solid (0.45 g.) upon standing in a freeze chest. After crystallization from acetone, there was thus obtained 0.08 g. more of purified solid, m.p. 209–210°.

Several small lots of this solid, obtained as described above, were combined, resublimed, and again crystallized from acetone, m.p. 210–211° (uncor.) in a sealed tube. The solubility and superficial appearance were the same as were described above.

Anal. Calcd. for $C_6H_{18}Si_6O_9$: C, 17.9; H, 4.5; mol. wt., 402.66. Found: C, 18.1; H, 4.5; mol. wt., 374.

Infrared spectrograms of "hexamethyl T_6" and "octamethyl T_8" also were obtained, both as Nujol mulls. Both curves confirmed the complete absence of silanol, and showed no features inconsistent with the assumed structures. Evidence was sought for the presence of six-membered (cyclotrisiloxane) rings in "hexamethyl T_6,"[18] but an unequivocal answer to this question was not obtained.

Analyses.—For determination of alkoxyl, samples of suitable weight to give 0.03 to 0.09 g. OR were refluxed in aqueous 50% potassium hydroxide. Solution usually was complete in 0.5 hour. Free alcohol was distilled directly from the alkaline solution and was collected as a water–alcohol mixture. The alcohol was determined by measuring the percentage absorption at 475 mμ in 5-mm. cells of the colored complex formed with ammonium hexanitrato cerate.[19]

Silanol usually was determined by reaction with methylmagnesium iodide in dibutyl ether solution. In some cases, lithium aluminum hydride was used instead of the Grignard reagent. It is believed that the Grignard method, as employed for this work, is accurate to within 5 or, at most, 10%. Silanol values usually were checked qualitatively by infrared spectrograms.

The molecular weight determinations were carried out cryoscopically in benzene.

Acknowledgment.—We are indebted to E. M. Hadsell for precision distillations, to various members of the Analytical Chemistry Unit of this Laboratory for elementary analyses and molecular weight determinations, and to C. A. Hirt for the infrared absorption curves.

SCHENECTADY, N. Y.

---

[18] C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, THIS JOURNAL, **70**, 3758 (1948).

[19] F. R. Duke, *Ind. Eng. Chem., Anal. Ed.*, **17**, 572 (1945).

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Partial Hydrolysis of Ethyltriethoxysilane

BY M. M. SPRUNG AND F. O. GUENTHER

RECEIVED JANUARY 5, 1955

Appreciable yields of distillable liquids result from the acid-catalyzed reaction of three molar equivalents of water with ethyltriethoxysilane in benzene solution. The major components are polycyclic polysiloxanes that contain free silanol groups and residual ethoxyl groups. Lower yields are obtained in ethanol solution with an acid catalyst, and only gels are obtained with an alkaline catalyst. If smaller amounts of water are used, the major products are first less highly cyclic, and finally predominantly straight-chain polysiloxanes. Several ethoxy-substituted linear and monocyclic polysiloxanes were isolated. Co-hydrolysis of equimolar mixtures of ethyltriethoxysilane and ethyltrichlorosilane gives products similar in physical properties to those derived from the trialkoxysilane alone, but with much less residual ethoxyl and silanol. A sublimable high-melting solid obtained in small amounts was identified as octa-(ethylsilsesquioxane), $(C_2H_5SiO_{1.5})_8$. A lower melting solid frequently present in even smaller amounts was identified as hexa-(ethylsilsesquioxane), $(C_2H_5SiO_{1.5})_6$.

Introduction

The distillable liquids isolated in low yields when methyltriethoxysilane was treated with three molar equivalents of water in benzene solution are principally complex polycyclic polysiloxanes with ethoxyl and hydroxyl end-groups.[1] It was of considerable interest that complex silanols survived the rigorous catalytic and thermal treatment involved, including distillation at high still-pot temperatures.

Ethyltriethoxysilane is considerably more stable toward hydrolysis. Under the standard conditions previously described (*i.e.*, 1.5 moles of water allowed to react with 0.5 mole of the alkoxy silane, dissolved in 500 ml. of benzene and stirred rapidly at the boiling point[1]), about 2.5 to 3 hours is required to reach the equilibrium conditions that are established. An acid or alkaline catalyst must be employed. Two high-boiling fractions were obtained: (1) b.p. 149–158° at 1 mm., n^{20}D 1.4263; (2) b.p. 167–176° at 1 mm., n^{20}D 1.4308. The residue was a heavy, balsam-like liquid, in contrast to the gelled resin obtained from methyltriethoxysilane. The results of ultimate analyses, ethoxyl, hydroxyl and molecular weight determinations are shown in Table I. Infrared spectra of the distillable fractions confirmed the presence of Si–OH, Si–OC_2H_5 and Si–C_2H_5 bonds (peaks at 2.93, 7.73 and 7.99 μ). The two infrared curves were nearly indistinguishable.

TABLE I

HYDROLYSIS PRODUCTS OBTAINED WITH THREE MOLAR EQUIVALENTS OF WATER

	Fraction 1	Fraction 2	Residue
Mol wt. (in benzene)	540	574	1167, 1330
Carbon, %	33.9	33.1	31.8
Hydrogen, %	7.4	7.3	6.9
Silicon, %	29.2	29.9	31.2
—OC_2H_5, %	15.6	13.5	9.2
—OH, %	4.0	4.3 (av. of 6)	...

