tible to attack by hydroxyl ion. The silicon system should thus attain a reactivity corresponding to the carbon analog when it has a lesser degree of electronegative substitution in the Y positions.

When A is attacked by hydroxyl, that group of the four groups attached to A (3 Y's and one CX_3) which has the strongest attraction for electrons should be the one to dissociate. In an unsubstituted methyl siloxane, therefore, the dissociating group should be siloxy in preference to methyl. However, the resulting silanols may readily recondense under the reaction conditions. Silanol formation, however, will account for the extensive rearrangement of the siloxane system which is always observed to occur simultaneously with the cleavage reaction. Placing electronegative substituents in the X positions should increase the ratio of CX_3 dissociation to Y dissociation. Since the former is irreversible, it may appear as the only observable reaction.

In chloromethylsiloxanes, the relative selectivity of the cleavage reaction over C–Cl hydrolysis may also be interpreted as a result of the polarity of the C–Si bond, hydroxyl reacting more readily with the more positive center.

The ease of cleavage of the trimethylsilylmethyl group from mercury in the Kharasch criterion of electronegativity, found by Whitmore and Sommer,[7] can be explained on this basis; silicon, in the role of an electron source, making the carbon more negative, and hence more susceptible to electrophilic attack by hydrogen chloride.

Acknowledgments.—We are indebted to Mr. L. B. Bronk for the microelementary and chloride analyses and to Dr. L. V. McCarty for the Podbielniak distillation.

Summary

1. The chlorination of octamethylcyclotetrasiloxane and hexamethyldisiloxane is described.

2. The preparation and properties of heptamethylchloromethylcyclotetrasiloxane, dimethyldichloromethylsilanol and tetramethyl-1,3-bis-dichloromethyldisiloxane are reported.

3. The hydrolytic cleavage of methyl and chloromethyl groups attached to silicon by alkaline reagents has been demonstrated.

4. The hydrolytic cleavage is accompanied by rearrangement of siloxane linkages.

5. A mechanism for the alkali catalyzed hydrolytic cleavage is proposed.

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[7] Whitmore and Sommer, THIS JOURNAL, 68, 481 (1946).

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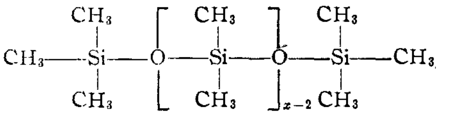
[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Equilibria between Linear and Cyclic Polymers in Methylpolysiloxanes

BY DONALD W. SCOTT[1]

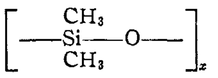
The equilibrium molecular size distributions in methylpolysiloxane systems have been studied by Wilcock.[2] He found that not only linear and branched species, but also cyclic species, were present in the "equilibrated" polymers, and that the molecular size distributions observed experimentally showed significant deviations from the theoretical distributions for systems consisting only of linear and branched species. In the present work, additional data were obtained for the molecular size distributions in equilibrium methylpolysiloxane systems containing monofunctional and difunctional units, and the theory of the molecular size distributions in these systems was extended to include cyclic as well as linear species.

The linear methylpolysiloxanes[3] have the general formula



$$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_{x-2}-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

and the cyclic methylpolysiloxanes[3,4] have the general formula



$$\left[-\overset{CH_3}{\underset{CH_3}{Si}}-O-\right]_x$$

where x is the number of silicon atoms in the molecule. For brevity, these compounds will be designated by $MD_{x-2}M$ and D_x, respectively, M denoting the monofunctional or chain terminating unit $(CH_3)_3SiO_{1/2}$ and D denoting the difunctional unit $(CH_3)_2SiO$.[5,6]

This paper reports the molecular size distributions found for two equilibrium methylpolysiloxane mixtures, the first prepared by equilibration without any diluent, in which case mostly linear compounds were present at equilibrium, and the second prepared by equilibration in dilute solution in an inert solvent (carbon tetrachloride), in which case the equilibrium was shifted more in favor of the cyclic compounds. The experimental methods were similar to those used by Wilcock.[2] Mixtures of appropriate composition were "equilibrated" with a suitable catalyst (sulfuric acid or

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[1] Present address: Petroleum Experiment Station, U. S. Bureau of Mines, Bartlesville, Okla.

