

## Rearrangement of a Polymethylsiloxane by Hydrogen Chloride

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### OBJECT

This research arose from an interest in preparing silicone resins with known structures and controlled degrees of crosslinking as, for example, by the condensation of tetraphenyldisiloxane diol,  $\text{HO—SiPh}_2\text{—O—SiPh}_2\text{—OH}$ , with methyltrichlorosilane. Further, silicone copolymers are commonly made by cohydrolysis of mixtures of aryl- or alkylchlorosilanes. In either case, much hydrogen chloride is formed and the aqueous layer may become strongly acid. The questions now arise: do the structures of the final copolymers isolated have much relation to the manner in which they were initially formed, or does hydrogen chloride cause rapid equilibration of siloxane units? Concentrated sulfuric acid is known to cause fairly rapid rearrangement of siloxane bonds at room temperature,<sup>1,2</sup> even though little of it dissolves. Since these experiments gave little indication of the effect of hydrogen chloride, the object of this work was to provide some semiquantitative information with the latter acid.

The results show that rearrangements of methylsiloxanes by 6*M* aqueous hydrochloric acid are negligible at room temperature, but that rearrangements by saturated solutions of hydrogen chloride, particularly in the presence of solvents such as methanol and tetrahydrofuran, may be rapid.

### METHOD

The following approach to the problem was used. Decamethyltetrasiloxane,  $\text{M—D}_2\text{—M}$  where  $\text{M} = \text{Me}_3\text{SiO}_{1/2}\text{—}$  and  $\text{D} = \text{—O}_{1/2}\text{—SiMe}_2\text{—}$ , was treated with hydrogen chloride and various solvents for various times at room temperature, about 23°C. Equilibration was then stopped by removing the acid and the recovered siloxanes were fractionally distilled. All the  $\text{M—D}_2\text{—M}$  and higher boiling material was isolated and weighed. The difference between this weight and the weight of starting material ("weight loss") is taken as the weight of lower boiling material formed. This weight loss represents the lower limit for the amount of  $\text{M—D}_2\text{—M}$  decomposed. To the extent that the decomposition,  $2\text{M—}$

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$D_2-M \rightarrow M_2 + D_4$ , occurs, this lower limit is correct. However, if equivalent quantities of  $M-D_3-M$  and  $M-D_4-M$  accompany formation of  $M_2$  and  $M-D-M$ , then the upper limit may be about three times the lower limit. For reactions with aqueous hydrogen chloride, both types of decomposition are indicated and the true extent of decomposition must lie between the two limits. Further complications occur in the presence of methanol and tetrahydrofuran. Nevertheless the method seems suitable for comparing related experiments.

## REARRANGEMENT OF $MD_2M$ BY HYDROGEN CHLORIDE AND WATER

Experiments are summarized in Table I, approximately in the order in which they will be discussed.

The first experiment (27) in Table I shows that 8.34 g. of  $MD_2M$  was recovered when 10.00 ml. (8.43–8.44 g., 0.0272 mole) was treated for a few seconds with hydrochloric acid and then recovered by the standard procedure, described later under "Experimental." This recovery is the standard from which losses are measured in the last column of Table I.

Experiments 1, 3, and 12 show that the extent of rearrangement of 10 ml. of  $MD_2M$  by an equal volume of reagent concentrated hydrochloric acid is nearly constant from 16–72 hours and this level is taken as an effective equilibrium. Rearrangement proceeds about 25% of the way to equilibrium in 4 hr. (expt. 2) and is nearly complete in some time less than 16 hr. Experiment 28 shows that more rearrangement occurs in the presence of a larger aqueous phase.

Addition of either benzene (expt. 20) or chloroform (expt. 21) has no marked effect on the equilibrium, but addition of tetrahydrofuran greatly increases both the rate (expts. 23 and 2) and extent (expts. 22 and 12) of reaction. In these experiments, recovered  $MDM$  and  $D_4$ , the former predominating, account for 40–60% of the weight loss. Experiment 29 was carried out in the presence of a surface-active agent which gave a fine dispersion. The result suggests that dispersion and the area of the interface are not major rate-controlling factors.

The initial rate of reaction with a 1:1 mixture of reagent concentrated hydrochloric acid and water (expt. 5) is less than one-tenth the initial rate with undiluted acid (expt. 2). When the aqueous acid is saturated with hydrogen chloride, the indicated initial rate (expt. 13) is nearly ten times that with "concentrated" acid.

