Table VI. Torsional Angles within the Phosphazene Ring

| Bonds | Angle, deg | Bonds | Angle, deg |
|---|---|---|---|
| P(1)-N(1)-P(3)-N(3) | −13.9 | N(3)-P(2)-N(2)-P(1) | 15.1 |
| N(1)-P(3)-N(3)-P(2) | 6.6 | P(2)-N(2)-P(1)-N(1) | −20.5 |
| P(3)-N(3)-P(2)-N(2) | −7.0 | N(2)-P(1)-N(1)-P(3) | 20.4 |

protonated segment. This could suggest some $d_\pi$-$p_\pi$ bonding involvement in the exocyclic P-N bonds. Of special interest is the angle P(3)-N(1)H-P(1), which is 126.9°. This can be compared to the 123° angle reported for a cyclotriphosphazene[3,5] and the 132° angle reported for the P-NH-P unit in II.[5] Apparently the bond angle at nitrogen is especially flexible and it responds more to the demands of the ring geometry as a whole than to the hybridization requirements at a particular site. The endocyclic ring angles at phosphorus are in the range of 109.6-114.5°, values that are unusally narrow compared with many other cyclotriphosphazenes. Similar effects were reported for II.[5] This could be a consequence of reduced ring $\pi$ bonding. The exocyclic N-P-N bond angles, which fall within the range 103.0-108.0°, are normal for cyclotriphosphazenes,[27] and, as expected, the N(exo)-P-N(exo) planes are oriented approximately at right angles to the adjacent N(ring)-P-N(ring) plane.

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**Registry No.** $[HN_3P_3(NMe_2)_6]_2[Mo_6O_{19}]$, 37369-90-7; $MoO_3$, 1313-27-5.

**Supplementary Material Available.** A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2963.

(27) Reference 3a, Appendix I.

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Contribution from the Department of Chemistry,
California State University, San Diego, California 92115

# Pyrolysis of Halodisilanes and the Formation and Insertion Reactions of Chlorosilylene and Fluorosilylene

R. L. JENKINS, A. J. VANDERWIELEN, S. P. RUIS, S. R. GIRD, and M. A. RING*

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The pyrolysis of $Si_2F_6$, $FSi_2H_5$, $ClSi_2H_5$, 1,1-$F_2Si_2H_4$, 1,1-$Cl_2Si_2H_4$, and $((CH_3)SiHCl)_2$ was examined as neat and in the presence of other silanes. The results from these pyrolyses demonstrated that all six disilanes decomposed into a silylene and a silane. In $((CH_3)SiHCl)_2$ the relative rate of the 1,2 hydrogen shift compared to the 1,2 chlorine shift was 4.4 ± 0.4. 1,2 halogen shifts were not observed in 1,1-$F_2Si_2H_4$ or 1,1-$Cl_2Si_2H_4$. The insertions of silylenes into the silicon-hydrogen bonds in ethylsilane were examined. The product ratios coupled with assumptions of the half-lives of the silylenes led to the following order for silylene insertion rates: $SiH_2 > ClSiH > FSiH \gg Cl_2Si, F_2Si$.

## Introduction

It was suggested that $Si_2(CH_3)_5H$ thermally decomposed by a 1,2 hydrogen shift to form $HSi(CH_3)_3$ and $Si(CH_3)_2$.[1] It has now been demonstrated that $Si_2H_6$,[2,3] $CH_3Si_2H_5$,[4] and 1,2-$(CH_3)_2Si_2H_4$[4] decompose *via* 1,2 hydrogen shifts producing a silane and a silylene. Methoxydisilanes also decompose into a silylene and a silane *via* a 1,2 methoxy shift.[5,6] In the above reactions, the silylenes have been chemically trapped.

It has also been suggested that $Si_2F_6$ decomposes similarly *via* a 1,2 fluorine shift.[7] Dichlorosilylene has been generated and chemically trapped in the flow pyrolysis of $Si_2Cl_6$ and $C_2H_2$.[8]

We have examined the pyrolysis (under flow conditions with low-temperature removal of products) of a number of substituted disilanes in order to determine the following: (i) the relative rate of a 1,2 hydrogen shift *vs.* a 1,2 chlorine shift when both hydrogen and chlorine are in the same environment; (ii) the effects of environment on the rates of 1,2 hydrogen shifts; (iii) the relative rates of $SiF_2$, $SiCl_2$, HSiF, HSiCl, and $SiH_2$ insertion into silicon-hydrogen bonds.

