

NMR STUDY OF THE EQUILIBRIUM BETWEEN TRIMERIC AND TETRAMERIC RING STRUCTURES OF DIMETHYLGERMANIUM OXIDE

KURT MOEDRITZER

Central Research Department, Monsanto Company, St. Louis, Missouri (U.S.A.)

(Received July 23rd, 1965)

In a series of papers^{1,2} Rochow has described the chemistry of dimethylgermanium oxide. In these studies the existence of three forms of dimethylgermanium oxide was established. A tetrameric form, m.p. 91–92°, was obtained by hydrolysis of dimethyldichlorogermane. The tetramer could be converted to an unstable trimeric form by heating at 210–220° for at least 24 hours. For both modifications a cyclic structure was proposed. In addition to these, there was also described a high-polymeric form, m.p. 132–133°, which is obtained upon evaporation of aqueous solutions of dimethylgermanium oxide. Infrared spectra in the 700 to 950 cm⁻¹ region and cryoscopic as well as tensimetric measurements corroborate the existence of these three forms of dimethylgermanium oxide.

The work reported here was prompted by a series of observations made while studying some reactions of dimethylgermanium oxide. In these investigations, it was found that proton nuclear magnetic resonance (NMR) spectra of carbon tetrachloride solutions of freshly prepared tetrameric dimethylgermanium oxide (m.p. 87–91°) showed two signals, at -0.495 and -0.472 ppm (relative to tetramethylsilane). The upfield resonance representing about 90% of the total area was assigned to the tetrameric form of dimethylgermanium oxide. The downfield peak, the area of which increased with time, was found to be the major peak when samples of the trimeric form, prepared² from the tetrameric form by heating at 200° and subsequent quenching, were investigated by NMR.

Further evidence for a fairly rapidly occurring transformation of the respective "pure" cyclic forms of dimethylgermanium oxide to an equilibrium controlled state in which both cyclic forms participate, was obtained from a study of scrambling equilibria³ in the systems [(CH₃)₂GeO] vs. (CH₃)₂GeX₂ (X = Cl, Br or I) involving the exchange of bridging oxygen atoms with halogens on the dimethylgermanium moiety. Based on the observed NMR line broadening, it was concluded in this study that the bridging oxygen-halogen exchange in the chain molecules at room temperature is very rapid, with average life-times of the order of 0.1 sec, and that the ring-ring interchanges are much slower.

In addition, it was also observed that a sample of the crystalline tetramer, after standing for ca. 1 year on the shelf in a taped screw-cap bottle, had converted to a solid hard mass having a melting point of 130°. The melting point and the insolubility at room temperature of this material in organic solvents (dissolution occurs upon heating above 100°) indicate that a solid state conversion of the crystalline tetramer had occurred to yield a high-polymeric form of the type described earlier². This re-

action probably is catalyzed by moisture². The thus obtained material, however, differs in appearance from the more fibrous high-polymeric dimethylgermanium oxide of the same melting point prepared by evaporation of aqueous dimethylgermanium oxide solutions.

All these observations suggested that a quantitative study of the equilibrium phenomena discussed above be undertaken.

RESULTS

Any of the forms of dimethylgermanium oxide or mixtures thereof, when dissolved in an inert solvent (heating to affect dissolution is required for the high-polymer species), tend to approach an equilibrium state. As evidenced by NMR spectroscopy this equilibrium state is characterized by the coexistence of the trimeric and tetrameric species, with the proportion of the two depending on the over-all concentration and temperature. Thus, the equilibrium observed in solutions of dimethylgermanium oxide may be represented by the following equation.



