Kinetics and Mechanism of Pyrolysis of Methyltrichlorosilane†

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The thermal decomposition of methyltrichlorosilane (MTS) was studied in a flow system in the temperature range of 825−977 K and pressure range of 10−120 Torr. Yields of products were measured by gas chromatography. The rate constant, k_1, for the initiation reaction was determined from the sum of the rates of the termination reactions. The Arrhenius expression for this reaction at the high-pressure limit was obtained from a nonlinear least-squares fit to the experimental data using the Troe factorization method, $k_{1\infty} = (9.6 \pm 2.5) \times 10^{19} \exp(-(392 \pm 18)\ \text{kJ mol}^{-1}/RT)\ \text{s}^{-1}$. The rate constants for hydrogen abstraction, k_2, and chlorine abstraction, k_3, from MTS by methyl radicals were also calculated on the basis of experimental measurements. The Arrhenius expression for hydrogen abstraction was $k_2 = (5.1 \pm 0.4) \times 10^8 \exp(-(61 \pm 3)\ \text{kJ mol}^{-1}/RT)\ \text{L mol}^{-1}\text{s}^{-1}$ and for chlorine abstraction was $k_3 = (1.5 \pm 0.5) \times 10^9 \exp(-(72 \pm 6)\ \text{kJ mol}^{-1}/RT)\ \text{L mol}^{-1}\text{s}^{-1}$.

Introduction

The chemistry of chlorinated organosilanes is of intrinsic interest because of their important role in chemical vapor deposition processes. Gas-phase study of chemical reactions is useful for determining the formation and consumption of reactive intermediates important to the film-growth rate, deposit composition, and reactor behavior in chemical vapor deposition (CVD) processes. Silicon carbide (SiC) prepared by CVD finds many structural and electronic applications.[1] CH_3SiCl3 (MTS) is one of the precursors which could be used in CVD processes to produce a coating film of silicon carbide SiC on the surfaces. The understanding of the kinetics of gas-phase pyrolysis of MTS is of particular interest. To the best of our knowledge, the kinetics of thermal decomposition of MTS is not studied in detail, experimentally.

Different groups have studied the kinetics of the deposition of some methylsilanes.[2]

Burgess and Lewis[3] in 1974 studied the kinetics of the reduction of MTS by hydrogen. They reported the following Arrhenius expression for the decomposition of MTS.

$$k = 7.6 \times 10^{14} \exp(-336\ \text{kJ mol}^{-1}/RT)\ \text{s}^{-1}$$

They reported the dissociation products of MTS in the presence of hydrogen are likely to be $SiHCl_3$ and CH_4, although other species, such as $SiCl_2$, may be important.

In 1975, Kobayashi et al.[4] worked on the formation of carbon-excess SiC from pyrolysis of MTS. They investigated pyrolysis of MTS in the presence of argon and hydrogen at high temperatures. They determined the effect of pressure and temperature on the C/Si ratio and the weight of the deposit. They also observed that the amount of excess carbon was larger in the presence of argon than in the presence of hydrogen. Their study suffers the lack of mechanistic explanation for their observation.

Davidson and Dean[5] have studied the kinetics and mechanism of pyrolysis of some methylchlorosilanes. They suggested that pyrolysis of these compounds proceeded mainly by radical chain mechanism.

In 1987, Gordon and Truong[6] studied the possible primary pyrolysis processes of methylsilane, H_3SiCH_3, theoretically. They suggested a chain radical mechanism for the pyrolysis of H_3SiCH_3. They investigated the way of formation of methane during the process. In 1991, Besmann and Sheldon[7] worked on the reaction of MTS and hydrogen. They suggested the formation of SiC and HCl as the overall products of the reaction. In 1991, Besmann and co-workers[8] in vapor-phase fabrication and properties of continuous-filament ceramic composites studied the characteristic of SiC film produced in chemical vapor deposition. In 1992, Besmann and co-workers[9] studied the depletion effect of silicon carbide deposition from MTS and dependence of SiC deposition on total system pressure. In their study, they reported the overall reaction $CH_3SiCl_3 \rightarrow SiC + 3HCl$ and they did not look at the mechanism of pyrolysis of MTS.

Allendorf and Melius[10] in 1993 studied the thermochemistry of molecules in the Si−C−Cl−H system including MTS.

In 1994, Cagliostro and co-workers[11] compared the pyrolysis products of dichloro-dimethylsilane in CVD process and formation of SiC on silica in the presence of hydrogen or argon.