[2] Wilcock, paper presented at the 110th meeting of the American Chemical Society, Chicago, Ill., Sept., 1946.

[3] Patnode and Wilcock, THIS JOURNAL, 68, 358 (1946).

[4] Hunter, Hyde, Warrick and Fletcher, *ibid.*, 68, 667 (1946).

[5] Hurd, *ibid.*, 68, 364 (1946).

[6] Wilcock, *ibid.*, 68, 691 (1946).

antimony pentachloride), the catalyst was washed out of each of them, and the mixtures were analyzed by fractional distillation.

Experimental

Equilibration without Diluent.—A mixture of 177 g. of hexamethyldisiloxane (MM), 323 g. of octamethylcyclotetrasiloxane (D_4), and 5 ml. of concentrated sulfuric acid was agitated at room temperature in a shaking machine for a period of twenty-one days. The approach to equilibrium was followed by periodically withdrawing small samples, extracting them with water to remove the acid, and determining their viscosity at 25.0°. The viscosity increased from 1.01 to 2.50 centipoises within the first five days and remained constant during the subsequent sixteen days. This constancy of viscosity was taken as satisfactory evidence that equilibrium had been attained. The "equilibrated" mixture was washed free of acid, dried with anhydrous sodium carbonate, and filtered. The material so obtained had a density, d^{25}_4, of 0.884 and a number average molecular weight, determined cryoscopically in cyclohexane, of 438 ± 20.

Equilibration in Carbon Tetrachloride Solution.—A homogeneous mixture of 177 g. of MM, 323 g. of D_4, 8040 g. of carbon tetrachloride, and 16 g. of antimony pentachloride was maintained at 25.0° for a period of twenty-three days. As before, the approach to equilibrium was followed by viscosity measurements. The viscosity at 25.0° increased from 0.904 to 0.932 centipoises within the first eight days and remained constant during the subsequent fifteen days. The "equilibrated" solution was washed with saturated sodium chloride solution to remove the antimony pentachloride, dried with anhydrous sodium carbonate, and filtered. Its density, d^{25}_4, was 1.512.

TABLE I

COMPOSITION OF EQUILIBRIUM METHYLPOLYSILOXANE MIXTURES

Without Diluent

Compd.	Weight per cent. Obs.	Weight per cent. Calcd.	Molar concentration Obs.	Molar concentration Calcd.
MM	6.5	7.6	0.354	0.415
MDM	8.7	8.7	.325	.325
MD_2M	9.7	9.0	.276	.255
MD_3M	10.0	8.7	.230	.200
MD_4M	8.3	8.2	.160	.157
MD_5M	7.8	7.4	.129	.123
MD_6M	6.6	6.6	.096	.097
D_4	3.1	3.6	.092	.107
D_5	$\sim$0.8^a	1.4	$\sim$ .019^a	.033
D_6	..^{b}	0.5	...^{b}	.011
D_7	..^{b}	0.2	...^{b}	.003
D_8	..^{b}	0.1	...^{b}	.001

$m = 3.85 \quad d = 7.70 \quad A = 0.6741 \quad p = 0.7845$

In CCl_4 Solution

Compd.	Weight per cent. Obs.	Weight per cent. Calcd.	Molar concentration Obs.	Molar concentration Calcd.
MM	(10.1)^c	11.3	(0.0551)^c	0.0618
MDM	11.7	11.2	.0438	.0420
MD_2M	10.5	10.0	.0299	.0286
MD_3M	9.0	8.4	.0207	.0194
MD_4M	6.5	6.8	.0125	.0133
MD_5M	5.5	5.4	.0091	.0090
MD_6M	4.3	4.2	.0063	.0061
D_4	21.3	20.2	.0639	.0602
D_5	7.2	6.9	.0172	.0164
D_6	$\sim$1.9^a	2.2	$\sim$ .0038^a	.0044
D_7	..^{b}	0.7	....^{b}	.0012
D_8	..^{b}	.2	....^{b}	.0003

$m = 0.386 \quad d = 0.772 \quad A = 0.1336 \quad p = 0.6800$

[a] No well-defined "flat" on the distillation curve—only a slight inflection. [b] Too little to detect—less than 1.0%. [c] Corrected for the loss which occurred when distilling off the carbon tetrachloride.

