Table V. Change in Concentration of Water in Typical Samples

Hr. Heated	Degree of Esterification, BuO/Si = 0.48		Degree of Esterification, BuO/Si = 0.31	
	Viscosity, cp.	H_2O, %	Viscosity, cp.	H_2O, %
0	1.21	0.07	1.23	0.14
10	...	0.16	...	0.25
20	...	0.25	1.23	0.33
30	1.21	0.24	1.235	0.20
40	...	0.18	...	0.23
50	1.21	0.14	1.25	0.30
65	...	0.22	...	0.31
76	1.23	0.26	1.28	0.34

It is postulated that the unesterified hydroxyl groups within the polysilicic acid molecule slowly undergo intramolecular condensation; thus they liberated water and account for the initial rise in the water content of the solution. This water may then be consumed in the hydrolysis of butoxy groups, liberating n-butyl alcohol and forming new hydroxyl groups, although this second increase in hydroxyl groups has not been checked by actual analysis. This process would lead to a decrease in the water content of the system. Finally, the newly formed hydroxyl groups may then permit intermolecular condensation and the growth of larger molecular units, water again being liberated in the process, and the viscosity increasing. This increase in viscosity may be due to the further mechanical entanglement of n-butyl alcohol solvent within the growing polysilicic ester molecular units.

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BUTOXYCHLOROSILANES....

Hydrolysis and Condensation

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BUTOXYSILOXANES are formed by controlled hydrolysis and condensation of n-butoxychlorosilanes in the presence of a tertiary amine as an acid acceptor. Hexa-n-butoxydisiloxane (n-butyl disilicate) is obtained from n-tributoxychlorosilane. High boiling liquid cyclic siloxanes $[(n\text{-BuO})_2\text{SiO}]_n$, where n ranges from 3 to 8 are obtained from the difunctional compound n-dibutoxychlorosilane. Although n-monobutoxychlorosilane gives only insoluble gels, soluble resinous products containing slightly over one butoxy group per silicon are obtained by interpolymerizing a mixture of the mono- and di-n-butoxychlorosilanes. The liquid cyclic butoxysiloxanes possess a high degree of thermal stability and low temperature coefficient of viscosity.

PRESENT knowledge of alkyl polysilicates, or, more properly, the alkoxysiloxanes[1], rests largely upon the work of Schumb and Holloway (7), who prepared ethoxysiloxanes from the corresponding chlorosiloxanes; Konrad, Bächle, and Signer (3), who studied the intermediate hydrolysis products of methyl orthosilicate; and Signer and Grosse (9), who investigated the cyclohexoxysiloxanes obtained by the reaction of cyclohexoxychlorosilanes with silver carbonate. More recently Peppard, Brown, and Johnson (5) have further demonstrated the possibility of preparing alkoxysiloxanes by hydroysis and condensation of alkoxychlorosilanes.

In view of the earlier background developed on the hydrolysis and condensation of alkyl and aryl chlorosilanes to yield liquid and resinous silicones, recently summarized by Rochow (6), it seemed worth while to investigate the preparation of similar polymeric products which might be obtained from typical alkoxychlorosilanes by hydrolysis under carefully controlled conditions. The n-butoxychlorosilanes n-$C_4H_9OSiCl_3$, $(n$-$C_4H_9O)_2SiCl_2$, and $(n$-$C_4H_9O)_3SiCl$ were chosen for this purpose.

In order to prepare polysiloxane structures analogous to the silicones, it was necessary to use a method of hydrolyzing the chloro groups and effecting subsequent condensation without hydrolyzing or causing rearrangement of the butoxy groups. It had been shown by Signer and Grosse (9) that this can be accomplished in the case of the cyclohexoxychlorosilanes by treatment with silver carbonate in ether. However, the same result can be more readily accomplished by treating alkoxychlorosilanes with a theoretical quantity of water (0.5 mole water per chlorine) in the presence of a slight excess of pyridine to act as an acceptor of hydrogen chloride. A similar technique, except that excess water was used, has recently been described by Peppard, Brown, and Johnson (5), who also found that, unless an acid acceptor is used, hydrolysis of alkoxychlorosilanes proceeds with simultaneous disproportionation to orthosilicate and silica.