Osterheld et al.[12] in 1994 studied dissociation reaction of MTS, theoretically. They studied different possible paths for the decomposition of this molecule. They used RRKM theory to calculate the rate constants for the three most probable paths for the decomposition of MTS. According to their results, Si−C bond cleavage to form CH_3 and $SiCl_3$ is the most likely path for the unimolecular decomposition of CH_3SiCl_3. The other two pathways for the decomposition of this compound are 1,2 elimination of HCl and C−H bound cleavage. They have reported high-pressure limiting values of the rate constants for each reaction in a temperature range of 800−1500 K.

In 1995, Gordon and co-workers[13] studied ab initio molecular orbital study on the unimolecular decomposition of $CH_3SiH_2^+$. In their study, they suggested a chain reaction mechanism for the pyrolysis of methylsilane.

The purpose of the present study is to investigate the pyrolysis of MTS at the temperature range of 825−977 K and pressure range of 10−120 Torr.

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Proposed Mechanism and Derivation of the Rate Laws. A chain reaction mechanism for the pyrolysis of MTS is proposed as

$$CH_3SiCl_3 \rightarrow CH_3 + SiCl_3 \quad (R1)$$

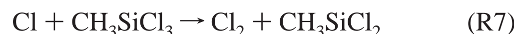
$$CH_3 + CH_3SiCl_3 \rightarrow CH_4 + CH_2SiCl_3 \quad (R2)$$

$$CH_3 + CH_3SiCl_3 \rightarrow CH_3Cl + CH_3SiCl_2 \quad (R3)$$

$$CH_3SiCl_2 \rightarrow SiCl_2 + CH_3 \quad (R4)$$

$$CH_2SiCl_3 \rightarrow CH_2SiCl_2 + Cl \quad (R5)$$

$$Cl + CH_3SiCl_3 \rightarrow HCl + CH_2SiCl_3 \quad (R6)$$


$$Cl + CH_3SiCl_3 \rightarrow Cl_2 + CH_3SiCl_2 \quad (R7)$$

$$CH_2SiCl_3 + CH_3 \rightarrow C_2H_5SiCl_2 \quad (R8)$$

$$2CH_2SiCl_3 \rightarrow (CH_2SiCl_3)_2 \quad (R9)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \quad (R10)$$

$$CH_3 + SiCl_3 \rightarrow CH_3SiCl_3 \quad (R11)$$

$$2SiCl_3 \rightarrow (SiCl_3)_2 \quad (R12)$$

$$CH_3SiCl_3 \rightarrow HCl + CH_2SiCl_2 \quad (R13)$$

$$SiCl_3 + CH_3SiCl_3 \rightarrow HSiCl_3 + CH_2SiCl_3 \quad (R14)$$

$$SiCl_3 + CH_3SiCl_3 \rightarrow SiCl_4 + CH_3SiCl_2 \quad (R15)$$

According to this proposed mechanism CH_4, CH_3Cl, $SiCl_2$, CH_2SiCl_2, and HCl would be the major products. The above mechanism consists of two unimolecular reactions R1 and R13. At low conversion of MTS, no active species such as radicals in reaction R13 are produced. Therefore, we do not expect any contribution of reaction R13 in the other reactions in the proposed mechanism at low conversion regime. Applying the steady-state approximation to the radicals in this mechanism, the rate of the initiation reaction R1 would be equal to the sum of the rates of the termination reactions, reactions R8−R12. This assumption would allow the calculation of the rate constant, k_1, for reaction R1 as

$$k_1 = (R_8 + R_9 + R_{10} + R_{11} + R_{12})/[MTS] \quad (1)$$

Here, R8−R12 are the steady-state rates of termination reactions, respectively. All these reactions are pressure dependent and to calculate the k_1 at high-pressure limit one must calculate rates of these termination reactions at high-pressure limit.