The methylpolysiloxane mixture was recovered from the solution by distilling the carbon tetrachloride solvent through a fractionating column. Under the conditions of the distillation, some of the lowest boiling methylpolysiloxane compound, MM, was carried over with the carbon tetrachloride. This loss of MM was estimated to have been 6.6% by weight of the methylpolysiloxane mixture,[7] and corrections to the data were made on this basis.

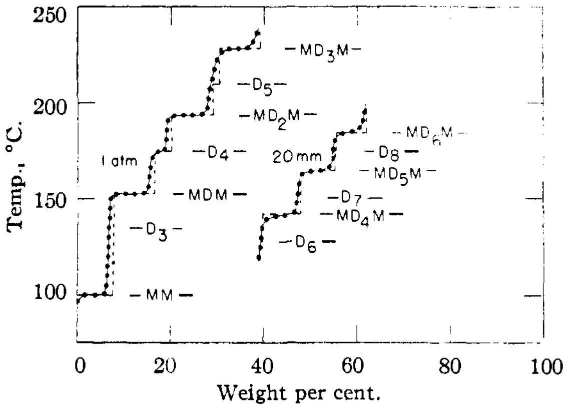

Fig. 1.—Distillation analysis of the methylpolysiloxane mixture equilibrated without diluent; -·-·-·-, distillation curve obtained experimentally; - - -, calculated ideal distillation curve. The boiling points of the various species are indicated.

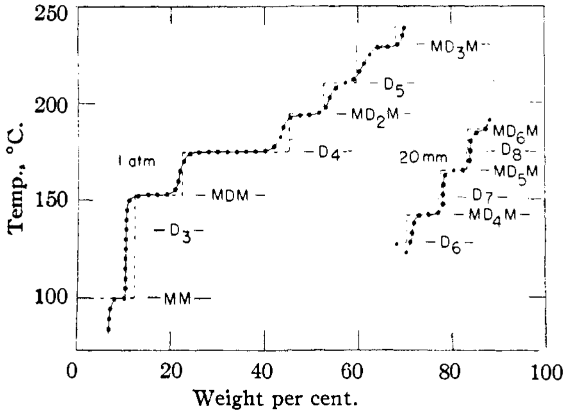

Fig. 2.—Distillation analysis of the methylpolysiloxane mixture equilibrated in carbon tetrachloride solution; -·-·-·-, distillation curve obtained experimentally, corrected for the loss of MM which occurred when distilling off the carbon tetrachloride; - - -, calculated ideal distillation curve. The boiling points of the various species are indicated.

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[7] To estimate the amount of MM carried over with the carbon tetrachloride, use was made of the equilibrium constants for reactions involving MM obtained from the data for the mixture equilibrated without diluent. The concentration of MM in the equilibrium solution in carbon tetrachloride was assumed to be that required by these equilibrium constants. Note that the entries of column 6, Table II, and any conclusions drawn from them, are independent of any assumptions regarding this loss of MM.

The recovered methylpolysiloxane mixture had a viscosity of 1.89 centipoises at 25.0° and a number average molecular weight, determined cryoscopically in cyclohexane, of 355 ± 15. When the appropriate correction is applied for the MM lost in distilling the carbon tetrachloride, the number average molecular weight of the methylpolysiloxane mixture in the equilibrium solution is computed to have been 329 ± 15.

Composition of the "Equilibrated" Mixtures.—The two methylpolysiloxane mixtures were analyzed by fractional distillation, using a 45 cm. × 10 mm. i. d. fractionating column packed with $^1/_8$" stainless steel helices. Compounds with boiling points below 240° were distilled at atmospheric pressure; those with higher boiling points at 20 mm. The distillation curves obtained are plotted in Figs. 1 and 2. Table I lists the amounts of the individual compounds in each of the two "equilibrated" mixtures, expressed in terms of weight per cent. of the total methylpolysiloxane mixture (column 2) and in terms of the molar concentration in the equilibrium solution (column 4).

