mide. The only product isolated from the attempted dehydration of 3-triphenylgermyl-3-pentanol was hexaphenyldigermoxane.

Ozonolysis of vinylgermanes and subsequent reduction of the ozonide was explored in an effort to find a general preparative method for α-germyl ketones. Germyl substituted phenyl ketones, but not germyl alkyl ketones, can be prepared from acid chlorides and triphenylgermyllithium.[15] A low yield of benzoyltriphenylgermane was obtained from the ozonolysis of 1-triphenylgermyl-1-phenylethylene, but, as summarized in Table III, either hexaphenyldigermoxane or the unreacted olefin was recovered from the ozonolysis of other vinylgermanes.

TABLE III

PRODUCTS OBTAINED FROM THE OZONOLYSIS OF VINYLGERMANES

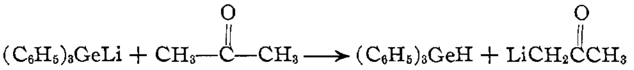
Olefin	Solvent	Temp., °C.	Product(s)	Yield, %
$(C_6H_5)_3Ge(C_6H_5)C{=}CH_2$	C_2H_5OAc	−78	$C_6H_5C(O)Ge(C_6H_5)_3$	5
$((C_6H_5)_3Ge)_2C{=}CH_2$	C_2H_5OAc	−78	$((C_6H_5)_3Ge)_2O$	45
$(C_6H_5)_3Ge(CH_3)C{=}CH_2$	Heptane	−78	$(C_6H_5)_3Ge(CH_3)C{=}CH_2$	27
			$((C_6H_5)_3Ge)_2O$	22
$(C_6H_5)_3Ge(CH_3)C{=}CH_2$	CCl_4	−20	$(C_6H_5)_3Ge(CH_3)C{=}CH_2$	53
$(C_6H_5)_3Ge(C_6H_5)C{=}CH_2$	CCl_4	−20	$(C_6H_5)_3Ge(C_6H_5)C{=}CH_2$	42

Discussion

The strong solvent dependence of the reaction of triphenylgermyllithium with ketones is demonstrated by the reactions of acetophenone and acetone in ether and in tetrahydrofuran. The sole product isolated from the reaction of acetophenone or acetone with triphenylgermyllithium in tetrahydrofuran was triphenylgermane. With ethyl ether as the solvent, the corresponding alcohol is obtained in good yield.

Triphenylgermane can result from one of two pathways. First, the triphenylgermane could arise from hydrolysis of unreacted triphenylgermyllithium; and second, it could result from abstraction of an acidic hydrogen from the ketone. The second path seems to be more likely. Triphenylgermyllithium has been shown earlier to react with carbonyl groups in carboxylic acid chlorides even at temperatures as low as −78°.[15] Benzophenone, which has no α-hydrogens available for reaction, gives the corresponding alcohol in 52% yield when allowed to react with triphenylgermyllithium in tetrahydrofuran.[16]

$$(C_6H_5)_3GeLi + H_2O \rightarrow (C_6H_5)_3GeH + LiOH$$



$$(C_6H_5)_3GeLi + CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 \longrightarrow (C_6H_5)_3GeH + LiCH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

Steric effects are probably important in explaining the failure to observe any alcohol resulting from reactions of *t*-butyl methyl ketone and 2-methylcyclohexanone with triphenylgermyllithium. Approach to the carbonyl group is severely hindered in each case.

No rearrangement of the α-hydroxygermanes to α-germyl ethers was observed. Formation of silyl ethers generally is observed in similar silicon systems.[17] The rearrangement in the silicon systems probably is due to the abnormally high Si–O bond energy.

The preparation of vinylgermanes from the dehydration of α-hydroxygermanes is especially useful in the synthesis of monosubstituted vinylgermanes in which the substituent is bonded to the same carbon atom as the germanium. Alternate Grignard syntheses or addition reactions leading to the preparation of such compounds have not been reported. Addition of triphenylgermane to monosubstituted acetylenes leads to the anti-Markownikoff product, *i.e.*, the germanium bonded to the least hindered carbon atom.

Acknowledgments.—This research was supported by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center, and by the Alfred P. Sloan Foundation.

---

(16) M. D. Curtis, unpublished results.

(17) A. G. Brook and N. V. Schwartz, *J. Am. Chem. Soc.*, **82**, 2435 (1960).

CONTRIBUTION FROM CENTRAL RESEARCH DEPARTMENT,
MONSANTO COMPANY, ST. LOUIS, MISSOURI

Scrambling of Oxygen with Halogens on Dimethylgermanium: Labile α,ω-Dihalopolydimethylgermoxanes

BY KURT MOEDRITZER AND JOHN R. VAN WAZER

Received July 20, 1965

Several new families of germanium compounds are described. These are the α,ω-dihalopolydimethylgermoxanes—with the halogen being either chlorine, bromine, or iodine. Proton nuclear magnetic resonance of the methyl groups shows that the chain compounds making up these families rapidly equilibrate (<1 sec.) with respect to exchange of parts. They also equilibrate somewhat more slowly with the trimeric and tetrameric cyclic dimethylgermoxanes—so that the ring molecules coexist with the chain molecules at equilibrium. Exchange of halogen with the methoxyl group on the dimethylgermanium moiety was also studied. In all cases, the minimum number of equilibrium constants needed to define the molecular distributions quantitatively were determined.

In a related study[1] of the exchange of bridging sulfur with halogen atoms on the dimethylgermanium moiety, we demonstrated the existence of α,ω-dihalopolydimethylgermanium sulfides and described the equilibria involving these compounds and the dimethylgermanium sulfide ring trimer. The ring compound was found to

---

(1) K. Moedritzer and J. R. Van Wazer, *J. Am. Chem. Soc.*, **87**, 2360 (1965).

be present in large amounts at equilibrium. On the other hand, no rings were found at equilibrium in α,ω-dihalopolydimethylsiloxanes[2] obtained by scrambling of bridging oxygen with halogen atoms on the dimethylsilicon moiety. It was therefore of interest to investigate the scrambling of bridging oxygen and halogen atoms on the dimethylgermanium moiety and to study the equilibria between the resulting α,ω-dihalopolydimethylgermoxanes and any cyclic structures present.

In addition, a study was also made of the scrambling of halogens with monofunctional oxygen atoms—oxygen atoms in which one of the two valences is blocked by a methyl group, with the O–CH_3 bond not participating in the scrambling reactions.

