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.

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

By WOLFGANG EISENHUTH[1] and JOHN R. VAN WAZER

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

$$\left[\begin{array}{cc} Cl & CH_3 \\ -Ge-N- \\ Cl \end{array} \right]_3$$
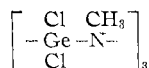
is the major species; whereas, when the amount of methylamine combined with the germanium tetrachloride is progressively decreased to zero, the last nitrogen-containing molecule to vanish in the equilibrated mixtures is $Cl_3GeN(CH_3)GeCl_3$. For all mole ratios of amine to germanium tetrachloride from 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

(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).
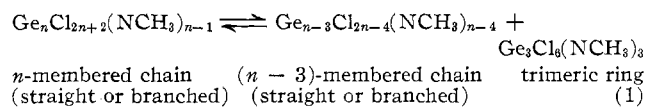
TABLE I

EQUILIBRIA AT 150° IN MIXTURES MADE FROM GERMANIUM
TETRACHLORIDE AND TRIMERIC
TRI-N-METHYLHEXACHLOROCYCLOTRIGERMAZANE

R = Cl/Ge	Nmr peak no.							All other combinations
	1	2	3[a]	4	5	6	7	
			(m—b)₃ or (m—m)₂	e—m except e—me				
	e—e	e—me	(m—m)₂	e—me	(m—m)₅	(m—m)₄	(m—m)₅	
3.46	45.1	3.5	1.3	6.3	42.9	0.9	...	...
	(43.4)[b]	(9.6)	(1.6)	(1.3)	(41.5)	(0.7)	(0.3)	(0.7)
	[42.9][c]	[9.3]	[6.6]	[1.2]	[38.2]	[0.7]	[0.3]	[0.8]
3.27	32.9	3.9	(1.5)	5.6	45.0	0.9	...	...
	(32.1)	(8.4)	(2.4)	(1.4)	(51.7)	(1.1)	(0.6)	(0.8)
	[32.1]	[8.4]	[6.9]	[1.3]	[48.6]	[1.0]	[0.5]	[0.9]
3.02	21.1	2.7	1.3	4.3	68.7	1.9	...	...
	(21.3)	(6.5)	(3.5)	(1.3)	(61.8)	(1.6)	(1.0)	(0.8)
	[21.6]	[6.8]	[7.1]	[1.3]	[59.6]	[1.5]	[0.9]	[1.1]
2.79	15.9	1.9	1.5	2.6	75.9	2.2	...	...
	(14.3)	(4.8)	(4.4)	(1.1)	(68.4)	(1.9)	(1.4)	(0.8)
	[14.8]	[5.2]	[7.1]	[1.1]	[67.2]	[1.9]	[1.3]	[1.1]
2.55	8.9	2.0	1.8	2.2	82.3	2.7	0.0	...
	(8.7)	(3.1)	(5.3)	(0.8)	(73.8)	(2.3)	(1.8)	(0.6)
	[9.2]	[3.6]	[7.1]	[0.8]	[73.7]	[2.3]	[1.8]	[1.1]
2.30	3.9	1.4	2.4	1.2	86.6	4.1	0.5	...
	(4.1)	(1.4)	(6.3)	(0.4)	(78.4)	(2.7)	(2.3)	(0.4)
	[4.5]	[1.9]	[7.0]	[0.5]	[79.7]	[2.7]	[2.3]	[1.0]
2.07	1.3	0.8	6.1	0.0	86.5	3.8	1.6	...
	(0.8)	(0.2)	(7.1)	(0.1)	(81.9)	(3.0)	(2.8)	(0.2)
	[0.9]	[0.4]	[6.9]	[0.1]	[84.5]	[3.0]	[2.8]	[0.8]
2.02	0.9	0.6	7.8	...	84.3	3.6	2.7	...
	(0.3)	(0.1)	(7.3)	(0.0)	(82.5)	(3.1)	(2.9)	(0.2)
	[0.3]	[0.1]	[6.9]	[0.0]	[85.4]	[3.1]	[2.9]	[0.8]
2.00	0.5	0.8	8.9	...	83.4	3.1	3.4	...
	(0.2)	(0.0)	(7.4)	(0.0)	(82.8)	(3.1)	(2.9)	(0.2)
	[0.0]	[0.0]	[6.8]	[0.0]	[85.8]	[3.2]	[3.0]	[0.8]