Discussion

Equilibria Involving Linear Species.—Applying Flory's statistical mechanical treatment of heterogeneous polymer solutions[8] to the reactions involving linear methylpolysiloxanes

$$MD_{x-2}M + MD_{y-2}M = MD_{x+z-2}M + MD_{y-z-2}M \quad \text{(a)}$$

leads to the two conclusions: (a) that it is acceptable to use equilibrium constants in terms of molar concentration, and (b) that these equilibrium constants will be unity regardless of the values of x, y and z. Thus, if we let c_x denote the molar concentration of the linear compound containing x units per molecule

$$K = c_{x+z}c_{y-z}/c_xc_y = 1 \qquad (1)$$

Table II lists values of K calculated from the data of Table I for fifteen different reactions involving linear methylpolysiloxanes. All of these values of K are close to the theoretical value of 1.00, the maximum deviation being +0.32. Actually the statistical mechanical treatment on which equation (1) is based applies to the limiting case of long chain molecules and would not necessarily be expected to apply to the very smallest species of a polymer series. However, the data show that this equation is a very satisfactory approximation for the equilibria involving the short linear methylpolysiloxanes considered here.

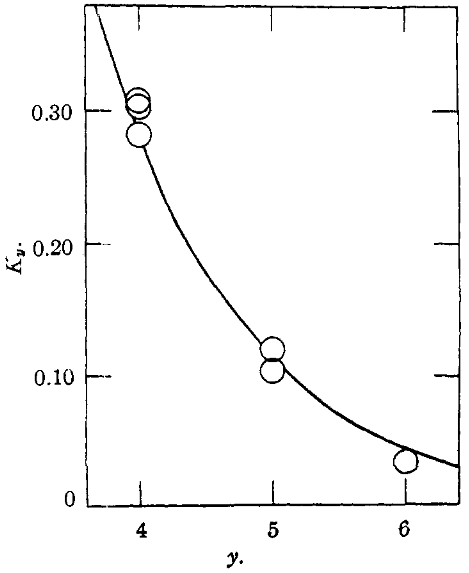

Fig. 3.—K_y as a function of y; ○, experimental values; the curve is a plot of equation (3b).

TABLE II

EQUILIBRIUM CONSTANTS FOR REACTIONS OF THE TYPE $MD_{x-2}M + MD_{y-2}M = MD_{x+z-2}M + MD_{y-z-2}M$

				K	
x	y	$x+z$	$y-z$	Without diluent	In CCl₄ soln.
2	4	3	3	1.08	See footnote (7)
2	5	3	4	1.10	
2	6	3	5	1.32	
2	7	3	6	1.14	
2	8	3	7	1.23	
3	5	4	4	1.02	0.99
3	6	4	5	1.22	1.13
3	7	4	6	1.05	0.94
3	8	4	7	1.14	0.99
4	6	5	5	1.20	1.15
4	7	5	6	1.03	0.95
4	8	5	7	1.12	1.00
5	7	6	6	0.86	0.83
5	8	6	7	0.93	0.87
6	8	7	7	1.08	1.05

Equilibria Involving Both Cyclic and Linear Species.—Reversible reactions of the type

$$MD_{x+y-2}M = D_y + MD_{x-2}M \qquad \text{(b)}$$

will now be considered. It will be assumed that for such reactions it is also acceptable to use equilibrium constants in terms of molar concentrations. Equation (1) requires that such equilibrium constants be functions only of y, the number of units in the cyclic molecule. Letting r_y denote the molar concentration of the cyclic species containing y units per molecule, such an equilibrium constant, K_y, is given by

$$K_y = r_yc_x/c_{x+y} \qquad (2)$$

No cyclic methylpolysiloxanes having fewer than four units per molecule were found in either of the two equilibrium mixtures. Therefore, to a sufficiently good approximation