Experimental

Materials.—Dimethyldichlorogermane, dimethyldibromogermane, and dimethyldiiodogermane were prepared according to a modified version[3] of Rochow's direct synthesis[4] from metallic germanium (purchased from A. D. Mackay, Inc., New York, N. Y.) and the respective methyl halide. Dimethyldimethoxygermane was prepared from dimethyldichlorogermane and methanol in the presence of triethylamine in 63% yield, b.p. 115–117° (lit.[5] 118–118.5°). Dimethylgermanium oxide in its tetrameric form was made by hydrolysis of dimethyldichlorogermane and recrystallization from petroleum ether, m.p. 87–91° (lit.[6] 91–92°). This material was used immediately after recrystallization.

Equilibration.—Equilibrium was achieved by heating the desired proportions of starting materials in sealed 5-mm. o.d. precision nuclear magnetic resonance (n.m.r.) tubes at 120° (for the cases involving dimethylgermanium oxide) or by letting the samples stand at room temperature (for samples with dimethyldimethoxygermane). The time required for reaching equilibrium was estimated on the basis of test runs at several different ratios of starting materials held for various time intervals until the proton n.m.r. spectra did not exhibit any further change. The reported equilibrium values generally correspond to much longer times.

Proton n.m.r. spectra were obtained on a Varian Model A-60 spectrometer as previously described[2] with the measurements being carried out on the neat liquids unless otherwise specified; *i.e.*, in those cases where the exchange rates were so fast as to cause line broadening or coalescence of two or more signals into one peak, carbon tetrachloride was used as solvent. Proton n.m.r. chemical shifts, which vary somewhat with the over-all composition, are reported only for compositions having the over-all composition $R \equiv X/Ge \approx 1$, where X = Cl, Br, or I. For the systems $(CH_3)_2GeX_2$ *vs.* $(CH_3)_2Ge(OCH_3)_2$, these shifts as obtained in the neat liquid samples are given below in terms of p.p.m. from tetramethylsilane (internal standard): $(CH_3)_2GeCl_2$, −1.113; $(CH_3)_2GeCl(OCH_3)$, −0.737 (CH_3Ge), −3.393 (OCH_3); $(CH_3)_2Ge(OCH_3)_2$, −0.362 (CH_3Ge), −3.335 (OCH_3); $(CH_3)_2GeBr_2$, −1.452; $(CH_3)_2GeBr(OCH_3)$, −0.935 (CH_3Ge), −3.425 (OCH_3); $(CH_3)_2Ge(OCH_3)_2$, −0.428 (CH_3Ge), −3.398 (OCH_3); $(CH_3)_2GeI_2$, −1.867; $(CH_3)_2GeI(OCH_3)$, −1.125 (CH_3Ge), −3.408 (OCH_3); $(CH_3)_2Ge(OCH_3)_2$, −0.450 (CH_3Ge), −3.450 (OCH_3). Chemical shifts observed in dilute samples of the composition $R \equiv X/Ge \approx 1$ for the systems $(CH_3)_2GeX_2$ *vs.* $[(CH_3)_2GeO]$ are reported in Tables III, IV, and V. The shifts are reported to the third decimal place because individual resonances lying as close as 0.2 c.p.s. (=0.003 p.p.m.) may be distinguished. Obviously, the absolute values are not known to this precision. Because of solvent shifts and other effects, one or two significant figures should be deleted from these values if they are employed out of the context of this paper.

Table I

Experimental and Calculated Equilibrium Data (in Mole %) for the Substituent Interchange X *vs.* OCH_3 in the Neat-Liquid Systems $(CH_3)_2GeX_2$ *vs.* $(CH_3)_2Ge(OCH_3)_2$ at 35°

X	$R \equiv X/Ge$	$(CH_3)_2GeX_2$	$(CH_3)_2GeX(OCH_3)$	$(CH_3)_2Ge(OCH_3)_2$
Cl	0.436[a]	0.2	44.6	55.2
	(0.450)[b]	(0.4)[c]	(42.9)	(56.8)
	0.819	3.9	77.1	19.0
	(0.849)	(3.0)	(75.9)	(21.1)
	1.156	21.1	76.4	2.5
	(1.186)	(19.0)	(77.5)	(3.4)
	1.433	46.0	53.2	0.8
	(1.452)	(44.1)	(55.2)	(0.8)
	1.707	73.7	26.3	...
	(1.737)	(70.9)	(29.0)	(0.1)
Br	0.523[a]	0.9	51.0	48.1
	(0.528)[b]	(0.6)[c]	(51.1)	(48.3)
	0.796	2.7	75.4	21.9
	(0.809)	(2.5)	(74.5)	(23.0)
	1.066	13.5	81.4	5.2
	(1.083)	(12.3)	(82.0)	(5.7)
	1.384	40.2	59.0	0.8
	(1.395)	(39.3)	(59.7)	(1.0)
	1.678	68.4	31.4	0.3
	(1.682)	(67.9)	(31.9)	(0.2)
I	0.612)[a]	4.0	53.4	42.6
	(0.614)[b]	(3.7)[c]	(53.9)	(42.4)
	0.832	11.3	65.7	23.0
	(0.883)	(8.9)	(65.4)	(25.7)
	1.172	(28.8	64.2	7.0
	(1.218)	(26.0)	(65.2)	(8.8)
	1.401	49.4	49.8	0.7
	(1.487)	(44.3)	(52.4)	(3.3)
	1.685	71.8	(28.2	0.1
	(1.716)	(69.2)	(30.1)	(0.7)

[a] Values are calculated from ingredients. [b] Values in parentheses are calculated from n.m.r. peak areas of the $(CH_3)_2Ge$ region of the spectra. [c] Values in parentheses are calculated from the equilibrium constants given in Table II.

Peak areas were determined by electronic integration and, in cases where there was considerable overlap or when the samples were very dilute, by cutting out and weighing Xerox copies of the spectra.

Results and Discussion

There are two types of reactions to be considered when studying the scrambling of halogens with oxygen on the dimethylgermanium moiety. In the first case, the halogens are scrambled with monofunctional oxygen, *i.e.*, with oxygen having one of its two valences blocked by a methyl group so that the C–O bond of the resulting methoxyl group remains intact during the scrambling. In the second case, scrambling of difunctional oxygen with halogens on the dimethylgermanium moiety leads to families of compounds based on the Ge–O–Ge backbone. In both cases, methyl groups directly attached to germanium do not participate in the exchange processes under the conditions employed.

Halogen *vs.* Methoxyl Exchanges.—The experimental data for the equilibrium described by eq. 1 are

$$(CH_3)_2GeX_2 + (CH_3)_2Ge(OCH_3)_2 \rightleftharpoons 2(CH_3)_2GeX(OCH_3) \quad (1)$$

presented in Table I. These data were used to calcu-

---

(2) K. Moedritzer and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 802 (1964).

