharpoons CH_3GeT_3 + CH_3GeZ_2T \qquad (2)$$

For Z = Cl and T = Br in eq 1 and 2, the constants K_1 and K_2 are obtained; for Z = Cl and T = I, the con-

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TABLE I

EQUILIBRIUM CONSTANTS[a] AS CALCULATED FROM THE EXPERIMENTAL DATA AT ROOM TEMPERATURE

		System A[b]	System B[b]
K_1	$= [Cl_3][Br_2Cl]/[BrCl_2]^2$	0.35 ± 0.02	0.41 ± 0.03
K_2	$= [Br_3][BrCl_2]/[Br_2Cl]^2$	0.45 ± 0.03	0.40 ± 0.03
K_3	$= [Cl_3][ClI_2]/[Cl_2I]^2$	0.61 ± 0.03	0.70 ± 0.11
K_4	$= [I_3][Cl_2I]/[ClI_2]^2$	0.76 ± 0.05	0.65 ± 0.13
K_5	$= [Br_3][BrI_2]/[Br_2I]^2$	0.40 ± 0.02	0.42 ± 0.04
K_6	$= [I_3][Br_2I]/[BrI_2]^2$	0.41 ± 0.02	0.39 ± 0.04
K_7	$= [Cl_3][Cl(OC_6H_5)_2]/[Cl_2(OC_6H_5)]^2$	...	0.13 ± 0.01
K_8	$= [(OC_6H_5)_3](Cl_2(OC_6H_5)]/[Cl(OC_6H_5)_2]^2$	...	0.14 ± 0.13
K_9	$= [Br_3][Br(OC_6H_5)_2]/[Br_2(OC_6H_5)]^2$	...	0.22 ± 0.04
K_{10}	$= [(OC_6H_5)_3][Br_2(OC_6H_5)]/[Br(OC_6H_5)_2]^2$	...	0.23 ± 0.22
K_{11}	$= [I_3][I(OC_6H_5)_2]/[I_2(OC_6H_5)]^2$	...	0.20 ± 0.14
K_{12}	$= [(OC_6H_5)_3](I_2(OC_6H_5)]/[I(OC_6H_5)_2]^2$	...	1.24 ± 1.61
K_{13}	$= [Br_2Cl][ClI_2]/[BrClI]^2$	0.31 ± 0.01	0.35 ± 0.03
K_{14}	$= [Br_2Cl][Cl(OC_6H_5)_2]/[BrCl(OC_6H_5)]^2$	...	0.16 ± 0.02
K_{15}	$= [ClI_2][Cl(OC_6H_5)_2]/[ClI(OC_6H_5)]^2$	...	0.55 ± 0.08
K_{16}	$= [BrI_2][Br(OC_6H_5)_2]/[BrI(OC_6H_5)]^2$	...	0.55 ± 0.08

[a] Weighted average values and their standard error; only the exchanging substituents, omitting the CH_3Ge central moiety, are shown in the equations. [b] Literature[7] values: $K_1 = 0.42 \pm 0.03$, $K_2 = 0.41 \pm 0.03$, $K_3 = 0.79 \pm 0.07$, $K_4 = 0.72 \pm 0.06$, $K_5 = 0.42 \pm 0.03$, $K_6 = 0.44 \pm 0.03$.

stants K_3 and K_4 are obtained; and for Z = Br and T = I, the constants K_5 and K_6 are obtained. One additional constant is required which determines the compound $CH_3GeBrClI$. Although there are three different ways of writing equilibria similar to eq 1 and 2 but involving $CH_3GeBrClI$, one is sufficient to fix the concentrations of this compound in the equilibrium mixture. Of the equations

$$2CH_3GeBrClI \rightleftarrows CH_3GeBr_2Cl + CH_3GeClI_2 \quad (3)$$

$$2CH_3GeBrClI \rightleftarrows CH_3GeCl_2Br + CH_3GeBrI_2 \quad (4)$$

$$2CH_3GeBrClI \rightleftarrows CH_3GeCl_2I + CH_3GeBr_2I \quad (5)$$

we have chosen the equilibrium described by eq 3 to represent the seventh required equilibrium constant, K_{13}. Values for the constants K_1 to K_6 and K_{13} corresponding to the equilibria of eq 1–3 are presented in Table I, where it is seen that the observed values of none of these constants are far from the statistically random values, which are 0.333 for K_1 to K_6 and 0.25 for K_{13}. These seven equilibrium constants represent the minimum number required to describe completely the equilibria in this system. The thus calculated theoretical equilibrium concentrations in this system are listed in parentheses under the experimental values in Table II. Generally excellent agreement between the calculated and experimental values is obtained.

