[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Kinetics and Thermodynamic Properties of the Disproportionation of Methylchlorosilanes

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It has been known for some time that organic compounds containing silicon undergo rearrangements under conditions which produce relatively little change in their carbon analogs.[1] Previous investigations[2] of the quantitative aspects of these and similar disproportionations with other metal alkyls indicate that a random distribution of groups attached to the metal prevails at equilibrium. In other words the heat of reaction is zero and the free energy of reaction and hence the equilibrium distribution depend solely on the entropy. A recent paper[3] described the disproportionation of methylchlorosilanes at elevated temperatures and pressures in the presence of a catalyst, usually aluminum chloride. The results showed that the equilibrium distribution of methylchlorosilanes did not correspond to that predicted on the basis of a purely random distribution of groups attached to silicon. This observation presented an interesting and heuristic deviation from the work of previous investigators. The present study was undertaken to refine further the observations of Sauer and Hadsell and if possible to discover a mechanism for the disproportionation.

Silicon tetrachloride and silicon tetramethyl in addition to all the methylchlorosilanes were used in this investigation. For the purposes of brevity the following symbols will be used to represent these compounds.

$Q = SiCl_4$
$T = CH_3SiCl_3$
$D = (CH_3)_2SiCl_2$
$M = (CH_3)_3SiCl$
$S = (CH_3)_4Si$

Experimental

Apparatus.—A diagram of the apparatus is presented in Fig. 1. The bomb was a standard high pressure vessel of 170-ml. capacity manufactured by the American Instrument Company. The bomb heater was one of a conventional design manufactured by the same company. The temperature was controlled by a Brown Pyrometer Controller which used a chromel–alumel thermocouple for its thermo sensitive element. The desired temperature was maintained to within ±2°.

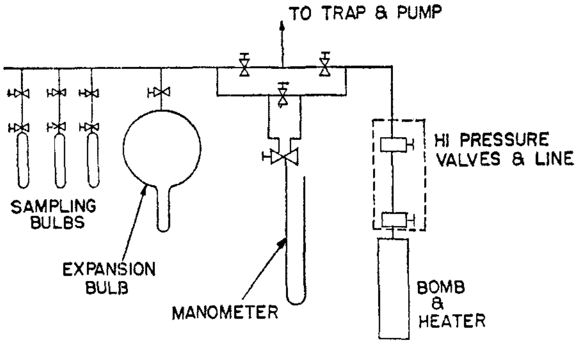

Fig. 1.—Schematic diagram of apparatus.

A General Electric analytical mass spectrometer fitted with a control to sweep the magnet current and with a Brown Electronik Recorder to record the peak height was used for the analyses.

Materials.—Trimethylchlorosilane, dimethyldichlorosilane and methyltrichlorosilane had been previously prepared in this Laboratory and were used without further purification.

The method of analysis using the mass spectrometer was sufficient to ascertain that these materials never contained more than traces of polysiloxanes.

Silicon tetrachloride of C.P. grade was obtained from the Stauffer Chemical Co. and was used without further purification.

The aluminum chloride was the C.P. material obtained from Eimer and Amend.

Tetramethylsilane was prepared by adding trimethylchlorosilane to methylmagnesium bromide in dibutyl ether. The material boiling below 142° was stripped out and subjected to distillation in a column of about ten theoretical plates. The material boiling between 26 and 27° was collected and again put through the same column. This time the material boiling between 26.0–26.5° was collected. It was analyzed on the mass spectrometer and showed the expected peaks resulting from fragmentation of $(CH_3)_4Si$. In addition, however, fairly large peaks occurred at mass numbers of 59, 45, 31 and 29. These could only be explained on the basis of fragments containing Si–H bonds. Even after treatment of a portion of the material with alkali the cracking pattern in the mass spectrometer was the same. Therefore it is concluded that the peaks result from some rearrangement in the spectrometer tube.