The apparent change in initial rate of rearrangement with equal volumes of diluted and saturated aqueous hydrochloric acids is about 100-fold. The spread in total hydrogen chloride concentration is much less (6, 12, and 13.4*M*), while the total spread in vapor pressures of hydrogen chloride is much greater (about 0.2, 200, and 760 mm., respectively). Thus, the rate is no simple function of acid concentration. In experiments 7 and 30 hydrogen chloride was passed through  $MD_2M$  without a solvent. The

TABLE I  
 Rearrangement of MD<sub>2</sub>M by Hydrogen Chloride

Expt. no.	Time, hr.	Reaction mixture		Products recovered, g.			
		Concd. <sup>a</sup> aq. HCl, ml.	Added material	MDM	D <sub>4</sub>	MD <sub>2</sub> M and higher boiling	Loss, <sup>b</sup> g.
27	0.01	10		0	0	8.34	0 (blank)
2	4	10		0.01	0.05	8.03	0.31
1	16	10		0.25	0.27	7.08	1.26
3	24	10		0.65	0.17	6.91	1.43
12	72.2	10		0.34	0.25	7.09 <sup>f</sup>	1.25
28	24	30		0.99	0.23	6.08	2.26
20	24	10	10 ml. benzene	0.17	0.30	7.22	1.12
21	24	10	10 ml. chloroform	0.41	0.27	7.23	1.11
23	4	10	10 ml. tetrahydrofuran	<0.4 <sup>c</sup>	0.3	<7.1 <sup>c</sup>	>1.3 <sup>c</sup>
22	24	10	10 ml. tetrahydrofuran	<1.2 <sup>c</sup>	0.3	<5.2 <sup>c</sup>	>3.2 <sup>c</sup>
29	1	10	8.4 mg. Atlas BRIJ 35 <sup>d</sup>		0.03	7.95	0.36
5	24	5	5 ml. water	0.01	0.02	8.22	0.12
13	1	10	Sat. with HCl	0.08	0.17	7.61	0.73
10	4	10	" " "	0.40	0.41	6.05	2.29
11	4	1	" " "	0	0	8.20	0.14
26	4	1	" " "	0.03	0.05	8.13	0.19
9	4	1	" " " e	0	0	8.29	0.05
24	4	2	" " "	0.72	0.51	6.44	1.90
25	4.13	2	" " " e	0	0	8.32	0.02
7	4	0	" " "	0	0	8.13	0.21
30	24	0	" " "	0.23	0.52	5.13	3.21
6	24	5	5 ml. methanol	0.84	0.39	6.40	1.97
14	4	0	0.3 ml. methanol	0.67	0.84	5.05	3.32
18	1	0	1.0 " "	0.70	0.35	6.56	1.81
19	1	0	1.0 " "	0.74	0.45	6.28	2.09
8	4	0	1.0 " "	0.73	0.17	6.48	1.89
16	4	0	1.0 " "	0.60	0.66	4.90	3.47
17	24	0	1.0 " "	0	0	1.03	7.34
15	4	0	3.0 " "	0.48	0.26	3.77	4.60

<sup>a</sup> Density of concentrated HCl was 1.143 g./ml. at 25° in expts. 1-13, 1.169 in expts. 20-30.

<sup>b</sup> Difference between blank and "MD<sub>2</sub>M and higher boiling" products recovered.

<sup>c</sup> The MDM fraction had an abnormally high refractive index and must have contained reaction products of the solvent. To the extent that the higher boiling products also contained solvent residues, their weights are too high and the losses are too low.

<sup>d</sup> Lauryl ether of polyethylene glycol.

<sup>e</sup> Reaction carried out in test tube without stirring.

<sup>f</sup> 0.2 ± 0.2% Cl.

mixture became hazy in about an hour, and then a second phase began to separate. After 24 hr., the second phase, presumably concentrated aqueous hydrochloric acid, amounted to about 0.3 g. The data show that the initial reaction is slow. They suggest that the rate of cleavage accelerates as the amount of aqueous phase increases. The formation of water, the

high loss of material, and the unusually low recovery of MDM and  $D_4$  establish that chlorosilanes were formed and swept away. The viscosity of the residue was scarcely higher than for  $MD_2M$ , and so very little higher molecular weight polymer was formed.

One group of experiments was carried out with various volumes of saturated aqueous hydrogen chloride and with a slow stream of hydrogen chloride passing through the reaction mixture. In all of these experiments, concentrations of all reagents in the oil phase should be equal. However, Table I shows that the extent of reaction in four hours increases with the volume of the aqueous phase ( $\sim 0.2$  g., 1.90, and 2.29 g. losses with 1, 2, and 10 ml. of hydrochloric acid, expts. 11, 26, 24, and 10). With 1 ml. of aqueous phase, little rearrangement occurs regardless of whether the mixture is stirred (expts. 11, 26, and 9), but, with 2 ml. of aqueous phase and stirring, rearrangement becomes much faster (expts. 24 and 25). The marked difference between experiments 26 and 24 indicates that the reaction is autocatalytic.

