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PROTON NMR STUDY OF THE EQUILIBRIA BETWEEN CYCLIC DISILTHIANES AND TRISILTHIANES

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SUMMARY

The equilibria in solution between the tetra-atomic ring structure of tetramethylcyclodisilthiane and the hexa-atomic ring structure of hexamethylcyclotrisilthiane were studied by proton nuclear magnetic resonance spectroscopy. Equilibrium constants determined at various temperatures and dilutions show that in accordance with the principle of Le Chatelier high (low) temperatures and high (low) dilutions favor the formation of the smaller (larger) sized ring structure. The ring strain energy in the cyclic dimer is about 3 kcal per monomer unit.

Ring compounds of alternating silicon and sulfur atoms have been known for several years[1-3]. Organometallic derivatives ("organocyclosilthianes") of these exist as tetra-atomic ring structures—tetraorganocyclodisilthianes (tetraorgano-1,3,2,4-dithiadisiletanes)—and hexa-atomic ring structures—hexaorganocyclotrisilthianes (hexaorgano-1,3,5,2,4,6-trithiatrisilins). Except for the finding[4] that tetraorganocyclodisilthianes "are thermodynamically unstable and rearrange to form hexaorganocyclotrisilthianes" and the observation that the tetraorganocyclodisilthianes may be regenerated from hexaorganocyclotrisilthianes by quenching the vapor phase, very little is known about the interrelationship between these two types of compounds. The evidence quoted above, in conjunction with our recently generated new ideas regarding exchange or redistribution equilibria[5] suggested that the interdependence of the two ring species may be equilibrium controlled and thus should follow the simple laws of chemical equilibria.

This paper presents a quantitative study of the equilibria between tetramethylcyclodisilthiane and hexamethylcyclotrisilthiane as a function of temperature and dilution using proton nuclear magnetic resonance (NMR) spectroscopy as analytical tool.

EXPERIMENTAL

Materials

Hexamethylcyclotrisilthiane[6] and dimethylbis(methylthio)silane[7] were prepared according to methods of the literature. Dimethyldiphenylsilane (used as solvent) was purchased from K & K Laboratories, Plainview, N.Y., and other solvents were commercially available reagent grade materials. Dimethyldiphenylsilane was selected as the solvent because of its thermal stability, inertness and the fact that its proton NMR signals do not overlap with those of the compounds studied.

Equilibration and measurements

Equilibrium was achieved by heating various portions of hexamethylcyclotrisilthiane in dimethyldiphenylsilane as inert solvent in the presence of 1% dimethylbis(methylthio)silane as catalyst in sealed standard 5 mm o.d. precision NMR tubes at 250°, 200°, and 150°, respectively. The time required for reaching equilibrium was estimated by recording the NMR spectra of the samples held for various time intervals at the respective temperature until all the proton NMR spectra did not exhibit any further change with time. The final data for the 250° runs were obtained after holding the samples for 22 h (5 h) at this temperature, the 200° data after 22 days (12 days), and the 150° data after 83 days (53 days). The times listed in parentheses indicate the heating interval after which the NMR spectra of the equilibrated sample did not change any further.

The proton NMR spectra were obtained at a probe temperature of 36° immediately after quenching the samples to room temperature in a jet stream of air. The validity of this procedure is apparent from the observed agreement of the NMR spectra of equilibrated samples obtained in one case after rapid quenching from 150° to room temperature in the above manner and in the other case by recording the spectra at a NMR probe temperature of 150°. Although one would not expect as much deviation from the equilibrium when quenching from 150° to 36° as when quenching from a higher temperature, the quenching procedure for obtaining the 200° data was preferred to operating the NMR probe of the A-60 at its upper limit of operation. The 250° data were also obtained by quenching. Considering the relatively slow rates of equilibration at these temperatures (evidenced by the approximate times required for complete equilibration listed in parentheses in the preceding paragraph) the error due to shift of the equilibrium during the relatively fast quenching process should be quite small. The Varian A-60 Spectrometer used in this study has been modified to provide a 25 Hz sweep-width setting. Peak areas were determined by electronic integration or by using a Du Pont Model 310 Curve Resolver.

