3,3,3-TRIFLUOROPROPYL(METHYL)CYCLOSILOXANES

II. The Rearrangement of 3,3,3-Trifluoropropyl(methyl)dimethylcyclotetrasiloxanes in Solution*

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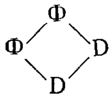
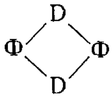
The influence of the number of 3,3,3-trifluoropropyl(methyl)siloxane links (Φ/Φ) in the cyclotetrasiloxanes $\Phi_m D_{4-m}$, where D represents the dimethylsiloxane link and m = 0-4, on the rearrangement of these compounds in acetone solution under the action of sodium siloxanolate has been studied. The rearrangement takes place with the formation of a linear polysiloxane the degradation of which yields, in addition to the initial ring, cyclosiloxanes with a different structure. The rate of rearrangement of $\Phi_m D_{4-m}$ and of the formation of a linear polysiloxane rises with an increase in m from 0 to 3. The equilibrium concentration of the linear polysiloxane formed from $\Phi_m D_{4-m}$ is inversely proportional to m. Results have been obtained on the kinetics of the formation of the cyclosiloxanes $\Phi_m D_n$, where m = 0–5, n = 0–5, and m + n = 3–6, in the rearrangement of the rings ΦD_3, $\Phi_2 D_2$, $\Phi_3 D$, and Φ_4. The reactivity of the siloxane links rises in the sequence $\sim (CH_3)_2Si{-}O{-}Si(CH_3)_2 \sim\ <\ \sim (CF_3CH_2CH_2)(CH_3)Si{-}O{-}Si(CH_3)_2 \sim\ <\ (CF_3CH_2CH_2)(CH_3)Si{-}O{-}Si(CH_3)(CH_2CH_2CF_3) \sim$. Because of the negative inductive effect transferred through the siloxane links, the 3,3,3-trifluoropropyl groups strongly activate the siloxane ring with respect to nucleophilic reagents.

Two of us have previously shown [1] that the cleavage of the siloxane bond in the disiloxanes, $[(CF_3CH_2CH_2)_n(CH_3)_{3-n}Si]_2O$, where n = 0–3, by nucleophilic reagents takes place the more readily the larger n; hexamethyldisiloxane (n = 0) being cleaved to only a small extent. In order to study the influence of 3,3,3-trifluoropropyl groups on compounds containing several siloxane bonds, it is convenient to use cyclosiloxanes containing both 3,3,3-trifluoropropyl(methyl)siloxane (Φ) and dimethylsiloxane (D) links. A method was developed previously for the chromatographic analysis of mixtures of the cyclosiloxanes $\Phi_m D_n$ (where m = 0–5, n = 0–5, and m + + n = 3–6) containing up to 18 components [2,3]. It has also been established [4] that under the action of bases both cyclic and linear trifluoropropyl(methyl)polysiloxanes dissolved in acetone undergo a rearrangement at room temperature giving an equilibrium mixture of cyclosiloxanes consisting mainly of 1,3,5,7-tetra(3',3',3'-trifluoropropyl)-1,3,5,7-tetramethylcyclotetrasiloxane (Φ_4) and 1,3,5,7-9-penta-(3',3',3'-trifluoropropyl)-1,3,5,7,9-pentamethylcyclopentasiloxane (Φ_5).

In the present work we studied the rearrangement of the cyclopentasiloxanes $\Phi_m D_{4-m}$, where m = 0–4, in acetone solution under the action of sodium siloxanolate at room temperature.

The cyclosiloxanes ΦD_3, $\Phi_2 D_2$, $\Phi_3 D$, and Φ_4 have been isolated and characterized previously. $\Phi_2 D_2$ apparently consists of a mixture of isomers with different arrangements of the links in the ring:


(I) and

(II). However, it was impossible to detect their presence chromatographically or by other methods.