Method.—The procedure in making a run was as follows: weighed amounts of aluminum chloride and of the chlorosilanes were introduced into the bomb and the bomb closed as rapidly as possible. It was then put in the heating mantle and attached to the vacuum line. The line including the large expansion bulb was then evacuated and the air flushed out of the bomb by opening the high pressure valves and alternately opening and closing the expansion bulb stopcock until the manometer indicated the same pressure between two successive openings. While this procedure introduced some uncertainty into the weight of chlorosilanes in the bomb it will be shown later this was of no consequence. The bomb was then brought to the desired temperature and sampling was begun.

The method of sampling was as follows: a sample of the gas mixture was admitted to the section of line between the two high pressure valves and was pumped away. Then another sample was admitted to this section and transferred to the expansion bulb by freezing it there with liquid air. This procedure removed a maximum of 1% of the bomb charge per sample. When transfer was complete the stopcock on the expansion bulb was closed and the liquid air was removed. After coming to room temperature a portion of the expanded gas was transferred to the sampling bulb and analyzed on the mass spectrometer. In the kinetic runs a sample was taken immediately after the bomb had reached the desired temperature and at appropriate intervals thereafter until five samples had been removed. In the runs where only the equilibrium conditions were determined the reaction was allowed to proceed for fifteen to twenty hours before

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(1) Dolgov and Volnov, *Zhur. Obschi Khim*, I, 1-104, (1931).

(2) Calingaert, Soroos and Hnizda, THIS JOURNAL, **62**, 1107 (1940).

(3) Sauer and Hadsell, *ibid.*, **70**, 4258 (1948).

the first sample was taken and at least one and sometimes two samples were taken thereafter at three to four hour intervals. Determinations of equilibrium constants were always made from both sides of the equilibrium.

The samples were analyzed on the mass spectrometer by determining the relative heights of several predetermined peaks characteristic of the individual methylchlorosilanes and applying the formula

$$\frac{P_a}{P_b} = F_{AB}\frac{h_a}{h_b} \tag{1}$$

where P_a and P_b are mole percentages of components A and B, respectively, h_a and h_b are the peak heights and F_{AB} is a factor determined by calibration of the mass spectrometer with known mixtures. These calibration mixtures were made up by pipetting, weighing and mixing the liquid chlorosilanes under investigation. This was done in glass stoppered flasks which when open to the air had a slow stream of dry nitrogen passing through them. The quantities of the chlorosilanes used (*ca.* 25–50 g.) were handled rapidly while exposed to the air and were large enough so that the hydrolysis during this time was negligible. This was demonstrated by the presence of only negligible amounts of polysiloxane fragments in the mass spectrometer. It has been shown that the deviation from random distribution results in systems composed at the most of three methylchlorosilanes[3] in measurable amounts. These systems were: $(CH_3)_4Si$, $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$, (SMD system); $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, CH_3SiCl_3, (MDT system); and $(CH_3)_2SiCl_2$, CH_3SiCl_3 and $SiCl_4$, (DTQ system). The peaks used for the analysis of the various systems and the fragments represented thereby are given in Table I.

TABLE I

PEAKS USED IN ANALYSIS OF METHYLCHLOROSILANES BY THE MASS SPECTROMETER

Mass no.	Fragment	Fragment from	System	Used to analyze for
168	$SiCl_4^{35}+$	Q	DTQ	Q
148	$CH_3SiCl_3^{35}+$	T	DTQ, MTD	T
135	$SiCl^{37}Cl_2^{35}+$	T	MTD	T
133	$SiCl_3^{35}+$	T	MTD	T
128	$(CH_3)_2SiCl_2^{35}+$	D	DTQ, MTD	D
113	$(CH_3)SiCl_2^{35}+$	D	SMD	D
108	$(CH_3)_3SiCl^{35}+$	M	MTD	M
93	$(CH_3)_2SiCl^{35}+$	D, M	SMD[a]	M
73	$(CH_3)_3Si^+$	M, S	MTD, SMT[a]	M, S[a]