(3) K. Moedritzer, *Inorg. Chem.*, submitted for publication.

(4) E. G. Rochow, *J. Am. Chem. Soc.*, **69**, 1729 (1947).

(5) R. West, H. R. Hunt, Jr., and R. O. Whipple, *ibid.*, **76**, 310 (1954).

(6) M. P. Brown and E. G. Rochow, *ibid.*, **82**, 4166 (1960).

TABLE II

EQUILIBRIUM CONSTANTS FOR THE EXCHANGE OF HALOGENS WITH THE METHOXYL GROUP OR WITH BRIDGING OXYGEN ATOMS IN CHAINS

X	K^a		$K_1{}^b$	
Cl	0.011[c]	(0.005)[d]	0.020	(0.006)
Br	0.011[c]	(0.002)	0.043	(0.007)
I	0.054[c]	(0.017)	0.27	(0.11)
Ideal randomness	0.250		0.25	

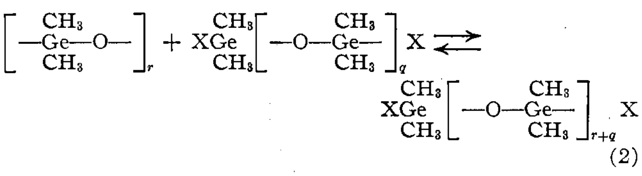
[a] $K = [(CH_3)_2GeX_2][(CH_3)_2Ge(OCH_3)_2]/[(CH_3)_2GeX(OCH_3)]^2$ at 35° for exchange of halogen with methoxyl groups. [b] $K_1 = [(CH_3)_2GeX_2][(CH_3)_2Ge(O_{1/2}-)_2]/[(CH_3)_2GeX(O_{1/2}-)]^2$ at 35° for exchange with the bridging oxygen atoms of polydimethylgermoxanes. [c] Equilibrium is reached in less than 24 hr. at 35°; the data correspond to 10 days at this temperature. [d] The standard deviation is given in parentheses.

late[7] the equilibrium constants presented in the second column of Table II for the interchange of halogens and methoxyl groups on the dimethylgermanium moiety. These equilibrium constants were then used to compute[7] the values given in parentheses in Table I. The agreement of experimental and calculated data in Table I is within the limits of experimental error. The equilibrium constants in Table II show that the exchange of halogen atoms with methoxyl groups on the dimethylgermanium moiety is quite nonrandom so that the proportion of the mixed compound $(CH_3)_2GeX(OCH_3)$ is large at equilibrium. The equilibrium constants for X = Cl and Br are smaller than that for X = I, indicating a more random system for the iodine compounds.

Assuming that the entropy term in the reaction of eq. 1 is due entirely to the entropy of mixing,[8] one can estimate that the enthalpy, ΔH, of formation of 1 mole of $(CH_3)_2GeX(OCH_3)$ from 0.5 mole each of $(CH_3)_2GeX_2$ and $(CH_3)_2Ge(OCH_3)_2$ will be small (<*ca.* 1 kcal.).

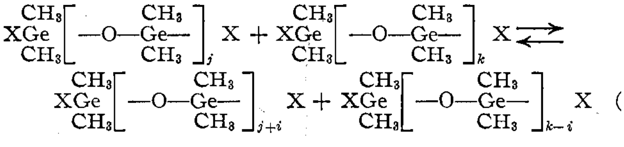
Halogen *vs.* Bridging-Oxygen Exchange.—A more complicated situation is found for the scrambling of difunctional oxygen with halogens on the dimethylgermanium moiety, since there are an infinite number of equilibria derived from the reactions of eq. 2 and 3.

Ring–Chain Reaction



$$\left[-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}-\mathrm{O}-\right]_r + \mathrm{X}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}\left[-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}-\right]_q \mathrm{X} \rightleftarrows \mathrm{X}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}\left[-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}-\right]_{r+q} \mathrm{X} \tag{2}$$

Chain–Chain Interchange



$$\mathrm{X}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}\left[-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}-\right]_j \mathrm{X} + \mathrm{X}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}\left[-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}-\right]_k \mathrm{X} \rightleftarrows \mathrm{X}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}\left[-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}-\right]_{j+i} \mathrm{X} + \mathrm{X}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}\left[-\mathrm{O}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}-\right]_{k-i} \mathrm{X} \tag{3}$$

where $r = 3$ or 4, $q \geq 0$, $j \geq 0$, and $k \geq i \geq 1$. The reaction described by eq. 2 represents a formal route whereby equilibria between rings and chains are achieved, while eq. 3 covers equilibration between various sized chains.

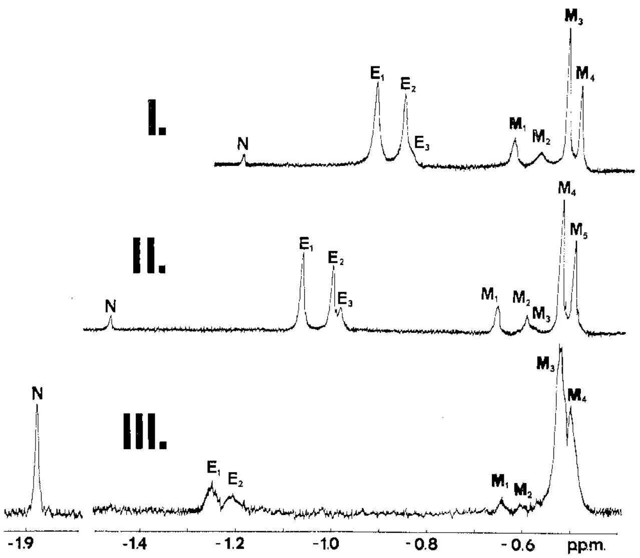
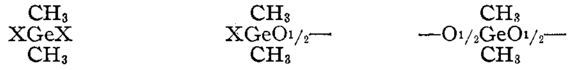


Figure 1.—Proton n.m.r. spectra of equilibrated samples in the system $(CH_3)_2GeX_2$ *vs.* $[(CH_3)_2GeO]$ for compositions defined by $R \equiv X/Ge$. I.: X = Cl, R = 0.472, dilution (volume of CCl_4 per volume of neat sample) 63; II.: X = Br, R = 0.140, dilution 31; III.: X = I, R = 0.443, dilution 127. N = *neso* compound, E = end groups, and M = middle groups.