The proton chemical shifts of the compounds seen at equilibrium are also listed in Table II. It is seen that, when substituting consecutively one substituent by another, the resulting shifts vary linearly and are in agreement with the shifts measured previously in the pertinent binary equilibrium systems. The shift of $CH_3GeBrClI$ is approximately equal to the average of the shifts of the three methylgermanium trihalides where the halogens are all of one kind: calcd, −2.17 ppm; found, −2.11 ppm.

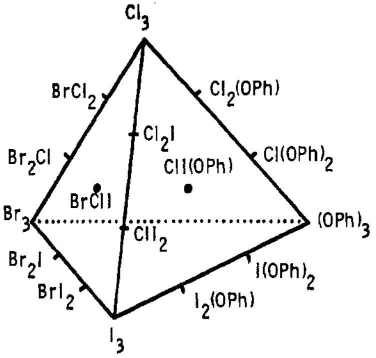

Figure 1.—Diagram showing the possible compounds present at equilibrium in the quaternary system CH_3GeCl_3–CH_3GeBr_3–CH_3GeI_3–$CH_3Ge(OC_6H_5)_3$. The central moiety CH_3Ge is not shown, OPh = OC_6H_5. Also not shown are the two compounds at locations on the tetrahedron faces which do not face the viewer and the two on the backside edge.

Still more complex equilibria result when four kinds of exchangeable monofunctional substituents are undergoing redistribution on the methylgermanium moiety. The number of possible compounds may be deduced from the diagram in Figure 1. At the apices of the tetrahedron there are the four unmixed compounds; at the six edges of the tetrahedron there are the binary mixed compounds—two per edge, resulting in a total of twelve; and, in the center of the four faces of the tetrahedron, there is a total of four ternary mixed compounds. This adds up to twenty possible species to be considered. As shown by the experimental data in Table III, all of these species have been identified in equilibrium mixtures.

The equilibrium state in this system, in addition to the constants K_1 to K_6, accordingly is determined by six additional equilibria of the form of eq 1 and 2, where Z = Cl, T = OC_6H_5 (yielding K_7 and K_8), Z = Br, T = OC_6H_5 (yielding K_9 and K_{10}), and Z = I, T = OC_6H_5 (yielding K_{11} and K_{12}). Furthermore, the four ternary mixed species are determined by K_{13} to K_{16} of which K_{13} is derived from eq 3 and K_{14} to K_{16} are derived from the equilibrium reactions

$$2CH_3GeBrCl(OC_6H_5) \rightleftarrows CH_3GeBr_2Cl + CH_3GeCl(OC_6H_5)_2 \quad (6)$$

$$2CH_3GeClI(OC_6H_5) \rightleftarrows CH_3GeClI_2 + CH_3GeCl(OC_6H_5)_2 \quad (7)$$

$$2CH_3GeBrI(OC_6H_5) \rightleftarrows CH_3GeBrI_2 + CH_3GeBr(OC_6H_5)_2 \quad (8)$$

The constants for these 16 equilibria are tabulated in Table I where it is seen again that nearly random values are predominant. The random value for K_1 to K_{12} is 0.333, and for K_{13} to K_{16}, it is 0.25. Good agreement is observed between corresponding constants as obtained in systems A and B and also as obtained in other studies of exchange equilibria on methylgermanium.[7]

The proton nmr chemical shifts of the methyl groups in the various compounds seen at equilibrium are pre-

TABLE II

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA (IN MOLE PER CENT) IN THE SYSTEM CH_3GeCl_3–CH_3GeBr_3–CH_3GeI_3 AT ROOM TEMPERATURE