The results above point to the following conclusions. (1) The "loss" data arise from two different but related reactions: a cleavage of siloxanes, to silanols and chlorosilanes, and a rearrangement of siloxanes. The rearrangement presumably results from reverse of the cleavage reactions. The rearrangement products have been found in fractional distillation. The chlorosilanes are inferred from the formation of water and the large weight losses in a stream of hydrogen chloride. Silanols must be present because both chlorosilanes and water are present and because water-soluble cleavage products are necessary to account for larger weight losses at equilibrium with larger volumes of aqueous layers. (2) Steady states are attained in closed systems, but not in streams of hydrogen chloride, where large weight losses occur. (3) Because the *rates* (as well as the extents) of cleavage and rearrangement depend on the volume of the aqueous phase and are sensitive to the concentration of hydrogen chloride, these reactions involve siloxanes, silanols, and unhydrated hydrogen chloride, with most of the reaction occurring in the water phase. The reactions seem to be autocatalytic. (4) In the approach to equilibrium (as opposed to simple hydrolysis and condensation), interfaces are not an important site of reaction. Agitation of the two phases is important but degree of dispersion apparently is not. (5) The vigorous reaction of the lower chlorosilanes with water is due to the high heat of hydration of hydrogen chloride. Easy interconversion of chlorosilanes and silanols (as well as siloxanes) occurs when water is saturated with hydrogen chloride.

### REARRANGEMENT OF $MD_2M$ BY HYDROGEN CHLORIDE AND METHANOL

Since contemporary work in the same laboratory showed that methanol participated in the condensation of silanols,<sup>3</sup> it seemed probable that methanol would also affect the rearrangement of siloxanes. To relate the

two researches, the following experiments listed in Table I were carried out. Although dilution of concentrated hydrochloric acid with an equal volume of water (expts. 5 and 3) greatly decreased rearrangement, dilution with an equal volume of methanol (expt. 6) appreciably increased rearrangement.

In the last group of experiments in Table I, the methanol and MD<sub>2</sub>M were continuously saturated with hydrogen chloride. Two phases were present, but the initial compositions (but not the volumes) of the respective phases should have been identical in all experiments. Experiment 17 shows that, in a 24-hr. run, the gentle stream of hydrogen chloride swept out most of the reaction mixture as volatile cleavage products. The small amount of residue had a viscosity (i.e., flow time through a capillary) 12.4 times that of MD<sub>2</sub>M.

In the 1-hr. and 4-hr. experiments with methanol, the weight losses apparently depended more on the flow rate of hydrogen chloride (not measured) than on the time or proportion of methanol. However, 1 ml. of methanol (expts. 18, 19) causes a much faster reaction than 1 ml. of water (expts. 11, 26), both being saturated with hydrogen chloride.

These experiments with methanol support in general the conclusions reached with water solutions. The rearrangement goes farther and faster in methanol, partly because of the greater solubility of the intermediates and products in the high-methanol phase but also because the methanol participates<sup>3</sup> in the rearrangements. The experiments suggest also that the large weight losses in experiments 17 and 15 other than those due to MDM and D<sub>4</sub> may result from volatilization of methyl ethers of silanols as well as of chlorosilanes.

The mechanisms of these acid-catalyzed reactions have been discussed elsewhere.<sup>2,3</sup>

## EXPERIMENTAL

Reactions always employed 10 ml. of MD<sub>2</sub>M (available in the laboratory)<sup>1</sup> and were usually carried out in a 100-ml. round-bottom flask, with stirring. Hydrogen chloride gas, from a steel cylinder, was introduced near the bottom of the reaction vessel through a capillary tube. Aqueous solutions and the 3 ml. of methanol were saturated and allowed to cool before addition of MD<sub>2</sub>M. Other methanol solutions were saturated before or after addition of MD<sub>2</sub>M without a consistent difference in results.

When less than 10 ml. of aqueous reagent was employed, water was added to make 10 ml. at the end of the reaction. The aqueous layer was then separated and the oil was washed with 5 ml. of saturated aqueous sodium bicarbonate, then with 5 ml. of water. The washed product was then distilled at 50 mm. pressure through an externally heated, vacuum-jacketed column. This column contained a platinum spiral 20 cm. long instead of packing, and was arranged so that several fractions could be collected without interruption. Transfers of material were made quantitative by

rinsing with a few milliliters of ether. In the runs with added solvents, benzene was used for transfer. In the tetrahydrofuran runs, most of the solvent entered the hydrogen chloride rather than the silicone layer. The acid layer was therefore extracted with two 5-ml. portions of benzene. The benzene extract was washed with bicarbonate solution and with water. The benzene was then distilled off, leaving 0.15 g. and 0.20 g. of silicones in experiments 22 and 23, which were combined with the main lots.