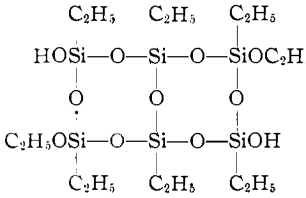
The close similarity of the analytical constants, and the trends from lower to higher molecular weight components, suggest that the individual components are very closely akin. The data for the lower boiling fraction conform closely to those required for a compound of the empirical composition $C_{14}H_{36}Si_5O_9$: *i.e.*, $(C_2H_5)_5Si_5O_6(OC_2H_5)_2(OH)$ (calcd.: mol. wt., 488.7; C, 34.4; H, 7.4; Si, 28.7; –OC_2H_5, 18.4; –OH, 3.5[2]). The analytical data for the higher boiling fraction do not lead

---

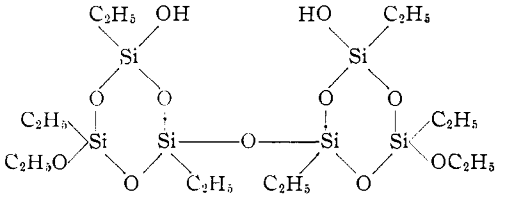
[1] M. M. Sprung and F. O. Guenther, THIS JOURNAL, **77**, 3990 (1955).

[2] Reasonable structural formulas would be 5,7-diethoxy-(3,9)-epoxy-1-hydroxy-1,3,5,7,9-pentaethylcyclopentasiloxane or 1,7-diethoxy-(3,9)-epoxy-5-hydroxy-1,3,5,7,9-pentaethylcyclopentasiloxane

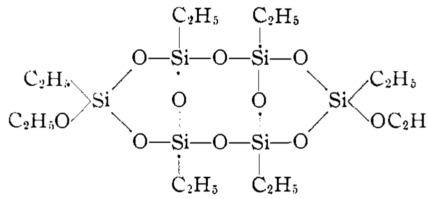
to a single empirical formula. However, a mixture of I (or Ia) and II, differing only by a molecule of water, would yield these analytical data. (Calcd. for $C_{16}H_{42}Si_6O_{11}$ (I or Ia): mol. wt., 578.9; C, 33.2; H, 7.3; Si, 29.1; $-OC_2H_5$, 15.6; $-OH$, 5.9. Calcd. for $C_{16}H_{40}Si_6O_{10}$ (II): mol. wt., 560.8; C, 34.2; H, 7.2; Si, 30.0; $-OC_2H_5$, 16.0; $-OH$, 0.0.)



I



Ia



II

These structures are analogous to (in fact, homologous with) those assigned the major distillable hydrolysis products obtained from methyltriethoxysilane under similar conditions.[1] It should be emphasized again that closely related substances having more or less than this number of $-OH$ and $-OR$ groups are probably present in small amounts, and that less probable isomeric species also must be taken into account. These data again demonstrate how readily structures containing a plurality of relatively small rings are formed from trifunctional organosilanes.

The non-volatile residue can be represented as a mixture of polymer-homologs of the distillable components. The average composition corresponds to $(C_2H_5)_{12}Si_{12}O_{17}(OC_2H_5)_2$ (related to II) (calcd. for $C_{28}H_{70}Si_{12}O_{19}$: mol. wt., 1047.5; C, 32.1; H, 6.8; Si, 32.2; $-OC_2H_5$, 8.6).

A two-mole hydrolysis gave only a slightly greater yield of distillable products, owing probably to longer heating times during concentration and distillation. This product was redistilled in a spinning-band column, and cuts were taken at the midpoints of the fractions described above (fraction 2, b.p. 155–156° at 4 mm.; fraction 6, b.p. 166–167° at 1 mm.). Except for low silanol contents, they were analytically similar to original fractions 1 and 2. (*Anal.* Found (fract. 2): Si, 29.0; $-OH$, 2.1, 2.2. (Fract. 6): mol. wt., 540; C, 33.6; H, 7.0; Si, 30.8; $-OC_2H_5$, 13.5; $-OH$, 0.7.) The decrease in hydroxyl content was confirmed qualitatively by infrared analysis. The complex silanols obviously are destroyed by long heating. In this particular case, an increase in the relative proportions of II compared to I might be expected.

The Effect of Ethanol on the Initial Reaction Products.—Higher yields of cyclic ethoxylated products might be realized if the sensitive silanol groups were converted to alkoxyl previous to distillation. Accordingly, a half-mole of ethyltriethoxysilane was hydrolyzed and, after the solvents had been removed, an equal volume of absolute ethanol containing the usual catalytic concentration of hydrochloric acid was added. This mixture was heated again as before. Vacuum distillation gave a materially increased yield of liquid products (28.1 g., b.p. 132–225° at 0.3 mm., $n^{20}D$ 1.4233, 26.5% $-OC_2H_5$). The balsam-like residue (21.1 g.) had 19.7% $-OC_2H_5$. On redistillation of the volatile portion in a spinning-band column, the fractions shown in Table II were taken.

Azeotropic separation of water after hydrolysis then was omitted. Solvents were removed immediately under vacuum. Absolute ethanol and hydrochloric acid were added again, the mixture heated under reflux as before, and distilled. The yield of crude distillate was 20.0 g. (b.p 135–195° at 1 mm., $n^{20}D$ 1.4208, $-OC_2H_5$ 28.7%) and of residue, 29.0 g. (20.6% $-OC_2H_5$). The volatile liquid was redistilled again through a spinning-band column (Table III).

To determine if siloxane bonds were split by reaction with ethanol, the non-volatile residue from a standard half-mole hydrolysis (average $-OC_2H_5$ content, 12.0%) was heated under reflux for 21 hours with absolute ethanol and hydrochloric acid. Distillation gave a small fraction (2.2 g., 20.5% $-OC_2H_5$), but the boiling range was above that to which the original distillation had been carried. Since lower boiling fractions were not obtained, siloxane-bond cleavage is apparently not important.

Characterization of Hydrolysis Products through Physical Properties and End-group Analysis.—A multiplicity of complex polysiloxanes, polysiloxanols, alkoxy polysiloxanes and alkoxy polysiloxanols are encountered in the hydrolysis products of trifunctional organosilanes. A systematic method of classification based on structure is needed. However, for the present purposes, a scheme that considers only the relative extensiveness of the hydrolytic attack is useful. With increasing hydrolysis, the major products are first linear, then monocyclic, then polycyclic and finally "cage-like." The concomitant changes in composition can be expressed in terms of the $-OR'$- to $-R_2Si_2O_3$ ratio. Polymer growth by polycondensation usually occurs randomly. However, in polysiloxane systems, the relative ease of ring closure and the high probability of formation of eight-membered rings lend a certain statistical preference to some types of ring structures. These considerations furnish a key to the nature of the substances present.