TYPES OF PRODUCTS OBTAINED

The polymeric products synthesized by this technique appeared, in general, similar in structure to the methylpolysiloxanes as

reported by Patnode and Wilcock (4). These range from liquids through resins to gels, depending upon the ratio of butoxy groups to silicon. Oily polymers were produced where the ratio of BuO/Si was greater than about 1.4, whereas viscous sirups or resins were found with ratios of 1.0 to 1.4, and insoluble gels below 1.0. (Throughout this paper Bu refers to the n-butyl group.) However, the analogy with methylsiloxanes is by no means complete, the course of the polymerization apparently having been modified by the presence of butoxy groups.
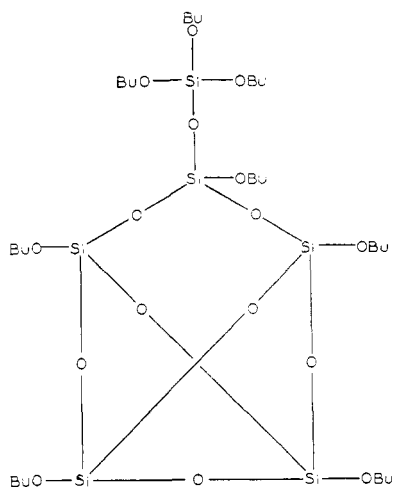

Figure 1. Possible Structure of Higher Boiling Fraction

From tributoxychlorosilane, $(BuO)_3SiCl$, a high yield of hexabutoxydisiloxane was obtained, a result completely analogous to the preparation of hexaethoxydisiloxane reported by Peppard, Brown, and Johnson (experiment 1). From dibutoxydichlorosilane, $(BuO)_2SiCl_2$, there resulted a clear, viscous, oily product having the general formula $[(BuO)_2SiO]_n$. Upon careful distillation this was found to consist almost entirely of high boiling, cyclic siloxanes containing from three to eight siloxane units (SiO) per ring. In contrast with the higher-molecular-weight hydrolysis products of dimethyldichlorosilane, reported by Patnode and Wilcock (4) and Hunter, Hyde, Warrick, and Fletcher (1), practically no higher-molecular-weight ring or straight-chain products were found (experiments 2 to 7, inclusive). From monobutoxytrichlorosilane, $BuOSiCl_3$, there was obtained a viscous, nonvolatile sirup which formed a weak, brittle gel when heated under vacuum to 300° C.; this is not surprising in view of the fact that the monomer is trifunctional (experiment 9).

Mixtures of mono- and dibutoxychlorosilanes gave products ranging from resinous masses containing slightly over one butoxy group per silicon atom to high boiling oils; this indicated considerable interpolymerization (experiment 10a). However, in the case of an equimolar mixture of monobutoxytrichlorosilane and tributoxychlorosilane there was less evidence of interpolymerization, since the principal products were hexabutoxydisiloxane and a soft resin containing 1.17 butoxy groups per silicon atom (experiment 10b). Nevertheless, some interpolymerization had actually occurred, since some intermediate high boiling oils were also found, and the residue was soluble in chloroform, in contrast with the brittle, insoluble polymer which would otherwise have been produced from the monobutoxytrichlorosilane.

In experiment 10b, small quantities of two high boiling oils were recovered having rather unusual compositions. In spite of the low molecular weight, which corresponded to only five or six silicon atoms per molecule, the BuO/Si ratios found in these oils were surprisingly low—1.89 and 1.48, respectively. The structure of these obviously highly cyclized compounds offers interesting speculation. For example, the higher boiling fraction (350–410° C. at 3 mm.) appears to contain about six silicon atoms and eight to nine butoxy groups per molecule, based on analysis and molecular weight data. Knowing the tendency of the siloxanes to form cyclic bodies, and assuming that only monobutoxy and tributoxy silyl groups are present, one possible structure is indicated in Figure 1. A similar methylpolysiloxane is described by Scott (8).