Nmr signal	Chem shift^a	Assignment	Experiments						
			1	2	3	4	5	6	7
1	−2.775	CH_3GeI_3	2.4^b	1.5	27.8	7.1	3.9	2.0	10.4
			(2.4)^c	(1.5)	(27.3)	(7.0)	(3.8)	(2.2)	(10.5)
2	−2.513	CH_3GeBrI_2	4.3	8.3	20.5	13.3	6.9	6.9	21.1
			(4.2)	(8.9)	(20.7)	(13.6)	(6.7)	(7.5)	(21.3)
3	−2.333	CH_3GeClI_2	7.5	2.3	16.2	9.2	8.8	5.0	8.1
			(7.5)	(2.2)	(16.5)	(9.4)	(8.9)	(4.9)	(8.0)
4	−2.273	CH_3GeBr_2I	2.9	20.7	6.2	10.5	4.5	10.1	17.3
			(3.0)	(20.9)	(6.4)	(10.7)	(4.8)	(10.4)	(17.4)
5	−2.108	$CH_3GeBrClI$	13.1	12.7	12.2	18.2	15.6	17.0	16.3
			(12.4)	(12.2)	(11.9)	(17.4)	(14.9)	(16.0)	(15.3)
6	−2.063	CH_3GeBr_3	1.0	20.4	0.8	3.5	1.4	6.0	5.6
			(0.8)	(19.6)	(0.8)	(3.4)	(1.4)	(5.8)	(5.7)
7	−1.959	CH_3GeCl_2I	16.5	3.6	7.1	9.6	14.9	9.2	4.5
			(17.4)	(2.4)	(7.6)	(9.6)	(15.7)	(8.4)	(4.6)
8	−1.923	CH_3GeBr_2Cl	5.9	20.1	2.6	10.0	7.5	16.1	9.1
			(6.3)	(20.7)	(2.7)	(9.9)	(7.7	(16.1)	(9.1)
9	−1.793	$CH_3GeBrCl_2$	20.8	9.0	4.3	12.7	19.4	19.6	6.1
			(21.2)	(9.9)	(4.0)	(13.1)	(19.3)	(20.1)	(6.5)
10	−1.671	CH_3GeCl_3	25.5	1.5	2.3	6.1	17.1	8.1	1.5
			(24.7)	(1.6)	(2.1)	(6.0)	(16.8)	(8.7)	(1.6)
Composition Parameters									
R_1 = I/Ge			0.622^d	0.622	1.817	1.038	0.779	0.624	1.259
			(0.633)^e	(0.627)	(1.823)	(1.046)	(0.781)	(0.661)	(1.277)
R_2 = Br/Ge			0.614^d	1.777	0.583	0.979	0.716	1.189	1.156
			(0.588)^e	(1.728)	(0.570)	(0.957)	(0.701)	(1.139)	(1.131)
R_3 = Cl/Ge			1.764^d	0.601	0.601	0.985	1.504	1.191	0.593
			(1.776)^e	(0.648)	(0.607)	(1.003)	(1.518	(1.200)	(0.592)

[a] In ppm relative to internal tetramethylsilane. [b] From the nmr spectra. [c] Calculated with the equilibrium constants K_1–K_6 and K_{13} of system A in Table I. [d] From the ingredients. [e] From the nmr data.

sented in Tables II and III. Whereas the shifts in Table II agree quite well with those obtained previously for like compounds in the studies of the equilibria in the binary systems,[7] the shifts in Table III for the corresponding compounds are generally about 0.1–0.2 ppm further upfield. This effect is attributable to the methyltriphenoxygermane and the methylhalophenoxygermanes acting as "aromatic" solvents which are known to affect the chemical shifts of polarizable compounds.[13] However, the order in which the various signals appear as well as the approximate distance between peaks does not seem to be affected.