For distillation cuts of narrow boiling limits, the nature of the predominant component can be determined from the ethoxyl content and boiling range only (knowing other physical constants, such as refractive index and density, or having an infrared spectrogram of the sample, is naturally helpful). The ethoxyl content, in turn, need not always be determined directly (although this was generally done as a matter of course) but can be estimated from the specific gravity. The correlation between these two quantities in a series of closely related cyclic alkoxy siloxanes is shown in Fig. 1.

The predominant components of distillation cuts given in Tables II and III were deduced in this way. Treatment with ethanol in the presence of acid did, indeed, convert some of the

TABLE II

REDISTILLATION OF A REACTION PRODUCT PREVIOUSLY TREATED WITH EXCESS ETHANOL

Fraction	Vol., ml.	B.p., °C. at 1 mm.	$n^{20}D$	Wt. of 1 ml.	$-OC_2H_5$,[a] %	Probable predominant component[b] $-OEt/Et_2Si_2O_3$	$-OH/Et_2Si_2O_3$	Theor. % $-OC_2H_5$
1	1.3	105–124	1.4137	1.023	41.1	4:2[d]	...	38.1
2	0.9	124–120	1.4158	...	...	...	...	...
3	1.6	120–127	1.4193	1.066	31.8	3:2[e]	1:2[e]	30.4
4	1.5	127–131	1.4220	1.095	25.6	3:2.5	...	26.1
5	1.1	131–136	1.4232	...	...	...	...	...
6	1.3	136–144	1.4223	1.106	23.4	3:3	1:3	22.3
7	1.6	144–151	1.4221	1.070	31.0	4:3	...	28.4
8	1.6	151–155	1.4216	1.080	28.8	4:3	...	28.4
9	1.0	151–168[c]	1.4215	...	...	...	...	...
10	1.5	168–158	1.4237	1.102	24.1	4:4	...	22.6
11	1.1	158–167	1.5252	...	...	...	...	...

[a] Estimated from the specific gravity. [b] Adduced from the residual ethoxyl and the physical constants. [c] The pressure became erratic at this point in the distillation. [d] Tetraethyltetraethoxycyclotetrasiloxane. [e] Hydroxytetraethyltriethoxycyclotetrasiloxane.

TABLE III

REDISTILLATION OF A REACTION PRODUCT PREVIOUSLY TREATED WITH ETHANOL[a]

Fraction	Vol., ml.	B.p., °C. at 1 mm.	$n^{20}D$	Wt. of 1 ml.	$-OC_2H_5$,[b] %	Probable predominant component[c] $-OEt/Et_2Si_2O_3$	Theor. % $-OC_2H_5$
1	0.9	94–122	1.4108	...	...	...	...
2	1.8	120–121	1.4155	1.041	37.2	4:2[d]	38.1
3	1.5	121–130	1.4192	1.073	30.4	...	...
4	1.2	132–133	1.4220	1.102	24.2	4:2.5	26.1
5	1.5	131–146	1.4208	1.096	25.4	4:2.5	26.1
6	1.6	146–151	1.4194	1.064	32.2	4:3	28.4
7	1.0	143–155	1.4200	...	...	...	...
8	0.6	153–155	1.4216	...	...	...	...
9	1.2	155–162	1.4237	...	...	...	...

[a] Dean–Stark trap separation of water omitted. [b] Estimated from the specific gravity. [c] Adduced from the residual ethoxyl and physical constants. [d] Tetraethyltetraethoxycyclotetrasiloxane.

silanol-rich components to alkoxy compounds, but did not reduce the complexity of the reaction product. The distillable products in both cases were predominantly polycyclic, having OEt/$Et_2Si_2O_3$ ratios between 4:2 and 4:4.

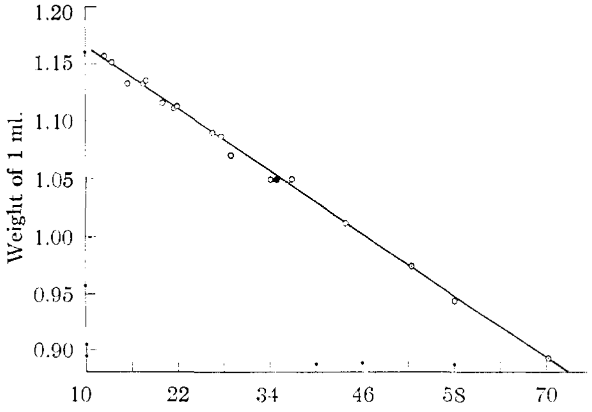


Fig. 1.—Density *vs.* %-C_2H_5O relationship of distilled hydrolysis products of ethyltriethoxysilane.

Infrared absorption spectra were obtained for the products described in Table II and these data added considerable support to the assumed structures. For example, in the crude distillate obtained after treatment of the hydrolyzate with excess alcohol, the peak heights at 7.75 and 2.93 μ indicated a relatively large amount of ethoxy and a silanol content of around 1 to 2%. In fraction 1 of the redistilled product the silanol peak was virtually absent, but reappeared in somewhat reduced intensity in fraction 3. In fraction 7 the silanol peak again was virtually absent. The Si–OC_2H_5 peak at 7.75 μ was, however, nearly as prominent as in fractions 1 or 2. These observations accord well with the data in Table II.

