carbonyl compounds are formed, as yet unidentified, some of which may also be expected to play a role as intermediates. The present paper supports these views, the spectroscopic evidence showing the overwhelming effect of furfurals on the absorption, while the polarographic data show that the wave found in darkened extracts cannot be accounted for exclusively in terms of furfurals, as determined spectroscopically.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Thermal Transformations of Methylchlorosilanes

BY ROBERT O. SAUER AND E. M. HADSELL

The methylchlorosilanes, $(CH_3)_nSiCl_{4-n}$, apparently possess reasonable thermal stability since their synthesis has been reported at temperatures of 300 to 400°.[1] Objectives of the present study were a more precise definition of the thermal stability of these compounds and at least a qualitative knowledge of their decomposition products. In particular we sought to effect an interchange of chlorine atoms and methyl groups and to ascertain the conditions necessary to produce such interchange.

The first observation on the migration of hydrocarbon radicals attached to silicon is that of Ladenburg,[2] who reported small amounts of diethyldiphenylsilane and tetraethylsilane by the interaction of zinc ethyl and phenyltrichlorosilane at 175°. Dolgov and Volnov[3] reported a study of similar rearrangements on heating tetrasubstituted alkyl- and alkyl-arylsilanes at 300° for twenty-four to forty-eight hours with an initial pressure of 100 atmospheres of hydrogen. In addition to rearrangements these investigators noted the hydrogenolysis of silicon–carbon bonds which, in this case, resulted in the formation of disilanes and hydrocarbons. The interchange of alkyl groups in tetra-alkylsilanes was studied again by Calingaert, Soroos and Hnizda[4] who reported that a "random equilibrium mixture" containing all five possible tetraalkylsilanes was obtained by heating under reflux approximately equimolar amounts of tetraethylsilane and tetra-*n*-propylsilane at 175–180° for five hours with 2.5 mole per cent. of aluminum chloride.

During the progress of this work the random rearrangement of the chlorobromosilanes and the chloroiodosilanes at 600° and without a catalyst was reported.[5] With aluminum chloride "partial" rearrangement could be effected in seven hours at 140°. Interchange of hydrogen and chlorine was similarly carried out by Stock and Somieski[6] in their synthesis of chlorosilane from silane and dichlorosilane.

At the start we planned to study the thermally induced transformations of the methylchlorosilanes by heating the individual compounds up to 450° in a closed steel vessel and in the presence of a variety of inorganic chlorides as possible decomposition or rearrangement catalysts. As it soon became apparent that interchange of the substituents on silicon could be brought about, a second projection of the problem was to establish whether or not an equilibrium existed and, if so, to ascertain the concentrations of the various components at equilibrium. The nature of the side reactions, pronounced at temperatures of 375° and higher, as well as the extension of the rearrangement studies to systems containing two types of hydrocarbon radicals, logically constituted part of the broad problem.

Experimental

A. Redistribution of the Methylchlorosilanes

Reaction Conditions.—A steel Aminco rocking autoclave operated under autogenous pressure was used in our experiments. The temperature range covered was from 250°, at which temperature the extent of reaction was very small, to 450° which was about the upper limit of our heating jacket. Since the critical temperatures of the methylchlorosilanes are in the range 225–275° no liquid phase was expected during the experiments. In general about one liter of liquid methylchlorosilanes was charged to the 3.4-l. autoclave; this corresponds to about 2.3 moles per liter (gas phase). The pressures developed in the bomb were linear with temperature. In Fig. 1 some of the experimental points obtained on six 1.0-kg. charges of dimethyldichlorosilane are plotted (Curve I) to show the lower pressures obtained experimentally as compared to those predicted by the ideal gas laws (Curve II). At comparable molar concentrations substantially the same pressure–temperature behavior was shown by trimethylchlorosilane, by methyltrichlorosilane, by equimolar mixtures of these two, and by a 2:1 mixture of the former with silicon tetrachloride.

Since it was established fairly early in the investigation that aluminum chloride was an effective catalyst (whereas zinc chloride, ferric chloride, cuprous chloride and boron chloride were much inferior) in accelerating the attainment of the equilibria all of the experiments described in this paper employed either this compound or no added catalyst.

The heating times given represent the elapsed time at the stated temperature. Actually at the higher temperatures the reaction times are appreciably longer (possibly two or three hours longer) than the times given because of the heat capacity of the bomb and heater. In some cases (and these are designated as "quenched") the autoclave was removed immediately from the heater and chilled rapidly so

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[1] Rochow, THIS JOURNAL, **67**, 963 (1945).

[2] Ladenburg, *Ber.*, **7**, 387 (1847).

[3] Dolgov and Volnov, *J. Gen. Chem.* (*U. S. S. R.*), **1**, 91 (1931).

[4] Calingaert, Soroos and Hnizda. THIS JOURNAL, **62**, 1107 (1940).

[5] Forbes and Anderson, THIS JOURNAL, **66**, 931 (1944).

[6] Stock and Somieski, *Ber.*, **52**, 719 (1919).