In an attempt to obtain nongelled products containing less than one butoxy group per silicon, the interpolymerization of mixtures of dibutoxydichlorosilane and silicon tetrachloride was tried (experiments 11 and 12). Most of the silicon tetrachloride was apparently converted to an insoluble polymer during the course of the hydrolysis, but there was definite evidence of some interpolymerization with the dibutoxydichlorosilane, since there was only a low yield of cyclic dibutoxysiloxanes which would otherwise have been formed from the latter intermediate. Instead there was a low yield of high boiling oils having BuO/Si ratios ranging from about 2.0 down to 1.48, along with a considerable portion of a nonvolatile, viscous, oily residue having the analysis and molecular weight corresponding to $[(BuO)_{1.05}SiO_{1.5}]_{10}$. Apparently all polymeric products containing less than about one butoxy group per silicon atom were insoluble in the reaction mixture and were removed by filtration along with the pyridine hydrochloride.

PROPERTIES OF CYCLIC BUTOXYSILOXANES

Under ordinary conditions the cyclic butoxysiloxane oils appear to be completely stable, in contrast with the lower esters, such as ethyl orthosilicate, which are readily hydrolyzed by atmospheric moisture. These mixed oils having the formula $[(BuO)_2SiO]_n = 3$ to 8 were quite resistant to hydrolysis when shaken with water at ordinary temperature, but tended to precipitate silica when the dispersion was heated. Semiquantitative tests indicate that there is appreciable hydrolysis when these cyclic siloxanes are heated in distilled water for 48 to 72 hours at 95° C., the cyclic trimer being less stable than the tetramer and higher cyclic products (experiment 13). However, none of the cyclic products was quite as resistant to hydrolysis as the hexabutoxydisiloxane and n-butyl orthosilicate. (The lower stability of the trimer toward hydrolysis may be the result of strain in the siloxane ring. Hunter, Hyde, Warrick, and Fletcher (1) report that the hexamethyltrisiloxane is thermally less stable than the tetra- or pentasiloxane.)

The unusual thermal stability of the butoxysiloxanes was indicated by the fact that no decomposition was observed during distillation under vacuum at temperatures up to 380° C. Even a small amount of decomposition would have been noted, since the evolved gases would have caused an immediate drop in pressure. However, when air was blown through the oil at 220–300° C., there was a 38% loss in weight, at which point the material became very viscous and started to gel (experiment 14). Sodium alcoholate brought about a disproportionation of the mixed cyclic butoxysiloxanes; this resulted in the formation of a fraction consisting largely of butyl orthosilicate and a highly viscous residue (experiment 15). Concentrated nitric acid, hydrofluoric acid, or ammonium hydroxide, when warmed with the cyclic oils, caused rapid decomposition.

The following properties were observed (determined on a composite of products obtained from $(BuO)_2SiCl_2$ in experiments 2 to 7, distilling in the range from 200–360° C. at 3 mm.):

Specific gravity, d_{20}^{20}	1.0028	Viscosity, cp.	
Flash point (C.O.C.), ° F.	405	+100° F.	10.15
Fire point (C.O.C.), ° F.	475	−40° F.	119.0
Pour and cloud point, ° F.	Under −75		

Particular attention should be called to the low change in viscosity with temperature, which approaches that of the alkyl silicone oils.

TABLE I. HYDROLYSIS AND CONDENSATION

Expt. No.	Butoxychlorosilanes, Mole	H₂O, Mole	Pyridine, Mole	Distillate					Residue		
				Wt., g.	Range, °C.	Mm.	BuO/Si	Mol. wt.	Wt., g.	BuO/Si	Mol wt
1	(BuO)₃SiCl, 0.2	0.2	0.22	26.6	175–180	3	3.0	......	1.0 oil	...	...
9	BuOSiCl₃, 0.2	0.3	0.6	None	To 320	3	...	......	Insol. gel	...	....
10a	BuOSiCl₃, 0.101 + (BuO)₂SiCl₂, 0.044	0.198	0.395	1.5	To 420	0.5	1.6	.....	14.0 resin	1.13	2030
10b	BuOSiCl₃, 0.1 + (BuO)₃SiCl, 0.1	0.2	0.4	14.0	175–180	3	3.0	577	9.7 resin	1.17	
				2.8	285–325	3	1.89	1100			
				3.5	350–410	3	1.48	972			
11	(BuO)₂SiCl₂, 0.1 + SiCl₄, 0.1	0.3	0.6	6.6	175–380	3	2.2 to 1.5	588 to 1200	6.0 viscous oil	1.06	
12	(BuO)₂SiCl₂, 0.05 + SiCl₄, 0.10	0.25	0.05	1.8	210–300	3	....	......	2.3 oil	1.05	1200