Calculations

All equilibrium calculations were performed with an IBM 7044 using computer programs developed in this laboratory[8] and applied on previous occasions[9,10].

RESULTS AND CONCLUSIONS

NMR chemical shifts

The proton NMR signal given by a neat liquid sample of hexamethylcyclotrisilthiane is a single sharp line at −0.66 ppm relative to internal tetramethylsilane ($\delta = 0$ ppm). Dissolution of tetramethylcyclodisilthiane in the above sample results in a new single peak which lies *ca.* 0.05 ppm downfield of the original one. As shown in Fig. 1, these two resonances representing the cyclic dimer and trimer of $[(CH_3)_2SiS]$ are well separated and therefore may be integrated electronically quite accurately thus permitting rapid determination of the relative proportions of the two species

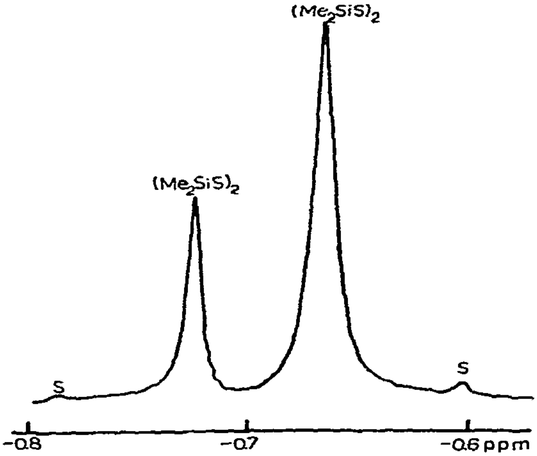

Fig. 1. Proton NMR spectrum of a neat equilibrated sample (at 200°) of tetramethylcyclodisilthiane and hexamethylcyclotrisilthiane with internal tetramethylsilane as reference (s denotes satellites due to proton spin-spin coupling with ^{29}Si).

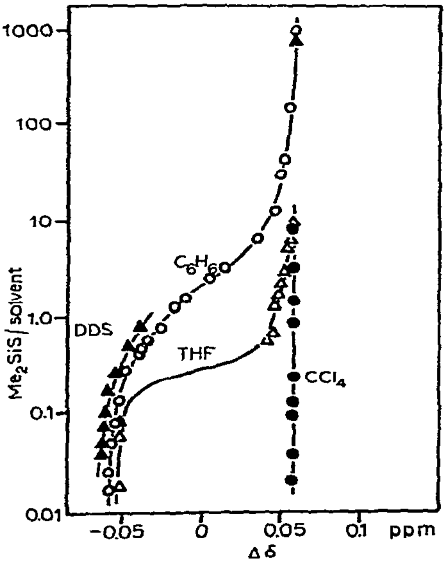

Fig. 2. Proton NMR chemical shift difference $\Delta\delta = \delta(Me_2SiS)_3 - \delta(Me_2SiS)_2$ in ppm (TMS = 0) as a function of the dilution expressed in volume of [Me_2SiS] per volume of solvent; DDS = dimethyldiphenylsilane, THF = tetrahydrofuran.

present in a mixture.