$$K_y = 0 \quad y < 4 \qquad \text{(3a)}$$

The data of Table I for the mixture equilibrated in carbon tetrachloride solution yield values of K_y for values of y of 4, 5 and 6. These are plotted in Fig. 3, which shows that the data fit the equation

$$K_y = (11.0)(0.40)^y \quad y \geqslant 4 \qquad \text{(3b)}$$

Values of K_y obtained from the data for the mixture equilibrated without diluent have larger experimental uncertainties; however, they agree with equation (3b) within the limits of these larger uncertainties. The molecular size distributions of the two equilibrium mixtures are con-

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[8] Flory, *J. Chem. Phys.*, **12**, 425 (1944).

sistent with the assumption that equation (3b) is also valid for all values of y greater than 6. It may be well to emphasize here that equation (3b) is entirely empirical and is based only on the data for this particular polymer system. Actually, as subsequent discussion will show, an equation of this form would *not* be expected to hold for the equivalent equilibria in many other polymer systems. Consequently equations of the form of (3b) [and (5b) and (7b), which are derived from it] should not be applied to other polymer systems unless supported by adequate equilibrium data.

Equilibrium Molecular Size Distribution.—Equation (1) is satisfied by the relation

$$c_x = Ap^x \qquad (4)$$

where A and p are constants for a given equilibrium methylpolysiloxane mixture. Substituting (3) and (4) in (2) leads to

$$r_y = 0 \quad y < 4 \qquad (5a)$$

$$r_y = (11.0)(0.40\,p)^y \quad y \geqslant 4 \qquad (5b)$$

Since there are two M-units in each linear methylpolysiloxane molecule, the total molar concentration of M-units, m, is given by

$$m = \sum_{x=2}^{\infty} 2c_x \qquad (6a)$$

Similarly, the total molar concentration of D-units, d, is obtained by summing over all species, both linear and cyclic

$$d = \sum_{x=2}^{\infty} (x-2)c_x + \sum_{y=4}^{\infty} y\,r_y \qquad (6b)$$

Substituting (4) in (6a), and (4) and (5b) in (6b), evaluating the resulting summations, and simplifying yields

$$m = 2Ap^2/(1-p) \qquad (7a)$$

$$d = \frac{Ap^3}{(1-p)^2} + \frac{(44.0)(0.40\,p)^4 - (33.0)(0.40\,p)^5}{(1-0.40\,p)^2} \qquad (7b)$$

For given concentrations of M and D units, the values of A and p are obtained by simultaneous solution of (7a) and (7b). Substituting these in (4) and (5b) yields values of the concentrations of the individual species, both linear and cyclic.

The concentrations of the individual species, calculated in this manner for each of the two equilibrium methylpolysiloxane mixtures investigated, are listed in Table I, column 5, for comparison with the experimentally observed values. The corresponding calculated weight percentages are given in column 3. In Figs. 1 and 2, the calculated ideal distillation curves are compared with those obtained experimentally. Figure 4 shows that the logarithm of the molar concentration for both linear and cyclic species is a linear function of the number of units in the molecule, as required by equations (4) and (5b). These various comparisons show that the scheme outlined above gives a satisfactory representation of the equilibrium molecular size distribution for a methylpolysiloxane system.