RESINOUS BUTOXYSILOXANE POLYMERS

From a mixture of monobutoxytrichlorosilane containing a minor proportion of dibutoxydichlorosilane (experiment 10a), the principal product was a viscous sirup having the empirical formula [(BuO)₁.₁₃SiO₁.₄₄]₁₃.₄ calculated from the analysis for carbon, hydrogen and silicon, and molecular weight. Since it was evident that harder resins might be obtained if the ratio BuO/Si were slightly lower, an attempt was made to produce a polymer using a still smaller proportion of dibutoxydichlorosilane. However, from a mixture of 0.04 mole of dibutoxydichlorosilane with 0.36 mole of monobutoxytrichlorosilane, only a gel was obtained upon evaporation of the solvent from the filtered reaction mixture.

Attention was therefore turned to the possibility of obtaining the desired resin by the partial hydrolysis of butoxy groups, starting with pure dibutoxydichlorosilane. As indicated in experiment 16, this was accomplished by emulsifying a solution of dibutoxydichlorosilane in benzene in a mixture of pyridine and ice water. Isolation of the polymeric product from the solvent yielded a resin containing slightly over one butoxy group per silicon, from which no volatile material could be detected when heated to 360° C. at 3 mm. (experiment 16). However, when ammonium hydroxide and sodium bicarbonate were used in place of pyridine, no resinous material could be isolated from the solvent layer, which contained only a small amount of oil boiling at 160–200° C. at 3 mm. (experiment 17).

The resinous material produced in experiment 16 had unusual thermal stability. Polymers of this type have been heated in vacuum (2 mm.) to 475° C. without evolving sufficient gas to cause a noticeable drop in pressure in the system. However, thermal decomposition occurs at an appreciable rate at 525° C. The resin is soluble in chloroform, benzene, and acetone. Firm, highly adherent films were obtained on glass by evaporation of these solutions. Although these films remained unchanged in contact with the atmosphere over a period of several weeks, they became loose and brittle when exposed to steam for several hours or permitted to stand in the laboratory atmosphere for several months. Analyses indicated that organic matter was lost during exposure to moist air; this suggested that partial hydrolysis had occurred.

MONOBUTOXYTRICHLOROSILANE

In a 3-liter flask, fitted with stirrer, 1410 grams of silicon tetrachloride (8.3 moles) were cooled to 15° C., and a mixture of 610 grams of n-butyl alcohol with 450 grams of benzene was added, with good agitation and cooling, over a period of 3 hours. The mixture was permitted to stand 18 hours and then fractionally distilled through a 1-inch-diameter, 2-foot column packed with ¹/₈-inch Fenske spirals. The desired product was collected at 82–85° C. at 100 mm. pressure, with a yield of 810 grams (47% theoretical based on SiCl₄). Analysis for C₄H₉OSiCl₃: calculated Cl = 51.25%; found = 50.0%. [This material may have contained as much as 5–6% (BuO)₂SiCl₂.]

DIBUTOXYDICHLOROSILANE AND TRIBUTOXYCHLOROSILANE

In a 3-liter three-necked flask, fitted with condenser and stirrer 757 grams of silicon tetrachloride (4.45 moles) and 1000 grams of benzene were mixed and cooled to 15° C. Over 2.5 hours 658 grams of anhydrous n-butyl alcohol (8.9 moles) were added, with good agitation and cooling. After standing for 24 hours at room temperature, the mixture was fractionally distilled into three rough cuts, from which the following fractions were isolated by separate distillations:

CRUDE BUTOXYTRICHLOROSILANE. Boiling point 31–45° C at 11 mm.; 100 grams (10.8% of theoretical) were obtained.

