Journal of Organometallic Chemistry, 194 (1980) 139—145

CYCLIC POLYSILANES

XIX *. A TEMPERATURE STUDY OF REDISTRIBUTION EQUILIBRIA BETWEEN PERMETHYLCYCLOPOLYSILANES

LAWRENCE F. BROUGH and ROBERT WEST *

Department of Chemistry, University of Wisconsin, Madison, WI 53706 (U.S.A.)

(Received November 23rd, 1979)

Summary

Equilibria among the cyclic compounds $(Me_2Si)_n$ where $n = 5$, 6 and 7 have been studied between 30—58°C. Thermodynamic values for the redistribution reactions between pairs of compounds are, for $n = 5 \rightarrow 6$, $\Delta H = -18$ kcal/mole, $\Delta S = -20$ cal/deg. mole; for $n = 7 \rightarrow 6$, ΔH —3, ΔS +33; for $n = 7 \rightarrow 5$, ΔH +18, ΔS +51. The enthalpies indicate that the stabilities of the rings increase in the order $(Me_2Si)_5 < (Me_2Si)_7 < (Me_2Si)_6$. The differences are smaller than corresponding differences among the cycloalkanes, probably because the silicon compounds are less affected by steric repulsions and angle strain.

Introduction

Although ring—ring and ring—chain equilibria for skeletal systems containing repeating Si—O, Si—S and Si—N units have been studied in considerable detail [2], little information is presently available concerning redistribution reactions of this kind in homonuclear, catenated molecules [3]. Kumada [4,5] has, however, examined the room temperature equilibria for systems containing $Ph_3Si(Me_2Si)_nSiPh_3$ (n = 1—6) and $(Me_2Si)_{5,6}$; the five- and six-membered rings alone; and also $PhMe_2Si(Me_2Si)_nSiMe_2Ph$ (n = 0—3) and $(Me_2Si)_6$, in the presence of a catalytic amount of triphenylsilyllithium or phenyldimethylsilyllithium. Redistribution reactions of linear and cyclic polysilanes have also been found to be synthetically useful [6—9].

During a study [10] of the reaction of dimethyldichlorosilane with sodium-potassium (Na/K) alloy in tetrahydrofuran (THF), a temperature-dependent equilibrium was observed between $(Me_2Si)_5$ and $(Me_2Si)_6$. Reproducible changes

---

* For part XVIII see ref. 1.

in the $(Me_2Si)_6 : (Me_2Si)_5$ ratio were observed as the reaction mixture was allowed to equilibrate alternately at room temperature and at 65° C. Temperature cycling caused little or no change in the total amount of the cyclopolysilane ring compounds, as determined by GLC analysis. These results encouraged us to investigate this system under controlled conditions. This paper reports a study of the equilibration between $(Me_2Si)_5$, $(Me_2Si)_6$ and $(Me_2Si)_7$ in THF, catalyzed by Na/K alloy, at several temperatures. From the results the ΔH and ΔS values, as well as equilibrium constants, were determined between pairs of cyclics which make up the general scheme shown in equation 1.

$$\begin{tikzcd}
(Me_2Si)_5 \arrow[rr, leftrightarrows] \arrow[dr, leftrightarrows] & & (Me_2Si)_6 \arrow[dl, leftrightarrows] \\
 & (Me_2Si)_7 &
\end{tikzcd} \qquad (1)$$

Results and discussion

Results of the equilibration experiments are given as a function of temperature in Table 1. The usual starting material was $(Me_2Si)_6$, but one equilibration at 30° C was carried out starting with $(Me_2Si)_5$. The results were identical showing that the equilibrium is independent of starting material, as expected.