TABLE I

REARRANGEMENT OF TRIMETHYLCHLOROSILANE

Charge: $(CH_3)_3SiCl$, 0.85 kg.; $n = 3.00$

Expt.	Reaction conditions Temp., °C.	Time, hr.	Press., atm.	% cat.	Loss, wt. %	Product composition (wt. %) $SiMe_4$	Me_3SiCl	Me_2SiCl_2	res.	loss	n
1	300	15.3	54	2.3	0.0	7.8	76.4	9.1	2.3	4.5	3.02
2	300	15.0	52	2.3	0.0	5.7	79.0	9.3	1.3	4.7	3.00
3	350	10.0	...	1.2	4.8	8.2	69.5	14.9[b]	1.8	5.0	2.97
4	375	7.0	83	2.3[a]	0.0	4.5	69.2	14.2	7.4	4.7	2.93[a]
5	375	7.0	79	2.3	2.4	4.1	71.8	8.2	11.3	4.7	2.98
6	400	7.0	86	0.0	2.5	0.6	..	..	...	..	..
7	450	7.0	108	0.0	4.0	7.4	75.7	11.7	3.9	1.3	3.00
					Ave.	6.3	73.9	11.2			

[a] The moist catalyst from a run at $n = 1.0$ was reused here; this may account for the low n-value of the product.

[b] Also about 0.6% $MeSiCl_3$.

that the temperature of the contents fell to 200° in less than five minutes.

Analyses.—In most cases where complete analyses are reported the liquid product from the bomb was charged to a Claisen flask where it was stripped to a vapor temperature of 125°. The condensed volatiles were then distilled in a $^3/_8$ in. diameter, 7-ft. long, Stedman column rated at about 100 theoretical plates at total reflux. The boiling points of the various components present are as follows: $Si(CH_3)_4$, 27°; $HSiCl_3$, 32°; CH_3SiHCl_2, 41°; $SiCl_4$, 57°; $(CH_3)_3SiCl$, 58°; CH_3SiCl_3, 66°; $(CH_3)_2SiCl_2$, 70°. Further, an azeotrope of silicon tetrachloride and trimethylchlorosilane exists which distills at 54.7° (760 mm.). All fractions were analyzed for hydrolyzable chlorine and the interfractions apportioned according to the analytical results. The residue from the distillation in the Stedman column and the residue from the stripping still were combined. This material was charged to a small column of about ten plates and the remainder of the methylchlorosilanes (in general, a small amount of dimethyldichlorosilane) was distilled. The treatment of the residue from this operation will be described in a subsequent section. In general we feel that the distillation analyses are accurate to 3 wt.% for the more abundant components of the charge and to 2 wt.% for the less abundant; for example, a value of 10% lies in the range 8–12%.

Certain losses were experienced and occasionally these were of considerable magnitude. The losses on removing the liquid from the bomb were generally about 4% with a maximum of 11%. The losses on distillation varied with the volatility of the compounds present. For the samples containing tetramethylsilane the losses were 4–5% of the charge to the still; for the others, about 2–3%.

Results

The composition of the equilibrium mixtures of methylchlorosilanes should depend primarily on the concentration of methyl groups; hence, experiments at approximately the same methyl-to-silicon ratio (n) will be grouped together for purposes of ready comparison. Data on the reaction conditions and the analytical results for seven runs with charges of trimethylchlorosilane are listed in Table I.

The reaction conditions noted are the temperature in °C., the heating time in hours at that temperature, the pressure in atmospheres and the weight percentage of aluminum chloride used as the catalyst. The composition of the product is based on the weight from the bomb. With the exception of a small amount of methyltrichlorosilane found in experiment 3, tetramethylsilane, trimethylchlorosilane and dimethyldichlorosilane were the only compounds isolated of the general formula $(CH_3)_nSiCl_{4-n}$ ($n = 0, 1, 2, 3, 4$). The n-value of the methylchlorosilanes actually isolated is given in the last column. A comparison of the two experiments at 300° with the two at 375° indicates that the equilibrium concentration depends on the temperature. The results of exp. 7 at 450°, however, tend to disavow such a presumption. Hence, one must question whether or not this uncatalyzed reaction—or, possibly, the catalyzed reactions at 300° (expts. 1 and 2)—had attained equilibrium in the time allotted. In view of the uncertainties we feel that the temperature dependence has not been established in this work, and hence we shall use the averaged values in our discussion.

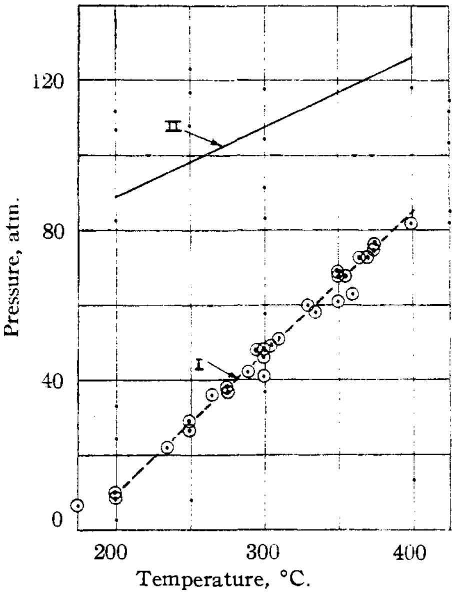


Fig. 1.—Pressure developed in reactor as a function of temperature: curve I, observed for d = 2.3 moles/liter; curve II, calculated by ideal gas law.

The average percentages of the three components assumed to be present at equilibrium (omitting expt. 6, however) are: tetramethylsilane, 6.3%; trimethylchlorosilane, 73.9%; dimethyldichlorosilane, 11.2%. These figures account for 91.4% of the weight from the reactor. Neglecting the residue and losses during analysis these amounts become, respectively, 6.9, 80.8 and 12.3%, based on the methylchlorosilanes actually isolated.