[a] The calculations in parentheses assume $(m—b)_3$; while those in brackets correspond to $(m—m)_2$ for peak 3. [b] Calculated from $K_1 = 0.14$, $K_2 = 0.10$, and $K_3 = 0.14$, with $K^0_3 = 53.3$, $K^0_4 = 6.2$, and $K^0_5 = 20$. [c] Calculated from $K_1 = 0.14$, $K_2 = 0.01$, and $K_3 = 0.01$, with $K^0_2 = 1.5$, $K^0_3 = 53.3$, $K^0_4 = 6.2$, and $K^0_5 = 20$.

methylamine were equilibrated with a benzene solution of germanium tetrachloride.

As can be seen in Table I, the combined areas of the resonances corresponding to the trimeric ring and dichain compound always represented more than 80% of the total peak area at equilibrium. This means that the ring-chain equilibrium for formation of the trimeric ring from any straight- or branched-chain molecule (not exhibiting ring closures) is shifted strongly toward the

$$\text{Ge}_n\text{Cl}_{2n+2}(\text{NCH}_3)_{n-1} \rightleftharpoons \text{Ge}_{n-3}\text{Cl}_{2n-4}(\text{NCH}_3)_{n-4} + \text{Ge}_3\text{Cl}_6(\text{NCH}_3)_3$$

| n-membered chain (straight or branched) | (n − 3)-membered chain (straight or branched) | trimeric ring (1) |

cyclic compound. The equilibria represented by eq 1 may be handled by the following expression[4] (with $r = 3$) for the equilibrium constant

$$K^0_r = m^0_r[e + 2m_c + 3b_c + 4q_c]^r / rV[2m_c]^r \quad (2)$$

where r is the number of germanium atoms in this cyclic structure; V is the molar volume of the mixture of ger-

(4) The underlying mathematics have been presented by D. W. Matula, L. C. D. Groenweghe, and J. R Van Wazer, *J. Chem. Phys.*, **41**, 3105 (1964); also see D. W. Matula and J. R. Van Wazer, *ibid.*, **46**, 3123 (1967); and for an example of the application of these mathematics to a related system, see J. R. Van Wazer and K. Moedritzer, *ibid.*, **41**, 3111 (1964). In the study reported here, a reorganization heat order of 2 is assumed and the proportions of the variously substituted *r*-sized rings is estimated on the basis of what may be called equal probability of pairs of joins around a given central moiety. Thus for the functionalities, *ν*, of 2, 3, and 4, the respective weightings for inclusion in rings are 1, 3, and 6. Fused rings (*i.e.*, a given Q atom participating in more than one ring structure) are not considered because of problems in the logic of the mathematics.

manium compounds under study; the symbols e, m, b, and q stand for the mole fractions of germanium in the following monogermano building units; and the subscripts r and c for these symbols indicate whether the respective units are in rings or chains.

b = three-way branch group q = four-way branch group
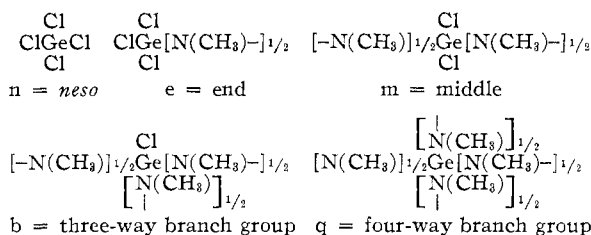
Except for the first and fifth resonances, the nmr peaks were always quite small so that the assignments of peaks 2, 3, 4, 6, and 7 were difficult and remain tentative. However, preliminary inspection of the variation of the peak areas with concentration indicates that a probable assignment for resonance 2 is the two methylamine bridges in the trichain molecule, *i.e.*, e—me. Likewise, peaks 3, 6, and 7 vary with concentration in such a way that they probably correspond to one of the following N-methyl linkages.[5] m—m, m—b, or, perhaps, m—q, with a good probability that these arrangements may be in cyclic structures. The final assignments of peaks 2, 3, 4, 6, and 7 were made by testing different values of the pertinent equilibrium constants chosen to give a good fit[6] to peaks 1 and 5 and simultaneously to find assignments which would be reasonable for the other peaks.