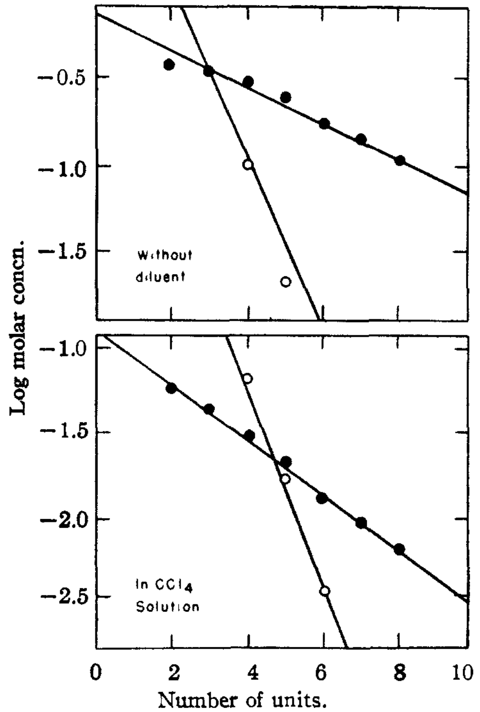

Fig. 4.—Logarithm of the molar concentration *vs.* the number of units in the molecule for methylpolysiloxane compounds in the two equilibrium mixtures: ●, linear compounds; ○, cyclic compounds: —, plots of equations (4) and (5b).

Average Degree of Polymerization.—The number average degree of polymerization of an equilibrium methylpolysiloxane mixture is given by

$$\overline{\mathrm{DP}}_{\mathrm{n}} = \frac{\sum_{x=2}^{\infty} xc_x + \sum_{y=4}^{\infty} yr_y}{\sum_{x=2}^{\infty} c_x + \sum_{y=4}^{\infty} r_y} = \frac{\frac{A(2p^2 - p^3)}{(1-p)^2} + \frac{(44.0)(0.40p)^4 - (33.0)(0.40p)^5}{(1-0.40p)^2}}{\frac{Ap^2}{1-p} + \frac{(11.0)(0.40p)^4}{1-0.40p}} \qquad (8)$$

The values of $\overline{\mathrm{DP}}_{\mathrm{n}}$ calculated from the cryoscopically determined molecular weights of the two equilibrium methylpolysiloxane mixtures are 5.7 ± 0.3 and 4.3 ± 0.2, in excellent agreement with the values predicted by equation (8), namely, 5.6 and 4.2.

Steric Aspects of Cyclic Methylpolysiloxanes.—The absence of any detectable amount of D_3 in the equilibrium methylpolysiloxane mixtures can be attributed to ring-strain in this compound. Sauer[9] and Mead find from dipole moment data that the normal silicon–oxygen–silicon angle in methylpolysiloxanes is 160 ± 15°; the normal oxygen–silicon–oxygen angle must be close to tetrahedral (109°28′). Formation of the D_3 ring requires that these angles be distorted

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[9] Sauer and Mead, THIS JOURNAL, 68, 1794 (1946).