[a] In the SMD system the parent peaks were too small to be usable for analysis. Hence the 93 and 73 peaks composed of fragments from *D* + *M*, and *M* + *S*, respectively, were used. The calculation of calibration factor were made using the following formulas

$$F_{MS} = \frac{P_m}{P_s}\left[\frac{h_{73} - R_{73}h_{93} + R_{73}R_{93}h_{113}}{h_{93} - R_{93}h_{113}}\right]$$

$$F_{MD} = \frac{P_m}{P_d}\left[\frac{h_{113}}{h_{93} - R_{93}h_{113}}\right]$$

where the "*F*'s" are the calibration factors, the "*P*'s" are the mole percentages of the component indicated by the subscript, the "h's" are the peak heights of mass numbers indicated by the subscripts and

$$R_{93} = \frac{h_{93}}{h_{113}} \text{ for pure } D$$

and

$$R_{73} = \frac{h_{73}}{h_{93}} \text{ for pure } M$$

Since the actual numerical values of the calibration factors are dependent upon the operating conditions and the geometry of the mass spectrometer they are not given.[4]

Equilibria

The MDT system at 350° was most extensively investigated both from equilibrium and kinetic viewpoint. The equilibrium constants, K_m, were calculated from

$$K_m = \frac{D_e^2}{M_e T_e} \tag{2}$$

where the subscript "e" denotes equilibrium concentration. Actually the percentage ratios as determined by the mass spectrometer were used directly as K_m is dimensionless and only the ratios of concentration are involved. Table II summarizes the results for the MDT system at 350°.

TABLE II

EQUILIBRIUM CONSTANTS FOR THE REACTION, M + T = 2D

Temp. = 350°; 1.15 g. $AlCl_3$; time, 15–20 hr.

Approx. total molar concentration	Starting materials	K_m
0.44	D	40.2
.25	D	39.3
.48	M + T (2/1)	40.3
.25	M + T (1/1)	40.1
		Av. 39.9

While no measurement of pressure was made in these cases, subsequent experiments and also Sauer's data show that the pressure for the larger amounts of materials was about 675 p. s. i. g. Presumably with the smaller bomb charge it was approximately one half that. While the small deviation of K_m shown in Table II is probably fortuitous no measurable effect of pressure upon K_m is observable. This leads to the conclusion that while the system is far from ideal, the activity coefficients change in such a way as to compensate for the non-ideality. Hence considerable reliance can be placed on manipulations of K_m to obtain thermodynamic data.

Table III summarizes all the thermodynamic data obtained for the SMD and the MDT systems.

The error in K_m is about 5%. This introduces an error of about 0.7 kcal. in $\Delta H°$ and $\Delta F°$ and about 0.5 e. u. in $\Delta S°$.

In order to prove conclusively that the catalyst had no effect on the equilibrium one run in the MTD system at 350° had four times (4.6 g.) the

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[4] Dr. F. J. Norton of this Laboratory is writing a paper for future publication on the details of analysis of methylcholorosilanes using the mass spectrometer.

TABLE III

EQUILIBRIUM CONSTANTS K_m; HEATS $H°$, ENTROPIES $S°$ AND FREE ENERGIES, $F°$, OF METHYLCHLOROSILANE DISPROPORTIONATION

Bomb vol. 170 cc., $AlCl_3$ = 1.15 g. Time 15–20 hr.

System	K_m 350°	K_m 420°	$\Delta H°$, kcal.	$\Delta S°$, e. u.	$\Delta F°_{350°}$, kcal.
SMD[a]	74.3	54.9	−3.6	2.8	−5.4
MDT	39.9	29.8	−3.6	1.6	−4.7

[a] $K_m = M_e^2/S_eD_e$.

normal amount of catalyst introduced into the mixture. The equilibrium constant in this case was 39.3, which is well within the experimental error of the measurements.