## Experimental Section

The silanes and alkylsilanes used were prepared by the reduction of the corresponding chloro compounds with $LiAlH_4$ or $LiAlD_4$. Hexafluorodisilane was prepared by reaction of $Si_2Cl_6$ with $SbF_3$.[9] 1,1-Dichlorodisilane was obtained from the reaction of $Si_2H_6$ with HCl over $Al_2Cl_6$,[10] while 1,1-$F_2Si_2H_4$ was obtained from the reaction of 1,1-$Cl_2Si_2H_4$ with $SbF_3$.[11] Chlorodisilane and $FSi_2H_5$ were prepared by chlorination of $Si_2H_6$[10] followed by fluorination of $ClSi_2H_5$ with $SbF_3$ in a flow reactor. The new compound 1,2-dichloro-1,2-dimethyldisilane, *sym*-$Cl_2Si_2H_2(CH_3)_2$, was prepared by the reaction of 1,2-$(CH_3)_2Si_2H_4$ with AgCl in a flow reactor as previously described[12] with the cold trap at −45° and the reactor at 25°.

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**Table I.** Neat Pyrolyses of Halodisilanes

| Expt | Reagent consumed (mmol) | Temp, °C | Cold trap, °C | Volatile products (mmol) |
|---|---|---|---|---|
| 1 | $Si_2F_6$ (0.8) | 405 | −55 | $SiF_4$ (0.8) |
| 2 | 1,1-$F_2Si_2H_4$ (0.3) | 400 | −78 | $F_2SiH_2$ (0.25), $F_2Si_3H_6$ (0.08) |
| 3 | $FSi_2H_5$ (0.5) | 390 | −78 | $H_2$ (0.01), $SiH_4$ (0.06), $FSiH_3$ (0.28), $Si_2H_6$ (0.01), 1-$FSi_3H_7$ (0.08) |
| 4 | 1,1-$Cl_2Si_2H_4$ (0.2) | 370 | −23 | $H_2$ (0.03), $SiH_4$ (0.04), HCl (0.02), $Cl_2SiH_2$ (0.08) |
| 5 | $ClSi_2H_5$ (0.7) | 390 | −63 | $H_2$ (0.02), $SiH_4$ (0.22), HCl (0.01), $ClSiH_3$ (0.18), 1-$ClSi_3H_7$ (0.16) |
| 6 | *sym*-$Cl_2Si_2H_2(CH_3)_2$ (0.5) | 395 | 0 | $H_2$ (0.02), HCl (0.04), $ClSiH_2CH_3$ (0.35), $Cl_2SiHCH_3$ (0.08), $Cl_2Si_3H_3(CH_3)_3$ (0.04) |

The compound *sym*-$Cl_2Si_2H_2(CH_3)_2$ was purified by trap to trap distillations. The product was found in a trap cooled to −45° having passed a trap cooled to −36°. The infrared spectrum of this compound consisted of the following absorptions (cm$^{-1}$): 2990 (w), 2160 (s), 1410 (w), 1265 (m), 872 (s), 788 (s), 735 (s), 705 (w), 625 (w), 542 (w), 509 (s). The mass spectrum at 10 V was due to the following heavy-atom ions (*m/e* in parentheses): $Si_2C_2Cl_2^+$ (44.6), $Si_2CCl_2^+$ (5.3), $Si_2C_2Cl^+$ (2.4), $CSiCl_2^+$ (5.3), $CSiCl^+$ (100), plus ions of lower mass. The relative intensities at *m/e* 158, 160, and 162 should be 100:72:15 based on isotope ratios of $^{35}$Cl, $^{37}$Cl, $^{28}$Si, $^{29}$Si, and $^{30}$Si and were 100:70:17. The neat proton nmr spectrum with TMS as an internal standard consisted of a $CH_3$ doublet at $\delta$ 0.70 and a poorly resolved Si–H quartet at $\delta$ 4.93 with relative intensities of 3.1:1. The absence of resonances between $\delta$ 3 and 4 clearly demonstrates the absence of $CH_3SiCl_2SiH_2CH_3$ and $(CH_3)_2Si_2H_3Cl$.[12] The appearance of the $CH_3SiCl_2^+$ in the mass spectrum is due to migrations in the mass spectrum.

1\. **Neat Pyrolyses.** Neat pyrolyses were carried out in Pyrex or Vycor tubes 9 mm in diameter and 15–20 cm long, which were wrapped with a heating tape and insulated with several layers of asbestos tape. A well was provided for a thermometer in order to monitor the temperature. Temperature control was effected by means of a Variac transformer. The thermal zone was connected to a "U" cold trap and an automatic Toepler pump for cycling the reactants. The cold trap removed any products less volatile than the reagent undergoing thermal decomposition. The inner wall of the pyrolyses tubes were coated with a silicon mirror to prevent Pyrex catalysis. No decomposition of the disilanes occurred when the disilanes were cycled at 25°. The results from typical neat decompositions are listed in Table I.