A typical nmr spectrum of an equilibrated sample in the system of Table III is shown in Figure 2. From this figure, it is also apparent how the assignments in the 20-line spectrum at the bottom were made. The shifts of methylgermanes having two kinds of exchangeable substituents are readily obtained from the study of the spectra of binary mixtures, *e.g.*, CH_3GeI_3–$CH_3Ge(OC_6H_5)_3$. Methylgermanes having three kinds of exchangeable substituents are seen in ternary mixtures, *e.g.*, in the center spectrum of Figure 2, where nine of the ten signals could be assigned according to the above technique from the binary mixtures. The tenth peak seen at equilibrium, therefore, must be due to the compound which could have formed only in the ternary system CH_3GeI_3–CH_3GeBr_3–$CH_3Ge(OC_6H_5)_3$ and therefore is that of $CH_3GeBrI(OC_6H_5)$. In a similar manner, the locations in the spectrum of the other three ternary compounds, $CH_3GeBrClI$, $CH_3GeBrCl(OC_6H_5)$, and $CH_3GeClI(OC_6H_5)$, were determined. No overlap of peaks was observed although, in each of three instances, three peaks are clustered quite closely together. The assignments made in Tables II and III are confirmed by the good agreement of the composition parameters R_1, R_2, R_3, and R_4 as obtained from the ingredients of the original mixtures (values not in parentheses in Tables II and III) with the ones calculated from the experimentally determined mole percentages on the basis of these assignments (value listed in parentheses in Tables II and III).

Rates.—Qualitative experiments have shown that the exchange of halogens or phenoxyl groups with each other on methylgermanium proceeds very fast, probably at half-life times of the order of minutes. Studies of the variation of nmr line widths with temperature for sample no. 5 in the system of Table III showed increasing line width of the proton nmr peaks with increasing temperature. Furthermore in the range of 80–120°, the close-lying signals merged to single broad peaks. These groups of peaks are (compare Figure 2): $CH_3GeI_2(OC_6H_5)$ and $CH_3GeBrClI$; $CH_3GeBrI(OC_6H_5)$ and CH_3GeBr_2Cl; $CH_3GeClI(OC_6H_5)$ and $CH_3GeBrCl_2$. Calculation of the average preexchange lifetime, τ, using the equation

$$\tau = 1/[2\pi(w - w_0)] \qquad (9)$$

where w is the line width (in cps) of the broadened peak and w_0 the line width when there is no exchange, shows that, at 200°, τ is of the order of 0.1 sec; at 100°, *ca.*

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[13] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance," Pergamon Press Ltd., London, 1966, p 258.

TABLE III

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA (IN MOLE PER CENT) IN THE SYSTEM CH_3GeCl_3–CH_3GeBr_3–CH_3GeI_3–$CH_3Ge(OC_6H_5)_3$ AT ROOM TEMPERATURE (Ph = C_6H_5)