The rearrangement of the cyclosiloxanes in solution takes place with the formation of linear polysiloxanes, the degradation of which partially regenerates the initial cyclosiloxane and also gives cyclosiloxanes with a different structure.

The kinetics of the rearrangement of the cyclosiloxanes $\Phi_m D_{4-m}$ and the formation of the corresponding linear polysiloxanes is illustrated in Fig. 1. The rearrangement of D_4 (curve 1) takes place very slowly under the action of sodium siloxanolate, which shows the relative resistance to nucleophilic attack of the D—D bond in this ring. When one dimethylsiloxane link is replaced by a 3,3,3-trifluoropropyl(methyl)siloxane link, i.e. on passing to ΦD_3 (curve 2), the rate of rearrangement in the initial period increases by a factor of approximately 18. Replacement of the following link ($\Phi_2 D_2$, curve 3) causes a further acceleration of the rearrangement by a factor of about 6, and the introduction of a third Φ group ($\Phi_3 D$, curve 4) a further increase by a factor of 2. Somewhat unexpected, at first sight, is the decrease in the rate of rearrangement on passing from $\Phi_3 D$ to Φ_4 (curve 5). However, one must take into consideration the fact that in the rearrangement of the cycles ΦD_3, $\Phi_2 D_2$, and $\Phi_3 D$ a large amount of other mixed cycles is formed and in the equilibrium mixtures (see table) the initial cyclosiloxanes are present in small amounts (14–19%), while only the cycles Φ_m (m = 3,5,6) are formed from Φ_4, and these, in their turn, give Φ_4 on rearrangement so that the amount of it in the equilibrium mixture is high (~55%). Since the cycles Φ_m undergo rearrangement rapidly, the "secondary" Φ_4 accumulates considerably faster than the "secondary" ΦD_3, $\Phi_2 D_2$, and $\Phi_3 D$, the probability of the formation of which from the linear copolymers is consequently lower than the probability of the formation of Φ_4 from the homopolymer Φ_p.

The rate of formation of a linear polysiloxane (Fig. 1, curves 1'–5') and the time it takes to reach its maximum concentration in the reaction mixture also depend on the number of Φ links in $\Phi_m D_{4-m}$. On passing from D_4 to ΦD_3, the initial rate of formation of the linear polymer rises approximately 17-fold, on passing from ΦD_3 to $\Phi_2 D_2$ approximately 5-fold, and on passing from

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*For part I, see [3].

Φ_2D_2 to Φ_3D approximately 1.6-fold. The maximum concentration of polymer is reached the more rapidly the greater the number of Φ links in the initial Φ_mD_{4-m}. In the rearrangement of Φ_4, the equilibrium concentration of the polymer is low and, apparently, is reached very rapidly since it remains practically constant (less than 1%) from the first minute up to the moment of achievement of equilibrium between the cycles, Φ_m.

The equilibrium concentration of linear polysiloxane is thus inversely proportional to the number of Φ links in Φ_mD_{4-m} (Fig. 2). Consequently, as dimethylsiloxane links are replaced by 3,3,3-trifluoropropyl(methyl)-siloxane links, the cyclic configuration of the siloxane becomes thermodynamically more favorable. This is also confirmed by literature data on the composition of the equilibrium systems obtained by the block polymerization of the cycles D_4 and Φ_3 [7,8].

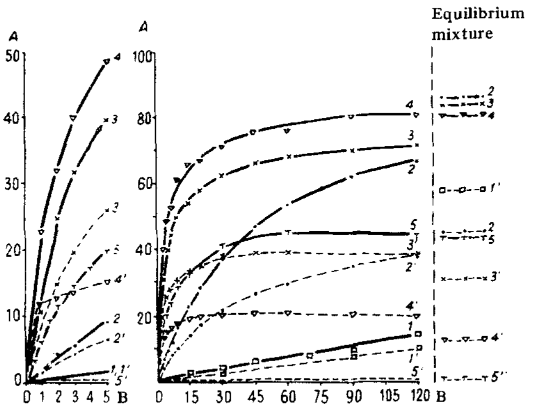
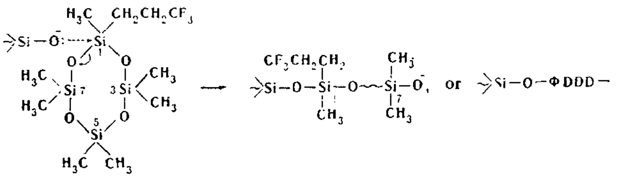


