Kinetics and Mechanism of Pyrolysis of Some Methylchlorosilanes

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The kinetics and products of pyrolysis of trimethylchlorosilane, dimethylchlorosilane, and methyldichlorosilane have been studied by low-pressure pyrolysis. It was concluded that all three pyrolyses proceeded mainly by radical chain mechanisms, with little involvement of silylenes or silenes. Nonchain conditions were achieved for the pyrolysis of trimethylchlorosilane, leading to a value of 366.5 ± 7 kJ mol^{-1} for the silicon–methyl bond dissociation energy in trimethylchlorosilane. Sulfur hexafluoride was found to be a useful trap for silyl radicals.

Introduction

Methylchlorosilanes, the precursors to siloxane polymers, are prepared industrially by the direct synthesis, the catalyzed thermal reaction of chloromethane with silicon.[1] Many products of differing commercial value are formed; accordingly, studies of the mechanism of pyrolysis of methylchlorosilanes are of commercial importance as well as being of academic interest.

The pyrolysis of organosilicon compounds may be initiated by σ-bond rupture to form organosilyl radicals, but the preferred primary pyrolysis step may be formation of silylenes, which are readily produced thermally in the singlet state from suitable precursors;[2,3] as shown in eq 1,

$$\mathrm{Me\ddot{Si}R \rightarrow HRSi{=}CH_2} \qquad (1)$$

methylsilylenes isomerize reversibly to silenes,[4] which may also be formed directly by molecular elimination. Consequently, several different types of intermediate may be involved simultaneously in the pyrolysis of organosilicon compounds. Silylene formation may be competitive with silyl radical formation,[3] and both silyl radical and silylene chains (the latter propagated by insertion reactions[5]) may ensue.

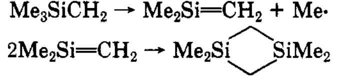
Against that background, we report kinetic studies of the low-pressure pyrolysis (LPP) of trimethylchlorosilane (I), dimethylchlorosilane (II), and methyldichlorosilane (III). Since silicon–chlorine is stronger than silicon–carbon or carbon–hydrogen bonds,[6] pyrolysis of I would be expected to resemble that of tetramethylsilane,[7] for which first-order rate constants were given by $\log k/\mathrm{s}^{-1} = (11.2 \pm 0.1) - (239.3 \pm 1.5)$ kJ mol$^{-1}/2.303RT$ between 840 and 950 K, while between 955 and 1055 K the parameters were $(17.6 \pm 0.3) - (355.3 \pm 6)$ kJ mol$^{-1}/2.303RT$. In the lower temperature region these results were explained in terms of the short radical chain reaction in Scheme I. While methane was the main product, the other products required by Scheme I were observed, notably 1,1,3,3-tetramethyl-1,3-disiletane. When the temperature was increased, the chain length tended to decrease below unity, with the result that the Arrhenius parameters at higher temperature approached those for the initiation reaction (2). Hence, the activation energy obtained above 955 K was identified with E_2, i.e. $D(\mathrm{Me_3Si{-}Me}) = 355 \pm 6$ kJ mol^{-1}, in agreement with the value of 356 ± 16 kJ mol^{-1} obtained from electron-impact experiments.[8] Subsequently, Walsh[6] has suggested a value of 374 ± 13 kJ mol^{-1} from thermochemical arguments. The main emphasis of our work on I was to see if a more reliable value for the silicon–methyl bond dissociation energy could be obtained from kinetic experiments. The expected chain sequence for I, analogous to Scheme I, is in Scheme II. While pyrolysis of II and III might also be initiated by silicon–methyl homolysis, other possibilities are silylene formation resulting from 1,2 H shifts[3,9] from silicon to carbon (reaction 10) or to chlorine (reaction 11).