Peak number	Chem. Shift[a]	Compound	Experiments 1	2	3	4	5
(1)	-2.618	CH_3GeI_3	2.7[b] (2.8)[c]	1.2 (1.2)	0.5 (0.6)	1.3 (1.2)	7.7 (6.4)
(2)	-2.343	CH_3GeBrI_2	7.7 (8.1)	4.9 (5.0)	3.2 (3.5)	2.9 (2.9)	12.5 (11.2)
(3)	-2.157	CH_3GeClI_2	4.1 (4.1)	2.3 (2.2)	1.7 (2.1)	3.1 (3.1)	5.1 (4.8)
(4)	-2.093	CH_3GeBr_2I	9.2 (9.1)	7.9 (8.1)	7.3 (7.5)	3.0 (2.7)	7.8 (7.7)
(5)	-1.950	$CH_3GeI_2(OPh)$	1.4 (2.5)	1.2 (1.9)	1.2 (0.5)	1.3 (2.1)	3.8 (7.0)
(6)	-1.925	$CH_3GeBrClI$	10.5 (10.3)	7.8 (7.9)	8.8 (9.9)	7.2 (6.6)	7.5 (7.3)
(7)	-1.872	CH_3GeBr_3	4.3 (4.3)	5.7 (5.5)	7.2 (6.8)	1.0 (1.1)	2.3 (2.2)
(8)	-1.768	CH_3GeCl_2I	4.2 (3.9)	2.6 (2.6)	4.2 (4.3)	5.5 (5.3)	2.1 (2.3)
(9)	-1.733	$CH_3GeBrI(OPh)$	5.5 (4.8)	4.5 (5.2)	1.3 (1.9)	3.1 (3.4)	8.2 (8.2)
(10)	-1.722	CH_3GeBr_2Cl	8.3 (8.9)	10.8 (9.9)	17.3 (16.5)	5.5 (4.8)	4.4 (3.9)
(11)	-1.585	$CH_3GeClI(OPh)$	4.6 (4.0)	3.6 (3.7)	1.8 (1.9)	5.6 (6.2)	5.3 (5.8)
(12)	-1.581	$CH_3GeBrCl_2$	7.9 (7.5)	7.4 (7.1)	17.0 (16.0)	9.3 (8.6)	3.4 (2.7)
(13)	-1.548	$CH_3GeBr_2(OPh)$	5.2 (5.6)	8.8 (8.6)	4.1 (4.2)	3.2 (3.4)	5.7 (5.8)
(14)	-1.453	CH_3GeCl_3	2.9 (2.5)	2.2 (2.1)	6.7 (6.3)	6.9 (6.3)	0.9 (0.8)
(15)	-1.416	$CH_3GeBrCl(OPh)$	11.2 (10.9)	14.9 (14.5)	9.4 (9.7)	13.9 (14.1)	10.1 (9.6)
(16)	-1.363	$CH_3GeI(OPh)_2$	0.2 (0.4)	0.5 (0.6)	0.1 (0.1)	0.4 (0.8)	1.1 (1.6)
(17)	-1.297	$CH_3GeCl_2(OPh)$	6.4 (6.5)	7.5 (7.5)	6.8 (6.7)	18.3 (18.1)	4.9 (4.9)
(18)	-1.202	$CH_3GeBr(OPh)_2$	1.5 (1.6)	2.8 (2.9)	0.7 (0.6)	2.0 (2.6)	3.2 (3.3)
(19)	-1.089	$CH_3GeCl(OPh)_2$	2.1 (2.2)	3.2 (3.5)	0.8 (0.9)	6.2 (6.7)	3.8 (3.9)
(20)	-0.855	$CH_3Ge(OPh)_3$	0.1 (0.1)	0.2 (0.2)	-- (0.0)	0.3 (0.3)	0.4 (0.4)
		R_1 ≡ I/Ge	0.701[d] (0.687)[e]	0.499 (0.473)	0.396 (0.372)	0.449 (0.433)	0.984 (0.979)
		R_2 ≡ Br/Ge	1.031[d] (1.026)[e]	1.121 (1.144)	1.184 (1.194)	0.629 (0.648)	0.839 (0.876)
		R_3 ≡ Cl/Ge	0.838[d] (0.865)[e]	0.822 (0.842)	1.139 (1.159)	1.244 (1.284)	0.576 (0.597)
		R_4 ≡ (OPh)/Ge	0.430[d] (0.422)[e]	0.558 (0.541)	0.281 (0.278)	0.678 (0.635)	0.602 (0.554)

[a] In ppm relative to internal tetramethylsilane [b] From the nmr spectra [c] Calculated from the equilibrium constants [d] From the ingredients [e] From the nmr data

2 sec; and, at room temperature, *ca.* 5 sec. The line-width measurements also indicate that at a given temperature the preexchange lifetimes for the individual species present at equilibrium increase in the order in which the respective signals appear in the upfield direction in the spectrum of Figure 2. The measured preexchange lifetimes at 200° for CH_3GeI_3 and the neighboring three peaks in the upfield direction are *ca.* 0.07 sec whereas this value for the three most upfield signals is 0.7 sec.

Discussion

Multicomponent scrambling equilibria, such as in system B of this paper, are of interest inasmuch as they yield a number of equilibrium constants in one simple set of experiments. In the present case, values for the constants K_7 to K_{16} are reported here for the first time, whereas K_1 to K_6 have been measured separately in previous studies of binary mixtures. Although the simultaneous determination of a large number of equilibrium constants from one set of experiments appears advantageous, it also poses some problems. These lie in the fact that the absolute concentration of each species present at equilibrium is relatively small and therefore the measured concentrations generally show larger errors than when determined in equilibria with a fewer number of participating species.