Mechanism of Siloxane Bond Formation.—A sample of crude distillate from a 1-mole hydrolysis run under normal conditions (19.5 g., b.p. 128–163° at 0.8 mm., $n^{20}D$ 1.4286, 15.1% $-OC_2H_5$, 2.3% OH) was heated under a water-cooled reflux condenser and under a pressure of 20 to 35 mm. for 105 minutes at 190–230°. A volatile product weighing 0.66 g., caught in a Dry Ice trap, was determined, by physical properties, to be mostly ethyl alcohol. The oil then was distilled, giving: (1) 6.2 g., b.p. 128–190° at 0.5 mm., $n^{20}D$ 1.4270, 14.8% $-OC_2H_5$; (2) 12.2 g. of non-volatile residue having 11.5% $-OC_2H_5$; and (3) 0.07 g. more of the volatile product. The average alkoxy content dropped from 15.1% (initial) to 12.6% (final), and the average silanol content from 2.3 to 0.5%. The stoichiometry of the reaction insofar as it affects functional groups can be represented as

$$1.4 -\overset{|}{\underset{|}{\text{Si}}}\text{OEt} + 2.0 -\overset{|}{\underset{|}{\text{Si}}}\text{OH} \longrightarrow$$

$$1.4\ \text{EtOH} + 0.3\ H_2O + 1.7 -\overset{|}{\underset{|}{\text{Si}}}\text{O}\overset{|}{\underset{|}{\text{Si}}}-$$

TABLE IV

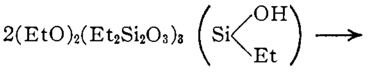
ACID-CATALYZED HYDROLYSIS IN BENZENE WITH VARYING AMOUNTS OF WATER

Fraction	B.p., °C. at 1 mm.	Wt., g.	$n^{20}D$	$-OC_2H_5$, %	Probable predominant component	Theor. % $-OC_2H_5$
		(A) $EtSi(OEt)_3:H_2O = 1:1.5$				
1	103–115	4.2	1.4165	36.9, 34.1	Monocyclic[a]	38.1
2	122–134	4.7	1.4222	27.6	Polycyclic[b]	26.1
3	134–144	7.2	1.4252	21.9	Polycyclic[c]	22.3
4	147–168	6.4	1.4275	...	...	...
5	173–193	7.2	1.4292	17.9	Polycyclic[d]	17.6
Residue	...	18.5	...	15.1	Polycyclic siloxanols	...
		(B) $EtSi(OEt)_3:H_2O = 1:1.125$				
1	44–69[f]	6.7	1.3923	...	Monomer	...
2	74–94	5.2	1.4024	60.1	Linear dimer	58.1
3	130–150	4.7	1.4152	38.9, 42.9	Cyclic tetramer	38.1
4	159–181	5.1	1.4217	26.7	Polycyclic[e]	28.4
5	188–196	2.0	1.4237	...	...	...
Residue	...	28.0	...	20.2	Polycyclic	...
		(C) $EtSi(OEt)_3:H_2O = 1:0.75$				
1	50–66[f]	30.3	...	69.8	Monomer	70.5
2	67–79	4.9	1.4022	56.1	Linear dimer	58.1
3	120–145	2.5	1.4138	40.1	Cyclic tetramer	38.1
4	148–184	2.4	1.4212	...	...	...
Residue	...	21.5	...	20.3	Polycyclic	...

[a] Average of 4 –OEt groups for 2 $Et_2Si_2O_3$ units. [b] Average of 3 –OEt groups for 2.5 $Et_2Si_2O_3$. [c] A verage of 3 –OEt and 1 –OH for 3 $Et_2Si_2O_3$. [d] Average of 3–OEt and 1 –OH for 4 $Et_2Si_2O_3$. [e] Average of 4 –OEt for 3 $Et_2Si_2O_3$. [f] At 20 mm.

On this basis, the 0.73 g. of volatile product consisted of 0.675 g. of ethanol and 0.055 g. of water. The reactions giving alcohol and water can be formulated as

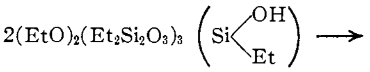
(A)



$$2(\mathrm{EtO})_2(\mathrm{Et_2Si_2O_3})_3\left(\mathrm{Si}\begin{matrix}\diagup\mathrm{OH}\\ \diagdown\mathrm{Et}\end{matrix}\right)\longrightarrow$$

$$(\mathrm{EtO})_4(\mathrm{Et_2Si_2O_3})_6(\mathrm{Et_2Si_2O}) + \mathrm{H_2O}$$

(B)



$$2(\mathrm{EtO})_2(\mathrm{Et_2Si_2O_3})_3\left(\mathrm{Si}\begin{matrix}\diagup\mathrm{OH}\\ \diagdown\mathrm{Et}\end{matrix}\right)\longrightarrow$$

$$(\mathrm{EtO})_3(\mathrm{Et_2Si_2O_3})_6(\mathrm{Et_2Si_2OOH}) + \mathrm{EtOH}$$

The ratio of ethanol to water in the volatile product (as calculated from the ethoxyl and silanol analyses) indicates that the probability of reaction B is about 4.5 to 5 times as great as that of reaction A.

Some Variations in Experimental Conditions.—Considerable effort was made to obtain higher yields of distillable products. The standard batch consisted of 0.5 mole of ethyltriethoxysilane, 500 ml. of benzene, 2.5 ml. of 0.5 *N* hydrochloric acid and 24.5 ml. of water. Doubling the batch size increased the total yield of distillate only slightly (21.2 g., $n^{20}D$ 1.4286, 15.1% $-OC_2H_5$). Quadrupling the batch size reduced the yield to 17.2 g. again. No gain resulted from doubling the concentration of reactants; from one mole of starting material there was obtained 16.7 g. of oil (b.p. 145–175° at 0.3 mm., 16.5% $-OC_2H_5$, 2.0% –OH) and 70 g. of residue.

A normal yield of distillate was obtained if the mixture was washed with water before concentration. However, omission of the Dean–Stark trap operation for separation of water resulted in a very low yield of distillate and a nearly quantitative yield of gelled residue, even if the acid was removed before distillation, by repeated washing with water or by neutralization with an amine. A prolonged period of heating, with continuous removal of water (7 hours instead of the normal 2) did not materially affect the yield (18.3 g., b.p. 140–170° at 0.5 mm.; average $-OC_2H_5$ content, 15.6%; average silanol content, 3.0%). The effect of slow removal of water thus is to form more stable intermediates than those first formed. Ethoxy compounds apparently are reformed by reaction of silanols with alcohol. The concentration of acid also continuously decreases during this operation, and this is a second stabilizing influence.