The many kinds of molecular species present at equilibrium are made up of the three types of structure-building units



$$\mathrm{X}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}\mathrm{X} \qquad \mathrm{X}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}\mathrm{O_{1/2}}- \qquad -\mathrm{O_{1/2}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Ge}}}\mathrm{O_{1/2}}-$$

neso, n end, *e* middle, *m*

and it is advantageous[9] to evaluate the equilibria in terms of such building units or groups of building units.

This approach is particularly useful since the experimental data obtained by n.m.r. are readily interpretable in terms of the building units in overlapping segments of molecules. Typical n.m.r. spectra of equilibrated samples in the systems $(CH_3)_2GeX_2$ *vs.* $[(CH_3)_2GeO]$ are shown in Figure 1. These spectra were obtained on quite dilute solutions, since the exchange rates in the neat-liquid samples were so rapid as to cause broadening and coalescence of fine structure. Dilution with carbon tetrachloride, however, slowed the exchange process down sufficiently to enable the n.m.r. to show up detailed fine structure.

Interpretation and N.m.r. Assignments.—Two relatively sharp signals in the range of −0.527 to −0.507 and −0.500 to −0.483 p.p.m., depending upon the dilution of the sample and the type of halogen X, were seen in all three systems. The shift of the latter of these resonances was identical with that of a sample of pure tetrameric dimethylgermanium oxide. The first peak was identical with the signal seen in solutions of the tetramer which had been stored for several hours at room temperature. In a separate study,[10] it has been

---

[7] L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964).

[8] K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 139 (1964).

[9] D. W. Matula, L. C. D. Groenweghe, and J. R. Van Wazer, *J. Chem. Phys.*, **41**, 3105 (1964).

[10] K. Moedritzer, *J. Organometal. Chem.*, in press.

demonstrated that this newly appearing signal is due to the alleged trimeric dimethylgermanium oxide[6] and that there is a concentration-dependent equilibrium (catalyzed by $(CH_3)_2GeX_2$) between the tetrameric and trimeric ring structures with the interconversion rate in *ca.* 1 M solution being of the magnitude of hours at room temperature in the absence of a catalyst. Therefore these two peaks seen in the equilibrated samples in the system $(CH_3)_2GeX_2$ *vs.* $[(CH_3)_2GeO]$ are assigned to the trimeric and tetrameric ring structures of dimethylgermanium oxide, respectively.

For the system $(CH_3)_2GeCl_2$ *vs.* $(CH_3)_2GeO$, the *neso* resonance (N in Figure 1) was seen at −1.193 p.p.m. in addition to resonances at −0.918 (E_1), −0.860 (E_2), and −0.850 p.p.m. (E_3). From the fact that the latter three resonances form a cluster of signals and from the variation of the relative intensities of these resonances with the composition parameter $R \equiv Cl/Ge$, these signals were assigned to end groups in molecules of differing chain length. The peak, E_1, which was the first one to appear upon decreasing R from its maximum value of 2 was attributed to the **e**_e_ molecule,[11] E_2 to the end groups in the **e**_me_ molecule, and E_3, which is seen as a shoulder on the upfield side of peak E_2, to the end group of the sequence **e**_mm_. The latter resonance comprises all end groups in chains consisting of four or more germanium atoms.

Further upfield from the end-group resonances, there are four additional resonances, M_1 to M_4. These four resonances, which include the signals for the trimer and tetramer dimethylgermanium oxide ring compounds, are attributable to middle groups exhibiting different n.m.r. chemical shifts due to differing shielding effects of building units attached to them. The resonance, M_1, at −0.635 p.p.m. is readily assigned to the middle in the _e_**m**_e_ molecule because of its approximate 1:2 intensity relationship with E_2 throughout the entire series of compositions measured. The signal, M_2, at −0.577 p.p.m. is attributed to the _e_**m**_m_ arrangement, with the shoulder on its upfield side indicating that it probably consists of two or more closely related signals representing the arrangements _e_**m**_me_, _e_**m**_mme_, and _e_**m**_mmm_. As noted above, the next two resonances, M_3 and M_4, at −0.522 and −0.495 p.p.m., respectively, represent the middle groups in the trimeric and tetrameric ring structures of dimethylgermanium oxide. Since a fifth order of environment[11] is seen in these spectra for the end groups, it is reasonable to assume the same order of environment for the middle groups. Thus, we have to conclude that the resonance for the expected sequence of middle groups, _m_**m**_m_, in the longer chain molecules is buried by the relatively large peaks, M_3 and M_4. At this point, however, it is not possible to decide which of the two peaks lies on top of the resonance for _m_**m**_m_ in chains.

Similar assignments can be made in the system $(CH_3)_2GeBr_2$ *vs.* $[(CH_3)_2GeO]$. The *neso* compound, $(CH_3)_2GeBr_2$, is seen at −1.472 p.p.m. (N). The signal E_1 at −1.072 p.p.m. is assigned to the **e**_e_ molecule, E_2 at −1.008 p.p.m. to the **e**_me_ molecule, and E_3 to **e**_mm_. The remaining peaks are attributed to middle groups, with M_1 at −0.660 p.p.m. being assigned (in spite of the observed trend for E_2/M_1 to increase from 1.1 to 2.8 with increasing R) to _e_**m**_e_, M_2 at −0.600 p.p.m. to _e_**m**_me_, and the somewhat poorly resolved signal, M_3 to _e_**m**_mm_. Again, the two resonances at −0.527 and −0.500 p.p.m. (labeled as M_4 and M_5) represent the trimeric and tetrameric rings, respectively, and also cover the resonances for chain structure _m_**m**_m_ which, in accord with the clear fifth order of environment seen for the end groups, should encompass the expected separate resonances for _em_**m**_me_, _em_**m**_mm_, and _mm_**m**_mm_.

In the system $(CH_3)_2GeI_2$ *vs.* $[(CH_3)_2GeO]$, the signal N at −1.883 p.p.m. was assigned to the *neso* compound, E_1 at −1.243 to the **e**_e_ molecule, and E_2 at −1.183 p.p.m. to **e**_m_, with the signals located further upfield being assigned to middle groups. Of these, M_1 at −0.657 p.p.m. was assigned to _e_**m**_e_, M_2 at −0.583 p.p.m. to _e_**m**_m_, and M_3 and M_4 at −0.507 and −0.438 p.p.m. to the trimeric and tetrameric ring structures of dimethylgermanium oxide, respectively. Again, these two signals cover the resonance expected for the _m_**m**_m_ arrangement in the chain molecules.