Fig. 1. Kinetics of the rearrangement of cyclotetrasiloxanes Φ_mD_{4-m}: a) Degree of conversion of the cyclosiloxane, % (full lines) or content of linear polysiloxane, wt. % (broken lines, numbers with dashes); b) time, min: 1,1'–D_4; 2,2'–ΦD_3; 3,3'–Φ_2D_2; 4,4'–Φ_3D; 5,5'–Φ_4.

It was stated above that on passing from D_4 to ΦD_3 the rearrangement accelerates approximately 18-fold. The cause of this may be a marked difference in the reactivity of the D—D and Φ—D bonds. Let us, however, consider the rearrangement of ΦD_3 in somewhat more detail. The linear tetrasiloxane formed as a result of an attack by the active center of the ~ > Si—O—Si < ~ bond in the cyclotetrasiloxane enters the growing polymer chain in the form of a whole fragment. This has been shown experimentally [9] for the cationic polymerization of D_4. In ΦD_3, the silicon atom attached to the trifluoropropyl group is the most electropositive. Consequently, in the attack of an anion on the Φ—D bond the appearance of the following linear fragment may be expected.



(1)

If the main attack in ΦD_3 is on a Φ—D bond, the polymer formed must have the structure

$$\sim>Si—O—\Phi DDD—\Phi DDD—\Phi DDD— \\ —\Phi DDD—\Phi DDD—\Phi DDD—.$$

The destruction of such a polymer predominantly at the Φ—D bonds must lead to the formation of Φ_2D_3, D_3, and the initial ΦD_3. In actual fact, in the rearrangement of ΦD_3 (Fig. 3), even in the first few minutes ΦD_4 and Φ_2D_2 are formed, besides Φ_2D_3, which shows the true structure of the polymer and the fact that the participation of the D—D bonds in the rearrangement is more active than was assumed. Evidently, the trifluoropropyl group activates with respect to nucleophilic reagents not only the siloxane bonds of "its own" silicon atom but also the ring as a whole. The reason for this may be the transfer of the inductive influence of the trifluoropropyl group through siloxane bonds from the Si_1 atom to the Si_3 and Si_7 atoms and, moreover, to the Si_5 atom. As a result, the D—D bonds in ΦD_3 become more reactive than those in D_4.

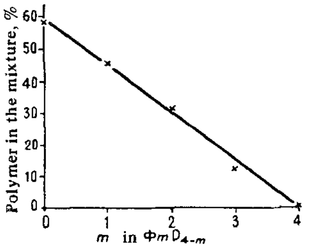


Fig. 2. Content of linear polysiloxanes in equilibrium mixtures.

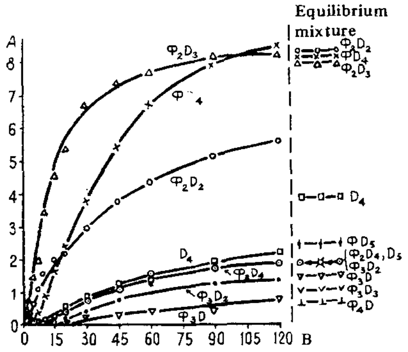


Fig. 3. Kinetics of the formation of cyclosiloxanes Φ_mD_n in the rearrangement of ΦD_3: A) content of cyclosiloxanes, wt. %; B) time, min.