DIBUTOXYDICHLOROSILANE. Boiling point 82–84.5° C. at 7.5 mm.; 320 grams, or 28.2% yield based on SiCl₄, were obtained. Analysis: calculated Cl = 28.98%; found = 28.2%. For hydrolysis experiments this material was redistilled, and a middle cut boiling at 103° C. at 20 mm. was isolated: found, 28.9% Cl.

TRIBUTOXYCHLOROSILANE. Boiling point 126–128° C. at 10 mm.; 236 grams (19.0% of theoretical) were obtained. Analysis. calculated Cl = 12.54%; found = 12.65%. Approximate specific gravities of these products at room temperature were as follows (BuO)₃SiCl, 0.97; (BuO)₂SiCl₂, 1.05; and BuOSiCl₃, 1.17.

HYDROLYSIS AND CONDENSATION

The results obtained upon hydrolysis and condensation of tributoxymonochlorosilane, monobutoxytrichlorosilane, and various butoxychlorosilane mixtures are summarized in Table I. In these experiments the indicated quantities of pyridine and water in 200–300 cc. of anhydrous ether were added to the butoxychlorosilanes in 200–300 cc. of anhydrous ether, with vigorous agitation. The mixture was then refluxed for 18 hours under continuous agitation, care being taken to exclude atmospheric moisture. At the end of this period the precipitate of pyridine hydro-

TABLE II. HYDROLYSIS AND CONDENSATION OF (BuO)₂SiCl₂

Expt. No.	(BuO)₂-SiCl₂, Mole	H₂O, Mole	Pyridine, Mole	Reaction Medium, Cc.	Addn. of H₂O	% Product Distilling below 260° C., 3 mm.	Residue
2	0.2	0.2	0.4	Ether 600	With pyridine	51	<3%
3	0.2	0.2	0.4	Benzene 300 + dioxane 50	In dioxane after pyridine	65	<3%
4	0.2	0.2	Excess	Pyridine 300	With pyridine	55	<3%
5	0.2	0.2	0.4	None	With pyridine	38	<5%
6	0.2	0.2	0.4	Dioxane 200 + ether 450	In dioxane before pyridine	0.025 mole (BuO)₄Si	Gelled
7	0.1	0.1	None	Dioxane 150	In dioxane	0.020 mole (BuO)₄Si	Viscous, BuO/Si = 1.0

·hloride which had formed was separated from the reaction mixture by filtration, and the ether was then removed from the filtrate by distillation at atmospheric pressure. The residue was then subjected to fractional distillation at 3 mm. pressure until either the residue in the distilling flask had gelled or the temperature within the flask had reached 400–500° C.

In experiment 1, in which twice the stoichiometric quantity of water required for hydrolysis and condensation was used, a considerable proportion of the tributoxychlorosilane was decomposed to a fine white powder which was isolated by dissolving the pyridine hydrochloride out of the precipitate which separated from the reaction mixture. After being dried for several hours at 110° C. in an air oven, this powder had the following analysis: Si, 30.33; C, 21.60; and H, 4.01%. This corresponds to 0.416 butoxy group per silicon atom, which indicates that the excess water brought about considerable hydrolysis of the butoxy groups In experiment 9 no volatile products were observed in the final vacuum distillation; the liquid in the distilling flask suddenly gelled when the temperature reached 320° C. In experiments 10a and 10b the nondistillable residues were viscous liquids at 475° C., but, when permitted to cool under vacuum to room temperature, the materials were found to be slightly tacky resins. It was noted that, at the highest temperature, the entry of a slight amount of air into the flask caused superficial gelling, probably as a result of oxidation. In experiments 11 and 12 it was obvious that a considerable proportion of starting materials was converted to insoluble products which were discarded, along with the pyridine hydrochloride precipitate. The isolated products therefore represent only the soluble portions of the polymeric materials produced.

