A Note on Some Alkoxydisilanes

By Rokuro ŌKAWARA, Toshio TANAKA and Keiichi MARUO

(Received November 8, 1954)

Many alkoxy-monosilane and -polysiloxanes have been studied, but on the alkoxydisilanes only a few reports[1,2,3] have been presented. The difficulty encountered on preparing the alkoxydisilanes from hexachlorodisilane and alcohol is the fission of Si-Si bond during the reaction. In the fission product, usually, alkoxy-monosilane and -polysiloxanes were found. Among them, disiloxane has a boiling point close to that of disilane and it is difficult to separate these two compounds by distillation. This paper will describe in as great detail as possible the preparation of alkoxydisilanes in the pure state. And the properties of hexamethoxydisilane (I), hexaethoxydisilane (II) and hexaisopropoxydisilane (III) will be described.

As previously reported[3], to prepare (I) from hexachlorodisilane and methanol, the dehydrochlorination by bubbling of nitrogen should be carried out under 30°C to prevent the fission of Si-Si bond also any trace of chlorine compound contaminated in the product should be precipitated by dry ammonia. In the light of this experiment, the preparation method to give pure (II) reported by Martin[1] and followed by Abrahamson et al,[2] appeared questionable. To drive off a trace of chlorine compound from the reaction product, Martin added ethanol and distilled it repeatedly and finally he obtained the chlorine free (II). In our experiment, it was found very difficult to purge off all the chlorine compound by repeated addition of ethanol and by followed aeration even at about 92°–95°C. And the product obtained after distillation still contained a trace of chlorine compound which makes the product slightly turbid and on prolonged standing there was a little precipitation of a white substance.

To assure whether the elevated temperature treatment of dehydrochlorination may give the completely chlorine free product or not the following incompletely dehydrochlorinated mixture of ethanol (6 mol.) and hexachlorodisilane (1 mol.) was refluxed. The chlorine content gradually decreased as in the case of partially alkolyzed alkylchlorosilanes[4,5]. And there was obtained a completely chlorine free product which was assured by Beilstein test. On fractional distillation, tetraethoxysilane, hexaethoxydisiloxane contaminated with a very small amount of (II) and octaethoxytrisiloxane were obtained. From this experiment, it may be concluded that by prolonged heating at the reflux temperature the incompletely dehydrochlorinated ethoxydisilane becomes chlorine free, but the ethoxydisilane is decomposed to form the mixture of the ethoxy-monosilane and -polysiloxanes.

Hexaisopropoxydisilane (III), a crystalline solid having the melting point 84.5° to 84.7°C,

---

[1] G. Martin, *J. Chem. Soc.*, **105**, 2860 (1914).

[2] E.W. Abrahamson, I. Joffe and H.W. Post, *J. Org. Chem.*, **13**, 275 (1948).

[3] R. Ōkawara and T. Tanaka, This Bulletin, **27**, 120 (1954).

[4] R. Ōkawara, This Bulletin, **27**, 428 (1954).

[5] R. Ōkawara and I. Ishimaru, ibid., **27**, 582 (1954).

was obtained after repeated recrystallizations from isopropanol. The relation of its melting point and the silicon content was determined after each recrystallization.

Analytical data of silicon of (I) and (II) were somewhat lower than the calculated value, but it may be seen within the experimental error. It may be possible that these two liquid alkoxy-disilanes are contaminated with a small amount of corresponding disiloxane, which has a boiling point close to that of the disilane. To determine the contamination of disiloxane in disilane, the volumetric method of determination of hydrogen evolved on the reaction with a basic reagent may be the suitable one, since with the determination of silicon content it is not easy to differentiate these two compounds. But the volumetric method which was described by Abrahamson[2] and Schumb[6] may not be useful for the time being, for the hydrogen evolved by the fission of Si-Si bond was not quantitative in general.

It was further found that the prevailing method of preparation of alkoxymonosilane using pyridine as an acid acceptor throughout the reaction could not be applied to the preparation of alkoxydisilane, because in pyridine medium, the fission of Si-Si bond takes place and alkoxymonosilane becomes the main product.