When this investigation was started it was planned to obtain data on the DTQ system also. However, it was found that this system approached equilibrium so slowly at any obtainable temperature that it was impossible to get useful data.

With 5 g. of aluminum chloride at 420° starting with pure T after twenty hours the composition was 92% T, and 4% each of D and Q while starting with equal amounts of D and Q after the same time there was only 10% T and 45% each of D and Q. This slowness of reaction is probably due to a high energy of activation.

It is unfortunate that we were unable to obtain useful data on the DTQ system for had we been able to do so we would have been able, with the aid of data already available,[5] to calculate heats and entropies of formation of the methylchlorosilanes. As it stands it is impossible due to the form of the equations even to calculate these quantities relative to each other.

It will be noted in Table III that the heats of reaction for the disproportionation of both $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$ are the same while the difference in the numerical values of the equilibrium constants is due to the $\Delta S°$ terms. On the basis of random distribution,[6] the $\Delta S°$ terms should have been 1.9 e. u. and 0.4 e. u. for the SMD and MDT systems, respectively.

Kinetics

The majority of kinetic experiments were done on the MDT system at 350°. They were made at a variety of starting concentrations from both sides of the equilibrium, the aluminum chloride concentration also being varied. In order to determine whether the reaction was heterogeneous the bomb was packed with 11 g. of steel wool having a surface of about 200 sq. cm./g. This increased the available surface by a factor of about ten. Plots of concentration of D as a function of time were identical within experimental error, with similar runs made in the unpacked bomb. It is therefore concluded that this reaction is homogeneous. Furthermore, the system must be totally gas since 350° is well above the critical temperatures for all components except the aluminum chloride. This has a critical temperature of 357° and with the small amount present it was almost certain to be all gas.

Plots were then made of concentration of D *versus* time and it was found that the half time was fairly constant regardless of the bomb charge. However, since the zero time of the reaction was in doubt, the time required for the reaction to go from 25 to 50% completion was taken as the measure of reaction order. Completion was taken as the equilibrium concentration of reactants.

This time required to go from 25 to 50% completion is the time required to proceed one-third of the remaining distance to equilibrium ($t_{1/3}$). The results of these calculations are given in Tables IV and V.

TABLE IV

ONE THIRD TIMES FOR REACTION $2D = M + T$

Temp. 350°, bomb vol. 170 cc.

Approx. starting charges, moles	$AlCl_3$, g.	$t_{1/3}$, min.	$\frac{1}{t_{1/3} \times AlCl_3}$
0.48	1.15	82	
.44	1.15	71	
.37	1.15	95	
.15	1.15	85	
		Av. 83	0.0105
.49	2.30	58	.0075
.48	0.65	194	.0078

TABLE V

ONE THIRD TIMES FOR REACTION $M + T = 2D$

Temp. 350°, bomb vol. 170 cc.

Approx. starting charge, moles	Initial (M/T)[a]	$AlCl_3$, g.	$t_{1/3}$, min.	$\frac{1}{t_{1/3} \times AlCl}$
0.47	0.99	1.15	49	
.25	1.00	1.15	49	
.125	1.10	1.15	47	
.43	1.70	1.15	46	
.46	1.59	1.15	64	
.43	.855	1.15	63	
			Av. 53	.016
.50	1.07	0.65	123	.013
.50	.96	2.30	36	.012
.51	1.01	4.60	14	.015

[a] Calculated from the average difference in concentration of M and T as determined from mass spectrometer analysis. This eliminates any assumption as to relative amounts lost while removing air from bomb.

Also in these tables are given $1/(t_{1/3} \times AlCl_3)$. This function shows no drift with varying aluminum chloride concentration and hence the best approximation to the plot of $1/t_{1/3}$ *vs.* $AlCl_3$ is a straight line and since $1/t_{1/3}$ is proportional to the rate, the rate must be proportional to aluminum chloride concentration. Inspection of the results of Tables IV and V shows $t_{1/3}$ to be independent of starting concentrations of reactants provided the aluminum chloride concentration is kept constant. This means that the reaction is first order.

