Isopropoxypolysiloxanes

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The preparation of tetraisopropoxysilane from silicon tetrachloride and isopropanol was attempted in vain by Dearing[1]. Recently Bradley and his co-workers[2] reported briefly its formation from the same materials. We wish now to report on the preparation and properties of tetraisopropoxysilane $((CH_3)_2CHO)_4Si$ (I), hexaisopropoxydisiloxane $((CH_3)_2CHO)_3SiOSi((CH_3)_2CHO)_3$ (II), and octaisopropoxytrisiloxane $((CH_3)_2CHO)_3SiOSi((CH_3)_2CHO)_2OSi((CH_3)_2CHO)_3$ (III).

For the starting material isopropanol of Shell Chemicals (b.p. 82.2°C, n_D^{20} 1.3776) was used without further purification. For the preparation of (I) and (II) redistilled silicon tetrachloride (b.p. 57–58°C), and for the preparation of (III) octachlorotrisiloxane $Cl_3SiOSiCl_2OSiCl_3$ were used. This substance was obtained from the distillation residue of industrial silicon tetrachloride with rigorous fractionation through the helices packed column of about 20 plates under reduced pressure. (b.p. 73°C./13 mm., Anal. Calcd. for $Cl_8Si_3O_2$: Cl, 70.9. Found : Cl, 70.8.)

Preparation of Tetraisopropoxysilane (I) and Hexaisopropoxydisiloxane (II):—In the 1 *l*. three-necked flask equipped with an efficient stirrer, dropping funnel and reflux condenser, isopropanol (240 g., 4 mol.) was placed. Redistilled silicon tetrachloride (170 g., 1 mol.) was added with vigorous stirring for 2 hours. During the addition, the mixture was kept under 5°C. After addition the temperature was gradually raised to 40°C. for an hour and kept at this temperature for additional 3.5 hours. The mixture amounted to 360 g. (Cl content 62%). At this temperature, the mixture was dehydrochlorinated by bubbling dry air through the mixture until the chlorine content of the mixture became constant, the final value was 0.2% after 7 hours aeration. The volume of air passed was 400 *l*. At this stage the weight of the mixture amounted to 245g. (Yield : 91% theory). Hydrated sodium carbonate (5 g.), containing about 2 moles H_2O to Na_2CO_3, was added and the mix-

TABLE ISOPROPOXYPOLYSILOXANES

Name	Formula	Boiling Point °C./mm.	Refractive Index n_D^{20} n_D^{30}	Density d_4^{20} d_4^{30}	Molar Refraction Found (Calcd.)**	Molecular Weight Found*** (Calcd.)	% Si Found (Calcd.)
Tetraisopropoxy-silane	$[(CH_3)_2CHO]_4Si$ (I)	93–4/28*	1.3835 1.3787	0.8744 0.8656	70.7 (70.4)	267 (265)	10.59 (10.62)
Hexaisopropoxy-disiloxane	$[(CH_3)_2CHO]_6Si_2O$ (II)	82–3/2	1.3921 1.3875	0.9236 0.9150	110.1 (109.0)	420 (427)	13.14 (13.17)
Octaisopropoxy-trisiloxane	$[(CH_3)_2CHO]_8Si_3O_2$ (III)	121–2/2	1.3960 1.3912	0.9504 0.9419	148.9 (147.7)	585 (589)	14.37 (14.31)

* 74°C/13 mm., 116°C./85 mm. Bradley, *et. al., loc. cit.*

** Calculated from bond refrativities by E. L. Warrick, *J. Am. Chem. Soc.* 68, 2455 (1946)

*** Cryoscopic measurements in benzene

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[1] A.W. Dearing and E.E. Reid, *J. Am. Chem. Soc.*, **50**, 3058 (1928).

[2] D. C. Bradley, R. C. Mehrotra and W. Wardlaw. *J. Chem. Soc.*, **1952**, 5020.

ture was warmed to 80°C. with shaking. The filtrate (240 g.) was distilled under reduced pressure by a Claisen flask, and the fraction boiling at 90°–95°C./30 mm. was collected. (Crude (I), 230g., Yield: 85% theory) This fraction and the residue of several runs, from which the (II) was obtained, were fractionated rigorously by a Stedman column of about 20 plates respectively. The properties of these fractions are summarized in the following Table.

If the treatment of hydrated sodium carbonate was not carried out, the distillate obtained after several fractionations usually still contained a trace of isopropoxychlorosilane which fumes in moist air. After the treatment with an excess of hydrated sodium carbonate equivalent to convert Si–Cl to Si–O–Si no trace of fuming compound was found in the filtrate. Furthermore the decomposition of the isopropoxysilane was not observed even after prolonged heating at about 80°C.

Preparation of Octaisopropoxytrisiloxane (III):—In the 300 cc. three-necked flask equipped as above, was placed octachlorotrisiloxane. (40 g., 0.1 mol.) Isopropanol (48 g., 0.8 mol.) was added with vigorous stirring for 1.5 hours. During the addition, the temperature of the mixture was kept under5 °C. after which the temperature was gradually raised to 40°C. for 0.5 hour and kept at this temperature for additional one hour. The weight of the mixture amounted to 60 g. This mixture was aerated at this temperature until the chlorine content became constant. The volume of air passed was 280 l during a course of 8 hours and the final chlorine content was 1.2%. (Yield: 55 g., 94.8% theory) To this was added hydrated sodium carbonate (7 g.) and treated as above. The filtrate (51 g.) was rigorously fractionated by the Stedman column. About 5 g. of low boiling fraction (80°–110°C./2 mm.) was obtained. Judging from the boiling point, this may be considered to be hexaisopropoxydisiloxane (II) produced by a fission of siloxane chain, but was not further examined. The properties of constant boiling fraction (III) are given in the Table together with (I) and (II).

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