In an attempt to increase the yield of silanol-rich components, solvent stripping was carried out at 0–25° in vacuum. The initial liquid product (39.4 g.) had 4.6% hydroxyl. Attempts to separate silanol-rich fractions from this product by solvent extraction with a variety of solvents were unsuccessful.

For the isolation of components of the highly condensed, polycyclic hydrolysis products, the optimum conditions therefore are close to those first described.

Hydrolysis in Ethanol Solution.—Hydrolysis in ethyl alcohol, with hydrochloric acid as catalyst, gave a smaller yield of distillable partial hydrolysis products and a relatively higher yield of heavy, sirupy, high-boiling residue. In boiling ethanol with sodium hydroxide as catalyst, the sole product was "ethylsilicone gel."

Hydrolysis with Less than Three Molar Equivalents of Water.—Runs were made in benzene with 50, 37.5 and 25% of the normal quantity of water. The result was a shift from the highly cyclized molecules already described, through somewhat less highly condensed structures, and finally to predominantly linear products. These data are summarized in Table IV.

From 0.5 mole of starting material, in ethanol, with 50% of the normal quantity of water, there resulted 35.5 g. of distillable product (b.p. 86–199° at 0.5 mm., $n^{20}D$ (1.4119–1.4184, 34.8–34.9% $-OC_2H_5$), and 20.8 g. of heavy liquid residue (28.9% ethoxyl). The average ethoxyl content of the distillate is that of monocyclic polysiloxanes.

With 25% of the theoretical quantity of water, in ethanol, the fractions described in Table V were obtained. It was expected that five, and possibly six, of the linear partial hydrolysis products would be isolated on redistillation, but actually only four pure components could be separated: the monomer, the next two linear products and the cyclic trisiloxane (Table VI). The linear dimer and the linear tetramer were described previously by Andrianov.[3] The linear trimer and the cyclic trimer have not been reported previously.

Only a small amount of distillate (2.7 g.) resulted from an alkali-catalyzed hydrolysis in ethanol, using 1.5 molar equivalents of water containing 2.5 ml. of 0.5 *N* NaOH per 0.5 mole of ethyltriethoxysilane. With 0.75 molar equivalent of water, a 22.9-g. yield of distillate was obtained (Table VII).

Presumably the first three members of the linear series and at least one member of the monocyclic series, probably the cyclic tetramer, are present in the lower boiling fractions,

---

[3] K. A. Andrianov, *J. Gen. Chem.* (*USSR*), **8**, 1255 (1938).

TABLE V

ACID-CATALYZED HYDROLYSIS IN ETHANOL

Fraction	B.p., °C. at 0.2 mm.	Wt. g.	$n^{20}\text{D}$	$-OC_2H_5$, %	Probable predominant component	Theor. % $-OC_2H_5$
			$EtSi(OEt)_3:H_2O$ = 1:0.75			
1	58–71 (6.3 mm.)	4.1	...	...	Monomer + dimer	...
2	63–68	15.1	1.4022	61.1	Linear dimer	58.1
3	67–77	13.4	1.4026	54.3	Linear trimer	52.5
4	80–95	5.6	1.4058	54.8	Linear trimer	52.5
5	97–110	9.9	1.4084	52.3	Linear trimer	52.5
6	111–128	5.1	1.4107	47.6	Linear tetramer	49.5
7	130–150	4.6	1.4123	46.6	Linear pentamer	47.4
8	161–198	4.4	1.4158	41.7	Pentamer + monocyclic	46.0, 38.1
Residue	...	4.0	...	34.8	Monocyclic	38.1

TABLE VI

ACID-CATALYZED HYDROLYSIS PRODUCTS FROM $EtSi(OEt)_3$ AND 0.75 MOLE H_2O IN ETHANOL

					Analyses, %									
					Calculated				Found				Mol. Wt.	
Product	Formula	Yield, ml.	B.p., °C. at 1 mm.	$n^{20}\text{D}$	C	H	Si	$-OC_2H_5$	C	H	Si	$-OC_2H_5$	Calcd.	Found[a]
Linear dimer	$C_{12}H_{30}Si_2O_5$	26.2	74–77	1.4022	46.4	9.7	18.1	58.1	46.8	10.1	17.7	53.2	310.5	289, 296
Cyclic trimer	$C_{12}H_{30}Si_3O_6$	1.6	98	1.4125	40.7	8.5	23.8	38.2	40.4	8.9	23.2	...	354	385
Linear trimer	$C_{16}H_{40}Si_3O_6$	8.9	116–123	1.4078	44.8	9.4	19.6	52.6	45.0	9.6	19.3	53.1	429	466

[a] Cryoscopically in benzene.

TABLE VII

ALKALINE-CATALYZED HYDROLYSIS IN ETHYL ALCOHOL

Fraction	B.p., °C. at 0.6 mm.	Wt., g.	$n^{20}\text{D}$	$-OC_2H_5$, %	Probable predominant component	Theor. % $-OC_2H_5$
			$EtSi(OEt)_3:H_2O$ = 1:0.75			
1	49–57[c]	13.3	1.3918	...	Monomer	...
2	66–76	7.2	1.4016	59.6	Linear dimer	58.1
3	101–120	3.0	1.4178	52.9	Linear trimer	52.5
4	140–175	4.3	1.4242	36.3	Monocyclic	38.1
5	182–212	5.7	1.4264	25.7	Polycyclic[a]	22.6–28.4
6	214–234	2.7	...	...	...	...
Residue	...	15.0	...	20.2	Polycyclic[b]	18.8

[a] Average of 4 –OEt groups for 3 to 4 $Et_2Si_2O_3$ units. [b] Averages about 4 –OEt groups for 5 $Et_2Si_2O_3$ units. [c] At 9 mm.

whereas the higher-boiling components are predominantly polycyclic. A similar situation was found to prevail when methyltriethoxysilane was hydrolyzed under these conditions.[1]

Co-hydrolysis of Ethyltriethoxysilane and Ethyltrichlorosilane.—Equimolar proportions of ethyltrichloro- and ethyltriethoxysilane (0.25 mole of each) were hydrolyzed in benzene with three molar equivalents of water under conditions that approximated those used for ethyltriethoxysilane alone. A small amount of gel was formed. Distillation gave two cuts: (1) 7.2 g., b.p. 155–160° at 2 mm., $n^{20}\text{D}$ 1.4302; (2) 1.0 g., b.p. 160–170° at 2 mm., $n^{20}\text{D}$ 1.4311. The distillation residue (32.0 g.) was again a thick balsam-like liquid. The boiling points and refractive indices were close to those of the homohydrolysis products. However, analytical data indicate that these products are quite different.