Fig. 1 shows the variation of the relative proportions of dimethylgermanium oxide monomeric units between the trimeric and tetrameric ring structures as a function of the dilution at two different temperatures. In this graph the experimental

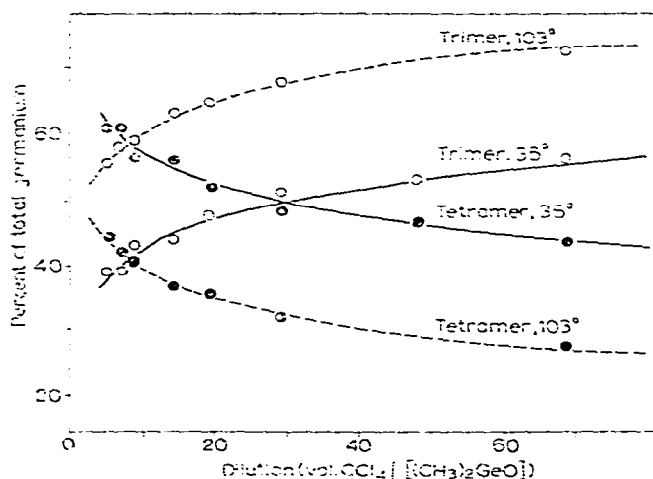


Fig. 1. Relative proportions of dimethylgermanium oxide units found in the trimeric or tetrameric form at various dilutions at 35 and 103°. Curves are calculated from the average equilibrium constants in Table I, assuming no long-chain species.

points as obtained by NMR are compared with theoretical curves calculated from the average equilibrium constants shown in Table I. Good agreement is observed between the experimental and calculated values. It is seen that, in agreement with the principle of Le Chatelier, low dilutions and low temperatures shift the equilibrium towards the tetramer, whereas high dilutions and high temperatures favor the formation of the trimer. The data of Fig. 1 were used to calculate equilibrium constants for the reaction

of eqn. (1). The constants in Table I were determined at various dilutions at 35 and 103° and were evaluated in terms of an average equilibrium constant for the given temperature, based on equal weighting of the individual values. From these average equilibrium constants, measured at two temperatures, the enthalpy for the formation of the tetramer according to eqn. (1) was determined to be $\Delta H = -8.2$ kcal.

TABLE I

CONSTANT FOR THE EQUILIBRIUM BETWEEN TRIMERIC AND TETRAMERIC DIMETHYLGERMANIUM OXIDE AT VARIOUS DILUTIONS AND TEMPERATURES

Dilution (vol. CCl_4 /vol. $[(\text{CH}_3)_2\text{GeO}]$)	$K_{4,3}^{2,1} = \frac{[(\text{CH}_3)_2\text{GeO}_3]^3}{[(\text{CH}_3)_2\text{GeO}_4]}$ in $l/mole$	
	at 35°	at 103°
5.13	5.94	0.60
6.65	7.23	0.50
8.98	5.11	0.54
14.48	7.06	0.48
19.55	5.49	0.52
29.45	4.93	0.48
48.33	6.33	—
68.76	5.73	0.52
Average \pm std. dev.	5.98 \pm 0.3	0.52 \pm 0.02

Rate studies of the equilibration reaction were performed by diluting a fairly concentrated equilibrated solution of dimethylgermanium oxide with additional solvent. Observation by proton NMR of the re-equilibration process to attain the trimer/tetramer ratio determined by the resulting higher dilution gave the kinetic curves shown in Fig. 2. In this figure it is seen that the re-equilibration process is fairly rapid with the new equilibrium being reached in a matter of hours at this