Applying the steady-state approximation, the ratios of rate constants for reactions R2 and R3 to the rate constants for reaction R10 may be calculated as

$$k_{10}/k_2^{\,2} = R_{10}\,[MTS]^2/(R_2)^2 \quad (2)$$

$$k_{10}/k_3^{\,2} = R_{10}\,[MTS]^2/(R_3)^2 \quad (3)$$

where R_{10}, R_2, and R_3 are the steady-state rates of formation of ethane, methane, and chloromethane, respectively. Reaction R10 has been studied extensively and the pressure and temperature dependence of its rate constant are reasonably well-known. Any pressure dependence of the rate constants k_1, k_8, k_9, k_{10}, k_{11}, and k_{12} can be analyzed using the factorization method of Troe:[14]

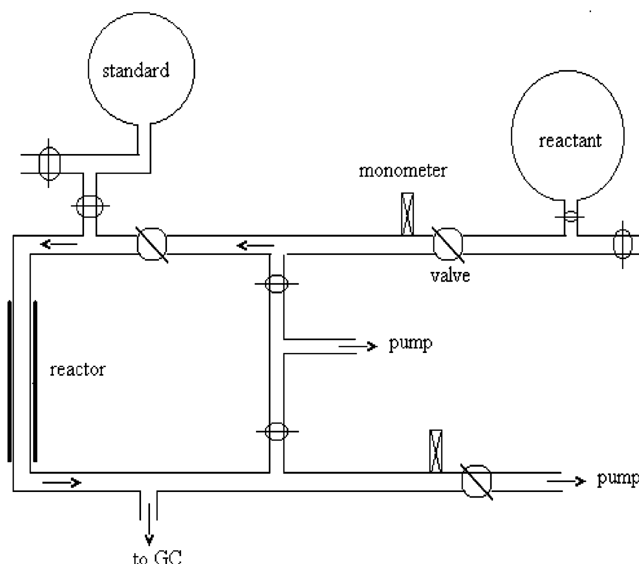


Figure 1. Schematic diagram of the apparatus used for the study of pyrolysis of CH_3SiCl_3.

$$k_1/k_{1\infty} = F_{LH}F_c^{\,SC}F_c^{\,WC} \quad (4)$$

$$F_{LH} = (k_{1,0}\,[M]/k_{1\infty})/(1 + k_{1,0}\,[M]/k_{1\infty}) \quad (5)$$

Here $k_{1,\infty}$ and $k_{1,0}$ are the limiting, high-pressure, first-order and limiting, low-pressure, second-order rate constants, respectively, for reaction R1. The same expressions might be written for the association reactions R8−R12, but the rate constants are second and third order, respectively.

Experimental Section

All experiments were performed in a flow system shown in Figure 1. The pressure in the storage bulb (10 L) and reactor were monitored by two pressure transducer (Druck DPI 705). The flow rate into the reactor was controlled by a needle valve. CH_3SiCl_3 of 98% purity (Fluka) was used in all experiments. During the experiments, a 40-cm-long section of the reactors was heated by a resistive furnace. The temperature of the reactor was controlled by a platinum/platinum-13%-rhodium thermocouple. The temperature was varied from 825 to 977 K. A FORTRAN program[15] was used to calculate the effective length and temperature of the reactor according to the temperature profile of the reactor and approximate activation energy of the overall reaction. The average residence time, t, of molecules in the reactor was calculated from the measured pressure, temperature, and effective cross section of the reactors and from the reactant flow rate. The conversion of reactant was between 1 and 3% to minimize the effect of possible secondary reactions. To examine the possible surface reactions, two 80-cm-long cylindrical quartz reactors with different surface-to-volume ratios were used. The cross sections of the reactors were 1.26 and 0.94 cm^2. The surface-to-volume ratios (s/v) for these reactors was 17.5 and 9.48 cm^{-1}. A six-way linear stainless steel gas sampling valve at the exit of the reactor was used to take samples in a 14 cm^3 sample loop and a gas chromatograph (Shimadzu GC-8A) was used to analyze the samples. The products were separated on a 3-m silicagel column (mesh 50/75) at different temperatures. Nitrogen was used as carrier gas. A flame ionization detector and a thermal conductivity detector

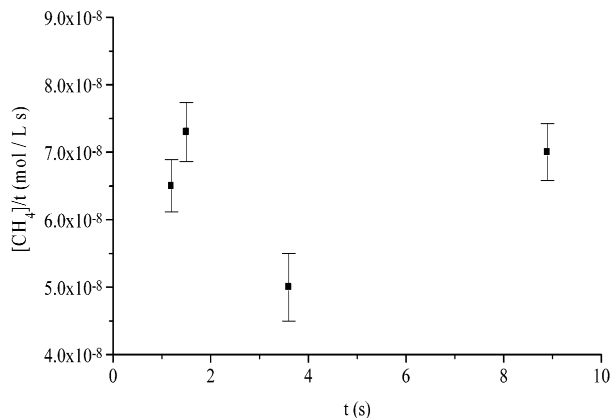


Figure 2. Chordal rate of formation of methane at 55 Torr and 825 K in a reactor with surface-to-volume ratio of 17.5 cm^{-1}.