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(5) Latimer, THIS JOURNAL, **44**, 90 (1922); Aston, *et al.*, *ibid.*, **63**, 2343 (1941).

(6) Calculated from $S° = -R \ln \sigma + \text{Const.}$, where σ = symmetry number.

Also, since it can be shown that $t_{1/2} = t_{1/3} \log {}^1/_2/\log {}^2/_3$, the half times were calculated to be 142 minutes for reactions in Table IV and 91 minutes for those in Table V where the aluminum chloride charge was 1.15 g.

Another pertinent property of this system was demonstrated by the following experiment. The bomb was charged with 53.4 g. of $(CH_3)_2SiCl_2$ and was brought to 350° and the pressure measured with a 2000 p. s. i. Ashcroft Laboratory gage with 10 p. s. i. subdivisions. Then the bomb was charged with the same weight of $(CH_3)_2SiCl_2$ but 4.60 g. of aluminum chloride was added and the pressure measured at the same temperature. Without the aluminum chloride present the pressure was 672 p. s. i. g., with the aluminum chloride present it was 678 p. s. i. g. Since this weight of aluminum chloride would have produced 75 p. s. i. assuming the gas was the dimer acting ideally, it must have been quite completely associated in some way with the chlorosilanes.

Any mechanism must take the following facts into consideration: (a) the rate is a linear function of the aluminum chloride concentration; (b) the reaction is first order in chlorosilanes; (c) the rate equations must reduce to an equilibrium constant, $K_m = D_e^2/M_eT_e$ when the change of concentration with time is zero; (d) substantially all the aluminum chloride is associated in some manner with the chlorosilanes.

The most reasonable mechanism that we have been able to develop that fits all these requirements is the following

$$(CH_3)_2SiCl_2 + AlCl_3 \xrightarrow{k_3} (CH_3)_2SiCl_2{\cdot}AlCl_3 \qquad (3)$$

$$(CH_3)_2SiCl_2 + (CH_3)_2SiCl_2{\cdot}AlCl_3 \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} (CH_3)_3SiCl + CH_3SiCl_3{\cdot}AlCl_3 \qquad (4)$$

$$CH_3SiCl_3{\cdot}AlCl_3 + (CH_3)_2SiCl_2 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} CH_3SiCl_3 + (CH_3)_2SiCl_2{\cdot}AlCl_3 \qquad (5)$$

Reaction 3 is very rapid and goes to completion before either reaction 4 or 5 starts to take place. Reaction 5 which merely involves transfer of aluminum chloride from a T molecule to a D molecule must be very much more mobile than reaction 4 which involves rupture and formation of both silicon–carbon and silicon–chloride bonds.

Letting $Y = (CH_3)_2SiCl_2{\cdot}AlCl_3$
$Z = (CH_3)SiCl_3{\cdot}AlCl_3$
C_0 = $AlCl_3$ added at start

This mechanism upon solving the usual steady state equations for

$$dY/dt = 0 \text{ and } dZ/dt = 0$$

yields

$$\frac{1}{C_0}\frac{dM}{dt} = \frac{k_{-4}k_{-5}(D^2/K_m - TM)}{k_{-4}M + k_{-5}T + (k_4 + k_5)D} \qquad (6)$$

letting $K_4 = k_4/k_{-4}$ and $K_5 = k_5/k_{-5}$, then

$$K_m = \frac{k_{-4}k_{-5}}{k_4k_5} = \frac{1}{K_4K_5} = \frac{D_e^2}{M_eT_e}$$

Also it can be shown that

$$\frac{Y}{Z} = \frac{k_{-4}M + k_5D}{k_4D + k_{-5}T} \qquad (7)$$

Letting $M = a - x$, $T = b - x$, $D = 2x$

Where a and b are initial concentrations or percentages, of M and T, respectively, and x is the concentration, or percentage, of each used up in time t, equation (6) integrates to