The hydrolysis and condensation of dibutoxydichlorosilane was carried out under a variety of conditions (Table II) in an attempt to vary the proportions of the cyclic siloxanes produced. In each case the dibutoxydichlorosilane was mixed in the reaction vessel with at least half of the indicated reaction medium (except in experiment 5 where no medium was used), and the water then added in the indicated manner with vigorous agitation, in most cases over a period of 30 minutes. In all cases the water content of the pyridine and solvent was determined, and this water was taken into account in calculating the total amount of water used. The mixture was then refluxed at least 1 hour; the pyridine hydrochloride and ether were then removed by the method already described, and the oily residue was fractionally distilled.

This procedure was varied in experiment 5 where no solvent was used; in this case the heat of reaction raised the temperature of the mixture to 120° C. The mixture was then further warmed to melt the pyridine hydrochloride, and stirring and heating were continued for 30 minutes. Agitation was then stopped to permit the pyridine hydrochloride layer to separate, and the mixture was permitted to cool. The upper oily layer was poured off the lower solidified layer of pyridine hydrochloride and fractionally distilled. In this case when the pyridine hydrochloride was dissolved in cold water it yielded a white precipitate, which, after being washed with water and methanol and dried in 110° C., weighed 3.0 grams. This indicated that the fused pyridine hydrochloride caused some side reactions, although no disproportionation to butylorthosilicate occurred, since no fraction boiling around 119° C. at 3 mm. was observed.

In experiments 6 and 7 butylorthosilicate, boiling at 115–121° C. at 3 mm., was identified by analysis for carbon and hydrogen:

	Calcd., %	Found, %
C	60.0	60.01
H	11.32	11.41
Si	8.8	8.4

In experiment 6 the residue was a brittle mass containing 23.67% silicon and 34.25% carbon; this suggested that the residue may have been silica gel saturated with high boiling butoxysiloxane oil. The residue obtained in experiment 7 was a viscous fluid at 475° C. which cooled to a soft resin soluble in acetone and benzene. The resin, which weighed 7.0 grams, contained 22.3% silicon, 7.19% hydrogen, and 38.2% carbon; this corresponded to about one butoxy group per silicon atom.

In experiment 8 the distillates from experiments 2 to 5, inclusive, were carefully fractionated through a $1/2$-inch-diameter 13-inch column packed with $1/2$-inch Fenske spirals. In this fractionation the various cuts from the previous experiments were added to the distilling flask when the temperature in the flask had reached the lower boiling point of the particular fraction. The distillation curve at 3.0 mm. is shown in Figure 2. The weights of the different fractions are indicated in Table III, the values in parentheses being the weights of the intermediate fractions. Analyses and molecular weights indicate that the various cyclic siloxanes were isolated in relatively pure condition, except perhaps for the highest boiling compound.

HYDROLYSIS OF BUTOXY SILOXANE OILS

In order to obtain a roughly quantitative idea of the relative resistance of the siloxane oils toward hydrolysis, weighed samples were sealed with 10.0 grams of water in clean $1/2$-inch Pyrex test tubes and heated to 98° C. (in boiling water) for 48 to 72 hours. The tubes were then cooled and opened, and a portion of the aqueous layer was clarified by filtering rapidly into a second tube through dry filter paper in a small covered funnel, to minimize evaporation. The concentration of n-butyl alcohol in the filtrate was then determined by refractive index (Table IV). Additional tests on the trimer and tetramer, together with the disiloxane and orthosilicate, are also included.