Scheme I. Partial Chain Mechanism for Pyrolysis of Tetramethylsilane

$$\mathrm{Me_4Si \rightarrow Me_3Si\cdot + Me\cdot} \qquad (2)$$

$$\mathrm{Me\cdot + Me_4Si \rightarrow CH_4 + Me_3Si\dot{C}H_2} \qquad (3)$$

$$\mathrm{Me_3Si\dot{C}H_2 \rightarrow Me_2Si{=}CH_2 + Me\cdot} \qquad (4)$$



(5)

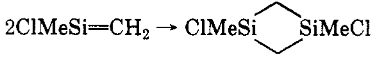
terminated by various radical combination reactions

Scheme II. Partial Chain Mechanism for Pyrolysis of Trimethylchlorosilane

$$\mathrm{Me_3SiCl \rightarrow Me_2\dot{Si}Cl + Me\cdot} \qquad (6)$$

$$\mathrm{Me\cdot + Me_3SiCl \rightarrow CH_4 + ClMe_2Si\dot{C}H_2} \qquad (7)$$

$$\mathrm{ClMe_2Si\dot{C}H_2 \rightarrow ClMeSi{=}CH_2 + Me\cdot} \qquad (8)$$



(9)

$$\mathrm{XMeSiHCl \rightarrow CH_4 + {:}SiClX} \qquad (10)$$

$$\mathrm{XMeSiHCl \rightarrow HCl + {:}SiMeX} \qquad (11)$$

$$\mathrm{II,\ X = Me;\ III,\ X = Cl}$$

Results

1. Trimethylchlorosilane (I). In LPP studies of the pyrolysis of I between 1020 and 1110 K, the decomposition had an order of ca. 1.1; Arrhenius parameters for first-order rate constants in the above temperature range were given by $\log k/\mathrm{s}^{-1} = (14.2 \pm 0.3) - (311 \pm 7)$ kJ mol$^{-1}/2.303RT$. Methane was the main product, but minor products were hydrogen and dimethyldichlorosilane, with smaller amounts of methyltrichlorosilane and silicon tetrachloride; no disiletanes were observed. Some hydrogen chloride was always present; silenes would add rapidly to hydrogen chloride, while silyl radicals readily abstract chlorine from

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Scheme III. Additional Reactions in the Pyrolysis of Trimethylchlorosilane in the Presence of Hydrogen Chloride

$$\mathrm{ClMeSi{=}CH_2 + HCl \rightarrow Me_2SiCl_2} \quad (12)$$

$$\mathrm{Me_2\dot{S}iCl + HCl \rightarrow Me_2SiCl_2 + H\cdot} \quad (13)$$

$$\mathrm{H\cdot + RH \rightarrow H_2 + R\cdot} \quad (14)$$

other chlorosilanes[10] and from hydrogen chloride. Consequently, formation of other products at the expense of disiletanes may be explained by the reactions in Scheme III. The feasibility of reaction 12 was assessed in separate experiments in which $Me_2Si{=}CH_2$ was generated thermally from 1,1-dimethylsiletane in the presence of hydrogen chloride;[11] not only did the corresponding reaction 15 occur, but also it was so fast that its kinetics could not

$$\mathrm{Me_2Si{=}CH_2 + HCl \rightarrow Me_3SiCl} \quad (15)$$

be measured conventionally by competition with reaction 5. Instead, Arrhenius parameters for reaction 15 relative to the published parameters[12] for reaction 5 were estimated by measuring the onset of reaction 5 as the HCl was consumed by reaction 15. These parameters were then optimized by numerical integration, giving $\log k_{15}/\mathrm{dm^3\ mol^{-1}\ s^{-1}} = (7.5 \pm 0.5) - (10 \pm 7)\mathrm{kJ\ mol^{-1}}/2.303RT$. Hence, reactions 6–8 and 12–14 constitute a reasonable chain mechanism for the pyrolysis of I. At 950 K, the approximate upper limit for chain behavior in the pyrolysis of tetramethylsilane, the rate constant for decomposition was ca. 10 times smaller for I than for tetramethylsilane; it should therefore be easier to move into a nonchain region with I than it was with tetramethylsilane, thus leading to a more reliable estimate of the activation energy for silicon–methyl bond rupture. Accordingly, kinetic data for decomposition of I were collected between 1079 and 1130 K, keeping the extent of decomposition below 10%. Under these conditions the pyrolysis obeyed first-order kinetics, with rate constants for either decomposition of I or formation of CH_4 given by $\log k/\mathrm{s^{-1}} = (17.03 \pm 0.34) - (366.5 \pm 7.2)\ \mathrm{kJ\ mol^{-1}}/2.303RT$. The HCl that was always present in the pyrolysis of I could have arisen from heterogeneous hydrolysis of I by water adsorbed on the surface of the apparatus or by direct elimination, homogeneously or heterogeneously, in reaction 16, the reverse of reaction 15. The following experiments were done to try to assess