In an attack by an anion on the D—D bonds in ΦD_3, the most probable points of attack are the Si_3 and Si_7 atoms, and in an attack on the Φ—D bonds the Si atom. The structure of the polymer formed in this case is

$$\sim>Si—O—\Phi DDD—D\Phi DD—\Phi DDD—DDD\Phi—D\Phi DD— \\ —D\Phi DD—DDD\Phi—\Phi DDD—.$$

The possibility of the formation of the cycles ΦD_4, Φ_2D_2, Φ_2D_3, and also D_4 and Φ_2D_4 in the degradation of such a polymer is obvious. So far as concerns Φ_3D and Φ_3D_2, which appear only at the 20th minute (see Fig. 3), their formation can be explained by the participation in polymerization of the cycles Φ_2D_3 and Φ_2D_2 accumulating in the system.

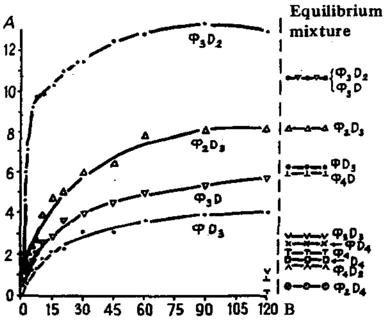


Fig. 4. Kinetics of the formation of the cyclosiloxanes Φ_mD_n in the rearrangement of Φ_2D_2: A) content of cyclosiloxane, wt. %; B) time, min.

In the rearrangement of Φ_2D_2, the isomer I may, in a similar manner to that described above, give the following fragments of polymer chain: ΦDDΦ, ΦΦDD, and (less probably) DΦΦD. Isomer II can give only ΦDΦD. The polymer formed from a mixture of isomers I and II must have the structure

$$\sim\!>\!Si{-}O{-}\Phi DD\Phi{-}\Phi DD\Phi{-}\Phi\Phi DD{-}\Phi\Phi DD{-}$$
$${-}D\Phi\Phi D{-}\Phi DD\Phi{-}\Phi D\Phi D{-}\Phi D\Phi D{-}.$$

This structure of the polymer satisfactorily explains the formation of Φ_3D_2, Φ_2D_3, Φ_3D, and ΦD_3 observed experimentally (Fig. 4). The Φ_4 and Φ_3D_3 appeared considerably later and are evidently the products of secondary reactions. The more rapid accumulation of Φ_3D_2 than of the other cycles is a convincing proof of the fact that the decomposition of the polymer at the Φ—Φ bonds takes place more readily than at the Φ—D bonds.

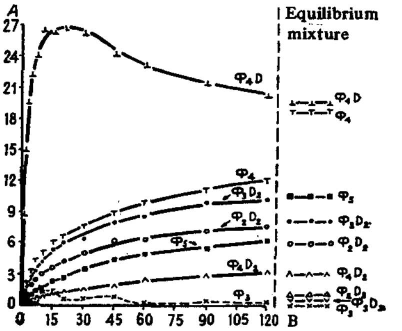


Fig. 5. Kinetics of the formation of the cyclosiloxanes Φ_mD_n in the rearrangement of Φ_3D: A) content of cyclosiloxane, wt. %; B) time, min.

The polymer formed in the rearrangement of Φ_3D must have the structure

$$\sim\!>\!Si{-}O{-}\Phi\Phi D\Phi{-}\Phi\Phi D\Phi{-}\Phi D\Phi\Phi{-}\Phi D\Phi\Phi{-}$$
$${-}\Phi\Phi D\Phi{-}\Phi D\Phi\Phi{-}\Phi\Phi\Phi D{-}\Phi\Phi D\Phi{-}.$$