The reagents used in these and other thermal decompositions and the known products of these reactions were identified and checked for purity both by infrared spectra, which were identical with those reported, and by mass spectra consistent with the formula. In addition, logical impurities ($Cl_2SiH_2$ and $SiH_4$ for $ClSiH_3$) were demonstrated absent by the absence of either strong infrared bands from the infrared spectra or parent ions from the mass spectra under conditions where the parent ions were easily detected. The purity of the compounds 1,1-$F_2Si_2H_4$, $FSi_2H_5$, 1,1-$Cl_2Si_2H_4$, and $ClSi_2H_5$ were also confirmed by proton nmr spectra which were identical with those reported in the literature.[13]

The fractionation temperatures used to separate the products in Tables I and II are listed in Table III while the new compounds generated were identified as described in section 3.

2\. **Pyrolyses of Halodisilanes in the Presence of Other Silanes.** The compounds thermalized neat in section 1 were also decomposed in the presence of thermally stable silanes. The results of these experiments are listed in Table II. These decompositions were carried out in the same manner as described in section 1. The gas-phase ratios were calculated from the relative vapor pressures measured at the cold-trap temperatures and the mole fractions of the compounds present. The products of the decompositions in the presence of deuteriosilanes were demonstrated free of silicon–deuterium bonds by the absence of silicon–deuterium stretching frequencies (1600 cm$^{-1}$). The new compounds obtained were identified as described in section 3.

3\. **Identification of New Products.** The following four compounds produced as described in Table I (experiments 2, 3, 5, and 6) were identified as follows.

**Experiment 2. $F_2Si_3H_6$.** This compound was contained in a trap cooled to −63°. The mass spectrum at 18 V consisted of the following heavy-atom fragments: $F_2Si_3H_x^+$ (16), $FSi_3H_x^+$ (2), $F_2Si_2H_x^+$ (9), $Si_3H_x^+$ (33), $FSi_2H_x^+$ (20), $F_2SiH_x^+$ (8), $Si_2H_x^+$ (100), $FSiH_x^+$ (23). The infrared spectrum consisted of the following absorptions (cm$^{-1}$): 2150 (s), 935 (s), 870 (s), 700 (s), 665 (m), 555–505 (w). The band at 700 cm$^{-1}$ is a doublet very much like the doublet in $Si_3H_8$ at 711 cm$^{-1}$.[14]

**Experiment 3. 1-$FSi_3H_7$.** 1-Fluorotrisilane was purified by distillation through a trap cooled to −63° and contained in a trap cooled to −95°. It was identified by a mass spectrum at 15 V of the following heavy-atom ions: $FSi_3H_x^+$ (14), $Si_3H_x^+$ (22), $FSi_2H_x^+$ (53), $Si_2H_x^+$ (100). The proton nmr spectrum consisted of a complex multiplet (–$Si_2H_5$) at $\delta$ 3.35 and a doublet ($H_2SiF$–) at $\delta$ 5.35 with $J_{H-F}$ = 43 Hz of relative integrated intensity of about 3 (calculated 2.5). The infrared spectrum consisted of the following absorptions (cm$^{-1}$): 2170 (s), 1270 (w), 940 (s), 900–860 (vs), 795 (m), 730 (s), 700 (s), 522 (m).

**Experiment 5. 1-$ClSi_3H_7$.** This compound was obtained by fractionation through a −63° trap and contained in a trap cooled to −95°. The compound was identified by the following spectra. The mass spectrum at 70 V consisted of the following heavy-atom fragments: $ClSi_3H_x^+$ (18), $ClSi_2H_x^+$ (43), $Si_3H_x^+$ (21), $ClSiH_x^+$ (47), $Si_2H_x^+$ (60), $Cl^+$ (100). The proton nmr spectrum consisted of a triplet ($ClSiH_2$–) at $\delta$ 4.92, a triplet (–$SiH_3$) at $\delta$ 3.42, and a complex multiplet (–$SiH_2$–) at $\delta$ 3.55. The integrated intensity of the resonance at $\delta$ 4.92 divided by the intensities at $\delta$ 3.55 and 3.42 was 0.55 (calculated 0.4). The infrared spectra consisted of the following absorptions (cm$^{-1}$): 2170 (s), 1267 (w), 933 (s), 880–870 (s), 815 (m), 795 (m), 766 (m), 718 (m), 690 (m), 540 (s).

**Experiment 6. $Cl_2Si_3H_3(CH_3)_3$.** This compound was contained in a trap cooled to −23°. The identification was based solely on a mass spectrum which contained peaks due to the parent ions $Cl_2Si_2(CH_3)_3H_{3-x}^+$. No heavier peaks were observed.

The following compounds and or mixtures produced as described in Table II (experiments 9–11, 15, and 16) were identified as described below.

**Experiment 9. $C_2H_5Si_2H_2D_3$.** This compound was identified by a proton nmr spectrum which consisted of two resonances at $\delta$ 0.87 ($C_2H_5$–) and at $\delta$ 3.13 (–$SiH_2D$) of relative intensities of 2.7:1. The mass spectrum had a strong parent ion at *m/e* 93 and other peaks consistent for $C_2H_5Si_2H_2D_3$. A very weak envelope was observed with a highest mass at *m/e* 123 which was probably due to $C_2H_5Si_3H_4D_3$.

