1-HYDRO-3-VINYLHEXAMETHYLCYCLOTETRASILOXANE AND ITS POLYMERIZATION

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1, 3-Dimethyl-3-vinyl-1, 3-dichlorosiloxane is prepared by partial cohydrolysis of methylvinyldichlorosilane and methyldichlorosilane, and its cohydrolysis with sym-tetra-methyldichlorodisiloxane gives 1-hydro-3-vinylhexamethyl-cyclotetrasiloxane. A study is made of the kinetics of the polymerization of the latter in CCl_4 in the presence of $H_2PtCl_6 \cdot 6H_2O$

It was of interest to us to prepare an organocyclotetrasiloxane, 1-hydro-3-vinylhexamethylcyclotetrasiloxane (I), with one $Si—CH = CH_2$ group and one Si—H—group in definite positions. We have synthesized this compound by cohydrolyzing sym-tetramethyldichlorosiloxane (II) with 1,3-dimethyl-3-vinyl-1,2-dichlorodisiloxane (III).

Up to the present the following have been the main methods of preparing linear sym-dichlorosiloxanes: partial hydrolysis of organodichlorosilanes [1,2], the action of oxygen-containing reactants on the appropriate alkylchlorosilanes [3,4], or heterofunctional condensation [5].

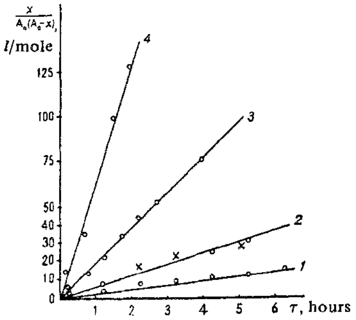
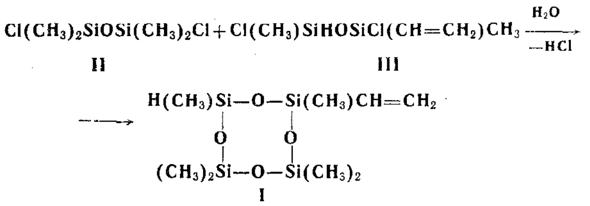


Fig. 1. Variation of $x/A_0(A_0-x)$ (A_0—initial concentration of starting material I, x—decrease in concentration in time τ) with reaction time at temperature t° C. 1) t = 50°, catalyst concentration $C = 1.4 \cdot 10^{-4}$ mole/l. 2) t = 65°, $C = 1.4 \cdot 10^{-4}$ mole/l. 3) t = 50° C, $C = 4.2 \cdot 10^{-4}$ mole/l. 4) t = 75°, $C = 4.2 \cdot 10^{-4}$ mole/l. x) Points obtained by determing the Si—H group content by treatment with ethanolic KOH.

Attempts to prepare III by heterofunctional condensation of methylvinylethoxychlorosilane with methyldichlorosilane gave a yield of only 11.7%. Reaction of methylvinyldichlorosilane and methyldichlorosilane with ferric oxide gave an even lower yield of III, 1.5%. Partial cohydrolysis of methylvinyldichlorosilane and methyldichlorosilane gave a 14.1% yield of III.

Cohydrolysis of II and III gave a 67.4% yield of I:



Polymerization of I in CCl_4 at 75° in the presence of $H_2PtCl_6 \cdot 6H_2O$ gives a polymer IV which is viscous at room temperature, and readily soluble in benzene and other organic solvents.

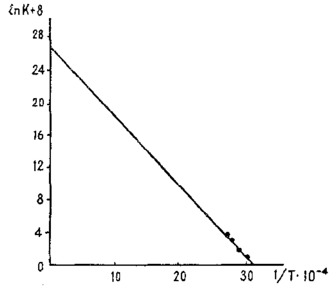


Fig. 2. Reaction rate constants for the polymerization of I (second order) as a function of 1/T (T—temperature, °K).

The PMR spectrum of IV (at 60 Mcps) gives along with the $SiCh_3$ peak, an unsplit peak characteristic of the $Si—CH_2$ group with a chemical shift (relative to the $SiCH_3$ group of IV) S = 0.35 ppm. The IR spectrum of IV lacks the 1370–1380 cm^{-1} absorption band characteristic of the $\underset{\mathrm{CH_3}}{\overset{—\mathrm{CH}—}{|}}$ group.