As also seen in the related study of the scrambling of dimethylgermanium sulfide with dihalodimethylgermanes,[1] Figure 1 shows that the n.m.r. signals for the *neso* compounds in the system $(CH_3)_2GeX_2$ *vs.* $[(CH_3)_2GeO]$ appear increasingly downfield when going from X = Cl to Br and I, thus extending the total range of the spectrum accordingly. In spite of this increased separation of the clusters for end and middle groups in the order Cl < Br < I, there is surprisingly little change in the separation of corresponding individual peaks within the respective clusters of signals. The distances between E_1 and E_2 as well as the distances between M_1 (the most downfield middle group) and the most upfield middle groups in each of the three systems change little when comparing the spectra for the chlorine, bromine, and iodine systems. Consequently there is also no increase in resolution of the fine structure in the spectra when going from Cl to Br to I.

Equilibrium Constants.—The experimental data representing the mole percentage of total germanium in specific building units at equilibrium are given in Tables III, IV, and V. Although the rate of equilibration at room temperature is quite fast, the data have been obtained on samples which have been kept at 120° for 3 to 30 days and then held at room temperature for at least 5 hr. before diluting. Each diluted sample was held overnight before its n.m.r. spectrum was run in

---

[11] This notation is precisely explained in ref. 9, p. 3108. In brief, the building unit observed by n.m.r. is shown in boldface type, with the arrangement of units affecting the chemical shifts (or another property under specific consideration) being shown by the italicized symbols. It should be noted that some of these arrangements (*e.g.*, **e**_e_ or _e_**m**_e_) correspond to building units in complete molecules, whereas others (*e.g.*, _e_**m**_m_) represent units in parts of molecules. An _n_th order of environment for chain molecules viewed from a nonexchangeable part of a building unit (such as a CH_3 directly bonded to the germanium) equals the maximum sequence of building units which affect the given property. Thus, if the **e**_mm_ arrangement is distinguishable from the **e**_me_, one would expect to distinguish _mm_**m**_mm_ from, say _em_**m**_mm_—a sequence of five building units—so that the order of environment would be five.

TABLE III

EXPERIMENTAL AND CALCULATED PERCENTAGE OF TOTAL GERMANIUM IN VARIOUS BUILDING UNITS[11] IN THE SYSTEM $[(CH_3)_2GeO]$ *vs.* $(CH_3)_2GeCl_2$ AT EQUILIBRIUM AT 35°

Assignment		*neso*	e*e*	e*me*	e*mm*	*e*m*e*	*e*m*m*	$(\text{m})_3$	[$(\text{m})_4$ + *m*m*m*]	$(\text{m})_4$	*m*m*m*
Chem. shift, p.p.m.		−1.193	−0.918	−0.860	−0.850	−0.635	−0.577	−0.522	−0.495		
R = Cl/Ge	Dilution[a]										
0.218[b]	127	. . .	12.2	6.3	5.0	2.8	4.6	40.1	29.1		
(0.235)[c]		(1.4)[d]	(13.1)	(4.8)	(2.8)	(2.9)	(2.8)	(45.3)	(27.5)	(26.7)	(0.8)
0.472	127	1.2	26.2	11.6	7.0	6.9	8.2	25.4	13.6		
(0.472)		(3.5)	(27.5)	(8.7)	(4.1)	(4.4)	(4.1)	(31.1)	(16.8)	(15.9)	(0.9)
0.720	63	2.6	38.4	18.1	11.0	10.3	6.8	8.9	4.9		
(0.717)		(5.6)	(42.3)	(12.7)	(5.5)	(6.4)	(5.5)	(14.0)	(8.0)	(6.8)	(1.2)
0.970	23	10.0	58.1	16.4	2.6	7.6	2.1	2.3	0.9		
(0.971)		(10.7)	(59.0)	(13.0	(3.7)	(6.5)	(3.7)	(2.2)	(1.3)	(0.8)	(0.5)
1.217	15	24.8	63.0	7.1	1.0	3.0	. . .	1.2	. . .	. . .	. . .
(1.207)		(24.8)	(63.7)	(6.5)	(0.8)	(3.3)	(0.8)	(0.2)	(0.1)	(0.0)	(0.1)
1.476	3	49.7	47.9	1.7	. . .	0.8	. . .	. . .	. . .		
(1.490)		(48.8)	(47.3)	(1.8)	(0.1)	(0.9)	(0.1)	(0.0)	(0.0)	(0.0)	(0.0)
1.736	3	74.7	24.4	0.5	. . .	0.4	. . .	. . .	. . .		
(1.743)		(74.5)	(25.0)	(0.3)	(0.0)	(0.2)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)

[a] Volumes of CCl_4 per volume of sample. These values correspond to the following concentrations in gram-atoms of Ge/l. (reading from the top of the table): 0.094, 0.088, 0.16, 0.41, 0.58, 2.21, 2.09. [b] From the ingredients. [c] Values in parentheses are calculated from the n.m.r. data. [d] Values in parentheses are calculated from $K_1 = 0.020$, $K_3° = 0.87$, and $K_4° = 1.40$, using the *R* values as determined from the n.m.r. data.

TABLE IV

EXPERIMENTAL AND CALCULATED PERCENTAGE OF TOTAL GERMANIUM IN VARIOUS BUILDING UNITS[11] IN THE SYSTEM $[(CH_3)_2GeO]$ *vs.* $(CH_3)_2GeBr_2$ AT EQUILIBRIUM AT 35°

Assignment		*neso*	e*e*	e*me*	e*mm*	*e*m*e*	em*me*	em*mm*	$(\text{m})_3$	[$(\text{m})_4$ + *m*m*m*]	$(\text{m})_4$	*m*m*m*
Chem. shift, p.p.m.		−1.472	−1.072	−1.008	−0.992	−0.660	−0.600	−0.587	−0.527	−0.500		
R = Br/Ge	Dilution[a]											
0.230[b]	7	. . .	5.7	5.3	12.1	4.9	2.1	7.5	14.5	48.0		
(0.231)[c]		(0.7)[d]	(5.9)	(4.3)	(11.5)	(2.2)	(3.1)	(8.4)	(22.4)	(41.6)	(26.2)	(15.4)
0.410	7	1.3	12.9	10.3	15.4	7.5	5.7	5.8	10.1	31.1		
(0.412)		(1.9)	(13.9)	(8.7)	(14.5)	(4.4)	(5.5)	(9.1)	(14.9)	(27.1)	(15.0)	(12.1)
0.668	7	3.8	28.7	16.9	14.0	11.0	7.7	2.9	5.1	9.9		
(0.672)		(5.3)	(29.6)	(14.1)	(12.8)	(7.1)	(6.7)	(6.1)	(7.0)	(11.2)	(5.4)	(5.8)
0.914	3	10.1	43.6	15.7	11.9	10.4	5.8	1.0	1.0	0.3		
(0.914)		(11.4)	(45.3)	(15.4)	(8.0)	(7.7)	(5.3)	(2.7)	(1.4)	(2.8)	(0.8)	(2.1)
1.200	7	28.6	51.7	12.2	1.2	5.5	0.8	. . .	. . .	. . .		
(1.223)		(28.9)	(54.1)	(8.7)	(1.7)	(4.4)	(1.4)	(0.3)	(0.3)	(0.2)	(0.1)	(0.2)
1.450	3	47.4	45.0	5.3	0.4	1.9	. . .	. . .	. . .	. . .		
(1.455)		(47.8)	(45.8)	(3.8)	(0.3)	(1.9)	(0.3)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
1.735	3	73.9	23.8	1.7	. . .	0.6	. . .	. . .	. . .	. . .		
(1.733)		(73.7)	(25.2)	(0.7)	(0.0)	(0.4)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)