**Experiment 10. $C_2H_5Si_2H_4F$.** Ethylfluorodisilane was obtained along with a large excess of $C_2H_5Si_2H_5$. The mass spectrum (15 V) of this mixture had weak peaks ending in the mass region *m/e* 110–104. The molecular weight of $FSi_3H_7$ is 110 while that of $C_2H_5Si_2H_4F$ is 108. When the mass spectrum of 1-$FSi_3H_7$ was removed from that of the mixture, considerable intensity remained at *m/e* 108. These results suggest that $FSi_3H_7$ and $C_2H_5Si_2H_4F$ were both present. When $FSi_2H_5$ was decomposed in the presence of $C_2H_5SiD_3$ (experiment 11), the mass spectrum of the least volatile fraction now ended at *m/e* 111. The *m/e* 111 peak can be assigned to $C_2H_5SiD_2(D)HSiF$. This latter result further suggests that $C_2H_5Si_2H_4F$ was obtained from the pyrolysis of $Si_2H_5F$ in the presence of $C_2H_5SiH_3$.

The nmr spectrum of the least volatile fraction from the $FSi_2H_5$-$C_2H_5SiH_3$ pyrolysis was primarily that of $C_2H_5Si_2H_5$.[15] In addition there were two resonances at $\delta$ 4.8 and 5.5. These two are probably from the fluorosilyl group in $FSi_3H_7$ and $C_2H_5Si_2H_4F$. If one assumes that the parent ions for $FSi_3H_7$ and $C_2H_5Si_2H_4F$ have the same intensity at the same pressure, then the mixture contained nearly

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**Table II.** Pyrolyses of Halodisilanes in the Presence of Other Silanes

| Expt | Gas-phase ratio | Temp, °C | Cold trap, °C | Volatile products (mmol) |
|---|---|---|---|---|
| 7 | $\frac{(CH_3)_2SiH_2}{Si_2F_6} = \frac{80}{1}$ | 415 | −63 | $SiF_4$ |
| 8 | $\frac{ClSiH_3}{Si_2F_6} = \frac{200}{1}$ | 415 | −63 | $SiF_4$ |
| 9 | $\frac{C_2H_5SiD_3}{1,1\text{-}F_2Si_2H_4} = \frac{30}{1}$ | 400 | −78 | $F_2SiH_2$ (0.29), $C_2H_5Si_2H_2D_3$ (0.22) |
| 10 | $\frac{C_2H_5SiH_3}{FSi_2H_5} = \frac{30}{1}$ | 390 | −78 | $SiH_4$ (0.06), $FSiH_3$ (0.28), $C_2H_5Si_2H_5$ (0.28),[a] $C_2H_5Si_2H_4F$ (~0.015),[a] $FSi_3H_7$ (~0.015)[a] |
| 11 | $\frac{C_2H_5SiD_3}{FSi_2H_5} = \frac{8}{1}$ | 390 | −78 | $H_2$ (0.02), $SiH_4$ (0.04), $FSiH_3$ (0.24), $C_2H_5Si_2H_2D_3$ and $C_2H_5Si_2HD_3F$ (0.24) |
| 12 | $\frac{(C_2H_5)_2SiD_2}{1,1\text{-}Cl_2Si_2H_4} = \frac{40}{1}$ | 370 | −23 | $SiH_4$ (0.02), HCl (0.01), $Cl_2SiH_2$ with $(C_2H_5)_2SiD_2$ |
| 13 | $\frac{C_2H_5SiH_3}{1,1\text{-}Cl_2Si_2H_4} = \frac{13}{1}$ | 370 | −23 | $H_2$ (0.04), $SiH_4$ (0.07), $Cl_2SiH_2$ (0.07), (no $C_2H_5Si_2H_3Cl_2$) |
| 14 | $\frac{N_2}{1,1\text{-}Cl_2Si_2H_4} = \frac{10}{1}$ | 370 | −23 | HCl (0.02), $SiH_4$ (0.03), $Cl_2SiH_2$ (0.03) |
| 15 | $\frac{C_2H_5SiD_3}{ClSi_2H_5} = \frac{60}{1}$ | 390 | −63 | $H_2$ (0.01), $SiH_4$ (0.10), $ClSiH_3$ (0.08),[b] $C_2H_5Si_2H_2D_3$ and $C_2H_5SiHD_3Cl$ (0.14) |
| 16 | $\frac{C_2H_5SiH_3}{ClSi_2H_5} = \frac{60}{1}$ | 390 | −63 | $H_2$ (0.02), $SiH_4$ (0.26), HCl (0.01), $ClSiH_3$ (0.20),[b] $C_2H_5Si_2H_5$ (0.20),[c] $C_2H_5Si_2H_4$-Cl (0.13) |
| 17 | $\frac{(C_2H_5)_2SiD_2}{sym\text{-}Cl_2Si_2H_2(CH_3)_2} = \frac{100}{1}$ | 395 | 0 | $H_2$ (0.02), $CH_3SiH_2Cl$ (0.13), $CH_3SiH_2Cl$ with $(C_2H_5)_2SiD_2$ |