Experimental

Starting Materials.—For the starting materials dehydrated methanol and ethanol, of which the water content was found by the Karl Fischer method to be 0.05% and 0.17% respectively, and isopropanol of Shell Chemicals (b.p. 82.2°C, n_D^{20} 1.3776) were used. The hexachlorodisilane used in this experiment was prepared by the reaction of chlorine and powdered 75% ferrosilicon at the temperature of 160°–250°C. As the catalyst a small amount of potassium chloride[7] was mixed with the ferrosilicon. The liquid product obtained was rigorously fractionated through a Stedman column of about 30 theoretical plates. The fraction having the boiling point 147°C/760 mmHg and the melting point −1.2°—0.8°C was taken as the starting material. Analysis for the hydrolyzable chlorine was carried out by breaking 0.2–0.5 g. of the weighed sample in water-methanol solution in a sealed vessel, and titrating the liberated acid with 0.1 N-NaOH solution.

Anal. Found: Cl, 79.0. Calcd. for Cl_6Si_2: Cl, 79.1%.

Preparation of Hexamethoxydisilane (I).—The preparation and properties of this compound were already described.[3] Data on this substance are given in Table I.

Preparation of Hexaethoxydisilane (II).—In a 500 cc. three-necked flask equipped with an efficient stirrer, a dropping funnel and a reflux condenser hexachlorodisilane (32 g., 0.119 mol.) was placed. Ethanol (33 g., 0.72 mol.) was added with vigorous stirring for 1 hour. During the addition the temperature was kept below 5°C. After the addition the temperature was raised to 30°C for 30 minutes. The mixture (52 g.) was aerated with dry nitrogen for 2 hours during which the temperature was gradually raised to 50°C. The weight of the mixture lessened to 40 g., where the chlorine content was 9.7%. Aeration was further continued at the room temperature by adding 5 g. of ethanol. After 1.5 hours a product (37 g.) containing 2% chlorine was obtained. A slight excess of pyridine (3 g.) was added to precipitate any trace of chlorine compound. The filtrate (30 g.) was fractionated through a semi-micro Stedman column of about 20 theoretical plates. After a slight excess of pyridine and a small amount of tetraethoxysilane were distilled off, the product was fractionated under 0.8 mmHg. The constant boiling fraction (12 g., 31% of the theory) was obtained, the middle portion of which was analysed. The results are given in Table I.

(i) Preparation of Hexaethoxydisilane (II) by Dehydrochlorination at 95°C.—At the room temperature (10°C), 31 g. (0.115 mol.) of hexachloro-

TABLE I

ALKOXYDISILANES

Formula	Boiling Point °C/mmHg	Melting Point °C	Refractive Index n_D^{20}	Density d_4^{20}	Molecular Weight Found** (Calcd.)	% Si Found (Calcd)
$(CH_3O)_6Si_2$	100–1/20	—	1.4070	1.095	235	23.00
(I)					(242)	(23.18)
$(C_2H_5O)_6Si_2$*	75–6/0.8	—	1.4102	0.9728	318	17.18
(II)					(327)	(17.20)
$(i\text{-}C_3H_7O)_6Si_2$	164–6/38	84.5–7	—	—	415	13.68
(III)					(411)	(13.68)

* G. Martin, loc. cit., B. P., 123/15, $n_D^{14.5}$ 1.4134, d_4^{17} 0.9718

** Cryoscopic measurement in benzene

---

[6] W.C. Schumb and R.A. Lefever, *J. Am. Chem. Soc.*, 75, 1513 (1953).

[7] D.F. Stedman, U.S.P. 2, 621, 111; *Chem. Abstr.* 47, 3037 (1953).

disilane and 32 g. (0.7 mol.) of ethanol were mixed with vigorous stirring during the course of 40 minutes. The mixture was gradually heated to 60°C for 1.5 hours. At this temperature dehydrochlorination was carried out by bubbling a slow stream of dry nitrogen through the mixture. After 1 hour, the weight of the mixture amounted to 37 g., and the chlorine content was found to be 4.1%. To complete the dehydrochlorination, ethanol (2 g.) was added and nitrogen was bubbled for 3 hours at 70°–80°C. But the product (34 g.) which contains still 2.3% chlorine was obtained. Finally, the product (27 g.) of which chlorine content 0.7% was obtained after repeated addition of 2–3 g. of ethanol (the total amount was 7 g.) and by followed aeration for 8 hours with nitrogen at the temperature of 92°–5°C. After adding a small amount of ethanol, the product was rigorously fractionated through the semi-micro Stedman column under the reduced pressure. The following three fractions were obtained.