$$\mathrm{Me_3SiCl \underset{15}{\overset{16}{\rightleftharpoons}} Me_2Si{=}CH_2 + HCl} \quad (15), (16)$$

the extent to which reaction 16 occurred. (i) I was copyrolyzed with equal pressures of HCl at 996 K; the rate of formation of CH_4, normalized to a standard initial pressure of I, increased on average by ca. 20%. The rate of formation of Me_2SiCl_2 increased similarly. (ii) At temperatures above 1000 K copyrolysis of I with HBr gave $Me_2SiBrCl$ and Me_3SiBr. The latter product was still produced between 713 and 941 K, but the results of these experiments were particularly irreproducible, with evidence for surface-catalyzed reactions. (iii) Copyrolysis of I with O_2 gave complex mixtures of products, with mass spectrometric evidence [$(M - Me)^+$ ions] for $Me_3SiOSiMe_2Cl$, $(ClMe_2Si)_2O$ or its isomeric $Me_3SiOSiMeCl_2$, and $ClMe_2SiOSiMeCl_2$.

2. Dimethylchlorosilane (II). II was pyrolyzed by LPP between 994 and 1042 K. The main products were hydrogen, methane, methyldichlorosilanes $RMeSiCl_2$ (R = H, Me), and hydrogen chloride. Mass spectrometric fragmentation patterns indicated that the main methyldichlorosilane was Me_2SiCl_2. Reproducible kinetic data for II were difficult to obtain; integrated first-order plots for decomposition of II were only linear up to 20–30%; corrections had to be made for adsorption of II at low temperature, while rate constants >0.2 s^{-1} could not be measured reliably. Despite these difficulties, the Arrhenius parameters in Table I were obtained for decomposition of II and formation of methane and $RMeSiCl_2$. Approximate rate constants for formation of hydrogen were of comparable magnitude to those in Table I. Possible primary reactive intermediates in the pyrolysis of II are silyl radicals resulting from silicon–methyl bond rupture and silylenes formed in reactions 10 or 11. While attempting to use SF_6 as an "inert" energy-transfer gas, we found that it is an excellent trap for silyl radicals

$$\mathrm{R_3Si\cdot + SF_6 \rightarrow R_3SiF + \cdot SF_5}$$

the abstraction reaction is exothermic by some 290 kJmol^{-1}, yielding products that are easily identified mass spectrometrically. We therefore pyrolyzed II in excess SF_6 at 1030 K. New mass spectrometric peaks were observed at m/e 97^+ and 99^+, of relative intensity ca. 3:1, implying the presence of the $MeSiFCl^+$ ion and hence of $\cdot SiMeHCl$ and/or $\cdot SiMe_2Cl$ radicals.

Table I. Kinetic Data for Pyrolysis of II

kinetic measurement	log A/s^{-1}	E/kJ mol^{-1}	k_{1000K}/s^{-1}
decomposition of II	11.35 ± 0.21	246.9 ± 4.1	0.0284
formation of CH_4	11.38 ± 0.13	247.4 ± 2.6	0.0286
formation of $RMeSiCl_2$	11.19 ± 0.19	247.1 ± 3.8	0.0192

Table II. Kinetic Data for Pyrolysis of III

kinetic measurement	log A/s^{-1}	E/kJ mol^{-1}	k_{1000K}/s^{-1}
decomposition of III	11.10 ± 0.20	244.1 ± 4.0	0.0223
formation of CH_4	11.73 ± 0.13	267.6 ± 2.6	0.00564
formation of $RSiCl_3$	8.49 ± 0.16	201.3 ± 3.3	0.00944

Table III. Kinetic Data for Formation of Methane from Methylsilanes

methylsilane	log A/s^{-1}	E/kJ mol^{-1}	k_{1000K}/s^{-1}	k_{rel}	ref
Me_3SiH	16.4 ± 0.7	320 ± 2	0.483	63	7
Me_4Si	17.6 ± 0.3	355 ± 6	0.114	15	7
Me_3SiCl	17.03 ± 0.34	366.5 ± 7.2	0.00768	1	this work