[a] This mixture was analyzed by a combination of nmr and mass spectrometry. See details in section 3. [b] The $ClSiH_3$ was reduced to $SiH_4$ for separation from ethylsilane. [c] From nmr integration of a mixture of $C_2H_5Si_2H_5$ and $ClSi_2H_5$.

**Table III.** Slush-Bath Temperatures for Separation

| | Temp, °C | | | Temp, °C | |
|---|---|---|---|---|---|
| Compd | Pass | Stop | Compd | Pass | Stop |
| $H_2$ | −196 | | $CH_3SiH_2Cl$ | −95 | −130 |
| $SiH_4$ | −160 | −196 | $CH_3SiHCl_2$ | −78 | −95 |
| HCl, $FSiH_3$ | −145 | −160[a] | $(CH_3)_2SiH_2$ | −95 | −130 |
| $F_2SiH_2$ | −130 | −160 | $C_2H_5SiH_3$ | −112 | −130[c] |
| $ClSiH_3$ | −112 | −145[b] | $(C_2H_5)_2SiD_2$ | −63 | −95 |
| $Cl_2SiH_2$ | −95 | −112[b,c] | | | |

[a] Not complete retention; nearly quantitative for very short fractionations. [b] Separation of $ClSiH_3$ and $Cl_2SiH_2$ by fractional distillation is not quantitative but this separation was not required. [c] The separation of $Cl_2SiH_2$ and $C_2H_5SiH_3$ was not completely quantitative but reasonable estimates of product yields were made from relative intensities of infrared bands.

equal quantities of these two compounds. With this assumption and with integrated nmr intensities, quantities of $C_2H_5Si_2H_4F$ and $FSi_3H_7$ could be estimated. It is obvious that the error in these values could be large.

**Experiment 11. $C_2H_5Si_2HD_3F$.** This compound was identified by a mass spectrum which contained a peak from the parent ion. No heavier peaks were observed.

**Experiment 15. $C_2H_5Si_2HD_3Cl$.** This compound was identified solely by a mass spectrum which contained a peak from the parent ion. No heavier peaks were observed.

**Experiment 16. $C_2H_5Si_2H_4Cl$.** This compound was identified by a mass spectrum containing peaks due to the following ions: $C_2H_xSi_2H_yCl^+$ (51), $CH_xSi_2H_yCl$ (9), $Si_2H_yCl$ (100), $C_2H_xSi_2H_y$ (44), and smaller ions. The nmr spectrum consisted of four resonances at $\delta$ 0.2 ($-CH_2-$), 1.1 ($CH_3-$), 3.73 ($-SiH_2-$), and 4.85 ($-SiH_2$-Cl). The integrated intensities were respectively 0.6:1:0.6:0.6. A sample was available and the spectrum was of poor quality. The infrared spectrum consisted of the following absorptions ($cm^{-1}$): 2970 (s), 2930 (m), 2890 (m), 2170 (vs), 1268 (w), 1075 (m), 1020 (m), 935 (s), 878 (s), 821 (s), 790-770 (vs), 537 (s).

## Results and Discussion

### 1. Initial Decomposition Mode of Disilanes.

The first step in the thermal decomposition of the disilanes investigated in this study consisted solely of 1,2 atom shifts forming a silane and a silylene as found for $Si_2H_6$.[2,3] Most of these silylenes then underwent insertion into silicon-hydrogen or silicon-deuterium bonds. This general mechanism is consistent with the following experimental results.

Initial decomposition *via* silicon-hydrogen and silicon-halogen bond rupture can be eliminated since $H_2$ and HCl were very minor products and HF was not produced (no $SiF_4$). Another possibility, homolytic silicon-silicon bond rupture as found in $Si_2(CH_3)_6$,[16] can also be eliminated. The decompositions of the disilanes in this investigation took place under the same conditions as our earlier $Si_2H_6$ pyrolysis.[2] The quantities decomposed were very similar indicating that the decomposition rates were all within an order of magnitude of each other. The activation energy for the decomposition of $Si_2H_6$ is 49.5 kcal/mol.[17] The value of $D(SiH_3\text{-}SiH_3)$ is 81 kcal/mol[18] and halogen substitution should increase this value when one considers the effects of halogen substitution on the per cent s character of the silicon orbitals in the silicon-silicon bond.[19] Thus, if the disilanes decomposed by silicon-silicon rupture, the activation energies would be 80 kcal/mol or greater and the decomposition rates would be orders of magnitude lower than observed.