The reaction involved may apparently be represented by eq. 1 although the existence of an

$$(CH_3)_4Si + (CH_3)_2SiCl_2 = 2(CH_3)_3SiCl \quad (1)$$

equilibrium has not been unequivocally demonstrated by approaching the attained concentrations from the tetramethylsilane–dimethyldichlorosilane side.

The analytical data on the eight experiments in which dimethyldichlorosilane was charged to the bomb are not as complete as those obtained for trimethylchlorosilane. Nevertheless, a three-component equilibrium is again indicated as shown by the constancy of the concentrations of methyltrichlorosilane and trimethylchlorosilane obtained in the experiments 10–14, inclusive, which are listed in Table II. Further, neither tetramethylsilane nor silicon tetrachloride could be detected by our distillation procedures. The average weight percentages of $(CH_3)_3SiCl$ and CH_3SiCl_3 based on the liquid from the reactor are 8.6% and 12.6%, respectively, using the data of experiments 10–14, inclusive. Assuming a figure of 7.0% for the combined loss and residue the average amount of $(CH_3)_2SiCl_2$ is 71.8%. On a methylchlorosilane basis these figures reduce to: $(CH_3)_3SiCl$, 9.3%; $(CH_3)_2SiCl_2$, 77.1%, CH_3SiCl_3, 13.6%. The reaction involved may be represented by eq. 2.

TABLE II

REARRANGEMENT OF DIMETHYLDICHLOROSILANE

Charge: $(CH_3)_2SiCl_2$, 1.0 kg. $n = 2.00$

	Reaction conditions					Product composition	
Expt.	Temp., °C.	Time, hr.	Press., atm.	% cat.	Loss, wt. %	Me_3SiCl	$MeSiCl_3$
8	250	6.0	..	2.0	6.0	0.4	1.6
9	300	7.2	..	3.0	11.2	4.0	6.0
10	300	48.5[a]	47	2.0	1.1	7.6	12.6
11	350	7.0	64	2.0	0.3	9.2	12.6
12	375	7.0	..	2.0	3.0	8.5	12.6
13	375	7.0[a]	76	2.0	8.4	9.7	13.1
14	375	14.0	..	2.0	2.6	7.9	12.0
15	375–400	3.5	83	0.0	11.4	<0.2	<0.2
					Av.	8.6	12.6

[a] Quenched.

$$CH_3SiCl_3 + (CH_3)_3SiCl = 2(CH_3)_2SiCl_2 \quad (2)$$

At this n-value we have also established the forward reaction by approaching the equilibrium value from the methyltrichlorosilane–trimethylchlorosilane side (Table III).

In experiment 16 the reaction time of 7.3 hours was apparently insufficient to allow equilibrium to be established from an equimolar mixture of CH_3SiCl_3 and $(CH_3)_3SiCl$ at 300°. However, at 375° in experiment 17 essentially the same final concentrations were obtained as in the experiments listed in Table II. No silicon tetrachloride nor silicon tetramethyl was noted in these experiments either, even in experiment 18 where the charge to the autoclave was one-third silicon tetrachloride.

Attainment of the expected equilibrium (eq. 3)

$$(CH_3)_2SiCl_2 + SiCl_4 = 2CH_3SiCl_3 \quad (3)$$

is more difficult at $n = 1.0$ as shown by the data of Table IV and V. Only very approximate values of the equilibrium concentration of methyltrichlorosilane could be obtained. We can say, however, that at $n = 0.91$–0.92 the weight percentage at equilibrium of methyltrichlorosilane in the volatile portion of the reaction mixture lies between 82% (expt. 20) and 63% (expt. 24). It seems probable that the true value is in the range 75–80%.

Miscellaneous Additional Experiments.—Several additional experiments designed to check the equilibrium concentrations at n-values of 2.5, 2.0 and 1.5 were carried out. Although equi-

TABLE III

ADDITIONAL EXPERIMENTS AT $n = 2.00$; CHARGE, 1.0 KG.

	Reaction conditions					Product composition, wt. %					
Expt.	Temp., °C.	Time, min.	Press., atm.	% cat.	Loss, wt. %	Me_3SiCl	Me_2SiCl_2	$MeSiCl_3$	res.	loss	n
16[a]	300	7.3	49	3.0	0.0	15.8	53.5+	21.9	9.0		2.00
17[a]	375	7.0	..	2.0	0.6	8.3	72.2	12.6	2.5	4.4	1.99
18[b]	375	23.5[c]	74	2.0	7.4	6.5	..	13.8	...	...	....

[a] Equimolar Me_3SiCl and $MeSiCl_3$. [b] Two moles Me_3SiCl to one mole of $SiCl_4$. [c] Quenched.

TABLE IV

REARRANGEMENT OF METHYLTRICHLOROSILANE

	Reaction conditions						Product composition, wt. %					
Expt.	Charge, g.	Temp., °C.	Time, hr.	Press., atm.	% cat.	Loss, wt. %	Me_2SiCl_2	$MeSiCl_3$	$SiCl_4$	res.	loss	n
19	993	375	7.0	64	2.1	2.9	3.1	94.0	Trace	1.3	1.6	1.03
20	1193	450	7.0	100	1.7	4.6	2.8	66.0	11.4	17.2	2.6	0.91

TABLE V

ADDITIONAL EXPERIMENTS AT $n = 1.0$; CHARGE, *ca.* 1.0 KG.