Table 1 also shows equilibrium constants between each pair of molecules, defined as follows: $K^{oo}_{6,5}$ = [mole fraction $(Me_2Si)_6]^5$/[mole fraction $(Me_2Si)_5]^6$; $K^{oo}_{6,7}$ = [mole fraction $(Me_2Si)_6]^7$/[mole fraction $(Me_2Si)_7]^6$; $K^{oo}_{5,7}$ = [mole fraction $(Me_2Si)_5]^7$/[mole fraction $(Me_2Si)_7]^5$. Agreement between duplicate runs is very good for the equilibrium between $(Me_2Si)_5$ and $(Me_2Si)_6$, but for the constants involving $(Me_2Si)_7$ there is somewhat more scatter, resulting from the difficulty in accurately measuring the small amounts of the seven-membered ring present at equilibrium. The constants are independent of concentration when the mole fraction of starting polysilane is less than 1.2×10^{-2} (0.14 *M*), but change slightly at higher concentrations, probably because of changes in activity coefficients. Therefore only the values at 0.14 *M* and below were used in further calculations. No larger permethylcyclosilanes such as $(Me_2Si)_8$ or

TABLE 1

DATA FOR EQUILIBRATION BETWEEN $(Me_2Si)_5$, $(Me_2Si)_6$ AND $(Me_2Si)_7$

Conc. [a] $\times 10^2$	*T* (°C)	$(Me_2Si)_5$ (wt. %)	$(Me_2Si)_6$ (wt. %)	$(Me_2Si)_7$ (wt. %)	Log $K^{oo}_{6,5}$ [b]	Log $K^{oo}_{6,7}$ [b]	Log $K^{oo}_{5,7}$ [b]
5.50	58	8.87	89.88	1.26	6.87	10.22	0.50
2.52	58	9.05	89.52	1.43	7.14	9.53	−0.39
1.21	58	9.15	89.43	1.41	7.43	9.25	−0.96
0.79	58	9.71	88.93	1.36	7.45	9.14	−1.07
0.47	58	10.42	88.32	1.26	7.47	9.10	−1.14
1.21	46	7.29	91.24	1.47	8.07	9.20	−1.74
0.47	46	9.30	89.49	1.22	7.79	9.22	−1.41
1.21	30	6.22	92.27	1.50	8.50	9.19	−2.27
0.47	30	7.11	91.73	1.16	8.54	9.43	−2.12
0.57 [c]	30	7.00	91.83	1.17	8.58	9.41	−2.17

[a] Concentration refers to mol-fraction of $(Me_2Si)_6$ as starting material. [b] Defined in text. [c] Starting material was $(Me_2Si)_5$.

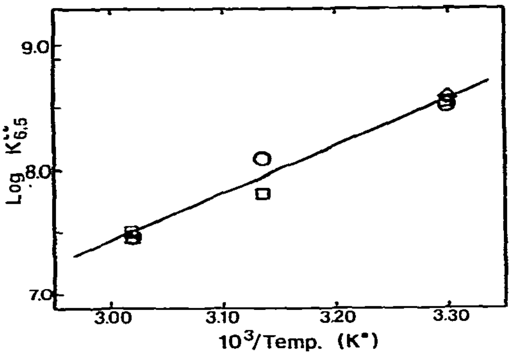

Fig. 1. Log $K^{oo}_{6,5}$ vs. 10^3/Temp. (K°) with ○ = 1.21 × 10^{-2}, △ = 0.79 × 10^{-2} and □ = 0.47 × 10^{-2} mole fraction using $(Me_2Si)_6$ as starting material and ◇ = 0.57 × 10^{-2} mole fraction using $(Me_2Si)_5$ as starting material.

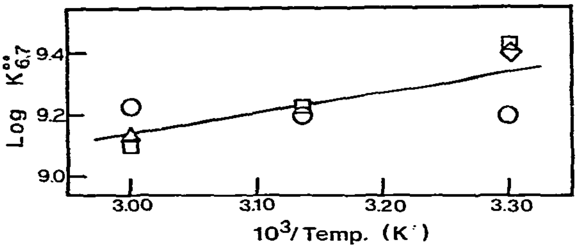

Fig. 2. Log $K^{oo}_{6,7}$ vs 10^3/Temp. (K°) with ○ = 1.21 × 10^{-2}, △ = 0.79 × 10^{-2} and □ = 0.47 × 10^{-2} mole fraction using $(Me_2Si)_6$ as starting material and ◇ = 0.57 × 10^{-2} mole fraction using $(Me_2Si)_5$ as starting material.

