to crystallize this compound were without success. Cut 4 also contained hexaphenylcyclotrisiloxane. The residue was subjected to a molecular distillation and was collected in four fractions of increasing viscosity. The chlorine content of these cuts was 5.4, 4.3, 4.1, and 5.2%, respectively.

When 1.5 moles of diphenyldichlorosilane per mole of water was used, the yield of tetraphenyl-1,3-dichlorodisiloxane decreased while larger yields of hexaphenyl-1,5-dichlorotrisiloxane and hexaphenylcyclotrisiloxane were obtained.

Part B. Ratio of 1:1 and 0.67:1.—The method of hydrolysis was similar to that described in Part A, except that ratios of chlorosilane to water used were 1:1 and 0.67:1. In both cases almost the theoretical quantities of hexaphenylcyclotrisiloxane were obtained. No α,ω-diols were isolated.

The occurrence of hexaphenylcyclotrisiloxane in the partial hydrolysis products would indicate that diphenylsilanediol was formed and subsequently dehydrated and polymerized through the action of hydrochloric acid. It is also conceivable that due to the steric effect of the *gem* diphenyl group the —O—Si—O— angle is reduced to a point where the formation of the cyclic trimer from the open chain intermediates (dichloro-, dihydroxy- or chlorohydroxypolysiloxanes) is facilitated.

Tetraphenyldisiloxane-1,3-diol.[3]—When tetraphenyl-1,3-dichlorodisiloxane was hydrolyzed in the same manner as was diphenyldichlorosilane, it gave the corresponding diol. The rate of hydrolysis was approximately one-eighth that observed for diphenyldichlorosilane. The reaction may be accelerated somewhat if the aqueous layer is changed several times during the hydrolysis. The diol was recrystallized from benzene and *n*-heptane; yield (from 20 g. of dichloride), 17 g., 92%, m. p. 113–114°.

Anal. Calcd. for $C_{24}H_{22}Si_2O_3$: C, 69.52; H, 5.35; Si, 13.55; OH/molecule, 2.00. Found: C, 69.9; H, 5.36; Si, 13.5; OH/molecule, 1.90.

Hexaphenyltrisiloxane-1,5-diol.[3]—Hexaphenyl-1,5-dichlorotrisiloxane was hydrolyzed to hexaphenyltrisiloxane-1,5-diol in 64% yield. The two-phase hydrolysis system was used for this hydrolysis also. The hydrolysis took two days to complete. The diol was purified by crystallizing from boiling *n*-heptane, m. p. 111°.

Anal. Calcd. for $C_{36}H_{32}Si_3O_4$: C, 70.54; H, 5.27; Si, 13.74; OH/molecule, 2.00. Found: C, 71.1; H, 5.52; Si, 13.9; OH/molecule, 2.05.

Hydrolysis of Molecular Distillation Cuts.—The two most viscous cuts of the molecular distillation were hydrolyzed in the two phase system giving non-crystalline taffy-like products.

Thermal Dehydration of Diphenylsilanediol.—Twenty grams of diphenylsilanediol was heated in a small distillation flask so that the volatile and low-molecular weight reaction products could be removed by distillation. Water was obtained as the first product and when no more could be recovered by elevating the distillation temperature, vacuum was applied and 6.3 g. of impure hexaphenylcyclotrisiloxane was obtained at 298–310° (1 mm.). At 315–330° (1 mm.) 1.3 g. of very impure hexaphenylcyclotrisiloxane was obtained. A high boiling residue weighing 7.5 g., which probably contains higher molecular weight cyclopolyphenylsiloxanes, remained.

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Summary

1. The hydrolysis of diphenyldichlorosilane in a homogeneous medium with less than one mole of water per mole of chlorosilane has been shown to yield polyphenyl-α,ω-dichloropolysiloxanes and hexaphenylcyclotrisiloxane.

2. Tetraphenyl-1,3-dichlorodisiloxane and hexaphenyl-1,5-dichlorotrisiloxane were isolated and hydrolyzed to the corresponding α,ω-diols.

3. Acids favor the formation of hexaphenylcyclotrisiloxane, while alkalies favor the formation of octaphenylcyclotetrasiloxane in the dehydration-polymerization of diphenylsilanediol.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Octaphenylcyclotetrasiloxane

BY CHARLES A. BURKHARD, BEULAH F. DECKER AND DAVID HARKER

The adequate characterization of octaphenylcyclotetrasiloxane[1] by Kipping[2] has been questioned in a recent publication.[3] As this compound has been encountered a number of times in experimental procedures, it became necessary to identify and definitely characterize it. Kipping isolated octaphenylcyclotetrasiloxane in two forms, depending on the crystallization temperature. From warm ethyl acetate or acetone he isolated long, slender, very imperfect prisms, while at ordinary temperatures either well-defined, almost rectangular, plates or long, well-defined prisms were obtained, m. p. 200–201°. The crystals obtained from cold ethyl acetate became opaque on being warmed to temperatures less than 100°. Using the well-defined, almost rectangular plates Kipping[2b] found that the crystals belong to the triclinic (anorthic) system; subclass, holohedral; $a:b:c::0.5614:1:0.5770$; $\alpha = 83°56'$, $\beta = 103°52'$, $\gamma = 96°44'$.