From the calculations, it is quite certain that the ring-chain constant, K^0_3, for eq 2 is equal to 53 mol/l. and that the chain-chain constant dominating this part of the composition range, $K_1 = nm/e^2$, has a value around 0.14. If we assume that the other chain-chain constants $K_2 = eb/m_2$ and $K_3 = mq/b^2$ are small ($\leq \sim 0.1$), resonances 6 and 7 have been rather arbitrarily assigned to simple cyclic molecules based on four and five germanium atoms, respectively, alternating with an equal number of nitrogen atoms. The respective ring-chain constants of the form of eq 2 are $K^0_4 = 6$ and $K^0_5 = 20$ mol/l., respectively. Resonance 4 has been assigned to all of the e—m arrangements in chain molecules except for e—me which corresponds to peak 2. Resonance 3 may be due to the ring based on two germanium atoms, corresponding to an equilibrium constant for $r = 2$ in eq 2 of 1.5 mol/l. On the other hand, if K_3 is about as large as K_1, resonance 3 may be due to the m—b linkage in substituted trimeric rings.[4] The calculated values of the various peak areas on the basis of the above assignments is given in parentheses in Table I and the corresponding composition diagram is given in Figure 1.

(5) The notation used here, where, for example, e—mm stands for the resonance of the italic hydrogens in the Cl₃Ge-N(CH₃)-Ge(Cl₂)-N(CH₃)-Ge(Cl₂)- group, is a slight modification of that previously described by J. R. Van Wazer, K. Moedritzer, and M. D. Rausch, *J. Chem. Phys.*, **42**, 3302 (1965). The symbol (m—m)ₙ refers to the [GeCl₂(NCH₃)]ₙ cyclic compound.

(6) These calculations were carried out with a computer program developed by Dr. L. C. D. Groenweghe according to the mathematical logic presented in ref 4.
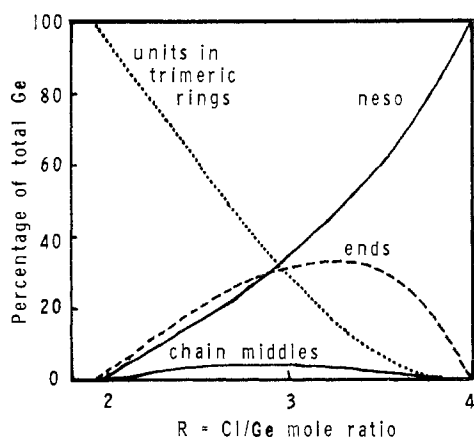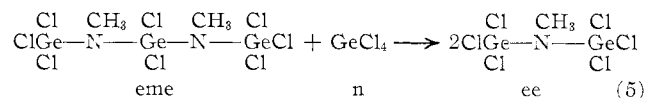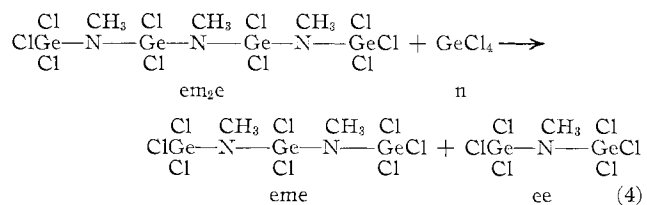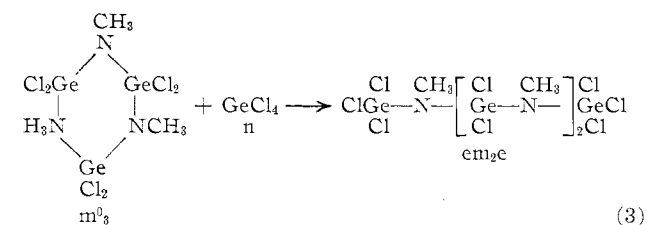
Figure 1.—Partial completed equilibrium diagram for the N-methylated perchlorogermazanes at 150° as calculated from the observed equilibrium constants: $K_1 = 0.14$ and $K^0_3 = 53$ mol/l. on a molecular basis, with K_2 set equal to 0.1. Neso represents $GeCl_4$; ends, $Cl_3Ge[N(CH_3)-]_{1/2}$; chain middles, $Cl_2Ge\{[N(CH_3)-]_{1/2}\}_2$; and units in trimeric rings, $Cl_iGe-\{[N(CH_3)-]_{1/2}\}_{4-i}$ with $i \leq 2$.