Anal. Calcd. for $C_{18}H_{46}Si_8O_{13}$: mol. wt., 694.9; C, 31.2; H, 6.7; Si, 32.3; $-OC_2H_5$, 6.5; –OH, 2.45. Found (lower-boiling fraction): mol. wt., 648, 680; C, 31.8; H, 7.0; Si, 32.4; $-OC_2H_5$, 6.75; –OH (estimated from the infrared spectrogram), <3.0. Found (resin): mol. wt. (av.), 2500, 2600; C, 31.2; H, 6.9; Si, 33.5; $-OC_2H_5$, 4.6. Found (gel): C, 30.0; H, 6.8; Si, 33.5; $-OC_2H_5$, 4.5.

$C_{18}H_{46}Si_8O_{13}$ would be a polycyclosiloxane having one ethoxyl and one hydroxyl. The simplest molecule of this empirical composition would be 9 - ethoxy - 1 - hydroxy - (3,15)(5,13)(7,11) - triepoxy - 1,3,5,7,9,11,13,15 - octaethylcyclooctasiloxane. There is only one monoethoxymonosilanol having this particular polysiloxane skeletal structure. It is interesting to note the close similarity in analytical composition of the soluble resin and the insoluble gel. Although the gel is presumably much more highly cross-linked, the average molecular weight is not necessarily greater than that of the resin.

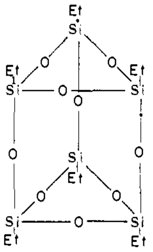
The co-hydrolysis, repeated several times, consistently gave about the same yield of distillable liquid, with 6 to 7% residual ethoxyl in contrast to 14 to 16% for the homohydrolysis product.

A co-hydrolysis of one-half mole each of the trichloro and triethoxy compounds, but with only half the normal amount of water, gave 35.0 g. of distillate with 14.0% residual ethoxyl. Under similar circumstances, ethyltriethoxysilane alone produced a distillate with over 25% average ethoxyl. The highest-boiling fraction (12.2 g., b.p. 175–197° at 1 mm., $n^{20}\text{D}$ 1.4288) was analyzed. Found: mol. wt., 654; C, 32.4; H, 6.8; Si, 30.6;

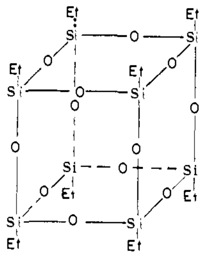
$-OC_2H_5$, 13.2; –OH, 2.8. The major component is probably $C_{18}H_{46}Si_7O_{12}$. Calcd.: mol. wt., 651.2; C, 33.2; H, 7.1; Si, 30.2; $-OC_2H_5$, 13.8; –OH, 2.6. A reasonable structure would be a tetracyclic heptasiloxane with two ethoxyl groups and one hydroxyl group.

Total Hydrolysis Products.—In "ethyl T-gel" $(C_2H_5SiO_{1.5})_n$, the usual total hydrolysis product of ethyltriethoxysilane, the value of *n* is indeterminate, but presumably large. Low molecular weight polymers of this composition are of great interest. Barry and Gilkey[4] prepared a compound, $(C_2H_5SiO_{1.5})_8$, but an adequate characterization was not given.

During a slow redistillation of a hydrolysis product obtained with three molar equivalents of water, small amounts of a solid were observed in the distillate. About a gram of this solid was filtered from the oil. The melting point was 57–58°, after preliminary softening at 44°. An analysis, though inconclusive (Found: C, 30.3, 30.6; H, 6.4, 6.4; Si, 32.1, 32.4; –OH, 0.1) virtually eliminated from consideration any molecule containing functional groups and strongly suggested a polycyclic silicone. The most probable structures are those of hexa-(ethylsilsesquioxane) (III) or octa-(ethylsilsesquioxane) (IV).



Hexa-(ethylsilsesquioxane) (III)



Octa-(ethylsilsesquioxane) (IV)

Analogous structures were shown to occur in the "methylsilicone" series.[1] Octa-(ethylsilsesquioxane) now has been prepared in small yields by several methods. The best method is to cohydrolyze equimolar quantities of ethyltrichloro- and ethyltriethoxysilane in benzene at twice the "normal" concentration with 50% of the "normal" amount of water. Octa-(ethylsilsesquioxane) appears in the final distillate as an insoluble solid; it is filtered and purified by vacuum sublimation, followed by recrystallization from acetone. The average yield is about 0.9 g. from 0.5 mole each of reactants. A smaller yield results from cohydrolysis with three molar equivalents of water. Small amounts are also obtained during alkaline-catalyzed hydrolysis of ethyltriethoxysilane in ethanol with 1.5 molar equivalents of water.

Octa-(ethylsilsesquioxane) forms small needles or plates during sublimation in vacuum at temperatures of 160–180° or on crystallization from acetone or benzene. It is soluble in *n*-pentane, benzene, chloroform, carbon tetrachloride and acetone; insoluble in methanol, ethanol and water. The solid, twice recrystallized from acetone, melted at 278–280° in a sealed tube. The solubility is considerably greater than that of octa-(methylsilsesquioxane) ("methyl T-8,") as is the ease of sublimation; the melting point is appreciably lower, since "methyl T-8" does not melt below 410°.