Fraction	b.p. (°C/mmHg)	n_D^{20}	%Si (Found)	Weight of the fraction (g.)
A′	79/32	—	—	0.5
B′	75–6/0.8	1.4122	17.28	10
C′	108–10/0.8	1.3963	—	2

The fractions A′, B′ and C′ may be considered tetraethoxysilane (reported[8]: b.p. 77/32, n_D^{20} 1.3837), hexaethoxydisilane (II) and octaethoxytrisiloxane (reported[9]: b.p. 126/0.5, n_D^{20} 1.3948; unpublished author's data: b.p. 107/0.8 mm, n_D^{20} 1.3952). But the fraction B′ was contaminated by a small amount of chlorine compound, which was assured by the Beilstein test. Further the fraction B′ became turbid in moist air and it was difficult to weigh.

(ii) **Dehydrochlorination at the Refluxing Temperature.**—At the room temperature (10°C), 41 g. (0.15 mol.) of hexachlorodisilane and 42.5 g. (0.9 mol.) of ethanol were mixed with vigorous stirring during the course of 1.5 hours and the mixture was gradually heated to 60°C for 2 hours. Then the mixture (49 g.) of which chlorine content 6.6% was heated to its refluxing temperature in a small flask fitted with a condenser, the upper end of which was connected to a calcium chloride tube. As a volatile chlorine compound was gradually evolved from the mixture, the refluxing temperature rose gradually. After 50 hours of refluxing, the temperature attained to 187°C and the chlorine was not found in the mixture by the Beilstein test. The product (41 g.) was rigorously fractionated through the semi-micro Stedman column. The following three fractions were obtained.

Fraction	b.p. (°C/mmHg)	n_D^{20}	%Si (Found)	Volume of the fraction (cc.)
A	57/10	1.3822	—	14
B	76–7/1	1.3928	16.26	4
C	105/1	1.3956	17.46	3

The fractions A, B and C may be considered tetraethoxysilane, hexaethoxydisiloxane (Anal. Calcd. Si, 16.40%. reported[9]: b.p. 94/0.5, n_D^{20} 1.3914) and octaethoxytrisiloxane (Anal. Calcd. Si, 17.68%).

From the silicon content, hexaethoxydisilane (II) which may appear in the fraction B was not found in this experiment. A qualitative test of Si-Si bond in the fraction B and in the residue by the saturated potassium hydroxide solution, showed that the fraction B evolved a very small volume of hydrogen, while the residue evolved hydrogen violently, showing the presence of the compound having Si-Si bond.

From the result of the elevated temperature treatment described here, it was clearly shown that the preparation of alkoxydisilane should be carried out at as low a temperature as possible.

Hexaisopropoxydisilane (III).—In a 300 cc. three necked flask equipped with an efficient stirrer, a dropping funnel and a reflux condenser, hexachlorodisilane (40 g., 0.15 mol.) was placed. Isopropanol (54 g., 0.9 mol.) was added with vigorous stirring for 70 minutes. During the addition the temperature was kept below 5°C. After addition the temperature was gradually raised to 80°C for 2 hours and at this temperature, the mixture was dehydrochlorinated by bubbling dry nitrogen through the mixture until the chlorine content of the mixture became constant (the final value, 2.7%, was attained after bubbling for 4 hours). At this stage the weight of the mixture amounted to 47 g. When the mixture was cooled to the room temperature (10°C), there was a deposit of crystalline matters. The crystals were filtered and recrystallized from ethyl ether, but the crystals could not be completely separated from the fuming matter which may be chloroisopropoxydisilane. To prepare the pure hexaisopropoxydisilane, 3.5 g. of pyridine and 3 g. of isopropanol were added to the mixture (47 g.) and the mixture was maintained at 60°C for 2 hours. The deposited pyridine hydrochloride was filtered off at the temperature of 85°C. The pure hexaisopropoxydisilane could be prepared from recrystallization (a) or distillation (b) of this mixture (40 g.).

(a) **Recrystallization.**—The crystal was recrystallized four times from isopropanol, and its melting point and silicon content were determined. The results were as follows:

Sample			Recrystallization times			
			1	2	3	4
(a) Filtered	m.p. (°C)	57–65	73–4	81–3	84.5–4.7	84.5–4.7
at 85°C	% Si	—	14.4	13.70	13.69	13.74
(b) (a) was simply	m.p. (°C)	72.5–6	84.5–4.7	84.5–4.7	—	—
distilled	% Si	13.9	13.63	13.65	—	—

---

[8] D. F. Peppard, W. G. Brown and W. C. Johnson, *J. Am. Chem. Soc.*, 68, 77 (1946).