Hyde and DeLong report, on the other hand, that the compound which Kipping reported as the tetramer, octaphenylcyclotetrasiloxane, is in reality the trimer, hexaphenylcyclotrisiloxane. In both cases cryoscopic data are used, together with other data, to identify the polymer. Kipping found molecular weights of 685, 674, and 669 in

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[1] A discussion of the nomenclature used in this paper has been given by Sauer [*J. Chem. Ed.*, **21**, 303 (1944)].

[2] (a) Kipping, *J. Chem. Soc.*, **101**, 2138 (1912); (b) Kipping, *ibid.*, **105**, 499 (1914).

[3] Hyde and DeLong, THIS JOURNAL, **63**, 1194 (1941).

benzene (theoretical 793).[4] Hyde and DeLong obtained a value of 589 using benzene, which is in very close agreement to the molecular weight of the trimer, 594.

Octaphenylcyclotetrasiloxane was prepared by the method outlined in a previous paper.[5] Cryoscopic measurements give for the molecular weight 810 in benzene and 802 in ethylene dibromide. These values are in agreement with the tetramer formula assigned by Kipping.

X-Ray diffraction work gave further support to Kipping's formula. A series of X-ray diffraction patterns was taken from a crystal which was oscillated about its needle axis. The X-ray diffraction patterns showed a plane of symmetry normal to the needle axis and a two-fold rotation axis parallel to the needle axis; the crystal is therefore monoclinic rather than triclinic (anorthic) as reported by Kipping. It was found possible to index all the spots on all the patterns on the basis of a cell with the dimensions: a_0 = 23.11kX, b_0 = 10.07kX, c_0 = 21.58kX, β = 121.32°; a:b:c::2.295:1.000:2.143.

The only reflections of the type $\{h0l\}$ to appear had l even. There is therefore a c-glide plane in the crystal perpendicular to the b axis. All types of $\{h1l\}$ and $\{h2l\}$ were observed; consequently the lattice is primitive. An attempt to discover which $\{0k0\}$ reflections occurred seemed to show only even orders, but the patterns were not good and it could not be concluded that the odd orders were really absent. On the basis of these observations, the space group of the crystal is $P2_1/c$, $P2/c$ or Pc, with the first of these the most probable.

The density, determined pycnometrically, is 1.185; the volume per $(C_6H_5)_2SiO$ unit is therefore 198.1 ÷ 1.185 = 167.2 cc. The molecular volume of the unit cell of the crystal, as calculated from the lattice constants, is 2599.7 cc. There are therefore 2599.7 ÷ 167.2 = 15.52 $(C_6H_5)_2SiO$ units per unit cell.[6] There cannot be a fractional number of atoms in the unit cell of a crystal of a pure substance; there are, therefore, 15 or 16 $(C_6H_5)_2SiO$ units in the unit cell, with 16 being more probable.

The presence of glide-planes of symmetry in the crystal requires that in each unit cell there be an even number of atoms of each kind; therefore there must be 16 (not 15) $(C_6H_5)_2SiO$ units in the unit cell. If the substance were the trimer, $[(C_6H_5)_2SiO]_3$, the number of $(C_6H_5)_2SiO$ units per unit cell would have to be a multiple of 3. Since this is not the case, the substance is not the trimer. If the substance is the tetramer, $[(C_6H_5)_2SiO]_4$, the number of $(C_6H_5)_2SiO$ units must be a multiple of 4; since 16 is a multiple of 4, the data do not exclude the tetramer.

The authors consider that the combination of cryoscopic and crystallographic data just presented prove that the substance dealt with in this investigation is the tetramer, octaphenylcyclotetrasiloxane.

Kipping's finding that the crystals are triclinic is not contradicted by the authors' finding that they are monoclinic, since this substance may show polymorphism. This possibility is suggested by Kipping's observation that the clear crystals obtained from cold ethyl acetate become opaque on warming to temperatures below 100°. The crystals used in this X-ray diffraction work were opaque white needles.

Acknowledgment.—The authors wish to express their appreciation to Mr. Eric T. Asp, who prepared the X-ray diffraction patterns.

Summary

1. The cyclic condensation product of diphenylsilanediol that melts at 201–202° has been shown to be the tetramer, octaphenylcyclotetrasiloxane.

2. The size of the monoclinic unit cell of crystalline octaphenylcyclotetrasiloxane is: a_0 = 23.11kX, b_0 = 10.07kX, c_0 = 21.58kX, β = 121.32°; a:b:c::2.295:1.000:2.143.

3. The molecular volume of the unit cell is 2599.7 cc.

4. The density is 1.185, giving 3.88 $\cong$ 4 molecules per unit cell.

5. The possible space groups are $P2_1/c$, $P2/c$ or Pc, the most probable being $P2_1/c$.

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[4] It is noted that these molecular weight data are low, but Kipping [*J. Chem. Soc.*, **101**, 2139 (1912)] also found a correspondingly low molecular weight for hexaphenylcyclotrisiloxane. The difference between the values for the trimer and the tetramer was 189 which corresponds very closely to the theoretical value of 198. He therefore believes that the results support the molecular formula assigned to the tetramer.

[5] Burkhard, THIS JOURNAL, **67**, 2173 (1945).

[6] This figure may be a little low, since the measured density may be decreased by internal flaws in the crystals.