Anal. Calcd. for $C_{16}H_{40}Si_8O_{12}$: C, 29.58; H, 6.22; Si, 34.62; mol. wt., 649.2. Found: C, 29.4; H, 6.4; Si, 34.4; mol. wt. (cryoscopically in benzene), 635, 591; (from the vapor density at 335°), 645–677.

The ~58° melting solid, in contrast, is highly soluble in numerous common organic solvents; *e.g.*, in pentane, heptane, benzene, cyclohexane, chloroform, carbon tetrachloride, carbon disulfide, acetone, ethyl alcohol, isopropyl alcohol, etc. It is, in fact, too soluble to permit recrystallization from any of these solvents. It is insoluble in water and of limited solubility only in methanol. Recrystallization from methanol, however, resulted in high losses, and sometimes only an uncrystallizable oil was recovered. If the solution was allowed to stand a half-hour at –10° only about 50% could be recovered, and standing overnight resulted in complete loss. This was, in itself, significant.[5] A sample was, nevertheless, recrystallized from methanol, working rapidly to minimize losses. The melting point was 59–60°.

Anal. Calcd. for $C_{12}H_{30}Si_6O_9$: C, 29.6; H, 6.2; Si, 34.6; mol. wt., 486.9. Found: C, 28.8; H, 6.6; Si, 35.1; mol. wt. (in cyclohexane), 473.

A number of oily distillates also were re-examined. A typical procedure was the following: A distillate of 16.7 g., b.p. 145–175° at 0.2–0.3 mm., obtained on acid-catalyzed hydrolysis of a mole of ethyltriethoxysilane in benzene, was slowly redistilled (in two portions) at about 0.5 mm. through a small 1/4" diameter platinum spiral column. Three cuts were taken. The lowest boiling portions (2.0–2.5 g., b.p. *ca.* 120–130°) slowly deposited solid on standing at –10°. The precipitate (0.51 g.) melted at 59.8–60.2° after crystallization from methanol. It was recrystallized from methanol, allowing the solution to stand at –10° for only 0.5 hour before filtering; m.p. 59.6–60.2°.

Anal. Calcd. for $C_{12}H_{30}Si_6O_9$: C, 29.6; H, 6.2; Si, 34.6; mol. wt., 486.9. Found: C, 29.9, 30.3; H, 6.0, 6.2; Si, 34.2; mol. wt. (in benzene), 484.

Experimental

Materials.—Ethyltriethoxysilane was obtained from the Linde Air Products Co. Ethyltrichlorosilane, from the same source, was redistilled, and a cut of boiling point 97.5°, 65.1% Cl, was used. Reagent grade benzene and U.S.P. anhydrous ethyl alcohol (U.S.I.) were used.

Hydrolysis of Ethyltriethoxysilane in Benzene with Three Molar Equivalents of Water.—One-half mole (96.2 g.) of ethyltriethoxysilane and 480 ml. of reagent-grade benzene were heated to 77° in a 1-liter, three-necked flask equipped with mechanical stirrer, Tru-Bore shaft, water-cooled condenser, thermometer and addition tube. A mixture of 24.5 ml. of water and 2.5 ml. of 0.5 *N* HCl was added, followed by 20 ml. of benzene. The mixture was maintained at the reflux temperature for 2.5 hours with vigorous stirring. The temperature of the liquid fell slowly from 71.1 to 66.0°, while the vapor temperature fell from 69.0 to 64.7°. The aqueous phase disappeared completely toward the end of the heating period. The addition tube was replaced by a modified Dean–Stark trap, and 23.5 ml. of liquid (mainly water) was collected during 2.0 hours. The liquid temperature rose to 68.0°. The Dean–Stark trap was replaced by a "downward" condenser, and the solvents (490 ml.) were distilled to 83° (pot temperature, 100°). From the refractive index (1.4795 at 20°) and the density (0.841 at 25°), it was estimated that 65 g. of ethanol was formed. The pale-yellow liquid residue was transferred to a still pot to which was attached a Claisen-type distilling head (Scientific Glass Apparatus Co., Catalogue No. J-1102). Residual solvents were removed at 25–40° and about 10 mm. The crude product was a heavy, pale amber liquid, weighing 51.9 g. The pressure was reduced to ~1 mm. Three grams distilled at about 149–158°, 14.2 g. at 167–176°; final pot temperature, 209°. The residue, a heavy, pale amber, balsam-like liquid, weighed 27.0 g.

Co-hydrolysis of Ethyltriethoxysilane and Ethyltrichlorosilane in Benzene with Three Molar Equivalents of Water.—The apparatus was the same as that used during the homohydrolysis, except that a Tygon tube led from the condenser

---

(4) A. J. Barry and J. W. Gilkey, U.S. Patent 2,465,188, March 22, 1949.

(5) Molecules that contain the strained cyclotrisiloxane ring react with methanol, giving methoxypolysiloxanols, by chain opening; private communication from Dr. W. T. Grubb.

outlet to a trap containing a concentrated solution of sodium hydroxide for absorption of gaseous HCl. Charged to the flask were 40.9 g. (0.25 mole) of ethyltrichlorosilane, 48.1 g. (0.25 mole) of ethyltriethoxysilane and 500 ml. of reagent-grade benzene. The reactants were cooled to 5° in an ice-bath. Water (27.0 ml.) was added during 17 minutes at 3.5–11°, with continuous stirring. The reaction mixture was then heated slowly to facilitate the removal of hydrogen chloride. During 85 minutes, the boiling point rose from 44 to 68°. A Dean–Stark trap now replaced the addition tube. The aqueous layer which was separated also contained ethanol, benzene, and some HCl; total volume, 62.3 ml. The gain in weight of the caustic absorber approached the theoretical value. The solvents were distilled (480 ml., b.p. to 86°). The residue (74.4 g.) was filtered from a small amount of gel and distilled using the Claisen-type head previously described. Three fractions were taken: (1) 6.7 g., b.p. 138–149°, 7.0% $-OC_2H_5$; (2) 2.6 g., b.p. 149–161°, 7.1%. $-OC_2H_5$; (3) 3.7 g., b.p. 161–176°, 6.2% $-OC_2H_5$. The residue, a stiff, balsam-like material, weighed 26.5 g. and contained 5.3% $-OC_2H_5$.