	Reaction conditions					Product composition, wt. %						
Expt.	Temp., °C.	Time, hr.	Press., atm.	% cat.	Loss, wt. %	Me_3SiCl	Me_2SiCl_2	$MeSiCl_3$	$SiCl_4$	res.	loss	n
21[a]	200	20.1[c]	49	1.7	5.5	0	..	0	..	..	...	1.00
22[b]	375	7.0	76	1.8	4.4	4.3	21.7	6.3	55.1	8.7	3.9	0.86
23[a]	375	17.0[c]	68	1.9	11.0	0	31.0	23.4	41.9	3.4	0.3	.99
24[a]	450	7.0	94	1.9	8.3	Trace	9.8	50.6	20.4	12.7	6.5	.92

[a] Charge: equimolar Me_2SiCl_2 and $SiCl_4$. [b] Charge: two moles $SiCl_4$ to one mole of Me_3SiCl. Quenched.

librium was not attained in some of these the results are of interest.

In the first, 912 g. of an *equimolar* mixture of *dimethyldichlorosilane* and *trimethylchlorosilane* was heated in the 3.4-l. Aminco hydrogenation bomb with 2.3 wt.% of aluminum chloride for seven hours at 375° (77 atm.). The loss on removing the liquid from the bomb was about average (2.85%), and no tetramethylsilane was found by distillation analysis. On this basis it was assumed that the equilibrium mixture at $n = 2.5$ consists of 45.6 wt.% of $(CH_3)_3SiCl$ and 54.4 wt.% of $(CH_3)_2SiCl_2$ (*i. e.*, equimolar).

A similar experiment was performed with 1114 g. of an *equimolar* mixture of *dimethyldichlorosilane* and *methyltrichlorosilane* (1.8% $AlCl_3$, seven hours at 375°, 76 atm.). In this case 5 g. of $(CH_3)_3SiCl$ (about 0.5 wt.% of the liquid from the bomb) was isolated. However, it is believed that the equilibrium concentrations in wt.% at $n = 1.5$ are approximately: CH_3SiCl_3, 54: $(CH_3)_2SiCl_2$, 46 (*i. e.*, about equimolar).

A third and similar experiment at $n = 1.5$ starting, however, with *equimolar silicon tetrachloride* and *trimethylchlorosilane* resulted in a considerable but not complete transformation to $(CH_3)_2SiCl_2$ and CH_3SiCl_3. After a heating time of 7.1 hours at 375° the $(CH_3)_2SiCl_2$ was present in the expected concentration of 46 wt.%, but the liquid from the bomb contained only about 30 wt.% of CH_3SiCl_3. Since some $(CH_3)_3SiCl$ and $SiCl_4$ remained (the *n*-value of the methylchlorosilanes found was still 1.50) it was concluded that seven hours is insufficient time to attain equilibrium from the starting components used.

The sluggishness of redistributions which involve several equilibria was also illustrated by heating *equimolar* amounts of *tetramethylsilane* and *silicon tetrachloride* with 2% aluminum chloride for thirteen hours at 290–325°. The composition of the product in mole per cent. was: $Si(CH_3)_4$, 5; $(CH_3)_3SiCl$, 58; $(CH_3)_2SiCl_2$, 3; CH_3SiCl_3, 0; $SiCl_4$, 34. Since it is known (expt. 18, Table III) that trimethylchlorosilane reacts with silicon tetrachloride to form dimethyldichlorosilane in the equilibrium amount this experiment was not repeated.

The rearrangement of *methyldichlorosilane* under these conditions yielded silane and the chlorosilanes as well as the methylchlorosilanes.

To the 3.4-l. Aminco bomb was charged 927 g. (8.05 moles) of CH_3SiHCl_2 and 20 g. of $AlCl_3$. This mixture was heated at 325° for twenty-four hours. The pressure rose from 69 to 83 atmospheres in the first four hours and then remained constant. After cooling to room temperature the pressure was 8 atm. On bleeding off, the gas ignited spontaneously (SiH_4!). Although most of the pressure was released by venting, a portion of the vapors distilled from the bomb up to a temperature of about 50° yielded the following fractions on low temperature distillation: SiH_4, b. p. −116 to −114°, 0.9 g.; HCl, b. p. −85 to −79°, 0.4 g.; H_3SiCl, b. p. −34 to −31°, 4.6 g.; H_2SiCl_2, b. p. 8–11°, 9.7 g. The residue from this distillation (28 g.) was principally $HSiCl_3$. The liquid remaining in the bomb weighed 680 g. Analytical distillation in the Stedman column indicated its composition (in wt.%) to be: $HSiCl_3$, 7.2; CH_3SiHCl_2, 30.7; CH_2SiCl_2, 29.5; $(CH_3)_2SiCl_2$, 17.5; residue, 1.6; loss, 13.5.

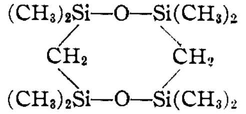
Although trichlorosilane is reported to be unaffected after forty-eight hours at 175° in the presence of aluminum chloride[7] our work indicates that at temperatures in the range 300–400° this compound disproportionates somewhat into dichlorosilane and silicon tetrachloride.