$$2\left(\frac{4 - K_m}{K_m}\right)C_0k_{-4}k_{-5}t = (2k_4 + 2k_5 - k_{-4} - k_{-5})\ln\left[\left(\frac{4}{K_m} - 1\right)x^2 + x(a + b) - ab\right] + \left\{2(a + b)(k_4 + k_5) + \frac{k_{-4}}{K_m}[K_m(a - b) - 8a] + \frac{k_{-5}}{K_m}[K_m(b - a) - 8b]\right\}\left\{\frac{x_e}{(a + b)x_e - 2ab}\right\}\ln\left\{\frac{x - \dfrac{abK_m}{x_e(K_m - 4)}}{x - \left[\dfrac{(a + b)x_e - ab}{x_e}\right]\left[\dfrac{K_m}{K_m - 4}\right]}\right\} + \text{Const.} \qquad (8)$$

where the subscript "e" denotes equilibrium value. In all the calculations of rate constants the concentrations were expressed in mole percents. This is permissible since the logarithmic functions must be dimensionless.

In the case where $a = b$ as when D was used, or where M was deliberately made equal to T at the start, equation (8) reduces to

$$2(K_m - 4)k_4C_0t = -(2 - K_mK_4)\ln\left[\left(\frac{4}{K_m} - 1\right)x^2 + x - 0.25\right] + \sqrt{K}_m(1 - 2K_4)\ln\left(\frac{x - 0.5\left[\dfrac{K_m + 2\sqrt{K_m}}{K_m - 4}\right]}{x - 0.5\left[\dfrac{K_m - 2\sqrt{K_m}}{K_m - 4}\right]}\right) + \text{Const.} \qquad (9)$$

provided that reaction 5 is considered much more mobile than 4 and hence the rates of 4 can be neglected when compared to those of 5. Plots of time *versus* the second logarithmic terms of eqns. 8 and 9 proved to be fair straight lines up to about 50% reaction; after that the curvature was upward. The constants k_4 and K_4 were calculated from the initial slopes of these plots and the results are given in Tables VI and VII.

It can be shown that when the logarithmic terms of Eq. (9) are plotted against each other the slope should approach the same value at infinite time whether equilibrium is approached from the M + T side or from the D side, this slope is $2 - K_mK_4/\sqrt{K}_m(1 - 2K_4)$; this permits an independent calculation of K_4 which when performed gave $K_4 = 0.142$ in good agreement with that given in Table VII. The average of these two values ($K_4 = 0.147$) was used to calcu-

TABLE VI

SUMMARY OF RATE DATA ON MDT SYSTEM

Temp. 350°, bomb vol. 170 cc.

Run	Starting materials	Approx. bomb charge	Initial (M/T)	$AlCl_3$, g.	Slopes $R \times 10^3$	$k_4C_0 \times 10^5$ min.$^{-1}$	$k_4 \times 10^5$ l. (min.)$^{-1}$ (g. $AlCl_3$)$^{-1}$
5[a]	D	0.48 mole	..	1.15	4.31	8.2	6.7
6[a]	D	.44	..	1.15	4.04	7.7	6.4
20[a]	D	.37	..	1.15	2.21	4.2	3.5
21[a]	D	.15	..	1.15	2.38	4.3	3.5
8[a]	M + T	.47	0.99	1.15	3.04	5.7	4.7
9[a]	M + T	.25	1.00	1.15	2.67	5.1	4.2
16[a]	M + T	1.25	1.10	1.15	2.67	5.1	4.2
(All above grouped together.)[a] Av. $R^a = 3.05$							
25	D	0.49	..	0.65	0.765	1.9	2.9
23	D	.48	..	2.30	3.87	9.5	4.1
17[b]	M + T	.43	1.70	1.15	1.95	4.1	3.6
18[b]	M + T	.40	1.59	1.15	1.41	4.3	3.7
19[b]	M + T	.43	0.86	1.15	2.97	4.4	3.9
24	M + T	.50	1.07	0.65	0.97	2.4	3.7
22	M + T	.50	0.96	2.30	3.40	8.4	3.6
26	M + T	.51	1.01	4.60	6.75	16.7	3.6
							(4.1 ± 0.7)