Rate Studies

When various proportions of $GeCl_4$ with $[Ge(Cl_2)N-(CH_3)]_3$ in benzene were heated at either 56 or 100°, it was found that the first resonance to appear in addition to that, $(m—m)_3$, for the trimeric ring was the e—e peak, followed shortly by the e—mm (peak 4) and then by the e—me peak. Further, at both temperatures, the e—mm resonance went through a pronounced maximum. These findings show that the major rate processes are

$$Cl_2Ge \overset{\overset{CH_3}{\underset{|}{N}}}{\underset{\underset{Ge}{\underset{|}{NCH_3}}}{\underset{H_3N}{\diagdown}}} GeCl_2 + GeCl_4 \longrightarrow ClGe-N-\begin{bmatrix} Cl \\ | \\ Ge-N- \\ | \\ Cl \end{bmatrix}_2 GeCl \quad (3)$$

$$\begin{matrix} Cl & CH_3 & Cl & CH_3 & Cl & CH_3 & Cl \\ ClGe-N & -Ge-N & -Ge-N & -GeCl \\ Cl & Cl & Cl & Cl \\ & & em_2e & & & & n \end{matrix} + GeCl_4 \longrightarrow$$

$$\begin{matrix} Cl & CH_3 & Cl & CH_3 & Cl & & Cl & CH_3 & Cl \\ ClGe-N & -Ge-N & -GeCl & + & ClGe-N & -GeCl \\ Cl & Cl & Cl & & Cl & Cl \\ & eme & & & & ee & (4) \end{matrix}$$

$$\begin{matrix} Cl & CH_3 & Cl & CH_3 & Cl & & Cl & CH_3 & Cl \\ ClGe-N & -Ge-N & -GeCl & + GeCl_4 \longrightarrow & 2ClGe-N & -GeCl \\ Cl & Cl & Cl & & Cl & Cl \\ & eme & & n & & ee & (5) \end{matrix}$$

The fact that the e—e resonance is the first to appear indicates that reactions 4 and 5 are somewhat faster than reaction 3. The e—m peak is obviously attributable to the tetrachain molecule, em₂e. Presumably the m—m resonance for this molecule is buried under the large peak corresponding to the trimeric ring. The e—me resonance, of course, represents the trichain molecule, eme.

The remaining resonances (peaks 3, 6, and 7) do not appear until rather late, give no evidence of maximizing with time, and never constitute more than a small frac-

tion of the total peak area. This indicates that the rate processes involved in forming rings other than the simple trimer are much slower than the reactions of eq 3–5.

From plots of the decrease of the $(m—m)_3$ resonance of the trimeric ring and the increase of the e—e resonance of the dimeric chain, an estimate was obtained for the activation energy and half-life of the over-all rate process represented by reactions 3–5. At 56°, the half-life estimated from the decrease in the trimeric-ring resonance is about 69 min; whereas, from the increase in the dichain resonance, a value of *ca.* 77 min is obtained. The activation energies separately estimated from the quarter-lives, half-lives, and three-quarter-lives at 56 and 100° were found to have an average value of 17 kcal/mol with a standard deviation of 2 kcal/mol. The values of the partial lives and of the activation energy were not seen to vary in a systematic manner with the ratio of the reagents (*i.e.*, the *R* value of Table I).