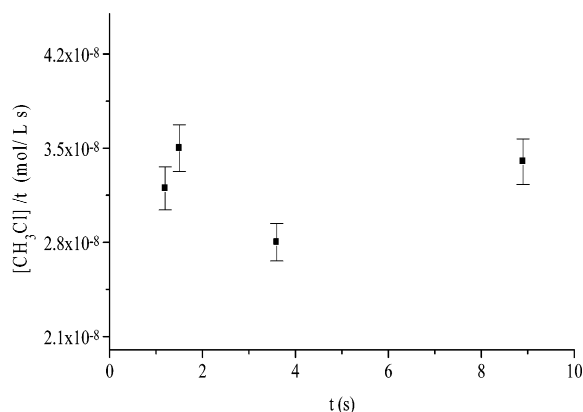


Figure 3. Chordal rate of formation of chloromethane at 55 Torr and 825 K in a reactor with surface-to-volume ratio of 17.5 cm^{-1}.

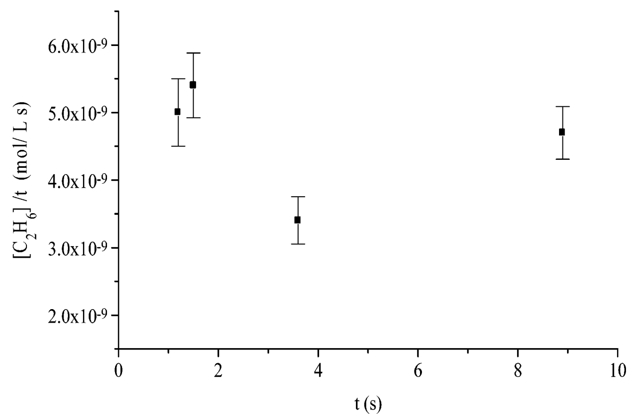


Figure 4. Chordal rate of formation of ethane at 55 Torr and 825 K in a reactor with surface-to-volume ratio of 17.5 cm^{-1}.

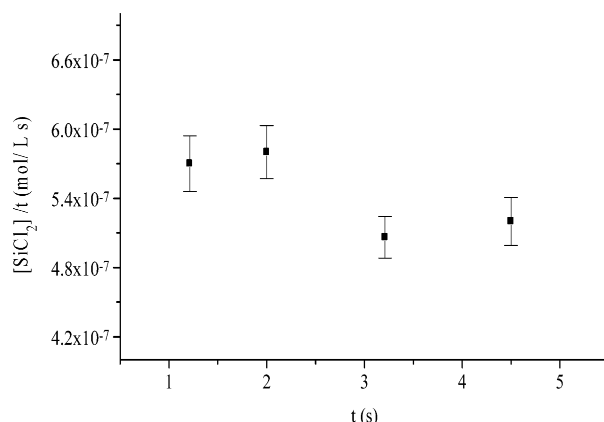


Figure 5. Chordal rate of formation of dichlorosilane at 70 Torr and 917 K in a reactor with surface-to-volume ratio of 17.5 cm^{-1}.

were used for the detection of possible different products. The spectrum of HCl at 2500−3300 cm^{-1} was detected qualitatively with a spectrophotometer (Shimadzu FTIR-8300).

Procedure. MTS was degassed by condensing with liquid nitrogen. It was then placed in the storage bulb, shown in Figure 1 by evaporation and was again degassed in liquid nitrogen. The storage bulb was covered with dark paper to prevent photolysis of the MTS. The vapor pressure of MTS could be monitored by a transducer. A needle valve controlled the flow rate of the MTS vapor into the reactor. The vapor of the MTS passed through the furnace. The temperature profile along the reactor was measured several times during each run to keep the temperature along the reactor constant. The pressure in the reactor was controlled by the pressure transducer and a needle valve. Normally, we tried to clean the surface of the reactors by passing air through the reactors at high temperatures.

Results

The reaction was studied in the temperature range of 825 ± 5 to 977 ± 5 K and the pressure range of 10 ± 2 to 120 ± 2 Torr. Depending on the temperature, the vapor pressure of pure MTS varied from 130 to 140 Torr. The main products observed were CH_4, CH_3Cl, $SiCl_2$, and CH_2SiCl_2 and the observed minor product was C_2H_6. Steady-state rates of formation of the primary products were calculated from their average rates of formation in the plateau region. We detected HCl qualitatively by means of an spectrometer.