[a] Volumes of CCl_4 per volume of sample. These values correspond to the following concentrations in gram-atoms of Ge/l. (reading from the top of the table): 1.50, 1.43, 1.34, 2.53, 1.19, 2.25, 2.12. [b] From the ingredients. [c] Values in parentheses are calculated from the n.m.r. data. [d] Values in parentheses are calculated from $K_1 = 0.043$, $K_3° = 0.87$, and $K_4° = 1.40$, using the *R* values as determined from the n.m.r. data.

order to achieve the ring–chain equilibrium corresponding to the exact dilution as well as the resulting chain–chain re-equilibration.

A cursory inspection of Tables III–V shows that most of the middle groups at low values of *R* and high dilutions (factors favoring ring formation) are to be found in the two types of ring structures and posssibly also in the *m*m*m* sequence in the chain structures. The total amount of middle groups in rings, however, may be calculated[9] by arbitrarily deducting various amounts of middle groups tentatively ascribed to rings from the total number of middles and then fitting[9] the resonances e*e* and e*me* (using a computer program) on the basis of random sorting of the remaining chain-building end and middle units into molecules (assuming a reorganizational heat order[9] of unity). This procedure yielded a preliminary estimate for the distribution of total middle groups into rings and chains as a function of the over-all composition and dilution.

These preliminarily estimated data were then used to calculate a set of equilibrium constants. One constant, K_1, relates the amounts of *neso*, end, and middle groups in chains

$$K_1 = [\text{neso}][\text{chain middles}]/[\text{ends}]^2 \quad (4)$$

TABLE V

EXPERIMENTAL AND CALCULATED PERCENTAGE OF TOTAL GERMANIUM IN VARIOUS BUILDING UNITS[11] IN THE SYSTEM $[(CH_3)_2GeO]$ *vs.* $(CH_3)_2GeI_2$ AT EQUILIBRIUM AT 35°

Assignment		*neso*	ee	e*m*	*e*m*e*	e*mm*	(m)$_3$	[(m)$_4$ + *m*m*m*]	(m)$_4$	*m*m*m*
Chem. shift, p.p.m.		−1.883	−1.243	−1.183	−0.657	−0.583	−0.507	−0.483		
R = I/Ge	Dilution[a]									
0.312[b]	127	5.0	6.1	3.1	2.5	...	51.0	32.3		
(0.192)[c]		(6.1)[d]	(4.3)	(2.7)	(0.8)	(1.0)	(52.4)	(32.6)	(32.3)	(0.3)
0.443	63	11.4	9.6	5.1	0.9	0.8	45.4	26.8		
(0.375)		(11.0)	(8.8)	(6.7)	(1.9)	(2.9)	(39.9)	(28.8)	(27.7)	(1.1)
0.697	63	20.0	12.6	7.3	3.3	2.5	35.5	18.8		
(0.599)		(18.8)	(13.6)	(8.7)	(2.7)	(3.4)	(31.8)	(21.1)	(20.0)	(1.1)
0.956	63	31.7	18.7	11.5	5.6	2.2	19.4	10.8		
(0.936)		(32.3)	(19.6)	(9.5)	(3.2)	(3.1)	(20.7)	(11.6)	(10.9)	(0.8)
1.202	63	47.1	19.6	11.1	4.9	1.9	11.7	3.6		
(1.249)		(47.1)	(22.8)	(8.1)	(3.0)	(2.1)	(11.6)	(5.3)	(4.9)	(0.4)
1.451	63	64.8	20.6	6.3	3.5	...	2.6	2.3		
(1.565)		(64.8)	(21.9)	(4.9)	(2.0)	(0.9)	(4.2)	(1.3)	(1.2)	(0.1)
1.736	63	73.8	20.7	3.7	1.3	0.6	...	...		
(1.720)		(75.4)	(18.3)	(2.8)	(1.2)	(0.4)	(1.6)	(0.4)	(0.3)	(0.0)

[a] Volumes of CCl_4 per volume of sample. These values correspond to the following concentrations in gram-atoms of Ge/l. (reading from the top of the table): 0.095, 0.17, 0.16, 0.15, 0.14, 0.13, 0.12. [b] From the ingredients. [c] Values in parentheses are calculated from the n.m.r. data. [d] Values in parentheses are calculated from $K_1 = 0.27$, $K_3° = 0.087$, and $K_4° = 1.40$, using the R values as determined from the n.m.r. data.

and two constants, $K_r°$, relate the amount of middle groups in chains[9] to those in the rings made up of three or four middle groups. This constant has the form

$$K_r° = \frac{[\text{middles in the } r\text{-sized rings}]}{(1 + D)[V_2 + (R/2)(V_0 - V_2)]} \left[\frac{[\text{ends}] + 2[\text{chain middles}]}{2[\text{chain middles}]}\right]^r \qquad (5)$$

where r is the size of the rings, which, in this case, is 3 or 4, D is the dilution expressed in volumes of diluent per volume of neat sample, V_0 is the volume of the *neso* compound in l./mole, and V_2 is the volume of the middle group (estimated from ring compounds) in l./mole, using no dilution. Furthermore, there is a ring–ring constant, $K°°_{4,3}$, relating the amounts of trimeric and tetrameric ring structures. This constant has the form

$$K°°_{4,3} = \{[(CH_3)_2GeO]_4\}^3/\{[(CH_3)_2GeO]_3\}^4 \qquad (6)$$

with the concentration of the two rings expressed in moles/l. The constant $K°°_{4,3}$ can be calculated from the ring–chain constants and, therefore, is not required when calculating the theoretical data listed in parentheses in Tables III, IV, and V. The final set of equilibrium constants was obtained by means of a computer program which calculated the statistical best fit to the observed n.m.r. peaks corresponding to the ee, *e*m*e*, and (m)$_3$ structures. This calculation gave the areas of all of the n.m.r. peaks in the spectra for the various R values as well as the set of equilibrium constants corresponding to the best fit.