[9] T. Takatani, *J. Chem. Soc. Japan* (*Pure Chem. Section*), 73, 409 (1952), (in Japanese).

(b) Distillation.—The mixture (40 g.) was distilled under reduced pressure. The first fraction distilled at the temperature 90°–164°C/38 mmHg (5 g.) and the second constant boiling fraction 164°–6°C/38 mmHg (22 g., 36% theory) of hexaisopropoxydisilane (III) was obtained. The residue was composed of a gelatinous mass and amounted to 12 g. By the analyses of silicon (13.9%) and its melting point (72.5°–76°C), the second fraction may be considered as the crude (III). Pure hexaisopropoxydisilane (III) was obtained by the recrystallization from isopropanol. The properties of this substance are given in Table I. The relation between the melting point and the silicon content after each recrystallization is already shown above together with (a).

Reaction of Hexachlorodisilane and Alcohol in Pyridine-Benzene Solution (i) *In isopropanol.*—In the 500 cc. three-necked flask cooled with ice-bath and equipped as above, 38 g. (0.14 mol.) of hexachlorodisilane diluted with 125 g. of benzene was placed. To this mixture 51 g. (0.85 mol.) of isopropanol mixed with 67 g. (0.84 mol.) of pyridine was added with vigorous stirring. After pyridine hydrochloride was filtered off and benzene was distilled, the product with slight excess of pyridine amounted to 49 g. The product was distilled under reduced pressure. The distillate boiling at the temperature of 70°–110°C/13 mmHg (33 g.) was washed with water and dehydrated with sodium sulphate. From the refractive index n_D^{20} 1.3850, and density d_4^{20} 0.8770 (reported:[10] b.p. 93.4°C/28 mmHg, n_D^{20} 1.3835 and d_4^{20} 0.8744), the distillate was found to be tetraisopropoxysilane, which was produced by the fission of Si-Si bond. The oily residue 17 g. was not further examined.

(ii) *In ethanol.*—To the mixture of hexachlorodisilane (30 g., 0.11 mol.) and benzene was added the mixture of ethanol (32 g., 0.7 mol.) and pyridine (55 g., 0.7 mol.) and treated in the same way as above. After simple distillation the fraction boiling at 55°–65°C/10 mmHg and the residue (10 g.) were obtained. The slightly turbid distillate was thoroughly washed with water and dehydrated on sodium sulfate. From its density (d_4^{20} 0.9330), the distillate may be considered to be tetraethoxysilane (reported[11] : d_4^{20} 0.9356).

Analyses

Silicon.—Silicon was determined by decomposing the sample with concentrated sulfuric acid.

Hydrogen.—Only qualitative tests were carried out with the three disilanes by using the Zerewitinoff apparatus. Hexamethoxydisilane (I) evolved about 94% theory of hydrogen by mixing butanol saturated with sodium hydroxide at the room temperature (8°C), while hexaethoxydisilane (II) on the same condition became a gel and scarcely evolved hydrogen. By adding a saturated aqueous solution of potassium hydroxide, hexaethoxydisilane (II) easily evolved hydrogen (ca. 94% of the theory), but by 30% aqueous solution, it was difficult to evolve hydrogen. Since isopropoxydisilane (III) floats on the surface of saturated aqueous solution of potassium hydroxide, it was dissolved in dry piperidine and mixed with wet piperidine. Hydrogen evolved very slowly and the volume of it reached to ca. 90% of the theory after standing over night.

Summary

1) Hexamethoxy-, hexaethoxy- and hexaisopropoxy-disilane were prepared and characterized.

2) Dehydrochlorination at an elevated temperature was not suitable for the preparation.

3) A trace of chlorine compound contaminated in the product could be completely taken off by dry ammonia or pyridine.

4) Alkoxydisilanes could not be prepared by using pyridine throughout the reaction as an acid acceptor.

5) The volume of hydrogen evolved by the fission of alkoxydisilanes varied with the reagents.

The authors wish to express their sincere thanks to Dr. Watase for his gracious encouragement and Miss Ukiko Takahashi for her aid during this experiment. Our thanks are also due to the Ministry of Education for aid in this research.

Department of Applied Chemistry,
Faculty of Engineering, Osaka
University, Osaka

---

[10] R. Ōkawara, T. Tanaka and I. Ishimaru, This Bulletin, 27, 45 (1954).

[11] H. D. Cogan and C. A. Setterstrom, *Ind. Eng. Chem.*, 39, 1364 (1947).