3. Methyldichlorosilane (III). The main products of low-pressure pyrolysis of III between 992 and 1139 K were hydrogen, methane, $RSiCl_3$ (R = H, Me), and hydrogen chloride; the trichlorosilane was mainly $MeSiCl_3$. Kinetic data were even more difficult to obtain than they were with II, and reliable Arrhenius parameters could not be measured for formation of hydrogen or hydrogen chloride. Those for the other products are in Table II. Rate constants for decomposition of III were about 4 times greater than for formation of methane (Table II), whereas rate constants for decomposition of II and formation of methane were about equal (Table I). Pyrolysis of III with excess SF_6 at 1030 K gave $SiFCl_2^+$ ions, from $MeSiFCl_2$ and/or $HSiFCl_2$; there was also some SiF_2Cl_2.

Discussion

1. Trimethylchlorosilane (I). The "high-temperature" Arrhenius parameters measured for formation of CH_4 from I between 1079 and 1130 K are in Table III, together with the corresponding parameters for the pyrolysis of Me_3SiH and Me_4Si. The relative rate constants (k_{rel}) in Table III confirm that the chain element

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is less in the pyrolysis of I than in the pyrolysis of Me_4Si. As the latter pyrolysis was close to the nonchain limit,[7] we believe that the Arrhenius parameters for I are those for reaction 6. Since reaction −6 would have zero activation energy, our results give $D(ClMe_2Si–Me) = 366 \pm 7$ kJ mol^{-1}. This is the most direct measure as yet for the silicon–methyl bond dissociation energy in a monosilane; it is consistent with Walsh's[6] more indirect estimate of 374 ± 13 kJ mol^{-1} for $D(Me_3Si–Me)$ in Me_4Si; substituent effects on $D(\equiv Si–Me)$ in monosilanes are believed to be small.[8] The A factor is entirely reasonable for a unimolecular bond rupture to form two radicals.[13]

The relative importance of the primary reactions 6 and 16 is a difficult question. By analogy with the elimination of HCl from chloroalkanes,[13] $\log A_{16} \geq 13.5$, while ΔH_{16} and hence E_{16} may be estimated from bond dissociation energies[6,13] as follows.

$$\Delta H_{16} = D(\text{–CH}_2\text{–H}) + D(\equiv\text{Si–Cl}) - D(\text{H–Cl}) - D_\pi(>\text{Si=C}<)$$
$$= 415 + 473 - 431 - 163 = 294 \text{ kJmol}^{-1}$$

Since E_{15} has been measured[11] to be 10 kJ mol^{-1}, $E_{16} \propto$ kJ mol^{-1}. These estimates give $k_{16} \geq 4 \times 10^{-3}$ s^{-1} at 1000 K, of comparable magnitude to k_6. However, k_{15} would be 9.5×10^6 s^{-1} at 1000 K; if reactions 16 and 15 are considered in isolation, I would only be 2% converted to $Me_2Si{=}CH_2$ and HCl at 1000 K. The enhancement of the rate of formation of CH_4 and Me_2SiCl_2 by added HCl might be due to the (16) $\rightleftharpoons$ (15) equilibrium being moved further to the left, thus increasing the amount of I available for decomposition as in Schemes II and III; but it might simply be due to the following new reactions 17 and 18 followed by reactions 8, 7, 19, and 20. Silenes being known

$$\mathrm{Me_2\dot{S}iCl + HCl \rightarrow H\cdot + Me_2SiCl_2} \tag{17}$$
$$\mathrm{H\cdot + Me_3SiCl \rightarrow H_2 + ClMe_2Si\dot{C}H_2} \tag{18}$$
$$\mathrm{Me\cdot + HCl \rightarrow CH_4 + Cl\cdot} \tag{19}$$
$$\mathrm{Cl\cdot + Me_3SiCl \rightarrow HCl + ClMe_2Si\dot{C}H_2} \tag{20}$$

to react rapidly with HBr,[11] formation of $Me_2SiBrCl$ in the copyrolysis of I with HBr could result from reaction 8 followed by reaction 21 but also from reaction 22. Like-

$$\mathrm{ClMeSi{=}CH_2 + HBr \rightarrow Me_2SiBrCl} \tag{21}$$
$$\mathrm{Me_2\dot{S}iCl + HBr \rightarrow Me_2SiBrCl + H\cdot} \tag{22}$$

wise, formation of Me_3SiBr might be taken as evidence for the presence of $Me_2Si{=}CH_2$ (reaction 23) but might equally be explained by reactions 24[10] and 25.