B. Side Reactions Accompanying Rearrangement

It is apparent from the data given in Tables I to V that the amount of "residue" increases very appreciably with temperature, particularly from 375° upward. In the runs at higher temperatures we noted an appreciable residual pressure after the reactor had cooled to room temperature. This proved to be due principally to methane. Subsequent examination of the residues revealed the presence of compounds containing methylene bridges between silicon atoms, such as $Cl_3SiCH_2SiCl_3$ and $Cl(CH_3)_2SiCH_2Si(CH_3)_2Cl$. One reaction accompanying redistribution then appears to be the elimination of methane from two methyl groups attached to silicon and the establishment of a methylene bridge between silicon atoms. This type of reaction is exemplified by eq. 4 and is probably not reversible.

$$2CH_3SiCl_3 \longrightarrow CH_4 + Cl_3SiCH_2SiCl_3 \qquad (4)$$

The new compound bis-(dimethylchlorosilyl)-methane formed similarly from trimethylchlorosilane was hydrolyzed yielding the cyclic dimer: 2,2,4,4,6,6,8,8-octamethyl-1,5-dioxa-2,4,6,8-tetrasilocane.[7a]



Experimental

bis-(Trichlorosilyl)-methane.—This compound has previously been prepared by Patnode and Schiessler,[8] who report the boiling point as 184–185° at 756 mm.

A. The residue of 123 g. from expt. 24 (Table V) was carefully distilled yielding 71.0 g. of impure bis-(trichlorosilyl)-methane, b. p. 185–186° (764 mm.). The chlorine contents of the various fractions were in the range 70.6 to 69.6% whereas $(Cl_3Si)_2CH_2$ requires 75.20% Cl. The most probable impurity is $Cl_3SiCH_2Si(CH_3)Cl_2$ (67.55% Cl) formed by the reaction

$$Cl_3SiCH_3 + (CH_3)_2SiCl_2 \longrightarrow CH_4 + Cl_3SiCH_2Si(CH_3)Cl_2 \qquad (5)$$

B. The residue from expt. 20 (Table IV) yielded 108 g. of crude bis-(trichlorosilyl)-methane which contained some aluminum chloride. Careful redistillation gave three fractions totalling 43.5 g. of substance, b. p. 185.1–185.5°, and which gave the analyses: 70.2, 70.2, 69.7% Cl, respectively.

bis-(Dimethylchlorosilyl)-methane. A.—From the residue of expt. 4, 30 g. of crude material, b. p. 179–191°, was isolated; this contained 37.1% Cl. Careful redistillation gave three fractions totalling 18.4 g. of slightly impure bis-(dimethylchlorosilyl)-methane, b. p. 174.5–175.8°, for which the respective chlorine analyses were: 35.3, 35.6, 35.7% (calcd. for $C_5H_{14}Si_2Cl_2$: Cl, 35.25). The most probable impurity is $Cl(CH_3)_2SiCH_2Si(CH_3)Cl_2$ (Cl, 48.00) (see also Bluestein[7a]).

B. The 95-g. residue from expt. 5 (Table I) was carefully distilled yielding four fractions totalling 39.4 g., b. p. 175.3–177.0°, and which gave the following analyses: 35.0, 35.4, 35.6, 35.7% Cl, respectively. These were considered to be slightly impure bis-(dimethylchlorosilyl)-methane (35.25% Cl).

2,2,4,4,6,6,8,8-Octamethyl-1,5-dioxa-2,4,6,8-tetrasilocane.—The seven fractions of bis-(dimethylchlorosilyl)-methane described above were combined (about 50 g. after

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[7] Stock and Ziedler, *Ber.*, **56**, 988 (1923).

[7a] Note added in proof: This compound has been mentioned by Goodwin, Baldwin and McGregor [THIS JOURNAL, **69**, 2247 (1947)] and has been described recently by Bluestein [*ibid.*, **70**, 3068 (1948)].

[8] Patnode and Schiessler, U. S. Patent 2,381,000, U. S. 2,381,002 (Aug. 7, 1945).

samples) and hydrolyzed by pouring in water. The oily layer was extracted with pentane, and the extract washed with potassium carbonate solution. After evaporation of the pentane the oily product was distilled in a Claisen flask. Two fractions were obtained: A, b. p. 212–221° (mostly at 213–213.5°), 5.0 cc., n^{20}_D 1.4341, d^{20}_4 (vac.) 0.9039, m. p. *ca.* 30°.; B, b. p. 213–235°, 1.8 cc.

Anal. Calcd. for $C_{10}H_{28}Si_4O_2$: C, 41.05; H, 9.58. Found (fract. A.): C, 41.1, 41.6, 41.0; H, 9.6, 9.9, 9.6.

The calculated specific refraction for the proposed structure is 0.2888 and that found for fraction A is 0.2882.

A liquid residue (15 g.) of higher boiling polymer remained in the flask. This gave n^{20}_D 1.4507; d^{20}_4 (vac.) 0.9463; R_D 0.2844.

C. Methylation of Phenyl- and Ethyl-trichlorosilanes

Our attempts to redistribute phenyl groups attached to silicon with or without aluminum chloride at 350° have so far been unsuccessful. Equimolar mixtures of diphenyldichlorosilane and silicon tetrachloride have given some phenyltrichlorosilane but this is believed to arise from the reaction

$$(C_6H_5)_2SiCl_2 + HCl \longrightarrow C_6H_5SiCl_3 + C_6H_6 \quad (6)$$

since benzene is produced in an approximately equivalent amount.