$(Me_2Si)_9$ [11] were detected in the equilibrium mixtures.

Enthalpy changes were determined from graphs of log $K^{oo}_{x,y}$ vs $1/T$ in the usual way. Figure 1 shows the plot for $K^{oo}_{6,5}$ at 30, 46 and 58°C from which ΔH for 6 $(Me_2Si)_5 \rightarrow 5\ (Me_2Si)_6$ may be determined as —18 kcal/mole. Similar plots for 6 $(Me_2Si)_7 \rightarrow 7\ (Me_2Si)_6$ (Figure 2) and 5 $(Me_2Si)_7 \rightarrow 7\ (Me_2Si)_5$ (Figure 3) give $\Delta H = -3$ and +18 kcal/mole respectively. The enthalpies of redistribution together with the corresponding entropies are listed in Table 2, along with the same data for the cycloalkanes.

The enthalpies of redistribution presented here are a measure of the relative stabilities of the five-, six- and seven-membered rings in dilute THF solution. The ΔH values for the redistribution reactions would be zero if the compounds

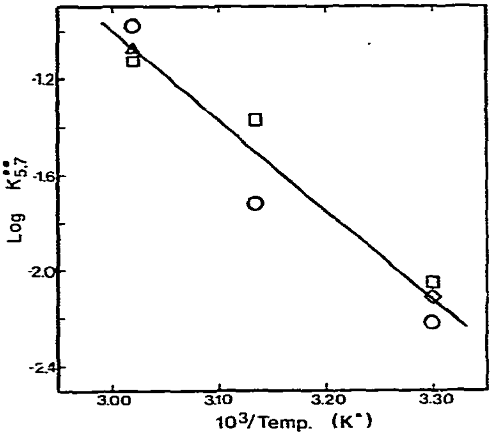

Fig. 3. Log $K^{oo}_{5,7}$ vs 10^3/Temp. (K°) with ○ = 1.21 × 10^{-2}, △ = 0.79 × 10^{-2} and □ = 0.47 × 10^{-2} mole fraction using $(Me_2Si)_6$ as starting material and ◇ = 0.57 × 10^{-2} mole fraction using $(Me_2Si)_5$ as starting material.

TABLE 2

ENTHALPIES AND ENTROPIES OF REDISTRIBUTION FOR CYCLOPOLYSILANES AND CYCLOALKANES

Redistribution	$H_{x,y}$ (kcal mol^{-1})	s [a]	r [b]	$S_{x,y}$ (cal K^{-1} mol^{-1})	s [c]
$6(Me_2Si)_5 \rightleftharpoons 5(Me_2Si)_6$ [a]	−17.7	1.2	0.99	−20 [e]	4.0
$6(Me_2Si)_7 \rightleftharpoons 7(Me_2Si)_6$ [d]	−3.0	1.2	0.71 [f]	+33 [e]	4.6
$5(Me_2Si)_7 \rightleftharpoons 7(Me_2Si)_5$ [d]	+18.4	1.6	−0.98	+51 [e]	5.7
$6\ C_5H_{10} \rightleftharpoons 5\ C_6H_{12}$ [g]	−34 [h]			−49 [i]	
$6\ C_7H_{14} \rightleftharpoons 7\ C_6H_{12}$ [g]	−34 [h]			−7 [i]	
$5\ C_7H_{14} \rightleftharpoons 7\ C_5H_{10}$ [g]	+12 [h]			+52 [i]	