$$\mathrm{Me_2Si{=}CH_2 + HBr \rightarrow Me_3SiBr} \tag{23}$$
$$\mathrm{Me_2\dot{S}iCl + Me_3SiCl \rightarrow Me_2SiCl_2 + Me_3Si\cdot} \tag{24}$$
$$\mathrm{Me_3Si\cdot + HBr \rightarrow Me_3SiBr + H\cdot} \tag{25}$$

Silenes are known to react with O_2 to form silanones,[11] which insert into silicon–chlorine bonds to form siloxanes (eq 26–28);[14] these reactions could account for the for-

$$\mathrm{ClMeSi{=}CH_2 + O_2 \rightarrow ClMeSi{=}O + CH_2O} \tag{26}$$
$$\mathrm{ClMeSi{=}O + Me_3SiCl \rightarrow Me_3SiOSiMeCl_2} \tag{27}$$
$$\mathrm{ClMeSi{=}O + Me_2SiCl_2 \rightarrow ClMe_2SiOSiMeCl_2} \tag{28}$$

mation of two of the observed new products from the silene formed in reaction 8 (Scheme II). Reactions 29 and 30 constitute an alternative to reaction 27, and the possible presence of $Me_2Si{=}CH_2$ may be confirmed by the formation of the third product, $Me_3SiOSiMe_2Cl$, by reaction 31. While this might be the strongest evidence yet for

$$\mathrm{Me_2Si{=}CH_2 + O_2 \rightarrow Me_2Si{=}O + CH_2O} \tag{29}$$
$$\mathrm{Me_2Si{=}O + Me_2SiCl_2 \rightarrow ClMe_2SiOSiMe_2Cl} \tag{30}$$
$$\mathrm{Me_2Si{=}O + Me_3SiCl \rightarrow Me_3SiOSiMe_2Cl} \tag{31}$$

reaction 16, the copyrolysis of I and O_2 is obviously complex, and none of the foregoing experiments had produced unambiguous evidence for the direct elimination of HCl from I; reaction 16 remains plausible but unproven.

2. Dimethylchlorosilane (II). The Arrhenius parameters in Table I are consistent with homogeneous gas-phase processes, being quite similar to those obtained[7] for the radical chain formation of CH_4 in the pyrolysis of Me_4Si ($\log A = 11.2$ and $E = 239$ kJ mol^{-1}). A reasonable radical chain sequence, initiated by the counterpart to reaction 6 and leading to H_2, CH_4, and $RMeSiCl_2$ as major products, is in Scheme IV; reactions 38 and 39 were included because some HCl was present. From published Arrhenius parameters for analogous reactions,[15] we estimate that reaction 34 would have about half the rate of reaction 33 at 1000 K when R = Me; H atoms are less selective than Me radicals in abstraction reactions. Because the silicon–hydrogen bond is stronger than silicon–methyl while the A factor for silicon–hydrogen bond dissociation is lower than that for silicon–methyl dissociation,[13] reaction 35 would be mainly a source of Me radicals, propagating the chain formation of CH_4. The main source of H atoms to propagate the H_2-forming chain would be reactions 38 and 39.