However, phenyltrichlorosilane with methylchlorosilanes gives methylphenyldichlorosilane. Because of the proximity of boiling points the parent compound (b. p. 201°) cannot be separated from its derivative (b. p. 204°) by distillation. In our experiments the mixtures of chlorosilanes was converted to a mixture of fluorosilanes which could then be readily separated. The conversion was accomplished *via* the ethoxy derivatives which were treated with anhydrous hydrogen fluoride rather than by heating the chlorosilanes directly with zinc fluoride. The latter process, though successful, gave considerable benzene.

Ethyltrichlorosilane may be methylated to yield similarly methylethyldichlorosilane. This was converted to the diethoxysilane and thence to methylethyldibromosilane.

Experimental

Diphenyldichlorosilane and Silicon Tetrachloride.—A. Into the copper liner of a 1.3-l., Aminco rocking autoclave was charged 386 g. (1.52 moles) of diphenyldichlorosilane and 258 g. (1.51 mole) of silicon tetrachloride (40% by wt.). The temperature of the mixture in the closed pressure vessel was raised slowly (three hours) to 350° (35 atm.) and held there for one hour. After heating at 375° for two hours longer the bomb was cooled and a 515-g. portion of the liquid contents distilled. From this, 187 g. of silicon tetrachloride was recovered. This is 91% of the amount expected on the basis of no reaction. About 4 g. of benzene and 7.4 g. of phenyltrichlorosilane (b. p. 194–202°) were also obtained.

B. To the 1.3-l. bomb (without the liner used in A) was charged 350 g. (1.38 mole) of diphenyldichlorosilane, 213 g. (1.25 mole) of silicon tetrachloride, and 4 g. of anhydrous aluminum chloride. After heating at 350° (32 atm.) for four hours with rocking the liquid reaction mixture was distilled yielding 213.2 g. (1.01 mole) of phenyltrichlorosilane, b. p. 197–200°, and 54.2 (0.7 mole) of benzene.

Phenyltrichlorosilane and Trimethylchlorosilane.—To the 3.4-l. Aminco autoclave was charged 396 g. (1.87 moles) of phenyltrichlorosilane, 207 g. (1.90 mole) of trimethylchlorosilane and 5.0 g. (0.037 mole) of anhydrous aluminum chloride. After heating at 325° for four hours the liquid product was removed from the autoclave and the $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, CH_3SiCl_3 and benzene removed up to a vapor temperature of 175°. The residue was distilled at atmospheric pressure over sodium chloride yielding 102 g. of liquid, b. p. 190–205°, 40.6% Cl. This was shown to contain methylphenyldichlorosilane by its conversion to *methylphenyldiethoxysilane* (51 g.), b. p. 217.5–223°. An authentic sample of this compound was prepared from methylphenyldichlorosilane and anhydrous ethanol; it distils at 221.5° whereas phenyltriethoxysilane boils at 235–237°.[9]

The methylphenyldiethoxysilane (51 g.) isolated as a derivative of the reaction mixture was treated with anhydrous hydrogen fluoride. The methylphenyldifluorosilane was extracted from the reaction mixture with pentane and distilled; 23.2 g., b. p. 141.2–141.7°, was obtained. Additional amounts of this compound were prepared from an authentic sample of methylphenyldichlorosilane. The first specimen, which distilled at 141.4–142.4°, was obtained *via* the ethanol–hydrogen fluoride treatment just described. A second sample was prepared directly by treating the chlorosilane with zinc fluoride, b. p. 142–142.5°. Phenyltrifluorosilane boils at 102°.

About 90 g. of methylphenyldifluorosilane was carefully redistilled. A heart cut (11 g.) was collected at 142.9–143.0° (767 mm.). Its density at 27° was 1.092 g./ml. with a temperature coefficient near 27° of 0.0012 g./ml./°C. The fluorine analysis was made in ethanol by acid–base titration in the presence of calcium chloride.

Anal. Calcd. for $C_7H_8SiF_2$: F, 24.04. Found: F, 23.8, 23.5.

Phenyltrichlorosilane and Dimethyldichlorosilane.—Into a 1.3-l., Aminco autoclave was charged 212.5 g. (1.00 mole) of diphenyldichlorosilane, 259 g. (2.01 moles) of dimethyldichlorosilane, and 10 g. of aluminum chloride. The autoclave was closed and heated at 350° (57 atm.) for four hours. The product was worked up as described above yielding, finally, about 29 g. (0.18 mole) of methylphenyldifluorosilane, b. p. 141–142°.

Ethyltrichlorosilane and Dimethyldichlorosilane.—Into the 3-l., Aminco hydrogenation bomb was placed 198.5 g. (1.54 mole) of dimethyldichlorosilane, 249.1 g. (1.53 mole) of ethyltrichlorosilane and 10 g. of aluminum chloride. After heating at 375° for five hours the charge was worked up in the usual way yielding 130 g. of a mixture of ethyltrichlorosilane (b. p. 100°) and methylethyldichlorosilane (b. p. 100.5°).[10] This mixture, which contained 57.7–57.8% of hydrolyzable chlorine, was treated with absolute ethanol. By this means 32.8 g. of *methylethyldiethoxysilane* was obtained. A heart fraction (14.3 g.) boiling at 140°, n^{20}_D 1.3950, was collected on fractionation.