The absence of homolytic silicon-silicon bond rupture to form silyl radicals can be confirmed by the results of the decompositions in the presence of deuterated silanes (Table II). As an example, the pyrolysis of $ClSi_2H_5$ in the presence of a gas-phase 60:1 excess of $C_2H_5SiD_3$ produced $SiH_4$ and

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$ClSiH_3$. If $ClSi_2H_5$ had decomposed into $SiH_3$ and $SiH_2Cl$ radicals, these radicals would have reacted with the excess $C_2H_5SiD_3$ to produce $SiH_3D$ and $DSiH_2Cl$. The complete absence of these compounds demonstrates that homolytic silicon–silicon rupture did not occur. Similar results were obtained for all of the systems investigated. For $Si_2F_6$ the case is similar. If $SiF_3$ radicals were produced, the pyrolysis of $Si_2F_6$ in the presence of excess $(CH_3)_2SiH_2$ (80:1) or $ClSiH_3$ (200:1) should have resulted in the formation of $HSiF_3$. The complete absence of this product eliminates this mode of decomposition.

We conclude that the disilanes investigated decomposed into a silane and a silylene. This conclusion is further supported by the observed insertion of most of the silylenes into silanes forming the appropriate polysilanes (experiments 2, 3, 5, 6, 9–11, 15, and 16 in Tables I and II).

The results listed in Tables I and II can be used to determine the major decomposition modes for the disilanes investigated. When more than one mode is operative, the relative rates can be determined by the ratio of the monosilanes produced. For a compound $XSi_2H_5$, the decomposition modes are represented by the reactions

$$XSi_2H_5 \xrightarrow{k_1} XSiH_3 + SiH_2 \qquad (1)$$

$$XSi_2H_5 \xrightarrow{k_2} XSiH + SiH_4 \qquad (2)$$

The ratio $k_1/k_2$ can be equated to (yield of $XSiH_3$)/(yield of $SiH_4$) when $XSiH_3$ is formed only by reaction 1 and $SiH_4$ is formed only by reaction 2 and when these compounds do not decompose or react once they are formed. We can demonstrate that these conditions were met in our system with estimated errors of less than 10%.

The silylene radicals ($SiH_2$ or $XSiH$) could insert into the trapping alkylsilane (reaction 3), into a product silane, or

$$SiH_2 + RSiH_3 \rightarrow RSi_2H_5 \qquad (3)$$

into the reactant disilane or could polymerize on the wall. In the reactions listed in Table II, the alkylsilanes were present in the gas phase in high concentrations compared to either the reactant disilane or the product silanes so that silylene insertions into the reactant disilane or the product silanes can be eliminated. It has been demonstrated that alkylsilanes trap silylenes as well as $SiH_4$ and much better than halosilanes.[20] The alkyldisilanes once formed were removed from the stream by the cold trap. To demonstrate that these alkyldisilanes did not decompose once formed, we can cite the following typical result. In the pyrolysis of $ClSi_2H_5$ in the presence of $C_2H_5SiD_3$ in a 60:1 excess, the products were $C_2H_5SiD_2SiDH_2$ and $C_2H_5SiD_2SiDHCl$. If these compounds decomposed, $SiH_2D_2$ and $SiD_2HCl$ would have been produced.[4] The absence of $SiH_2D_2$ and $SiD_2HCl$ demonstrates that the insertion products were completely removed by the cold trap.

Once formed, the compounds $SiH_4$ and $XSiH_3$ did not decompose to any great extent due to their greater thermal stability compared to the disilanes. This contention is verified by the low yield of $H_2$. The last potential problem is that of polymer decomposition. In a kinetic investigation of the pyrolysis (static conditions) of $Si_2H_6$ a polymer was obtained. The decomposition of this polymer was slow compared to that of disilane and the main product was $H_2$.[21] In our flow system, most of the polymer would deposit outside of the thermal zone further decreasing its decomposition. The suggestion that polymer decomposition did not affect our $XSiH_3$:$SiH_4$ product ratios is consistent with the fact that these ratios are similar in Tables I and II where per cent polymer formation was significantly different.