Figures 2−4 show the average rates of formation of methane, chloromethane, and ethane, respectively, at 825 K and 55 Torr. Figure 5 shows the average rate of formation of dichlorosilane at 917 K and 70 Torr. Each point in Figures 2−5 is the average of at least three measurements. Experiments were carried out at 825 and 977 K in each of the two reactors to test for any surface reaction. Table 1 shows the steady-state rates of formation of different products at different pressures and temperatures. To calculate the steady-state rate of formation of each product at different conditions in Table 1, a figure similar to Figures 2−5 was used. As Table 1 shows, with clean quartz reactors at identical pressures, there was no trend evident in the steady-state rates of formation of different products on changing surface-to-volume ratio. The magnitude of error for each rate in Table 1 was less than 10%. Calculated rate constants at different pressures and temperatures are also shown in Table 1.

The rate constant for reaction R1 was calculated using the sum of the rates of formation of termination products as in eq 1. Unfortunately, it was not possible to measure the heavy termination products; their retention time in GC column was longer than the retention time for MTS. A value of 6.6×10^{10} L mol^{-1} s^{-1} from ref 16 was used for the rate constant of reaction R11. Rate constant for reaction R12 was calculated according to eq 6.

$$R_{11} = m(R_{10}\, R_{12})^{1/2} \qquad (6)$$

Mousavipour and Pacey[15] have shown *m* is almost independent to the pressure and is very close to 2.

As we will discuss later, rates of reactions R8 and R9 are negligible compared to the rates of the other termination reactions R10−R12. We found rate of reaction R3 the major source for CH_3SiCl_2 is smaller than that for reaction R2 and

TABLE 1: Steady-State Rates and Rate Constants from Experiments at Different Pressures and Temperatures in Two Reactors[a]

P Torr	$R_2 \times 10^7$ mol L^{-1} s^{-1}	$R_3 \times 10^7$ mol L^{-1} s^{-1}	$R_d \times 10^7$ mol L^{-1} s^{-1}	$R_4 \times 10^7$ mol L^{-1} s^{-1}	$R_{10} \times 10^8$ mol L^{-1} s^{-1}	k_2^2/k_{10} L mol^{-1} s^{-1}	k_3^2/k_{10} L mol^{-1} s^{-1}	k_2/k_3	$k_1 \times 10^4$ s^{-1}
				$T = 977$ K, $S/V = 17.5$ cm^{-1}					
10	1.3	0.7	0.61						
20	1.7	0.5							
30	5.0	2.8	4.3		0.8	129	40	1.8	0.6
40	4.4	4.5			2.0	22	23	1.0	1.2
50	7.5	7.5			3.1	26	27	1.0	1.5
60	11	8.5		18	5.0	25	15	1.3	2.0
70	13	9.5	5.2		6.4	20	11	1.3	2.2
80	14	13		30	6.7	17	15	1.1	2.0
90	13	8.0	8.9		10	7	3	1.5	2.7
100	13	9.0			12	5	3	1.3	2.9
120	22	14			25	5	2	1.6	5.1
				$T = 977$ K, $S/V = 9.48$ cm^{-1}					
20	2.7	1.0			1.0	68	9	2.7	1.2
40	5.4	5.1			2.7	25	22	1.1	1.6
70	13.2	12			4.5	29	24	1.1	1.6
				$T = 917$ K, $S/V = 17.5$ cm^{-1}					
10	0.2	0.3	1.4		0.3	4.4	9.8	0.7	0.7
20	0.4	0.5			0.5	2.6	4.1	0.8	0.6
30	0.7	0.7	5.9		0.9	2.2	2.2	1.0	0.7
50	1.4	1.0	7.1		1.5	1.7	1.0	1.3	0.7
70	2.6	1.6	9.0	5.4	3.0	1.5	0.6	1.6	1.0
90	5.9	4.1	15		6.3	2.2	1.1	1.4	1.6
100	9.0	6.7			7.3	3.6	2.0	1.3	1.7
110	9.4	7.5			6.6	3.6	1.8	1.4	1.4
120	14	10			10	4.4	2.3	1.4	1.9
				$T = 882$ K, $S/V = 17.5$ cm^{-1}					
25	0.2	0.1			0.2	1.0	0.2	2.2	0.18
35	0.2	0.1			0.3	0.3	0.1	1.7	0.19
50	0.8	0.4			0.6	1.3	0.3	2.1	0.26
70	1.0	0.7			0.9	0.7	0.3	1.5	0.28
95	1.4	1.2			1.1	0.6	0.4	1.2	0.25
				$T = 825$ K, $S/V = 17.5$ cm^{-1}					
15	0.07	0.03			0.1	0.6	0.1	2.4	0.14
25	0.1	0.05			0.2	0.2	0.1	1.4	0.16
55	0.7	0.3			0.5	0.6	0.2	1.7	0.19
75	0.8	0.5			0.6	0.5	0.2	1.6	0.16
95	1.2	0.7			0.9	0.5	0.2	1.6	0.19
				$T = 825$ K, $S/V = 9.48$ cm^{-1}					
55	0.6	0.2			0.4	0.8	0.1	2.8	0.14
75	0.7	0.3			0.6	0.4	0.1	2.0	0.16
				$T = 909$ K, $S/V = 17.5$ cm^{-1}					
30	0.3	0.3			0.3	1.1	1.1	1.0	0.23
40	0.5	0.5			0.4	1.3	1.3	1.0	0.23
				$T = 891$ K, $S/V = 17.5$ cm^{-1}					
50	0.6	0.5			0.1	4.4	3.1	1.2	0.05
70	1.2	1.0			0.3	3.0	2.1	1.2	0.10
				$T = 831$ K, $S/V = 9.5$ cm^{-1}					
25	0.1	0.1			0.1	0.5	0.5	1.0	0.07
55	0.2	0.1			0.3	0.1	0.03	1.8	0.11
75	0.4	0.2			0.4	0.2	0.05	2.2	0.11