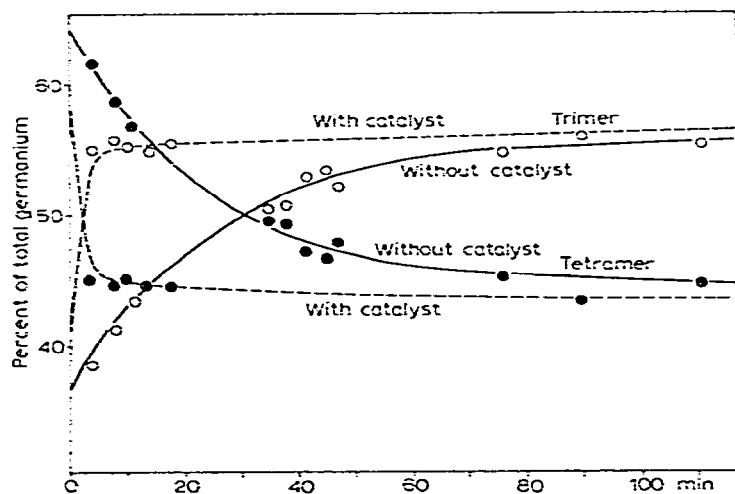


Fig. 2. Re-equilibration of a CCl_4 solution of dimethylgermanium oxide upon dilution from 7.5 to 58 volumes of CCl_4 per volume of $[(\text{CH}_3)_2\text{GeO}]$ at 35°. The solid lines represent the change with time of the relative proportions of dimethylgermanium oxide $[(\text{CH}_3)_2\text{GeO}]$ units in the trimer and tetramer species in the absence of a catalyst. The broken lines describe the same process in the presence of 1 wt.-% of dimethyldiiodogermane.

dilution. It was found that the re-equilibration reaction is catalyzed by dimethyldihalogermes, with the iodo compound being more effective than the chloro compound at comparable concentration levels.

Addition of 1% of dimethyldiiodogermes to an equilibrating solution of the oxide decreases the time required to reach the new equilibrium from several hours to *ca.* 10 minutes. It is assumed that by initiating a rapidly occurring exchange process³ between the bridging oxygen and the halogen the dimethyldihalogermes thus provides a new path—probably via chain-molecules—for the conversion of some of the tetrameric dimethylgermanium oxide to the trimer, the over-all process which is seen to occur upon dilution.

DISCUSSION

From the temperature and concentration dependence of the trimer-tetramer equilibrium of dimethylgermanium oxide, it may be concluded that at sufficiently high temperatures or dilutions only the trimer should be in existence; and, indeed, by rapid quenching this species has been isolated earlier² in pure form. Tensimetric measurements² of dimethylgermanium oxide have also shown that the average degree of polymerization at high temperatures (*ca.* 250°) and low pressures (*ca.* 100 mm) is 3, with this value increasing to *ca.* 3.2 at lower temperatures (*ca.* 160°). In further agreement with the type of equilibrium discussed here, pure crystalline tetrameric dimethylgermanium oxide is obtained by crystallization from a relatively concentrated solution at low temperatures.

Both of the cyclic forms, however, when isolated as crystalline materials do not appear to be stable indefinitely. Upon storage at room temperature they gradually convert to higher polymers which do not dissolve when brought into contact with organic solvents at room temperature. Depolymerization to give the equilibrium mixture of the trimer and tetramer occurs when these materials are heated in carbon tetrachloride in a sealed tube at 100°. On the other hand, solutions of the equilibrium mixture of the trimer and tetramer were found to remain unchanged and no higher polymers appear to form.

Proton NMR spectra of dimethylgermanium oxide melts or concentrated solutions in carbon tetrachloride (dilution ≤ 2) obtained at 100° display a single broad peak with half line widths of *ca.* 3–4 cps. Since these melts as well as the concentrated solutions at this temperature are quite mobile liquids, the broadening of the NMR line definitely cannot be ascribed to viscosity effects. Therefore, it is concluded that it is rather due to rapidly exchanging species at equilibrium. By applying the equation for coalesced NMR peaks⁴ it is estimated that the average life time of an exchanging species in the melt at 100° is *ca.* 0.3 sec.