Scheme IV. Partial Chain Mechanism for Pyrolysis of Dimethylchlorosilane

$$\mathrm{Me_2SiHCl \rightarrow Me\cdot + Me\dot{S}iHCl} \tag{32}$$
$$\mathrm{R\cdot + Me_2SiHCl \rightarrow RH + Me_2\dot{S}iCl} \tag{33}$$
$$\mathrm{R\cdot + Me_2SiHCl \rightarrow RH + \cdot CH_2SiMeHCl} \tag{34}$$
$$\mathrm{\cdot CH_2SiMeHCl \rightarrow CH_2{=}SiClR' + R\cdot} \tag{35}$$
$$\mathrm{CH_2{=}SiClR' + HCl \rightarrow R'MeSiCl_2} \tag{36}$$
$$\mathrm{RMe\dot{S}iCl + Me_2SiHCl \rightarrow RMeSiCl_2 + Me_2\dot{S}iH} \tag{37}$$
$$\mathrm{Me_2\dot{S}iH + HCl \rightarrow Me_2SiHCl + H\cdot} \tag{38}$$
$$\mathrm{RMe\dot{S}iCl + HCl \rightarrow RMeSiCl_2 + H\cdot} \tag{39}$$

R = Me, H; R′ = H when R = Me and vice versa

The energetics of the alternative silylene-forming primary reactions 10 and 11 may be estimated thus

$$\mathrm{MeSiHCl_2 = {:}SiMeCl + CH_4} \tag{10}$$
$$\Delta H_{10} = D(\equiv\text{Si–Me}) + D(=\text{Si–H}) - D(\text{Me–H})$$
$$= 366 + 268 - 435 = 199 \text{ kJ mol}^{-1}$$
$$E_{10} = \Delta H_{10} + E_{-10}$$
$$= 199 + \geq 123 \geq 322 \text{ kJ mol}^{-1}$$
$$\mathrm{Me_2SiHCl \rightarrow Me_2Si{:} + HCl} \tag{11}$$
$$\Delta H_{11} = D(\equiv\text{Si–Cl}) + D(=\text{Si–H}) - D(\text{H–Cl})$$
$$= 473 + 268 - 435 = 306 \text{ kJ mol}^{-1}$$
$$E_{11} = \Delta H_{11} + E_{-11}$$
$$= 306 + 28 = 334 \text{ kJ mol}^{-1}$$

$D(\equiv Si–Me)$ is from this work; other bond dissociation energies are from the literature,[6,13] as is[16] E_{-11}. E_{-10} is unknown, but 123 kJ mol^{-1} has been estimated[17] for the insertion of Me_2Si: into CH_4; E_{-10} is likely to be greater than that because chlorine enhances silylene stabilization.[6] Combining these activation energies with A factors[18] for analogous reactions of Me_2SiH_2 leads to the estimated

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Table IV. Estimated Arrhenius Parameters for Primary Reactions in the Pyrolysis of II

reaction	no.	log A	E/ kJmol^{-1}	k_{1000K}/s^{-1}
$Me_2SiHCl \rightarrow Me\cdot + Me\dot{S}iHCl$	(6)	17.0	366.5	7.68×10^{-3}
$Me_2SiHCl \rightarrow Me\ddot{S}iCl + CH_4$	(10)	14.8	≥ 322	$\leq 9.55 \times 10^{-3}$
$Me_2SiHCl \rightarrow Me_2Si{:} + HCl$	(11)	14.3	334	7.13×10^{-4}

Arrhenius parameters and rate constants in Table IV. The estimates for reaction 11 imply that its rate would be only 10% of the rate of reaction 6; the main reaction of $Me_2Si{:}$ would be reversible insertion into the silicon–hydrogen bond in II (eq 40). The analogous reaction of

$$Me_2SiHCl + Me_2Si{:} \rightleftharpoons ClMe_2SiSiMe_2H \qquad (40)$$

$ClMeSi{:}$ could lead to formation of Me_2SiCl_2 by a 1,2-chlorine shift (reaction 42), but that reaction would be slower than (−41).[19] In any case, k_{10} may be substantially

$$Me_2SiHCl + ClMeSi{:} \rightleftharpoons ClMe_2SiSiMeHCl \qquad (41)$$

$$ClMe_2SiSiMeHCl \rightarrow Me_2SiCl_2 + HMeSi{:} \qquad (42)$$

smaller than our upper-limit estimate. Isomerization of silylenes by reaction 1 would lead to observed products, as shown in reactions 43–46, but such reactions would be