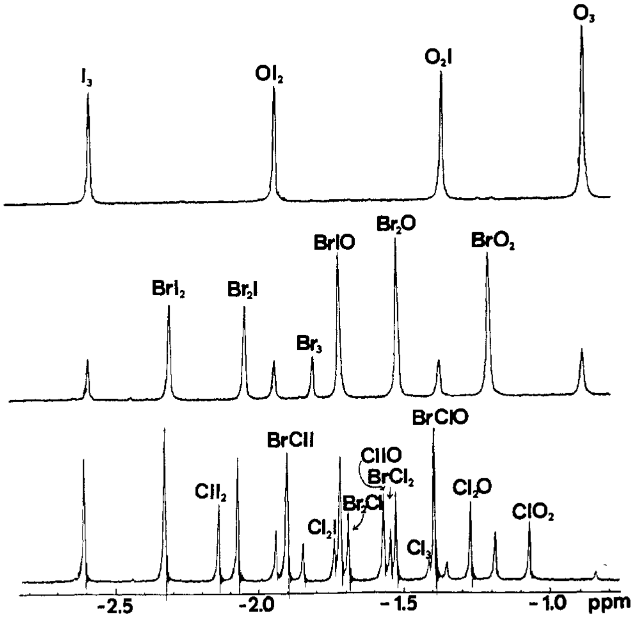

Figure 2.—Proton nmr spectra of equilibrated samples in the systems CH_3GeI_3–$CH_3Ge(OC_6H_5)_3$ [top spectrum; composition parameter R_1 = I/Ge = 1.254]; CH_3GeI_3–CH_3GeBr_3–$CH_3Ge(OC_6H_5)_3$ [center spectrum; composition R_1 = I/Ge = 0.770, R_2 = Br/Ge = 1.137, R_3 = OC_6H_5/Ge = 1.093]; and CH_3GeI_3–CH_3GeBr_3–CH_3GeCl_3–$CH_3Ge(OC_6H_5)_3$ [bottom spectrum; composition corresponds to experiment 5 in Table III]. In the notation for assigning the various peaks, only the exchangeable substituents (without the CH_3Ge central moiety) are shown.

The first six constants (K_1 through K_6) as well as K_{13} in Table I serve as a check on the reproducibility of equilibrium constants for the scrambling of substituents in situations where the various compounds do not have low-lying empty orbitals which may be filled by the donation of electron pairs from the solvent molecules. For all of the reactions of Table I, the equilibrium constant corresponding to statistically random sorting of the substituents is 0.333 and, to a first approximation, the heat of the reaction may be estimated[14] from the deviation of the observed constant from the random value. For small deviations from randomness, the meaningfulness[15] of such estimations of the enthalpy becomes questionable and it is important to build up a collection of values for a given equilibrium constant corresponding to the same equilibration in varying systems and solvents. This kind of evidence, as well as the equilibrations carried out in the gas as compared to the liquid phase,[16] is needed in order to justify discussion of these constants in terms of the electronic structure of the molecules. The data of

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(14) *E.g.*, see J. R. Van Wazer and L. Maier, *J. Am. Chem. Soc.*, **86**, 811 (1964).

(15) T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, **5**, 233 (1966).

(16) D. R. Weyenberg, *Ann. N. Y. Acad. Sci.*, in press.

Table I as well as the recent study[16] comparing liquid- and gas-phase data are both indicative that a theoretical analysis on the electron level would not be ill founded.

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N-Methylated Perchlorogermazanes and the Reaction of Germanium Tetrachloride with Methylamine

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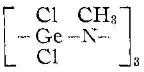
When a 3:1 molar mixture of methylamine and germanium tetrachloride in benzene is allowed to react to precipitate the amine hydrochloride and is then equilibrated, a new cyclic compound



$$\left[\begin{array}{c} \text{Cl}\quad\text{CH}_3 \\ -\text{Ge}-\text{N}- \\ \text{Cl}\qquad \end{array}\right]_3$$

is the major species; whereas, when the amount of methylamine combined with the germanium tetrachloride is progressively decreased to zero, the last nitrogen-containing molecule to vanish in the equilibrated mixtures is $Cl_3GeN(CH_3)GeCl_3$. For all mole ratios of amine to germanium tetrachloride from 0 to 3, these two compounds are the predominant species at equilibrium. Nuclear magnetic resonance (nmr) has been used to demonstrate the above and to estimate values of the pertinent equilibrium constants measured on mixtures made from the crystalline tri-N-methylhexachlorocyclotrigermazane with germanium tetrachloride. The first stage in the reaction between the amine and the tetrachloride is the exothermic formation of the amine hydrochloride plus precipitation of polymeric germazanes which further react with the free $GeCl_4$ to give smaller soluble molecules. When there is an excess of amine over that needed to react with all of the chlorine atoms, the monofunctional units of the soluble species are methylamino groups, $(CH_3)HN-$, which then slowly disappear through a process of hydrogen exchange to give bridging groups in a cross-linked amorphous polymer plus free CH_3NH_2.