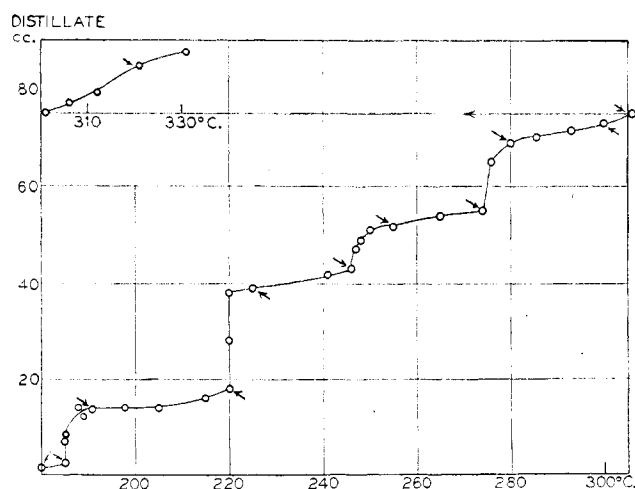Since the percentage hydrolysis in the cases of the orthosilicate

TABLE III. ANALYTICAL DATA ON CYCLIC BUTOXYSILOXANES

B.P. Range at 3 Mm.°C.	Wt., Grams[a]	Analysis, %			Refractive Index (20°C.)	[(BuO)₂SiO]ₙ	Mol. Wt.	
		C	H	SiO₂			Calcd.	Found
185–190	10.0(4.6)	50.94	9.73	31.16	1.4196	$n = 3$	571	602
220–225	19.7(3.3)	51.00	9.79	31.00	1.4220	$n = 4$	761	776
245–250	7.9(3.4)	50.96	9.69	31.03	1.4228	$n = 5$	951	983
275–280	13.4(3.4)	50.16	9.51	32.24	1.4230	$n = 6$	1142	1205
300–326	11.8(2.8)	48.90	9.34	34.07	1.4240	$n = 8$	1522	1585
Calcd. for (C₄H₉O)₂SiO		50.5	9.55	31.5				

[a] Figures in parentheses are weights of intermediate fractions.

Figure 2. Distillation Curve of Cyclic Butoxysiloxanes at 3 Mm. Pressure

TABLE IV. HYDROLYSIS OF BUTOXYSILOXANE OILS

Sample	Vol. Sample, Cc.	Vol. H2O, Cc.	Hrs. at 98° C.	Filtrate Refractive Index at 25.7° C.	n-BuOH in Filtrate Cc./100 Cc.	n-BuOH for Complete Hydrolysis, Cc./100 Cc.	Approx. Hydrolysis, %
n-BuOH {	0.1	10.0	...	1.3342	1.0	...	..
	0.2	10.0	...	1.3350	2.0	...	..
	0.5	10.0	...	1.3372	5.0	...	..
	1.0	10.0	...	1.3410	10.0	...	..
Distd. H2O	...	...	...	1.3333	...	...	..
[(BuO)2SiO]3	1.0	10.0	48	1.3369	4.6	9.7	47
[(BuO)2SiO]3	0.9	10.0	72	1.3395	8.0	8.7	92
[(BuO)2SiO]4	1.0	10.0	48	1.3333	0	9.7	0
[(BuO)2SiO]4	2.0	10.0	72	1.3391	7.5	19.4	39
[(BuO)2SiO]5	1.0	10.0	48	1.3336	0.5	9.7	5
[(BuO)2SiO]6	1.0	10.0	48	1.3335	0.3	9.7	3
[(BuO)3Si]2O	2.0	10.0	72	1.3342	1.0	21.5	5
(BuO)4Si	2.0	10.0	72	1.3342	1.0	22.8	5
[(BuO)3Si]2O	...	...	...	1.4152	...	...	..
Partially hydrolyzed sample of [(BuO)3Si]2O	...	...	...	1.4150	...	...	..
(BuO)4Si	...	...	...	1.4115	...	...	..
Partially hydrolyzed sample of (BuO)4O	...	...	...	1.4113	...	...	..
n-BuOH	...	...	...	1.4015	...	...	..

and disiloxane appeared to be so slight, it was suspected that n-butyl alcohol might have been held in the unhydrolyzed oily layer. However, this did not seem to be the case, since the upper layers after the hydrolysis experiments had refractive indices very close to the original values, as shown at the end of Table IV

OXIDATION OF HEXABUTOXYDISILOXANE AND CYCLIC TETRAMER

About 25 grams of hexabutoxydisiloxane were heated to 240° C., and air was bubbled slowly through the oil while the temperature was raised, over a period of 30 minutes, to 312° C. The viscosity increased rapidly, and the residue was extremely viscous at ordinary temperature and gelled on standing 1 week.