Although the rates of eq 4 and 5 are more rapid than that of eq 3, it appears from the kinetic curves that the constants probably do not vary by more than a factor of 10 for these three processes and that the formation of rings other than the starting trimer is about 100 times slower. The order-of-magnitude estimate for second-order rate constants corresponding to eq 3–5 is 10^5 mol/l. at 25°. No attempt was made to ascertain the effect of catalysts, including whatever trace amounts of HCl might be present in the reaction mixtures. However, the observed nonsystematic variation in half-life with changes in the starting composition was indirect evidence for only a small amount of catalysis. This variation corresponded to a mean deviation of *ca.* 20%.

Reaction of $GeCl_4$ with CH_3NH_2.—When 3 mol of methylamine per mol of Ge is bubbled through an ether solution of germanium tetrachloride at 0°, the precipitate is found to consist not only of the amine hydrochloride but also to contain appreciable amounts of germanium. However, upon refluxing the mixture for 1 day, it is seen that the germanium almost totally disappears from the precipitate and the solution exhibits the same nmr pattern as that found for the equivalent composition ($R = 2.00$) in Table I. A similar situation is found when smaller mole ratios of methylamine to germanium tetrachloride are employed.

As the mole ratio of methylamine to germanium tetrachloride is increased beyond 3 at the same temperature, it is seen that the nmr resonance due to the compound $[Ge(Cl_2)N(CH_3)]_3$ diminishes in the equilibrated solution phase, dropping from 83% for a reagent ratio of 3.0 to 74% for a ratio of 3.5 and to 10% for a ratio of 4.0. Simultaneously a resonance 0.05 ppm upfield from this peak and two resonances 0.08 and 0.15 ppm downfield from it are seen to maximize at a reagent mole ratio somewhere near 4. There are also other resonances, mostly quite broad, appearing for the compositions corresponding to a reagent ratio range of $3 < CH_3NH_2/GeCl_4 < 6$. The previously noted phenom-

enon of initial precipitation followed by partial dissolution of the germanium is also seen in this region of composition. However, upon increasing the mole ratio of methylamine to germanium tetrachloride from 3 to 6, the amount of precipitate either formed immediately or present at equilibrium is seen to increase steadily so that, at $CH_3NH_2/GeCl_4 = 6$, there is only a small amount of germanium and methylated nitrogen in the solvent at any time and the reaction product is nearly all in the form of a flocculent precipitate.

When more than enough methylamine to substitute all of the chlorine atoms on the germanium ($CH_3NH_2/GeCl_4 > 6$) is bubbled into germanium tetrachloride at $0°$, essentially complete precipitation of the germanium is first observed, followed by partial solubilization. Thus, for example, when a final $CH_3NH_2/GeCl_4$ mole ratio of 9 was achieved, starting with a 4.0 wt % solution of $GeCl_4$ in ether, it was found that a flocculent precipitate filled the entire volume of the solution in about 80 min at which time *ca.* 6 mol of methylamine had been added per mol of germanium tetrachloride. After another 40 min when all of the methylamine had been incorporated, the precipitate was greatly reduced in volume and appeared to be more granular. The supernatant liquid was then removed by centrifugation from the precipitate, which was found still to contain about 20% of the total germanium, and the excess methylamine was removed by vacuum. The nmr spectrum of the resulting precipitate-free solution showed two complicated sets of peaks centered at -2.55 and -2.88 ppm, respectively.