Anal. Calcd. for $C_7H_{18}SiO_2$: C, 51.81; H, 11.18. Found: C, 51.6, 51.9; H, 11.0, 11.0.

The above product was added to 146 g. of phosphorus tribromide and the mixture refluxed for six hours. After the ethyl bromide was distilled about 6 g. of reasonably pure *methylethyldibromosilane*, b. p. 139–141°, was obtained.

Anal. Calcd. for $C_3H_8SiBr_2$: Br, 68.90. Found: Br, 69.5, 69.8.

D. Discussion

The Rate of the Redistribution Reaction.—The rate of the uncatalyzed reaction in steel at temperatures below 400° is quite slow as shown by experiments 6 and 15. In fact, even the aluminum chloride-catalyzed reaction is slow at 300° for a reaction time of seven hours seems to be insufficient, on occasion, to obtain equilibrium as shown by experiments 9 and 16. At a methyl-to-silicon ratio of unity the reaction is extremely slow

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[9] Kalinin, *Compt. rend. Acad. Sci. U. R. S. S.*, **26**, 368 (1940).

[10] Lewis and Newkirk, THIS JOURNAL, **69**, 701 (1947).

under all conditions tried (Tables IV and V). Since the experiments were all performed at approximately the same molar concentration, not even a qualitative statement can be made on the expected accelerating effect of increasing the pressure of the components.

The Equilibrium Concentrations.—In the equilibria of equations 1 and 2 we have in each case the same number of molecules and the same number and types of bonds. To a first approximation ΔH for the reactions as written should be zero, as indicated by Stearn[11] in commenting on the redistribution reactions described by Calingaert, *et al.*[12] The controlling factor then in determining the equilibrium constant for a reaction such as that of eq. 2 should be the entropy change, the principal term of which concerns the randomness of distribution of the substituent groups around silicon. In computing such an equilibrium constant it must be remembered, though, that the activities of the components should probably not be replaced by their molar concentrations, particularly since the concentrations of the individual species at equilibrium are generally different. Further, considerable deviation from ideality exists and the magnitude of this deviation changes with temperature (Fig. 1). For example, the ratio $(P/P_0)_V$ of the pressure calculated from the ideal gas laws to the pressure observed at constant volume changes from 2.24 at 300° to 1.58 at 375°. From the ideal gas laws the temperature coefficient of pressure at constant volume $(\partial P/\partial T)_V$ is 0.187 atm./°C. for the system concerned, whereas the value actually observed between 200 and 400° is about 0.38 atm./°C. Because of these considerations one should probably not expect a random distribution of the products under the conditions we describe.

From the data presented in Tables I to III *temperature* does not seem to have a pronounced effect on the equilibrium concentrations at a given methyl-to-silicon ratio. This fact implies, of course, that ΔH for the redistribution reactions is approximately zero. Actually a disproportionate change in the activities of the components with temperature and possibly pressure (at constant volume) is quite possible and this would obscure any simple relationship between the concentrations measured and the fundamental thermodynamic quantities. What is seriously needed to interpret our results are equations of state for the molecular species involved.

The absence of any notable difference in equilibrium concentrations between the quenched and unquenched experiments shows again the inconsiderable magnitude of the temperature coefficient. However, it must be granted that the slow reaction rate might prevent retrogression from the equilibrium condition at the higher temperatures.

The effect of the *methyl-to-silicon ratio n* on the equilibrium concentrations is shown roughly in Fig. 2. The peaks of 81 ± 3 mole % of trimethylchlorosilane at $n = 3.0$ and of 78 ± 2 mole % of dimethyldichlorosilane at $n = 2.0$ are well-established but considerable uncertainty exists concerning the equilibrium concentration of methyltrichlorosilane at $n = 1.0$ (see experimental). Empirically the mole fraction m_2 of dimethyldichlorosilane in equilibrium at 375° may be represented as a function of n by eq. 7.

$$m_2 = 0.78[n - (n/2)^2]^7 \qquad (7)$$

Random distribution requires that the function should be given by eq. 8.

$$m_2 = 0.375[n - (n/2)^2]^2 \qquad (8)$$

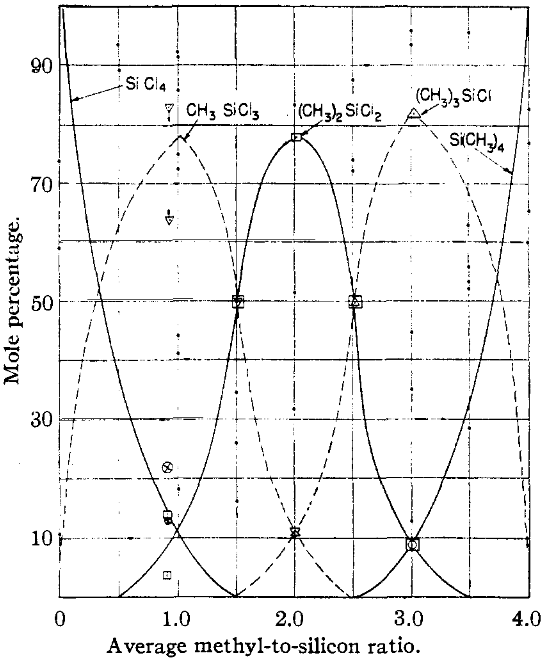

Fig. 2.—Rough graphical representation of molar concentrations of methylchlorosilanes in equilibrium mixtures at 300–450° as a function of the average methyl-to-silicon ratio.