A similar experiment, starting with 5.7 grams of octabutoxytetrasiloxane (cyclic tetramer), yielded a highly viscous product weighing 3.5 grams which was on the point of gelling.

In a third experiment, under identical conditions, 6.0 grams of the cyclic hexamer became extremely thick at the same point, the residue weighing 3.7 grams. Carbon analysis indicated that the very viscous, partially gelled product contained about 1.2 to 1.3 butoxy groups per silicon.

DISPROPORTIONATION OF CYCLIC BUTOXYSILOXANES CATALYZED BY SODIUM BUTYLATE

To 16.8 grams of the mixed cyclic butoxysiloxanes used in experiment 8 were added 50 cc. of anhydrous n-butyl alcohol, in which 0.2 gram of sodium had been dissolved. The mixture was refluxed at 100° C. under anhydrous conditions and then distilled at 3 mm. pressure. When the temperature in the still reached 230° C. the residue suddenly gelled to a highly viscous foamy solid. The fraction of the distillate selected between 115° and 160° C. (at the top of the distillation column) was found to be largely butyl orthosilicate. Molecular weight calculated, 320; found, 348; SiO2 calculated, 18.7; found, 17.6.

EMULSION HYDROLYSIS OF (BuO)3SiCl3

IN PRESENCE OF PYRIDINE. A mixture of 49 grams (0.20 mole) of (BuO)2SiCl2 in 400 cc. of anhydrous benzene were added, with violent agitation, to a mixture of 100 grams of pyridine in 400 grams of water, cooled at 0° C. with ice. Immediately after the addition was complete, the benzene layer was separated, partially dried by filtering through calcium chloride, and subjected at once to vacuum distillation to remove benzene and water. After these solvents had been removed at 66 mm. pressure, the residue was heated over a period of 15 minutes to 360° C. at 2 mm. pressure. No distillate was obtained under vacuum. A resinous product (18.3 grams) was obtained, containing 47.23% SiO2 and having a molecular weight of 4889. This analysis corresponds to slightly over one butoxy group per silicon.

IN ABSENCE OF PYRIDINE. A mixture of 24.5 grams of (BuO)2SiCl2 (0.1 mole) and 100 cc. of benzene was poured rapidly into 300 grams of a mixture of ice and water to which 42 grams of sodium bicarbonate had been added. The mixture was stirred vigorously for 3 minutes and the organic layer separated. Since it smelled strongly of hydrochloric acid, it was again slurried and mixed with the cold sodium bicarbonate solution to which 25 cc. of 1:1 ammonium hydroxide had been added. There was considerable emulsification. A portion (about 25 cc.) of the benzene layer was separated, filtered through anhydrous calcium chloride, and the benzene removed as in the previous experiment. The resulting 3.4 grams of liquid residue were distilled at 20 mm. pressure. All of the material had distilled when the temperature of the flask reached 200° C. No resinous polymer was produced.

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

In all experiments involving the preparation and hydrolysis of butoxychlorosilanes, precautions were taken to exclude atmospheric moisture from the reagents and reaction vessels by the use of Drierite tubes on all vents. Water determinations on all solvents were by means of the Karl Fischer reagent.

Analyses for carbon and hydrogen were made by the ordinary combustion method; care was taken to raise the temperature of the sample gradually and to complete the combustion in pure oxygen at bright red heat, since some of the silica residues tended to retain carbon in a form that was not readily oxidized. Silica was determined by decomposition of the samples in concentrated nitric acid, followed by gravimetric determination of silica in the residue by fuming with hydrofluoric and sulfuric acids.

Molecular weight determination was carried out by the freezing point method, using anhydrous benzene. In all cases the molecular weights were found to be lower than theoretical when the conventional freezing point constant for benzene was employed. However, as described by Hyde, Frevel, Nutting, Petrie, and Purcell (2), a freezing point constant for benzene of 58.4 is found in work with siloxanes. In the case of the butoxysiloxanes the molecular weights calculated with this constant were slightly higher than theoretical.

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