[a] Standard deviation. [b] Correlation coefficient. [c] Calculated from standard deviations of ΔH and $\log K^{oo}_{x,y}$ on a worst case basis. [d] In THF solution. [e] Calculated from $\Delta H_{x,y}$ and the average $\log K^{oo}_{x,y}$ at 30°C. [f] If the point at (3.300, 9.19) in Figure 2 is excluded r improves to 0.92, $\Delta H = -4.2$ ($s = 0.8$) and $\Delta S = 29.3$ ($s = 2.8$). [g] In liquid phase. [h] Calculated from literature values for ΔH_f at 25°C. See ref. 24. [i] Calculated from literature values for S^o at 25°C. See ref. 24.

were equally stable (i.e., had equal heats of formation per Me_2Si unit). The results show that $(Me_2Si)_6$ is significantly more stable than $(Me_2Si)_5$ and slightly more stable than $(Me_2Si)_7$. The six-membered ring is known [12] to adopt a "strainfree" conformation analogous to the chair form of cyclohexane [13], with minimal interaction between methyl group hydrogens. The destabilization of $(Me_2Si)_5$ and $(Me_2Si)_7$ relative to $(Me_2Si)_6$ is probably due to methyl—methyl interactions, combined with some angle strain at least in the five-membered ring *. Similar reasons account for the fact that cyclohexane is more stable than cyclopentane or cycloheptane [15].

Our thermodynamic data for the cyclopolysilanes in dilute THF solution cannot strictly be compared to that for the cycloalkanes, which is referred to the pure liquids **. However, the differences in solvation energy among the three cyclosilanes and among the three cycloalkanes as well as the net solvation energy for the latter molecules are probably quite small. (The enthalpy of mixing for cyclohexane in dilute solutions in THF is only 0.6 kcal per mole of cyclohexane [17].) A qualitative comparison of the enthalpies of redistribution across these two families therefore seems justified. In each series the six-ring is more stable than the five- or seven-ring, but the data indicate that the stability differences are much less for the cyclosilanes than for the cycloalkanes.

There is good reason to believe that methyl—methyl steric interactions in permethylcyclosilanes may be generally less than hydrogen—hydrogen repulsions in cycloalkanes. A conformational analysis [18] of $(Me_2Si)_6$ by the EFF method indicates that the energy differences between the ground state chair conformation and the less energetically favorable D_2 (twist), C_{2v} (boat) and C_2

---

* A recent crystal structure of cyclo-$Me_9Si_5Me_2Si[Fe(CO)_2(C_5H_5)]$ has been shown that the ring is puckered to about the same extent as cyclopentane. See ref. 14.

** Heats of formation are unknown for the permethylcyclopolysilanes, and indeed for polysilanes in general [16]. These data would be of much interest, but would be complicated by the (probably differing) heats of sublimation of the crystalline cyclosilanes. The values obtained in dilute solution may therefore be more suitable for comparing relative stabilities of the molecules as influenced by ring size.

conformations are much less than for cyclohexane. This is reflected experimentally by the observation [19] that even at —95°C the NMR spectrum of $(Me_2Si)_6$ shows no apparent broadening due to nonequivalence of the methyl protons in contrast to the well known behavior of cyclohexane [20]. Also, the rotational barrier of $Me_3SiSiMe_3$ has been calculated to be 1.05 kcal/mol while the rotational barrier of H_3CCH_3 is reported as 2.88 kcal/mol [21]. The lower rotational barriers in silicon than in carbon compounds are probably related to the large radius of silicon and consequent greater bond lengths in the silanes. In addition, silicon—silicon (and silicon—carbon) bonds may be less subject to loss of bond energy upon deformation from the preferred tetrahedral bond angles than are carbon—carbon bonds.