Hydrolysis in Ethanol Solution.—One-half mole (96.2 g.) of ethyltriethoxysilane and 500 ml. of absolute ethyl alcohol were charged to the reaction flask. The water (27.0 ml. containing 2.5 ml. of 0.5 *N* HCl) was added in 12 minutes at 27–33°. Heat was applied slowly; then the reaction mixture was maintained at the boiling point (78°) for 3 hours. A still-head was attached, and alcohol was distilled until the liquid temperature reached 93°. Vacuum distillation followed immediately, giving: 7.5 g., b.p. 143–154° at 0.5 mm., 20.1% $-OC_2H_5$; 3.5 g., b.p. 166–180° at 0.5 mm., 15.5% $-OC_2H_5$; 34.4 g. residue, 14.0 $-OC_2H_5$.

Alkaline hydrolysis in ethanol was carried out similarly, the HCl being replaced by an equivalent volume of 0.5 *N* sodium hydroxide. There was some gel present after the heating period. The mixture was cooled and blown with CO_2 for 1.5 hours to remove alkali. The carbonate formed and the gel present were removed by filtering through a bed of Dicalite. After ethanol was distilled, a second filtration produced 1–2 g. more of gel. The concentrate was washed several times with water. On vacuum distillation, only an inconsequential yield of liquid was obtained. The gelled residue weighed 22 to 32 g. on several trials. Using less than three molar equivalents of water, however, distillable reaction products were obtained, as described previously.

Acknowledgment.—The distillations involving the spinning-band columns were carried out by E. M. Hadsell and Mrs. Dorothea Ladd. The ultimate analyses and molecular-weight determinations were carried out by various members of the Analytical Chemistry Unit of this Laboratory. C. A. Hirt is responsible for the infrared spectrograms. We wish to thank all these individuals for their assistance.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE MOUNT SINAI HOSPITAL]

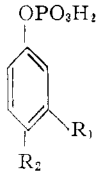
The Mechanism of the Hydrolysis of Organic Phosphates. III. Aromatic Phosphates[1]

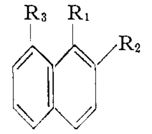
BY J. D. CHANLEY AND EDWARD FEAGESON

RECEIVED FEBRUARY 3, 1955

The rates of the hydrolysis, over the *p*H range 1–10, of the following six compounds: phenyl (I), *m*-carboxyphenyl(II), *p*-carboxyphenyl(III), α-naphthyl (IV), β-naphthyl (V) and 8-carboxy-α-naphthyl (VI) phosphates have been determined. First-order kinetics were observed in each instance. All six compounds exhibited a maximum rate of hydrolysis in an intermediate *p*H range, were quite stable at *p*H of 1, and completely stable at *p*H of 8 and above. An explanation for the observed *p*H dependency is offered and the influence of the carboxyl group is discussed. The *p*H *vs.* hydrolysis rate curve for compound VI differs fundamentally from that observed with the other compounds, but resembles that of *o*-carboxy-substituted aromatic phosphoric acid esters. This observation, in conjunction with other evidence, supports the view that the hydrolysis of compound VI proceeds, in contradistinction to compounds I through V, by a "participation" mechanism which involves the attack of the carboxylate anion on the phosphorus with formation of a seven-membered ring "transition state." The various ionization constants of compounds I through VI have been determined and the entropies and heats of activation evaluated.

In continuation of our studies[2a,b] on the hydrolysis of aromatic phosphoric esters, we wish to report on the hydrolysis of the following six compounds: phenyl (I), *m*-carboxyphenyl (II), *p*-carboxyphenyl (III), α-naphthyl (IV), β-naphthyl (V) and 8-carboxy-α-naphthyl (VI) phosphate to the parent phenol or naphthol and phosphoric acid. Compounds I, II and III were chosen for study, since they form—in conjunction with the previously investigated *o*-carboxyphenyl phosphate (salicyl phosphate)—a series, which lends itself particularly well to a study of the effect exerted on the hydrolysis by the intact carboxyl group and carboxylate anion. Compounds IV and V are related to *o*-carboxynaphthyl phosphates previously studied, while with compound VI the carboxyl group, albeit in the other ring, is so close to the phosphate grouping as to suggest "a priori" the possibility of behavior analogous to the *ortho* position.





I, R_1 = H; R_2 = H
II. R_1 = COOH; R_2 = H
III, R_1 = H; R_2 = COOH

IV, R_1 = OPO_3H_2;
R_2 = H; R_3 = H
V, R_1 = H;
R_2 = OPO_3OH; R_3 = H
VI, R_1 = OPO_3H;
R_2 = H; R_3 = COOH

***p*H Dependency and Rates.**—The rates of hydrolysis of compounds I through VI were determined at 80° over the *p*H range 1–10 in buffered medium of ionic strength $\mu = 0.1$ by analysis for liberated phosphoric acid. In each instance first-order kinetics obtained throughout the course of the reaction. All six compounds exhibited a maximum rate of hydrolysis in an intermediate *p*H region, were quite stable at *p*H *ca.* 1, and completely stable at *p*H of 8 and above (see Figs. 1

---

[1] This work was supported in part by a grant from the National Science Foundation. The material was presented in part at the Annual Meeting of the American Chemical Society in New York City, Division of Organic Chemistry, on September 16, 1954. For the preceding papers in this series see reference 2a,b.

[2] (a) J. D. Chanley, E. M. Gindler and H. Sobotka, THIS JOURNAL, **74**, 4347 (1952); (b) J. D. Chanley and E. M. Gindler, *ibid.*, **75**, 4035 (1953).