The rapid accumulation of Φ_4D and the formation of Φ_4, Φ_3D_2, Φ_2D_2, Φ_5, and Φ_4D_2 observed experimentally (Fig. 5) agree well with this structure for the polymer. In the rearrangement of Φ_3D, the products were also found to contain varying amounts of Φ_3 (from traces to 1.5%) and Φ_2D (from traces to 0.9%). In rearrangements of ΦD_3 and Φ_2D_2, small amounts (about 0.2–0.5%) of D_3, ΦD_2 and Φ_2D were found. The low content of cyclotrisiloxanes in these systems, which varies during the rearrangement, is due to the thermodynamically unfavorable formation of strained six-membered siloxane rings and their faster polymerization as compared with the cyclotetrasiloxanes. This is also confirmed by the practically complete absence of cyclotrisiloxanes in the equilibrium mixtures (see table). The upper limits of the variable concentrations of cyclotrisiloxanes are the greatest in the rearrangement of Φ_3D. It is obvious that in this case there is the possibility of the formation of Φ_3 and Φ_2D as a result of the splitting of only the Φ—Φ bonds, which are the most reactive.

In the rearrangement of Φ_4, the concentration of cyclosiloxanes Φ_m (m = 3,5,6) approaches the equilibrium concentration comparatively rapidly (Fig. 6).

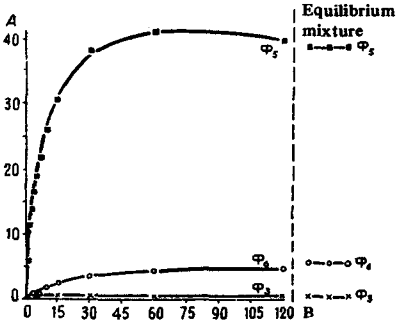
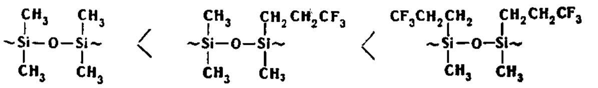


Fig. 6. Kinetics of the formation of cyclosiloxanes Φ_m in the rearrangement of Φ_4: A) content of cyclosiloxane, wt. %; B) time, min.

Data on the composition of the equilibrium mixture (see table) agree satisfactorily with the results obtained previously [4].

The increase in the rate of rearrangement of Φ_mD_{4-m} and the rate of formation of the corresponding linear polymer in the sequence $D_4 < \Phi D_3 < \Phi_2D_2 > > \Phi_3D$ and also the other data given above show that in reaction with nucleophilic agents the reactivity of the siloxane links rises in the sequence



$$\sim\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}\sim \;<\; \sim\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_2CH_2CF_3}{Si}}\sim \;<\; \sim\underset{CH_3}{\overset{CF_3CH_2CH_2}{Si}}-O-\underset{CH_3}{\overset{CH_2CH_2CF_3}{Si}}\sim$$

This increase in reactivity is evidently explained by the negative inductive effect of the trifluoropropyl group. The causes of the fall in the equilibrium concentration of polymer with an increase in m in Φ_mD_{4-m} are less clear. It is possible that it is connected with the steric influence of the trifluoropropyl groups. The study of this question is continuing.

Composition of the Equilibrium Mixtures Obtained by the Rearrangement of the Cyclotetrasiloxanes Φ_mD_{4-m}

Initial cyclosiloxane	Equilibrium concentration, wt.%																		
	D_4	D_5	ΦD_2	ΦD_3	ΦD_4	Φ_2D·	Φ_2D_2	Φ_2D_3	Φ_2D_4	Φ_3	Φ_3D	Φ_3D_2	Φ_3D_3	Φ_4	Φ_4D	Φ_4D_2	Φ_5	Φ_6	polymer
ΦD_3*	4.9	1.9	—	13.8	8.2	—	8.3	8.0	1.9	—	1.5	1.9	1.1	—	0.7	—	—	—	45.3
Φ_2D_2	1.8	—	—	6.3	2.6	—	14.9	8.3	0.5	—	10.7	10.7	2.9	2.2	6.1	1.6	—	—	31.4
Φ_3D	—	—	0.2	—	—	0.4	6.0	1.0	—	0.3	18.7	8.2	0.7	18.5	19.6	3.0	10.6	—	12.8
Φ_4	—	—	—	—	—	—	—	—	—	0.2	—	—	—	55.4	—	—	38.7	5.7	<1.0

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*2.5% of an unknown substance which judging from the residence time, is Φ D_5 was also detected in the mixture.