Although there is some literature on the reaction of germanium halides with primary amines and ammonia,[2] modern methods for the determination of molecules in mixtures have not been applied to these systems until now. In designing this study, we chose methylamine in order that a molecular assay could be carried out on the basis of the proton nuclear magnetic resonance (nmr) spectra of the N-methyl groups.

Experimental Section

The germanium tetrachloride was a gift from the Germanium Research Institute, Kansas City, Mo. The new crystalline cyclic compound, $[Ge(Cl_2)N(CH_3)]_3$, was made according to our previous description.[3] The methylamine was taken through a KOH drying tube from a lecture bottle purchased from the Matheson Co., East Rutherford, N. J. The nmr measurements were made on a Varian A-60 spectrometer running at room temperature and the reference standard (with downfield shifts being negative) was tetramethylsilane added to the solutions at the end of the runs. Measurements on the equilibrated samples were all done at a sweep width of 50 cps full scale, with use of the cut-and-weigh technique for area measurements.

The equilibrium studies were carried out by mixing various proportions of crystalline $[Ge(Cl_2)N(CH_3)]_3$ with germanium tetrachloride in benzene as solvent and sealing the samples in 5-mm precision nmr tubes. These were then heated at 150° for 4 days before quenching (by dropping in ice water) and measuring immediately thereafter. Preliminary rate data indicate that equilibrium was achieved in less than 1 day at this temperature. The rate studies were carried out in the same way, except that one set of samples was thermostated at 56° and the other at 100°. Since it took about 600 min to reach equilibrium at 100° and about 5000 min at 56°, the repeated quenching of a sample for measuring the nmr spectrum at a given time promptly followed by replacing the sample in the thermostat should have had an inappreciable effect on the resulting rate curves.

Results and Discussion

Equilibrium Studies.—Equilibration of various mixtures of germanium tetrachloride with the cyclic compound $[Ge(Cl_2)N(CH_3)]_3$ showed seven nmr peaks, exhibiting chemical shifts at a total of 2 mol of Ge/l. in benzene of -2.45, -2.47, -2.54, -2.56, -2.63, -2.68, and -2.72 ppm, of which the first and fifth peak listed always predominated. In benzene, these shifts vary somewhat with concentration and the overall composition of the mixture of germanium species. Indeed, for the neat liquid, the first peak lies downfield of the fifth: Dilutions greater than 2 mol of Ge/l. of benzene do not change the ordering of the resonances but cause them to be more widely separated. The nmr shift[3] of -2.68 for the pure cyclic $[Ge(Cl_2)N(CH_3)]_3$ under the same conditions was identical with that of the fifth peak in the above series and this assignment was confirmed by small additions of the cyclic molecule to equilibrated mixtures. The other predominating peak—the first one—was assigned to the dichain molecule, $Cl_3Ge-N(CH_3)-GeCl_3$, on the basis that it was the initially appearing resonance when increasingly larger trace amounts of

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[1] Postdoctoral fellow from Heidelberg University, Heidelberg, Germany, 1966-1967.

[2] *E.g.*, see J. G. A. Luitjen, F. Rijkens, and G. J. M. van der Kerk, *Advan. Organometal. Chem.*, **3**, 398 (1965); J. S. Thomas and W. W. Southwood, *J. Chem. Soc.*, **1931**, 2083; and W. C. Johnson and A. E. Sidwell, *J. Am. Chem. Soc.*, **55**, 1884 (1933).

[3] W. Eisenhuth and J. R. Van Wazer, *Inorg. Nucl. Chem. Letters*, **3**, 359 (1967).