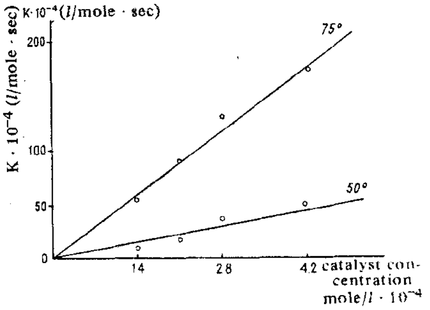


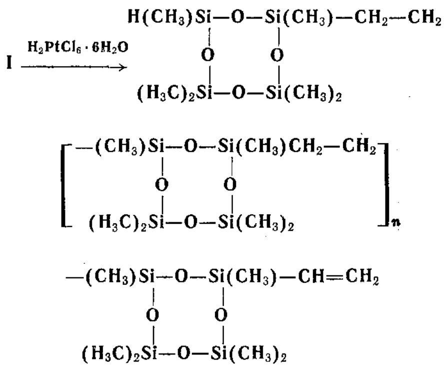
Fig. 3. Reaction rate constants for the polymerization of I at 50° and 75° as a function of catalyst concentration.

IV was first freed from monomer by vacuum heating 1 mm 75°, and its molecular weight then found ebullioscopically in benzene to be 2260.

Rate constants for polymerization of I(K)

Catalyst concentration (mole/*l*) × 10^{-4}	$K \cdot 10^{-3}$			
	50°	65°	75°	85°
1.4	0.675	1.72	5.7	7.8
2.1	1.76		9.45	
2.8	3.59		13.75	
4.2	5.38		13.87	

The experimental results show the polymerization of I to proceed without ring scission according to the equation



During operations with IV and in the above polymerization it was not found to undergo crosslinking.

The polymerization reaction kinetics for I were investigated by measuring the content of the → Si—H group during polymerization at different temperatures and for different concentrations of catalyst. The determinations were made spectroscopically, by finding the integrated absorption band intensity for ν(Si—H), when reproducible results were obtained. In addition (straight line 2, in Fig. 1), the content of the → Si—H group was also determined chemically, from the volume of hydrogen liberated on treatment with ethanolic KOH. The reaction rate constants found by the previously described method [6] (Fig. 1), are satisfactorily represented by a second order reaction equation. Table 1 gives the values of the reaction velocity constant (K).

For catalyst concentration $1.4 \cdot 10^{-4}$ mole/*l*, an activation energy $E = 17$ kcal/mole^{-1}, and an Arrhenius constant $A = 2.9 \cdot 10^{8}\ l \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$ were found graphically (Fig. 2). Fig. 3 shows the relationship between catalyst concentration and K. It is linear, and shows that polymerization of I proceeds with intermediate compound formation between monomer and catalyst. The polymerization reaction is first order with respect to catalyst concentration.

EXPERIMENTAL*

Sym-tetramethyldichlorodisiloxane (II) was synthesized by a known method [4].

1, 3-Dimethyl-3-vinyl-1, 3-dichlorodisiloxane (III). A mixture of 36 ml (2 mole) water and 36 ml dioxane was added dropwise in 30 min to a mixture of 282 g (2 mole) methylvinyldichlorosilane, 230 g (2 mole) methyldichlorosilane, and 500 ml ether which was stirred vigorously and kept below -20°C. After distilling off the solvent the products were distilled through a column, to give 56.8 g (14.1%) III, bp 141–142°; n_D^{20} 1.4190; d^{20}_4 1.0701. Found: C 23.98; H 5.47; Si 27.36; Cl 35.46; H(Si) 0.56%; MR_D 47.43. Calculated for $C_4H_{10}OCL_2Si_2$; C 23.88; H 4.98; Si 27.86; Cl 35.32; H(Si) 0.50%; MR_D 47.97.

1-Hydro-3-vinylhexamethylcyclotetrasiloxane (I). A mixture of 30.45 g (0.15 mole) II, 30.15 (0.15 mole) III, and 75 ml ether, was added over a period of 45 min, to a mixture of 100 ml 10% hydrochloric acid and 75 ml ether at about −15°. The ether solution was then washed with water until a neutral reaction was obtained, and dried over $CaCl_2$. Then it was distilled to give 29.8 g (67.4%) I, 58–60° (8 mm); n_D^{20} 1.4017; d^{20}_4 0.9703. Found: C 32.86; H 7.87; Si 37.79; H(Si) 0.38%; MR_D 73.75. Calculated for $C_8H_{22}O_4Si_4$: C 32.65; H 7.48; Si 38.09; H(Si) 0.34%; MR_D 74.35.

Polymerization of I was carried out in a flask with a reflux condenser and placed in an IT-12 thermostat. The measurements were all carried out till the instant when homogeneity ceased, when a precipitate appeared. An IKS-14 spectrometer with a LiF prism was used for determining the Si-H group content spectroscopically, the cell being a dismountable one LiFCd = 1 mm, and the range of molar concentrations (calculated for the S-H group/bond) was 0.05–0.005.

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