We conclude that the data in Tables I and II (especially II) can be used to determine the relative ratio of $k_1/k_2$. The results from Tables I and II lead to the following ratios for the decomposition of the disilanes investigated in this study

$$Si_2F_6 \longrightarrow SiF_2 + SiF_4 \qquad (4)$$

$$1,1\text{-}F_2Si_2H_4 \longrightarrow SiH_2 + F_2SiH_2 \qquad (5)$$

$$FSi_2H_5 \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} SiH_2 + FSiH_3 \qquad (6)$$

$$FSi_2H_5 \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} FSiH + SiH_4 \qquad (7)$$

$$k_6/k_7 = 5 \pm 1$$

$$1,1\text{-}Cl_2Si_2H_4 \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} SiH_2 + Cl_2SiH_2 \qquad (8)$$

$$1,1\text{-}Cl_2Si_2H_4 \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} SiCl_2 + SiH_4 \qquad (9)$$

$$k_8/k_9 \simeq 1^{22}$$

$$ClSi_2H_5 \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} SiH_2 + ClSiH_3 \qquad (10)$$

$$ClSi_2H_5 \underset{k_{-11}}{\overset{k_{11}}{\rightleftharpoons}} ClSiH + SiH_4 \qquad (11)$$

$$k_{10}/k_{11} = 0.80 \pm 0.1$$

$$sym\text{-}Cl_2Si_2H_2(CH_3)_2 \xrightarrow{k_{12}} ClSiCH_3 + ClSiH_2CH_3 \qquad (12)$$

$$sym\text{-}Cl_2Si_2H_2(CH_3)_2 \xrightarrow{k_{13}} HSiCH_3 + Cl_2SiHCH_3 \qquad (13)$$

$$k_{12}/k_{13} = 4.4 \pm 0.4$$

The results from the decomposition of *sym*-$Cl_2Si_2H_2(CH_3)_2$ (eq 12, 13) suggest that when a Cl atom and an H atom are in an identical ground state environment, the H atom shift is considerably more favored than the Cl shift. This result is in agreement with our data on 1,1-$Cl_2Si_2H_4$ where no Cl atom shift was observed while both types of H atoms apparently underwent 1,2 hydrogen shifts.

**2. Relative Insertion Rates of $SiH_2$, HSiCl, HSiF, $SiF_2$, and $SiCl_2$ into Si-H Bonds.** It has been established that $SiH_2$ insertions into silicon-hydrogen bonds are very facile reactions.[2,3] It has been estimated that these insertion reactions have nearly zero activation energies.[17] In contrast, it appears that $SiF_2$ is unreactive in the gas phase with a "half-life" of 150 sec.[23] Thus as expected, $SiF_2$, from the $Si_2F_6$ pyrolysis, did not insert into the silicon-hydrogen bonds in $(CH_3)_2SiH_2$ or $ClSiH_3$ in the gas phase. Similarly $SiCl_2$, generated from 1,1-$Cl_2SiH_2$, did not insert into the silicon-hydrogen bonds in $C_2H_5SiH_3$. Chlorosilylene and FSiH are intermediate between $SiH_2$ and $SiCl_2$ or $SiF_2$ and one might expect to observe their insertions into silicon-hydrogen bonds.

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[20] M. D. Sefcik and M. A. Ring, *J. Amer. Chem. Soc.*, 95, 5168 (1973).

[21] M. Bowery and J. H. Purnell, *Proc. Roy. Soc., Ser. A*, 321, 341 (1971).

[22] The $Cl_2SiH_2$:$SiH_4$ product ratio varied considerably from Table I to Table II. We have listed the result from Table II where a silylene trapping agent was present.

[23] P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Amer. Chem. Soc.*, 87, 2824 (1965).

Chlorodisilane decomposes by eq 10 and 11. From the determination of the $SiH_4$:$ClSiH_3$ ratio we have a measure of the ClSiH:$SiH_2$ ratio produced from $ClSi_2H_5$. If the half-lives of ClSiH and $SiH_2$ are the same, this ratio (1.25) would approximate the ClSiH:$SiH_2$ gas-phase ratio in our system. Since ClSiH probably has a longer half-life than $SiH_2$, this ratio would be a lower limit. In the pyrolysis of $ClSi_2H_5$ in the presence of $C_2H_5SiH_3$, $SiH_2$ and ClSiH reacted with $C_2H_5SiH_3$ forming $C_2H_5Si_2H_5$ and $C_2H_5SiH_2SiH_2Cl$ in a ratio of 1.54, respectively. This result suggests that the lower limit of $k_{14}/k_{15}$ is about 2.

$$SiH_2 + C_2H_5SiH_3 \xrightarrow{k_{14}} C_2H_5Si_2H_5 \qquad (14)$$

$$ClSiH + C_2H_5SiH_3 \xrightarrow{k_{15}} C_2H_5SiH_2SiH_2Cl \qquad (15)$$

If the half-life of ClSiH is much longer than that of $SiH_2$, this ratio would be considerably greater than 2.

Fluorodisilane decomposed *via* eq 6 and 7 to form $SiH_2$ and FSiH in a ratio of 5 ± 1. Since the half-life of FSiH is undoubtedly greater than that of $SiH_2$ the FSiH:$SiH_2$ ratio in our system was 0.2 or greater. Since the ratio of $C_2H_5Si_2H_5$ to $C_2H_5SiH_2Si(F)H_2$ from the $FSi_2H_5$ decomposition in the presence of $C_2H_5SiH_3$ was about 21, it is obvious that $SiH_2$ insertion into $C_2H_5SiH_3$ was considerably greater than that of FSiH.