$$Me_2Si{:} \rightleftharpoons CH_2{=}SiMeH \qquad (43)$$

$$CH_2{=}SiMeH + HCl \rightarrow Me_2SiHCl \qquad (44)$$

$$ClMeSi{:} \rightleftharpoons CH_2{=}SiHCl \qquad (45)$$

$$CH_2{=}SiHCl + HCl \rightarrow MeSiHCl_2 \qquad (46)$$

uncompetitive with reactions (48) and (49) because silylene insertion into silicon–hydrogen bonds is so rapid. Hence, while there may be some primary formation of silylenes by reactions 10 and 11, there are no obvious silylene chains that would account for the observed Arrhenius parameters in Table I. On the other hand, numerical integration of an extended version of the radical mechanism in Scheme IV, with no silylene reactions included, satisfactorily reproduced the experimental Arrhenius parameters. Furthermore, the results of the copyrolyses with SF_6 are entirely consistent with the presence of $RMe\dot{S}iCl$ radicals. We conclude that silylenes are not important intermediates in the pyrolysis of II, which proceeds mainly by the radical chain mechanism outlined in Scheme IV.

3. Methyldichlorosilane (III). Our conclusions regarding the pyrolysis mechanism for III clearly parallel those for II. The analogous radical chain mechanism is outlined in Scheme V. Unlike Scheme IV, Scheme V only embodies a chain sequence for the formation of H_2, not CH_4, in keeping with the experimental observation that H_2 and CH_4 were formed in comparable amounts in the pyrolysis of II, whereas relatively less CH_4 was formed from III.

Scheme V. Partial Chain Mechanism for Pyrolysis of Methyldichlorosilane

$$MeSiHCl_2 \rightarrow Me\cdot + H\dot{S}iCl_2 \qquad (47)$$

$$R\cdot + MeSiHCl_2 \rightarrow RH + Me\dot{S}iCl_2 \qquad (48)$$

$$R\cdot + MeSiHCl_2 \rightarrow RH + \cdot CH_2SiHCl_2 \qquad (49)$$

$$\cdot CH_2SiHCl_2 \rightarrow CH_2{=}SiCl_2 + H\cdot \qquad (50)$$

$$CH_2{=}SiCl_2 + HCl \rightarrow MeSiCl_3 \qquad (51)$$

$$R\dot{S}iCl_2 + MeSiHCl_2 \rightarrow RSiCl_3 + Me\dot{S}iHCl \qquad (52)$$

$$Me\dot{S}iHCl + HCl \rightarrow MeSiHCl_2 + H\cdot \qquad (53)$$

$$R\dot{S}iCl_2 + HCl \rightarrow RSiCl_3 + H\cdot \qquad (54)$$

$$R = Me, H$$

The silylene-forming primary reactions (10) and (11) are likely to be even less important in the pyrolysis of III. E_{-10} and E_{-11} would be higher than in the pyrolysis of II because of the stabilizing effect of chlorine substituents on silylenes; as there would be little difference in ΔH_{10} and ΔH_{11} between II and III, E_{10} and E_{11} would be even higher for III than for II. Again, numerical integration of an extended version of Scheme V without any silylene reactions agreed with the experimental Arrhenius parameters in Table II. The copyrolyses of III with SF_6 indicated the presence of $R\dot{S}iCl_2$ radicals. While SF_6 is useful in indicating which radicals are present, some caution is called for in view of the recent evidence that silylenes can undergo abstraction reactions.[20] The small amount of SiF_2Cl_2 observed in the pyrolysis of III with SF_6 may have originated from such a reaction:

$$:SiCl_2 + SF_6 \rightarrow \cdot SiFCl_2 \xrightarrow{SF_6} SiF_2Cl_2$$

Experimental Section

Compounds I–III were gifts from Dow Corning (Europe); purity was checked by gas chromatography and mass spectrometry.

The basic features of the LPP apparatus with analysis by quadrupole mass spectrometry have been described.[9] An improved version was used in this work, the output from the mass spectrometer peak selector being interfaced to a dedicated microcomputer (RML 380Z). Peak heights collected by the microcomputer were timed by its internal clock; time intervals between readings were normally $^1/_8$ or $^3/_8$ s. The resulting peak height/time data were subsequently analyzed in accordance with conventional kinetic methods to produce rate constants and Arrhenius parameters by software written in-house.

Partial pressures of I–III were between 0.01 and 0.1 torr; some experiments to verify product composition were done in a flow system with analysis by gas chromatography.[21]

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