Enthalpy changes of redistribution are also listed in Table 2, for the cyclosilanes and the cycloalkanes. No detailed interpretation is possible in the absence of knowledge of the total entropy content of at least one of the $(Me_2Si)_n$ molecules. However for reasonable values of the total entropy content of any of the cyclosilanes, the data suggest that the total entropies S^0 increase in the order $(Me_2Si)_5 < (Me_2Si)_6 < (Me_2Si)_7$, and that the differences are somewhat larger than for the cycloalkanes *. This is reasonable in view of the fact that methyl rotations and rocking motions, present in the cyclosilanes but not in the cycloalkanes, will increase with ring size and should make an additive contribution to the entropy content.

Attempts were made to study equilibration of the permethylcyclosilanes at temperatures above 58°C and below 30°C, but without success. In an experiment carried out in a sealed tube at 80°C, attack of Na/K alloy on the THF solvent apparently took place leading to destruction of the polysilanes. At low temperatures the equilibration becomes quite slow, and during the longer reaction time secondary reactions apparently occur between the Na/K and the cyclosilanes, again leading to their decomposition. Even in the 30—58°C range used for our experiments, the equilibrium mixture is not indefinitely stable. After a week in contact with Na/K, GLC of the THF solutions shows decreased amounts of cyclosilanes and growth of peaks due to decomposition products.

Experimental

Gas chromatograms were obtained on a Hewlett-Packard 5720A or a Barber Colman 5340 chromatograph using a 8 ft × $\frac{1}{16}$ in or a 15 ft × $\frac{1}{4}$ in column respectively. QF-1 silicone was employed as the liquid phase.

Commercially available Na/K alloy (Callery Chemical Co.) was used. The THF (Fischer) was predried over KOH and then distilled from $LiAlH_4$ after refluxing overnight. $(Me_2Si)_5$ and $(Me_2Si)_6$ were synthesized and purified as described earlier [23]. Each sample of the cyclic compounds was also sublimed to assure removal of small amounts of polymer. A GLC trace of $(Me_2Si)_5$ used as a starting material showed that it contained about 5% $(Me_2Si)_6$ and about 5% cyclic $Si_5Me_{10}O$ while $(Me_2Si)_6$ was free from other compounds.

---

* For example the data in Table 2 are approximately fitted by the following S^0 values in cal/deg, mol: $(Me_2Si)_5$, 100; $(Me_2Si)_6$, 116; $(Me_2Si)_7$, 130. S^0 values for the cycloalkanes are C_5H_{10}, 49; C_6H_{12}, 49; C_7H_{14}, 58. For discussions see ref. 22.

In each experiment a measured amount (5.00, 2.50, 1.25, 0.83 or 0.50 g) of cyclic material was weighed in a 25 ml volumetric flask and THF was added to the mark. The solution was transferred to a 50 ml round bottomed flask and about 0.4 g of Na/K alloy was added by syringe. The flask was placed in a constant temperature bath (±0.5°C) and monitored by GLC until equilibrium was reached. Standards were run and it was determined that the percent of each cyclic by weight was proportional to the peak area ($\%\ \mathrm{wt} = kA$). Proportionality constants k for $(Me_2Si)_5$, $(Me_2Si)_6$ and $(Me_2Si)_7$ are 0.89, 1.02 and 1.05 respectively. Percentages of the cyclics measured with the Hewlett-Packard GLC were taken as the average of 3—5 injections. Values obtained for percentages of compounds fell within a range of 0.3—1.0% for $(Me_2Si)_5$ and $(Me_2Si)_6$ and about 0.2% for $(Me_2Si)_7$. Because of the somewhat large range of yields observed between injections taken from the same sample for some equilibrations, the samples run at 30°C were evaluated using both the Hewlett-Packard GLC and a Barber-Colman GLC and standards were run on both instruments to determine k values. Agreement between the two instruments for both the equilibrium yields of the cyclics at 30°C and the k values was excellent.