The relative half-life of $SiF_2$ is about $10^5$ greater than that of $SiCl_2$.[23,24] From this, we assume that the half-life of HSiF is greater than that of HSiCl. Our data would then suggest that HSiCl inserts into silicon-hydrogen bonds faster than HSiF.

Our data with half-life assumptions (FSiH > ClSiH > $SiH_2$) suggest relative rates of silylene insertions into the silicon-hydrogen bonds of $C_2H_5SiH_3$ are in the order $SiH_2 > ClSiH > FSiH \gg SiCl_2, SiF_2$.

**3. Decomposition Modes of Disilanes.** Methyldisilane[4] and 1,1-$(CH_3)_2Si_2H_4$[25] decompose by both available 1,2 hydrogen shift routes in nearly statistical ratios. It is obvious that this observation cannot be made for the halodisilanes, especially for 1,1-$F_2Si_2H_4$ where only one route was observed.

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**Registry No.** $Si_2F_6$, 13830-68-7; 1,1-$F_2Si_2H_4$, 15857-41-7; $FSi_2H_5$, 14537-73-6; 1,1-$Cl_2Si_2H_4$, 20424-84-4; $ClSi_2H_5$, 14565-98-1; *sym*-$Cl_2Si_2H_2(CH_3)_2$, 42087-66-1; $F_2Si_3H_6$, 42086-09-9; 1-$FSi_3H_7$, 34551-82-1; 1-$ClSi_3H_7$, 31411-99-1; $Cl_2Si_3H_3(CH_3)_3$, 42086-10-2; $C_2H_5Si_2H_2D_3$, 42087-69-4; $C_2H_5Si_2H_4F$, 42087-70-7; $C_2H_5Si_2HD_3F$, 42087-71-8; $C_2H_5Si_2HD_3Cl$, 42087-72-9; $C_2H_5Si_2H_4Cl$, 42087-73-0.

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Department of Physical Chemistry of the Institute of Chemical
Engineering, Technical University of Gdansk, Gdansk, Poland

# Nature and Stability of the $CuCl^+$ Complex in Aqueous Solution

ZOFIA LIBUS

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Equimolal mixtures of the divalent transition metal perchlorates with magnesium perchlorate are proposed as effectively constant ionic media for the study of weak complexes of the type MX (M = a divalent metal cation, X = anion). Values of the stability constant, $\beta_1$, and the molar absorption coefficient, $\epsilon$, of the $CuCl^+$ complex have been determined in equimolal mixtures of copper(II) perchlorate with magnesium(II) perchlorate of the total molalities of 0.40, 1.34, and 2.39 mol $kg^{-1}$. $\epsilon$ is found to be approximately constant ($1115 \mp 80$) in dilute and moderately concentrate solutions, while at the highest concentrations of the ionic medium a slight increase in its value takes place, as indicated by additional experiments involving solutions of varying concentration of copper(II) perchlorate and a small concentration of NaCl. From the independently determined product $\epsilon\beta_1^\circ$, the value of $1.63 \mp 0.15$ $mol^{-1}$ $dm^3$ is found for $\beta_1^\circ$, the thermodynamic equilibrium constant of the $Cu^{2+} + Cl^- \rightleftharpoons CuCl^+$ reaction at 25°. The variation in the quotient of the activity coefficients of the latter reaction with the concentration of either copper(II) perchlorate or magnesium(II) perchlorate has also been calculated from the spectrophotometric data and is found to be practically the same for the two ionic media. The nature of the $CuCl^+$ complex is discussed on the basis of its uv and visible spectral characteristics and the conclusion is drawn that it consists mainly of the $[CuCl(OH_2)_5]^+$ coordination complex, in which the chloride anion replaces one of the two more distant water molecules of the hexaaquo complex, with a small contribution of the $\{[Cu(OH_2)_6]^{2+}Cl^-\}^+$ outer-sphere ion pair.

## Introduction

Constant ionic media are commonly used in determinations of the stability constants of metal complexes in order to maintain constant activity coefficients of reacting species.[1] However, this method becomes unsatisfactory when the ligands are ionic and the stabilities of complexes under investigation are low. It is necessary, in such cases, to vary the concentration of the complexing anion over a broad range, considerably changing, at the same time, the activity coefficients of the reacting species. Adjusting the concentration of the ionic medium so as to obtain a constant formal ionic strength does not, of course, fix the activity coefficients. The difficulties were discussed by Matheson in connection with the determination of the stability constant of the $CuSO_4$ complex in aqueous solution.[2] A new possibility of controlling the activity coefficients in determinations of stability constants of weak anionic complexes arises from our recent observations concerning the activity coefficients in aqueous solutions of a group of divalent metal perchlorates. It has been shown that equimolal solutions, pure or mixed, of $Mn(ClO_4)_2$,

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