Since the ring–ring constant must be the same for all systems, the value of $K°°_{4,3} = 4.8$ l./mole of $(CH_3)_2Ge$ moieties or 6.0 l./mole of molecules, found[10] for equilibrated samples of the pure dimethylgermanium oxide, was assumed in the calculation of the values of K_1, $K_3°$, and $K_4°$ for the three systems studied here. Regardless of the kind of chain-terminating group employed (Cl, Br, and I in this work), the ring–chain constants $K_3°$ and $K_4°$ must each have a fixed value, although the values of the chain–chain constants K_1 may differ greatly depending on the chain termination. [This assumes that solvent interactions (if any) are not changed by replacing one chain-terminating group by another.] When treated independently, the chlorine and iodine systems gave values of $K_3°$ of 0.21, 3.37, and 0.72, respectively. However, the dilution studies[10] on equilibrated samples of pure dimethylgermanium oxide showed that $K_4°$ should surely not be less than 1.3 and preferably is 1.4 or greater. The best fit to the data of this paper must correspond to the lower end of this allowed range for $K_4°$. Therefore, the value of $K_4° = 1.4$ and the corresponding value of $K_3° = 0.87$ were employed in calculating the theoretical n.m.r. peak areas given in Tables III, IV, and V. The best-fit values obtained from varying the chain–chain constants in the neighborhood of the ones obtained by treating the systems independently differed by no more than one standard deviation from the values for the situation where $K_4°$ and $K_3°$ were forced to equal 1.4 and 0.87, respectively. These latter values are presented in the third column of Table II. Each system is completely described by the three constants, K_1, $K_3°$, and $K_4°$. Obviously, the correct dilution was employed for each separate experimental run in using eq. 5 and 6.

The calculated data show that the best fit is obtained when it is assumed that the expected (but not observed) signals for the *m*m*m* arrangement in chain molecules are lumped together with the signals for the tetrameric ring compound. Test calculations based on the assumption that the *m*m*m* resonance is associated with the resonance of the trimeric ring compound resulted in

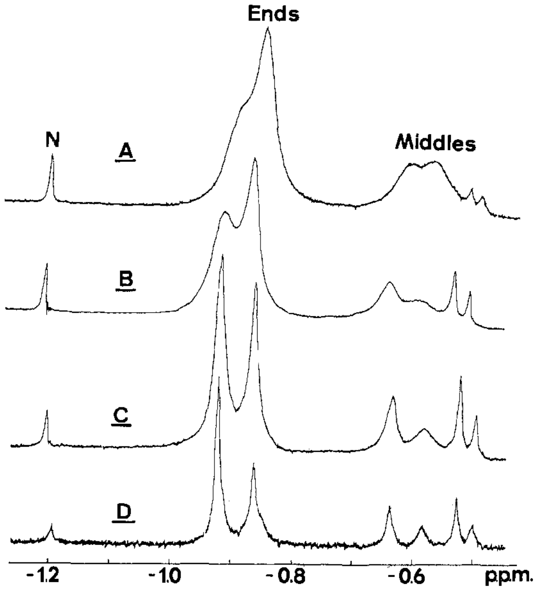


Figure 2.—Proton n.m.r. spectra of an equilibrated sample in the system $(CH_3)_2GeCl_2$ *vs.* $[(CH_3)_2GeO]$ of the composition R = 0.72 at various dilutions: A, neat liquid; B, diluted with three parts; C, 15 parts; D, 63 parts of carbon tetrachloride (v./v.); N = *neso* compound.

equilibrium constants which showed a systematic error when going from low to high R values.

Inspection of the chain–chain equilibrium constants listed in Table II indicates that the constant K_1 increases from X = Cl to Br and I. When compared with the constants K for the scrambling of methoxyl groups with halogens, the corresponding constants K_1 are larger—indicating more randomness in the scrambling of halogens with bridging oxygen than with methoxyl groups.

Equilibration Rates.—Proton n.m.r. spectra obtained from equilibrated samples in the neat-liquid form for X = Cl and Br show only one broad peak each for the end and middle groups in chain molecules, with the portion representing the two kinds of ring species being fairly well resolved and sometimes sitting as a double hump on top of the broad middle peak. For X = I, neat-liquid samples of certain compositions give only a single broad peak. However, upon dilution of these samples with carbon tetrachloride, fine structure becomes visible in this system also. This type of behavior is typical either for viscous solutions or for rapidly exchanging species at equilibrium. In the latter case, the exchange rate diminishes upon dilution due to increased separation of the exchanging molecules (Figure 2). We have excluded viscosity broadening as a significant factor because (a) the neat liquids corresponding to all but the lowest R values were quite limpid and (b) the broadening persisted to rather high dilutions.

The average lifetimes[8,12,13] of such exchanging species were estimated by applying the equations for line broadening or for saddle-shaped n.m.r. signals. A plot of the average lifetime, τ, as obtained separately from the shape of the end-group resonances and the chain middle-group resonances for all three systems is shown in Figure 3. It is seen that the exchange rates measured for the end groups are identical with those for the middle groups, and there is also good agreement between the data obtained from line broadening and those from saddle-shaped resonances. In the neat liquids, the average lifetimes of the chain molecules with respect to interchange of parts with each other is of the order of magnitude of <0.1 sec. Ring–ring and ring–chain equilibration is much slower as evidenced by the fact that, except for the iodine system at the higher concentrations, the two n.m.r. peaks for the ring molecules appear to consistently exhibit the natural line width. This may also be true for the iodine system where the broad coalesced n.m.r. peak of the chain molecules may merely obscure sharp resonances of the ring molecules.