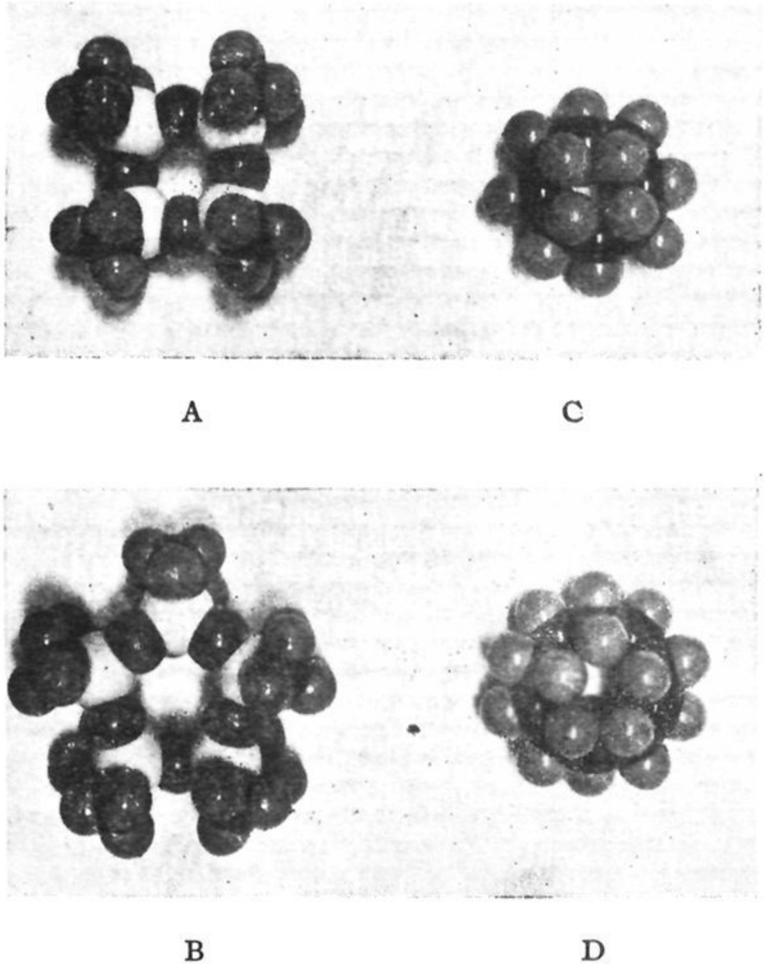

Fig. 5.—Models of the Fisher–Hirschfelder type, illustrating that the peripheral methyl groups of cyclic methylpolysiloxanes do not occupy positions of close proximity, as do the peripheral hydrogen atoms in cyclic hydrocarbons with the same number of atoms in the ring: A, $[(CH_3)_2SiO]_4$; B, $[(CH_3)_2SiO]_5$; C, cyclooöctane: D, cyclodecane. A value of 160° was assumed for the silicon-oxygen-silicon angle.

considerably from their normal values. The planarity of the ring in D_3, as indicated by the X-ray data of Frevel and Hunter,[10] is further evidence of ring strain in this compound.[4]

Strain arising from bond angles having less than their normal values occurs only in small rings. A second type of strain may be present in larger rings. This occurs if the rings must pucker in order to preserve the normal bond angles, and peripheral atoms or groups are forced toward the center of the ring where they are crowded against each other. Strain of this sort is present in cyclic hydrocarbons, esters, anhydrides, and ketones having from seven to about fifteen or twenty atoms in the ring.[11] Since the magnitude of this strain will in general vary in an irregular manner from member to member of a cyclic homologous series, no regularity in the thermodynamic properties of the members of such a series is to be expected when such strain is present. However, it is observed that the equilibrium constants for reactions of the type

$$MD_{x+y-2}M = D_y + MD_{x-2}M$$

involving D_4, D_5 and D_6 (and presumably also the higher members of this series) vary in a regular manner with the number of units in the ring. This would indicate that the cyclic methylpolysiloxanes with eight or more atoms in the ring are strain free.

That these cyclic methylpolysiloxanes are strain free, while compounds having similar sized rings of carbon and oxygen atoms are not, seems reasonable upon consideration of the steric factors involved. The normal silicon–oxygen–silicon angle of approximately 160° requires a siloxane ring to pucker less than a ring of carbon and oxygen atoms in which the normal angles are all close to tetrahedral. Furthermore, only alternate atoms in the siloxane ring carry attached methyl groups. These factors allow the peripheral methyl groups to remain sufficiently far apart that they do not interfere with one another and introduce strain into the molecule. The molecular models shown in Fig. 5 illustrate these steric relationships.

Summary

1. Data are reported for the equilibrium molecular size distributions in two methylpolysiloxane mixtures, one equilibrated without diluent and the other equilibrated in carbon tetrachloride solution.

2. The equilibrium constants found for the reactions involving linear species are in agreement with the predictions of current theories of polymer equilibria.

3. The equilibrium constants for a series of reactions involving cyclic species with four or more units per molecule vary in a regular manner with the number of units in the cyclic molecule. This is interpreted to indicate that these cyclic methylpolysiloxanes are strain-free.

4. Equations are given for calculating the molecular size distribution and number average degree of polymerization for equilibrium methylpolysiloxane mixtures containing both linear and cyclic species.

SCHENECTADY, NEW YORK RECEIVED JULY 3, 1946

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[10] Frevel and Hunter, *ibid.*, **67**, 2275 (1945).

[11] (a) Stoll and Stoll-Compte, *Helv. Chim. Acta*, **13**, 1185 (1930); (b) Carothers and Hill, THIS JOURNAL, **55**, 5043 (1933); (c) Spanagel and Carothers, *ibid.*, **57**, 929 (1935).