At 50 mm. pressure, some hexamethyldisiloxane ( $M_2$ ) was often found. Since it often evaporated during the remainder of the distillation, the quantities are not recorded here. Theoretically, every gram of  $D_4$  could be accompanied by 1.1 g. of  $M_2$ , with more  $M_2$  coming from other disproportionations. The first fraction was usually collected at about 70–76°, with a flat in the middle of the range. The second fraction was collected from about 76–94°, with a steep and steady rise in boiling point. All the first and half the second fraction is listed as MDM ( $n_D^{20}$ , 1.3849), although their indices of refraction were lower than corresponded to these compositions. There is apparently a small proportion of some unknown compound of lower refractive index boiling in this range. The other half of the second fraction is counted as cyclic octamethyltetrasiloxane,  $D_4$  ( $n_D^{20}$ , 1.3968). The third fraction, from 94–105°, and fourth fraction, b.p. 105–107 or 108°, were assumed to contain only  $D_4$  and starting product,  $MD_2M$  ( $n_D^{20}$ , 1.3896). Their refractive indices were used to calculate compositions since they corresponded to those expected from the shapes of the distillation curves. Fraction 3 averaged around 50%  $D_4$  and sometimes showed a flat at 96–97°. Fraction 4 was 90–95%  $MD_2M$ . Distillation was stopped when the boiling point became constant at 107 or 108°. The liquid in the warm column drained and evaporated cleanly. The residue was weighed and taken to be  $MD_2M$  and higher boiling products.

The recovery and purity of the product of the blank experiment establish the reliability of the analytical method. Although all weights were made to 0.01 g., the analyses are probably not reproducible to better than  $\pm 0.10$  g. for any product.

### References

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### Synopsis

Linear decamethyltetrasiloxane ( $MD_2M$ ) was treated with hydrogen chloride in the presence of various amount of water or methanol at room temperature. In the presence of water, the rate and extent of cleavage and rearrangement increased with the concentration of hydrogen chloride and the volume of the aqueous phase. In a slow stream of hydrogen chloride gas, significant proportions of the  $MD_2M$  were lost as chlorosilane vapors. Until an aqueous phase appears,  $M_2D_2$  is fairly stable to dry hydrogen chloride.

It is also stable to dilute aqueous hydrogen chloride, but, with an equal volume of saturated aqueous hydrogen chloride, 10-20% of the MD<sub>2</sub>M may react in an hour. Rearrangement and cleavage are accelerated by methanol and by tetrahydrofuran. The significance of these results is discussed.

### Résumé

Le décaméthyltétrasiloxane linéaire (MD<sub>2</sub>D<sub>2</sub>) était traité par l'acide chlorhydrique en présence d'une quantité variable d'eau et de méthanol à température ordinaire. En présence d'eau, la vitesse et le taux de rupture et de réarrangement augmentaient avec la concentration en acide chlorhydrique et le volume de la phase aqueuse. Dans un courant faible d'acide chlorhydrique gazeux, il y a une perte importante de MD<sub>2</sub>M sous forme de vapeurs de chlorosilane. Jusqu'à ce qu'une phase aqueuse apparaisse M<sub>2</sub>D<sub>2</sub> est assez stable à l'égard de l'acide chlorhydrique sec. Il est stable aussi à l'égard de l'acide dilué, mais en présence d'un volume égal d'une solution saturée d'acide chlorhydrique aqueux, 10 à 20% de MD<sub>2</sub>M réagissent endéans une heure. Les réarrangement et rupture sont accélérés par le méthanol et du tétrahydrofuranne. On discute la signification de ces résultats.

### Zusammenfassung

Lineares Decamethyltetrasiloxan (MD<sub>2</sub>M) wurde bei Raumtemperatur und in Gegenwart verschiedener Mengen Wasser oder Methanol mit Chlorwasserstoff behandelt. In Gegenwart von Wasser steigt die Geschwindigkeit und das Ausmass der Spaltung und Umlagerung mit der Konzentration des Chlorwasserstoffs und dem Volumen der wässrigen Phase an. In einem langsamen Strom von Chlorwasserstoffgas ging ein bedeutender Teil des MD<sub>2</sub>M als Chlorsilangas verloren. Bis zum Auftreten einer wässrigen Phase ist M<sub>2</sub>D<sub>2</sub> gegen trockenen Chlorwasserstoff recht stabil. Auch gegen verdünnten wässrigen Chlorwasserstoff ist es beständig, mit einem gleichen Volumen gesättigten wässrigen Chlorwasserstoffs jedoch reagieren 10-20% des MD<sub>2</sub>M in einer Stunde. Umlagerung und Spaltung werden durch Methanol und Tetrahydrofuran beschleunigt. Die Bedeutung dieser Ergebnisse wird diskutiert.

Received March 20, 1961