Upon dilution with carbon tetrachloride of a sample containing both of the two ring species in the neat liquid state the chemical shift of each of the two signals practically remains unaffected by the added solvent over a wide concentration range. In a plot of the shift difference $\delta(Me_2SiS)_3 - \delta(Me_2SiS)_2$ *versus* the dilution with solvent as shown in Fig. 2, this sort of behavior is represented by a vertical straight line. Other solvents, however, such as benzene, toluene, xylene, chlorobenzene, dimethyldiphenylsilane, tetrahydrofuran and diphenyl ether cause the position of these peaks to change relative to internal tetramethylsilane. Whereas the position of the signal of the trimer in the latter solvents is shifted somewhat upfield (less than 0.05 ppm) from that in the neat liquid sample with respect to internal tetramethylsilane, the chemical shift of this peak is not dependent upon the dilution of the sample with additional solvent. However, the position of the signal for the dimer species in these latter solvents shows, in addition to a similar slight upfield shift, a remarkable and unique dilution dependence. Upon increasing the dilution of the sample with solvent, this peak moves from a position downfield from the peak for the trimer to a position upfield of that signal. This is shown in Fig. 2 for a series of solvents. In this plot of the dilution of the equilibrated sample expressed in volumes $[(CH_3)_2SiS]$ per volume of solvent *versus* the shift difference $\Delta\delta = \delta_{\text{trimer}} - \delta_{\text{dimer}}$ in ppm it is seen that for large ratios $[(CH_3)_2\text{-}SiS]$/solvent, *i.e.*, high concentrations, $\Delta\delta$ is positive, indicating that the signal of the dimer is downfield of that of the trimer. When the above ratio decreases, *i.e.*, the solution is diluted, $\Delta\delta$ decreases also and goes through zero, at which point total overlap of the two peaks is seen. Upon further dilution the signal of the dimer emerges at the upfield side of the single peak consisting of the two overlapping signals. When infinite dilution is approached, the signal of the dimer remains at the position upfield from that of the trimer with the shift difference maintaining a constant value.

This pronounced effect of magnetically anisotropic solvent molecules[11] on the proton NMR chemical shift of the cyclic dimer as opposed to the minimal effect on that of the trimer probably is due to steric effects. Electron diffraction[12] studies have suggested a planar structure for the dimer and a chair configuration for the trimer.

Equilibria

From NMR peak area measurements of samples of $[(CH_3)_2SiS]$ equilibrated at various dilutions with dimethylphenylsilane as solvent at the three temperatures 150°, 200° and 250° the data points plotted in Fig. 3 were obtained. The graph shows

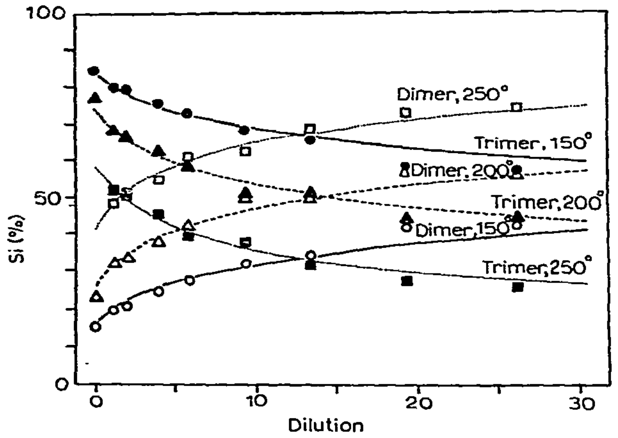

Fig. 3. Relative proportions of $[(CH_3)_2SiS]$ moieties (in percent of total Si) found in the cyclic dimer and trimer at various dilutions (volume of Si compound/volume of solvent) and temperatures (°C). The curves were calculated from the respective average equilibrium constants shown in Table 1. The diluent is dimethyldiphenylsilane.

the variation of the relative proportions of dimethylsilthiane monomer units between the dimeric and trimeric ring structures as a function of the dilution with dimethyldiphenylsilane at three temperatures. Each pair of data points in Fig. 3 was used to calculate an equilibrium constant of the form given below.

$$K = \{[(CH_3)_2SiS]_3\}^2/\{[(CH_3)_2SiS]_2\}^3 \text{ l/mole} \qquad (1)$$

Values for K as obtained for each individual pair of data points are summarized in Table 1. From the individual K values an average equilibrium constant K_{av} was calculated for each of the three temperatures based on equal weighting of the individual values. The average equilibrium constants were then evaluated in terms of the reaction enthalpy and entropy for the formation of the trimer from the dimer according to the reaction of eqn. (2).