When this solution was allowed to stand in a sealed nmr tube, it was found that the first resonances decreased and the methylamine resonance (at -2.18 ppm) appeared and grew in size, with continuing precipitation occurring after the $CH_3N</CH_3(H)N-$ ratio became greater than *ca.* 1.8. From this study and others, we concluded that the resonances around -2.88 ppm are due to methylimino bridges whereas the others around -2.55 ppm are caused by monofunctional methylamino groups, $CH_3(H)N-$. As would be expected for preferential incorporation of bridging groups into the precipitate, the long-term rate of decrease with time of the monofunctional methylamino groups was found to be considerably greater than that of the methylimino bridges. At $25°$, the rate of formation of methylamine prior to visible precipitation corresponds to 0.017% of the total nitrogen per min (for 15 wt % of total Ge compounds in solution), with the amount formed being proportional to time for at least 500 min.
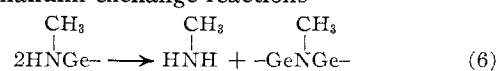
The onset of precipitation at a $CH_3N</CH_3(H)N-$ ratio of *ca.* 1.8 corresponds to a $CH_3(H)N/Ge$ ratio of *ca.* 0.83 at the gel point. Since the monofunctional substituent and the bridging group are both nitrogen atoms, we can assume that the chain–chain equilibrium constants are close to random and calculate from them the amount of the various building units at the gel point. From this and the general equation for the gel point,[7] we can further estimate the number of ring closures occurring in the solution just before precipita-

tion occurs, and this number comes out to be *ca.* 0.65 closure/Ge atom. Thus, in the solution over the precipitate, there must be a large number of highly cyclized molecules, including many exhibiting fused rings and bird-cage structures. In order to appreciate the value of 0.65 closure/Ge, it should be remembered that, when there are only four-way branch groups (q) in the structure, the gel-point equation corresponds to no more than 1 ring closure/Ge for the resulting three-dimensional network polymer in which each germanium is bridged to four neighboring germanium atoms, by N-CH_3 groups. Finally, all of the germanium is found to be precipitated from the solution in the form of chunks of a transparent glassy material (amorphous by X-ray diffraction) having about the same index of refraction as the benzene; and the only nmr peak then showing up in the solution is the one for free methylamine. From the material balance, it appears that the ratio of monofunctional methylamino groups to methylimino bridges in the glass is *ca.* 1:4 when the rate of formation of methylamine becomes excessively slow. Presumably, however, the proportion of methylamino groups continues to diminish at a very low rate owing to self-diffusion in the solid.

It should be noted that the only strongly exothermic step in these processes appears to be the initial precipitation of the amine hydrochloride. Analyses also showed that the precipitation of the amine hydrochloride in all cases was fast and essentially stoichiometric.

Conclusions

These studies indicate that the initial step in the reaction between methylamine and germanium tetrachloride is the formation of cross-linked polymers which further react (at a considerably slower rate than they are formed) with either excess germanium tetrachloride or excess methylamine to give an equilibrium distribution of chloro- or methylamino-terminated molecules which are sufficiently small so as to be soluble. An excess of methylamine over that needed to react with all of the chlorines on the $GeCl_4$ leads to methylamino-terminated structures in solution; whereas, an excess of the germanium tetrachloride leads to chlorine-terminated structures. It is believed that even in the precipitates, either chlorine or methylamine groups represent practically all of the monofunctional substituents except perhaps for the solid corresponding to a CH_3NH_2 to $GeCl_4$ reagent mole ratio of exactly 6 (a composition which offers many experimental problems because of continuing insolubility). Soluble molecules having methylamino end groups are not stable because of the hydrogen–germanuim exchange reactions

$$2HN\overset{\overset{\displaystyle CH_3}{|}}{Ge-} \longrightarrow HN\overset{\overset{\displaystyle CH_3}{|}}{H} + -Ge\overset{\overset{\displaystyle CH_3}{|}}{N}Ge- \qquad (6)$$

However, stable equilibria are reached in the case of solutions containing the chlorine-terminated molecules.

(7) J. R. Van Wazer, *J. Macromol. Sci. (Chem.)*, **A1**, 29 (1967); see eq 4 on p 46. This equation is a general one applying to all ring structures regardless of whether or not they are fused rings, in bird-cage molecules, or what kinds or sizes of molecules are involved in the over-all ring and chain distribution.