In the study³ of equilibria in the systems $[(\text{CH}_3)_2\text{GeO}]$ vs. $(\text{CH}_3)_2\text{GeX}_2$, where X = Cl, Br, or I, it was found that the middle groups in long chains exhibited the same chemical shift as those of the cyclic tetramer, $[(\text{CH}_3)_2\text{GeO}]_4$. If there had been an appreciable amount of long-chain polymer in with the cyclic trimer and tetramer in the equilibrium studies reported herein, the equilibrium constants of Table 1 should systematically decrease with increasing dilution. This behavior would be expected on the basis that (a) the long-chain polymer would have been included in the numerator of the expression for $K^{30}_{4,3}$ and (b) the ring-chain equilibrium constant of

eqn. (2) below demands that the fraction of total germanium in chain structures (probably terminated by trace impurities) would drop sharply with increasing dilution. These facts put a constraint on the ring-chain equilibrium constants which are thus fixed for a given ring size no matter what kind of group terminates the chain. The ring-chain equilibrium constant applicable to the derivatives of dimethylgermanium oxide has the following form⁵:

$$K^{\tau}_r = \frac{[\text{middles in the } r\text{-sized ring}]}{(1-D)V_2 + (R/2)(V_0 - V_2)} \left[\frac{[\text{ends}] + 2[\text{chain middles}]}{2[\text{chain middles}]} \right]^{\tau} \quad (2)$$

where τ 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 in l/mole of the compound $(\text{CH}_3)_2\text{GeX}_2$ where X is the chain-terminating group, V_2 is the volume in l/mole of the $(\text{CH}_3)_2\text{GeO}$ monomer, using no dilution, and R is a composition parameter defined as the ratio X/Ge. The two ring-chain constants are related to the ring-ring constant by the equation $K^{\tau}_3 = (K^{\tau}_4)^2/(K^{\tau}_3)^2$. In the limiting case of trace amounts of terminating groups X, the concentrations of all species at equilibrium must be the same regardless of the nature of X. Since the ring-ring equilibrium constant, K^{τ}_3 , of Table I was not seen to vary systematically with dilution, the ring-chain equilibrium constants K^{τ}_r , where $\tau = 3$ or 4, must have values which correspond to an analytically undetectable amount (< ca. 5%) of the total germanium present as long-chain polymers. This means that $K^{\tau}_4 \geq 1.3$ and $K^{\tau}_3 \geq 0.82$.

EXPERIMENTAL

Materials

The various forms of dimethylgermanium oxide were prepared according to the literature². Dimethyldichlorogermane, required as starting material, was made by an improved version⁶ of the direct synthesis⁷.

Equilibration

Equilibrium was achieved by heating the desired proportions of dimethylgermanium oxide and dry carbon tetrachloride in sealed 5 mm o.d. precision NMR tubes at 35 and 103° respectively. The time required for reaching equilibrium was estimated from test runs held for various time intervals at the respective temperature until the proton NMR spectra did not exhibit any further change. The data for the 35° runs were obtained after keeping the samples for 55 days at this temperature and the data at 103° were obtained after 24 hours at this temperature.

NMR measurements

Proton NMR spectra at 35° were obtained on a Varian A-60 Spectrometer which was modified to provide a 25 cps sweep-width setting. High-temperature NMR measurements were performed on a Varian A-56/60 Spectrometer equipped with a variable-temperature probe. Since the observed two peaks could not be resolved entirely (the valley between the two peaks did not quite reach the base line), peak areas were determined by cutting out and weighing of Xerox copies rather than by electronic integration.

ACKNOWLEDGEMENTS

I wish to thank Dr. JOHN R. VAN WAZER for helpful advice and Mr. RAY E. MILLER for obtaining some of the NMR spectra.

SUMMARY

The equilibria in solution between trimeric and tetrameric forms of dimethylgermanium oxide have been studied by proton NMR. From the data obtained in this study equilibrium constants for the reaction: $4[(\text{CH}_3)_2\text{GeO}]_3 \rightleftharpoons 3[(\text{CH}_3)_2\text{GeO}]_4$ were determined; $K_{4,3}^{25} = 5.9\text{S}$ at 35° , and 0.52 at 103° . The rate of equilibration has been studied in dilute solution and catalytic effects by dimethyldihalogermanes are interpreted in terms of oxygen-halogen exchange reactions.

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