TABLE 1

CONSTANTS FOR THE EQUILIBRIUM BETWEEN TETRAMETHYLCYCLODISILTHIANE AND HEXAMETHYLCYCLOTRISILTHIANE AT VARIOUS DILUTIONS AND TEMPERATURES

Dilution (vol. solvent[b]/vol. $[(CH_3)_2SiS]$)	Equilibrium constant[a] Temperate (°C)		
	150°	200°	250°
0	17.9	3.76	[c]
1.2	14.4	2.47	0.42
2.0	17.0	2.83	0.48
3.9	14.8	2.83	0.50
5.7	14.1	2.45	0.37
9.4	12.1	1.84	0.48
13.4	12.2	2.33	0.36
19.3	7.0	1.62	0.33
26.2	9.0	2.43	0.36
Average value	13.2	2.51	0.41
Standard deviation	3.5	0.62	0.07

[a] $K = \{[(CH_3)_2SiS]_3\}^2/\{[(CH_3)_2SiS]_2\}^3$ in l/mole. [b] Dimethyldiphenylsilane. [c] The sample solidified upon quenching to room temperature due to the presence at equilibrium of large amounts of tetramethylcyclodisilthiane, m.p. 113°.

$$3\,[(CH_3)_2SiS]_2 \rightarrow 2\,[(CH_3)_2SiS]_3 \qquad (2)$$

$$\Delta H = -17.1 \pm 2.2 \text{ kcal/mole}$$

$$\Delta S = -43.6 \pm 4.4 \text{ cal} \cdot \text{deg}^{-1} \cdot \text{mole}^{-1}$$

The value of ΔH was obtained by least square fitting of a straight line through the three equilibrium constants K in Table 1. The standard deviations were derived from the fit procedure. Based on the ΔH value a ring strain energy of about 3 kcal may be assigned to each monomer unit in the cyclic dimer.

The experimental data points in Fig. 3 as obtained from the NMR data may now be compared with theoretical curves calculated from the average equilibrium constants shown in Table 1. As seen by inspection of Fig. 3 there is good agreement between the experimental and calculated values.

In the absence of a catalyst or impurities the rate of equilibration in the neat liquid samples below *ca.* 200° is quite slow and only above this temperature half lives of the order of magnitude of hours were observed. However, impurities and compounds capable of acting as end groups and thus providing a mechanism for ring opening reactions were found to catalyze the dimer/trimer equilibration and consequently increase the rate of equilibration considerably. Although no detailed kinetic studies were made, the suggested reaction scheme of the ring–ring interconversion process is supported by previous studies of the redistribution equilibria in the systems[7] $(CH_3)_2SiX_2/[(CH_3)_2SiS]$, where X = halogen, SCH_3 or OCH_3. These studies have shown that in addition to ring–ring equlibria also ring–chain equilibria are established. In spite of the fact that cyclic species are favored at equilibrium and only relatively small amounts of chain molecules of rather limited chain length are present, the equilibrium concentration of the latter types of molecules is large enough to account for ring–ring interconversions as suggested by the equations given below:

$$(Me_2SiS)_2 + Me_2SiX_2 \rightleftarrows XSiMe_2{-}S{-}SiMe_2{-}S{-}SiMe_2X \tag{3}$$

$$XSiMe_2{-}S{-}SiMe_2{-}S{-}SiMe_2X + (Me_2SiS)_2 \rightleftarrows X(SiMe_2{-}S)_4SiMe_2X \tag{4}$$

$$X(SiMe_2{-}S)_4SiMe_2X \rightleftarrows (Me_2SiS)_3 + XSiMe_2{-}S{-}SiMe_2X \tag{5}$$

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