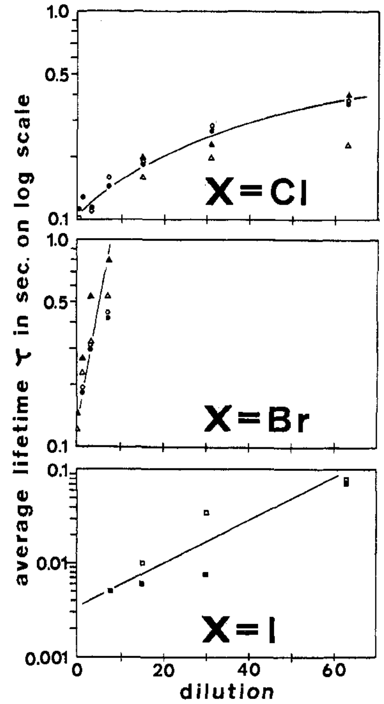


Figure 3.—Average lifetimes, τ, at 35° for equilibrated samples in the system $(CH_3)_2GeX_2$ *vs.* $[(CH_3)_2GeO]$ at various dilutions (volumes of CCl_4 per volume of neat liquid sample) for the composition ratios defined by $R \equiv X/Ge$. For X = Cl, R = 0.720; for X = Br, R = 0.668; and for X = I, R = 0.697. The data marked ● and ○ were obtained from saddle-shaped spectra of the end- or middle-group resonances, respectively. The data marked ▲ and △ were obtained from line broadening of two separated end-group resonances or middle-group resonances, respectively. The data ■ and □ for X = I were obtained from saddle-shaped spectra or from line broadening of the two signals representing total end and total middle groups, respectively.

Conclusions.—The analogous α,ω-dihalopolydimethylsiloxanes[2] equilibrate very slowly (with half-lives of *ca.* 3 hr. at 200° in the presence of $AlCl_3$ as catalyst) to form essentially all chain molecules, the lower members of which were readily isolable by distillation. In contrast, the α,ω-dihalopolydimethylgermoxanes exhibit a rapid rate of exchange of molecu-

---

(12) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **4**, 893 (1965).

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, pp. 220–225.

lar parts at room temperature as evidenced by the line broadening of the n.m.r. signals, with average lifetimes in the neighborhood of 0.1 sec. at 35°. These systems, therefore, are quite labile, thus rendering it a hopeless task to isolate even the shorter chain molecules by ordinary separation methods under the usual conditions. Perhaps low-temperature separation methods, such as chromatography, with Dry Ice cooling, might be applied successfully. However, any isolated species when brought to room temperature undoubtedly will rearrange rapidly to the equilibrium distribution of molecules as determined by the over-all composition of the species.

Superficial inspection of the experimental data obtained on the chloro-terminated dimethylgermanium and dimethylsilicon compounds exhibiting either oxygen or sulfur bridges would indicate that the siloxanes[2] have a much lesser tendency to form ring structures than either the silthians[14] or the equivalent oxygen- (studied here) or sulfur-bridged[1] compounds of germanium. This, however, is not true since the ring–chain equilibrium constants for the oxygen-bridged molecular systems based on silicon[15] have the same order of magnitude as the constants obtained in this work for the equivalent germanium system. The difference lies in the fact that rapid exchange between the germanium compounds forced us to study dilute systems, where the ring–chain equilibria are shifted toward the rings. The work on the silicon systems was carried out on the neat liquids.

We conclude from the study of the siloxanes and silthians and their related germanium compounds that the major difference in behavior between the silicon and germanium systems is with respect to the rate of equilibration, which is about a million times slower for silicon than for germanium. In both cases, the sulfur-bridged structures reorganize more slowly than the oxygen ones and, at equilibrium at the same dilution, exhibit a larger proportion of rings as compared to chains.

Acknowledgment.—We wish to thank Ray E. Miller for running some of the n.m.r. spectra and L. C. D. Groenweghe for assistance with the computer programs.

[14] K. Moedritzer, J. R. Van Wazer, C. H. Dungan, *J. Chem. Phys.*, **42**, 2478 (1965).

[15] The data of J. B. Carmichael and R. Winger, *J. Polymer Sci.*, **3A**, 971 (1965), corresponds to the following set of ring-chain constants of the form of eq. 5: $K_3° = 0.018$, $K_4° = 0.75$, $K_5° = 0.69$, $K_6° = 0.29$, $K_7° = 0.10$, and $K_8° = 0.04$. These constants are consistent with the data of ref. 2.

Contribution from the RCA Laboratories,
Princeton, New Jersey

The Crystal Structure of Scandium Sesquitelluride

By J. G. WHITE and J. P. DISMUKES

Received June 3, 1965

Scandium sesquitelluride has been prepared in single crystal form by a vapor transport technique. The crystals are rhombohedral with $a_h = 4.109 \pm 0.004$ Å., $c_h = 40.59 \pm 0.05$ Å., referred to the triply primitive hexagonal unit cell. The space group is $R\bar{3}m$ and the Te atoms are at ±0, 0, ·1247 and ±0, 0, ·2918 forming a 12-layer stacking sequence containing regions of both cubic and hexagonal close packing. All the Sc atoms are in octahedral sites, 2Sc in 0, 0, 0 and 0, 0, $^1/_2$, and $^2/_3$ Sc in ±0, 0, ·4150. The structure may be regarded as being made up of alternate regions of NaCl and NiAs structure types, with the metal sites common to both regions being only one-third occupied. A nonstoichiometric scandium telluride of approximate composition $Sc_{2.3}Te_3$ has been made which also has the Sc_2Te_3 structure, presumably with a higher scandium content in the partially occupied sites.

Introduction

Men'kov, *et al.*,[1] have reported X-ray powder diffraction data for Sc_2Te_3. They describe the structure as being similar to that of γ'-Al_2O_3,[2] which is a close-packed cubic structure for the anions with the cations being distributed statistically over all the possible octahedral and tetrahedral sites in the ratio of 70% in octahedral and 30% in tetrahedral sites. During an investigation of the occurrence of the Sc_2S_3 structure[3] among the higher atomic number rare earth (including Sc and Y) chalcogenides,[4] single crystals of Sc_2Te_3 were prepared, giving the opportunity of definitive structural investigation. Our X-ray powder pattern is quite different from that published by Men'kov, *et al.*, and it is possible that these authors had a different crystalline modification, although our experimental conditions were quite similar to theirs.

Experimental

Preparation.—Polycrystalline Sc_2Te_3 was prepared by direct reaction of the elements at 1000°, using a small amount of I_2 as a mineralizer. Single crystal plates of Sc_2Te_3 were then chemically transported with I_2 from a hot zone of 1050° to a cold zone of 950°.[4] About a 160-mg. sample was decomposed with nitric acid, and scandium was titrated by EDTA, as in the determina-

---

[1] A. A. Men'kov, L. N. Komissarova, Y. P. Simanov, and V. I. Spitsyn, *Dokl. Akad. Nauk SSSR*, **128**, 92 (1959).

[2] E. J. W. Verwey, *Z. Krist.*, **91**, 317 (1935).

[3] J. P. Dismukes and J. G. White, *Inorg. Chem.*, **3**, 1220 (1964).

[4] J. P. Dismukes and J. G. White, *ibid.*, **4**, 970 (1965).