[a] For the purpose of calculation of K_4 all these runs were grouped together and their slopes, R, averaged. This group was called P in calculation of K_4. [b] In these runs only were the concentrations of M and T far enough apart so that eqn. 8 was applied. In all other runs eqn. 9 was used.

TABLE VII

VALUES OF EQUILIBRIUM CONSTANT K_4

Pair of slopes takes	K_4
P + 17	0.190
P + 18	.230
17 + 19	.126
18 + 19	.167
	Av. 1.53

late the value of k_4C_0 and k_4 given in Table VI.

The values of k_4 and K_4 given above lead to

$$k_{-4} = 2.8 \times 10^{-4} \text{ liter (g. AlCl}_3)^{-1}(\text{min.})^{-1}$$
$$K_5 = 0.171$$

Two runs were made at 375° one with D and the other with M + T in equal amounts and with 1.15 g. of aluminum chloride in both cases. The results of these runs gave $K_4 = 0.147$, $K_5 = 0.174$, $k_4 = 7.3 \times 10^{-5}$ and $k_{-4} = 4.93 \times 10^{-4}$. It can be seen that there is very little change in the equilibrium constants for reactions 4 and 5 but that the rate has about doubled over the 25° temperature range. This gives an energy of activation of approximately 22 kcal. for reaction 4. This is normal for the temperature range in which this reaction proceeds at measurable rates.

It was found that although it took about two hours to heat the bomb up to the desired temperature, by the time the first sample was taken the reaction had progressed only 8–12% toward completion. Since the energy of activation is normal this leads to the conclusion that the abnormality may lie in a small entropy of activation. The reason for this is plausibly explained by considering the nature of the aluminum chloride–chlorosilane complex. Very probably the aluminum chloride is attached to the chlorine of the chlorosilane. This weakens the Si–Cl bond and when a collision occurs with another chlorosilane molecule the two silicons exchange $AlCl_4^-$ and CH_3^- or $AlCl_4^-$ and Cl^-. Since halogens attached to silicon exchange quite easily[7] the exchange being favored by their high electronegativity only a relatively few collisions will have the correct orientation to permit rupture of a Si–C bond to give the methyl interchange. This high degree of necessary orientation implies a low entropy of activation.

The proposed mechanism bears a formal resemblance to those proposed for a wide variety of other reactions involving RCl as one reactant[8] with aluminum chloride as a catalyst. However, in the proposed mechanism it will be noted that the first order kinetics arise from the rate controlling step being the reaction of the chlorosilane–aluminum chloride complex with the chlorosilane and not the dissociation of the complex into positive siliconium and negative tetrachloroaluminate ions. The fact that the aluminum chloride does not materially increase the pressure of the system necessitates this difference in mechanism. Further in reaction 4 it is improbable that any separation of ions occurs because the dielectric constant of the medium must be quite low. Rather the process is to be pictured as an exchange of the $Si–CH_3$ and Si–Cl bonds the latter having been much weakened by its attachment to the aluminum chloride.

Summary

Equilibrium constants have been determined for the disproportionation of methylchlorosilanes at 350 and 420°. Heats and entropies of the reactions were calculated. In corroboration of the work of Sauer and Hadsell it was found that the equilibrium distribution of groups attached to silicon is not random.

Rate measurements have been made on the reactions and a mechanism is proposed.

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[7] Forbes and Anderson, THIS JOURNAL, **66**, 932 (1944).

[8] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 291–328; Whitmore, Pietrusza and Sommer, THIS JOURNAL, **69**, 2108 (1947).