Mole fractions of silane were calculated using $\rho = 0.822$ for THF. (The fact that each gram of starting material displaced approximately 1 ml of THF during the preparation of the solutions was also taken into account.) Finally, checks using eicosane as an internal standard showed that the total amount of cyclosilanes is essentially unchanged during equilibration.

Acknowledgement

This work was supported by the U.S. Air Force Office of Scientific Research (NC)-AFSC, USAF Grant No. AF-AFOSR 78-3570.

References

1 L.F. Brough, K. Matsumura and R. West, Angew. Chem. Int. Ed. Engl., 18 (1979) 955.
2 (a) K. Moedritzer, in F.G.A. Stone and R. West (Eds.), Advances in Organometallic Chemistry, Vol. 6, Academic Press, New York, 1968, p. 171; (b) I. Haiduc, The Chemistry of Inorganic Ring Systems, Part 1, Wiley, New York, 1970, p. 36—48; (c) F. Armitage, Inorganic Rings and Cages, Edward Arnold, London, 1972; (d) W. Noll, Chemistry and Technology of Silicones, Academic Press, New York, 1968.
3 J.R. Von Wazer, in A.L. Rheingold (Ed.), Homoatomic Rings, Chains and Macromolecules of the Main-Group Elements, Elsevier, Amsterdam, 1977, Ch. 1.
4 M. Kumada, M. Ishikawa, S. Sakamoto and S. Maeda, J. Organometal. Chem., 17 (1969) 223.
5 M. Kumada, S. Sakamoto and M. Ishikawa, J. Organometal. Chem., 17 (1969) 231.
6 W.H. Atwell and D.R. Weyenberg, J. Organometal. Chem., 7 (1967) 71.
7 M. Ishikawa and M. Kumada, J. Chem. Soc. Chem. Commun., (1969) 567.
8 M. Ishikawa and M. Kumada, J. Chem. Soc. Chem. Commun., (1970) 157.
9 H. Watanabe, K. Higuchi, M. Kobayashi, T. Kitahara and Y. Nagai, J. Chem. Soc. Chem. Commun., (1977) 704.
10 L.F. Brough, Ph.D. Thesis, University of Wisconsin-Madison, 1979.
11 K. Matsumura, L.F. Brough and R. West, J. Chem. Soc. Chem. Commun., (1978) 1092.
12 H.L. Carrell and J. Donohue, Acta. Cryst. B, 28 (1972) 1566.
13 R. Kahn, R. Fourme, D. Andre and M. Renaud, Acta. Cryst. B, 29 (1973) 131.
14 T. Drahnak, J. Calabrese and R. West, J. Organometal. Chem., submitted for publication.
15 E.L. Eliel, Elements of Stereochemistry, Wiley, New York, 1969, p.
16 C. Pitt, in A.L. Rheingold (Ed.), Homoatomic Rings, Chains and Macromolecules of Main-Group Elements, Elsevier, Amsterdam, 1977, p. 223.

17 S. Murakami, M. Koyama and R. Fujishiro, Bull. Chem. Soc. Japan, 41 (1968) 1540.
18 J.P. Hummel, J. Stackhouse and K. Mislow, Tetrahedron, 33 (1977) 1925.
19 E. Carberry, R. West and G.E. Glass, J. Amer. Chem. Soc., 91 (1969) 5446.
20 F.A. Bovey, Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1969, p. 191.
21 D.A. Stanislawski, A.C. Buchanan III and R. West, J. Amer. Chem. Soc., 100 (1978) 7791 and references therein.
22 J.G. Aston, G.J. Szasz and H.L. Fink, J. Amer. Chem. Soc., 65 (1943) 1135.
23 R. West, L. Brough and W. Wojnowski, in D.F. Shriver (Ed.), Inorganic Synthesis, Vol. 19, Wiley, 1979, p. 265.
24 H.L. Finke, D.W. Scott, M.E. Gross, J.F. Messerly and G. Waddington, J. Amer. Chem. Soc., 78 (1956) 5469 and references listed therein.