The Side Reactions.—Although the redistribution reaction is remarkably clean-cut at 300–350° we have noted a serious decomposition of methyl groups at higher temperatures. This demethylation is an interesting new route to the synthesis of compounds with silicon–carbon–silicon bonding. Unfortunately from the synthetic viewpoint, rearrangement is a concomitant reaction and one more favored thermodynamically.

Mechanism of Rearrangement.—Speculation on the mechanism of the rearrangements we have studied and on the mode of catalysis by aluminum chloride would, we feel, be unwarranted at this time. These aspects of the problem are being studied by Dr. Fraser Price of

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[11] Stearn, *ibid.*, **62**, 1630 (1940).

[12] Calingaert and Beatty, *ibid.*, **61**, 2748 (1939); Calingaert, Beatty and Neal, *ibid.*, **61**, 2755 (1939); Calingaert and Soroos, *ibid.*, **61**, 2758 (1939); Calingaert, Beatty and Hess, *ibid.*, **61**, **3300** (1939).

our Laboratory who will report his conclusions at an early date.

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Summary

1. Thermal rearrangement of the methylchlorosilanes has been studied between 250 and 450° and at vapor concentrations of about 2.3 moles per liter.

2. The equilibrium concentrations of the redistribution products have been established at methyl-to-silicon ratios of 2 and 3 and have been found to deviate very considerably from the predictions of random distribution. This discrepancy is possibly related to the non-ideal gaseous behavior of these substances under the conditions employed to effect rearrangement. At $CH_3/Si = 1$ rearrangement was very slow and complicated by side reactions; for this reason accurate equilibrium values have not been obtained.

3. Demethylation occurs to an appreciable extent at 375° and above, resulting in the establishment of methylene bridges between silicon atoms. This reaction is illustrated by the formation of bis-(dimethylchlorosilyl)-methane from trimethylchlorosilane.

4. Methylphenyldichlorosilane and methylethyldichlorosilane have been prepared by heating phenyltrichlorosilane and ethyltrichlorosilane, respectively, with certain methylchlorosilanes.

5. The following new compounds have been prepared and characterized: methylphenyldiethoxysilane, methylphenyldifluorosilane, methylethyldiethoxysilane, and methylethyldibromosilane.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Reaction of Ferrous and Ferric Ions with 1,10-Phenanthroline. II. Kinetics of Formation and Dissociation of Ferrous Phenanthroline

BY T. S. LEE, I. M. KOLTHOFF AND D. L. LEUSSING

The equilibrium constants for the dissociation of ferroin (ferrous phenanthroline) and ferriin (ferric phenanthroline) have been determined and were reported in a previous paper.[1] The present paper deals with kinetics of the dissociation and of the formation of ferroin. Data are also given from which the rate of dissociation of ferriin can be calculated. However, the mechanism of this reaction is not understood.

Experimental

Materials.—Preparation of reagent solutions was described in a previous paper.[1]

Rate of Dissociation of Ferroin.—Five ml. of 0.00997 *M* phenanthroline solution was added to 5.00 ml. of 0.0104 *M* ferrous sulfate solution. Under these conditions the formation of ferroin is rapid and quantitative. The mixture was diluted in a volumetric flask to nearly 500 ml. and the desired amount of standard 2 *M* sulfuric acid was added. The mixture was then diluted quickly to 500 ml. with water. The final sulfuric acid concentration was 0.005, 0.05 or 0.5 *M*. The temperature of all solutions was maintained at 25 ± 0.1° before and after mixing. After various reaction periods portions of the reaction mixture were removed and the amount of ferroin determined with the Model DU Beckman spectrophotometer at a wave length of 500 mμ.

Rate of Formation of Ferroin.—Reaction mixtures were prepared by mixing together sulfuric acid, ferrous sulfate, and phenanthroline–sulfuric acid solutions. The final concentrations of the reactants are given in Table I. The temperature of the reagent solutions and reaction mixtures was 25 ± 0.1°. After various reaction periods portions of the mixtures were analyzed spectrophotometrically for ferroin.

Rate of Dissociation of Ferriin.—The experiments were described in the experimental part of a previous paper[1] under "Measurement of E. m. f. of the Cell Au | Fe^{++}, Fe^{+++}, H_2SO_4 | $FePh_3^{++}$, $FePh_3^{+++}$, H_2SO_4 | Au."

Rate of Dissociation of Ferroin

Figure 1 shows the rate of dissociation of ferroin in solutions of different acidities. The function log c_0/c is plotted against time, where c_0 is the initial concentration of ferroin and c is the concentration of ferroin at a given time. It is seen that the experimental points for the reaction mixtures which are 0.5 and 0.05 *M* in sulfuric acid fall on a straight line, indicating that the dissociation of ferroin is a first order reaction and that the rate is the same in 0.5 and 0.05 *M*. The curve for the reaction mixture which is 0.005 *M* in sulfuric acid is coincident with the straight line during the initial stages of reaction. After a reaction period of one hour the experimental curve approaches asymptotically a horizontal line. The horizontal line corresponds to the equilibrium concentration of ferroin in the reaction mixture. At the two higher acidities the rate of formation of ferroin is negligible as compared to the rate of dissociation.

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(1) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948).