EXPERIMENTAL

The work was carried out with the cyclosiloxanes $\Phi_m D_{4-m}$ obtained as described previously [3, 5, 6]. A solution of a cyclotetrasiloxane in anhydrous acetone was placed in a conical flask, with a magnetic stirrer, previously filled with argon. Then a solution of sodium 3, 3, 3-trifluoropropyl(methyl)siloxanediolate in anhydrous acetone was added to the flask. In all experiments, the concentration of cyclosiloxane was 0.835 mole/*l* and the concentration of catalyst $(2.78 \pm 0.01) \cdot 10^{-4}$N, and the temperature of the experiments was 22.5 ± 0.5° C. A stopwatch and the magnetic stirrer were switched on at the moment of introduction of the catalyst. The addition of the catalyst and the taking of samples were carried out under conditions excluding the access of moisture and CO_2. The samples taken after predetermined intervals of time were neutralized with acetic acid (3 moles per g-equiv. of catalyst). After 120 min, the catalyst was added to the reaction mixture to a concentration of $(4-5) \cdot 10^{-3}$ N and 22 hr after this a sample was taken; then catalyst was added to a concentration of $(14-16) \cdot 10^{-3}$ N. 72 hr after the beginning of the experiment the contents of the flask were neutralized with acetic acid. The acetone was distilled off from all the neutralized mixtures at 90° C. From the results of chromatography, the acetone distilled off contained no cyclosiloxanes.

The weighed residues were chromatographed and separated by heating in vacuum (up to 200° C at 1–2 mm) into a cyclic fraction (distillate) and a polymer fraction, which were also weighed and chromatographed (the polymer fraction qualitatively). To calculate the amount of polymer in the mixture before the vacuum distillations of the cyclosiloxanes, chromatographic data on the content in the mixture and in the distillate of one of the cyclosiloxanes (C) absent from the polymer fraction and present in the distillate in maximum amount were used. The calculation was performed using the formula $P = 100 - B(n_2/n_1)$, where P is the content of polymer in %, B is the amount of distillate in %, n_1 is the proportion of cyclosiloxane C in % of the total cycles in the mixture before distillation, and n_2 is the content of cyclosiloxane C in the distillate in %.

Twenty-two hours after the addition of the first amount of catalyst the reaction mixture had reached equilibrium in all cases except for D_4, since the second addition of catalyst and keeping the mixture for 48 hr caused no change in its composition. For the mixture obtained from Φ_2D_2, this was also confirmed by the addition of a more effective catalyst, potassium dimethylsiloxanediolate ($4.1 \cdot 10^{-3}$ g-equiv./*l*), and keeping the mixture for 24 hr. Under these conditions the composition of the mixture was the same as that obtained with the sodium siloxanolate. Since the rearrangement of D_4 in the presence of the sodium siloxanolate takes place very slowly, in this case the equilibrium mixture was obtained by the action of potassium dimethylsiloxanediolate ($7.3 \cdot 10^{-3}$ g-equiv./*l*) for 24 hr. Under these conditions, only 10 min after the addition of the catalyst the deposition of polymer from the solution was observed. The mixture was treated as described above. After vacuum distillation, the polymer contained no cyclosiloxanes. The composition of the distillate was not determined.

All the chromatographic analyses were carried out on a UKh-1 chromatograph with a katharometer as detector and helium as the carrier gas. For the analysis of the mixtures obtained by the rearrangement of D_4, ΦD_3, Φ_2D_2, and Φ_3D, SKTFT-50 rubber on Celite-545 was used as the stationary phase. The products of the rearrangement of Φ_4 were analyzed on a F column attached to the chromatograph, with siloxane oil on Inza brick as the stationary phase.

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