[a] R_2, R_3, R_d, R_4, and R_{10} are the steady-state rates of formation of methane, chloromethane, dichloromethylensilane, dichlorosilane, and ethane, respectively. S/V is the reactor surface-to-volume ratio.

also the possibility of reaction R5 could diminish the concentration of CH_2SiCl_3. Values of k_1 calculated at different pressures and temperatures are listed in Table 1 and shown in Figure 6. The Troe expression, eq 4, was fitted to the experimental data by nonlinear least squares to estimate the low- and high-pressure limiting values of k_1. The results showed that $k_{1\infty}$ was not sensitive to F_C^{WC} and that changing the collision efficiency from unity to 0.1 changed $k_{1\infty}$ by only 10%. Values of the Troe input parameters S_k, B_T, and F_C^{SC} for reaction R1 were calculated at different temperatures. Values of S_k varied from 10.227 to 11.285, B_T varied from 0.69 to 0.74, and F_C^{SC} varied from 0.107 to 0.074 as temperature increased from 825 to 977 K. An Arrhenius plot for $k_{1\infty}$ is shown in Figure 7. The Arrhenius expression for this rate constant from the present work was found by least-squares method to be

$$k_{1\infty} = (9.6 \pm 2.5) \times 10^{19} \exp(-(392 \pm 18)\ \text{kJ mol}^{-1}/RT)\ \text{s}^{-1}$$

In the present work, we also calculated the values of k_2 and k_3, the rate constants for hydrogen abstraction or chlorine abstraction from MTS by methyl radicals, respectively. Values

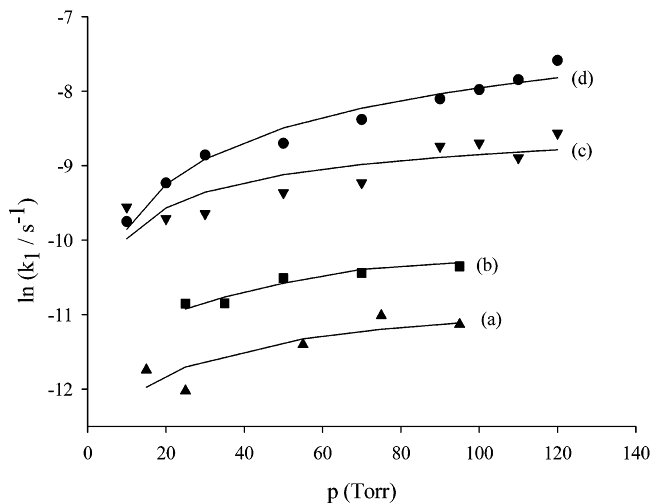


Figure 6. Dependence of k_1 on MTS pressure: a, 825 K; b, 882 K; c, 917 K; d, 977 K. Points, experimental data; solid lines, nonlinear least-squares fit of eq 4 to the data with $\beta_C = 1.0$.

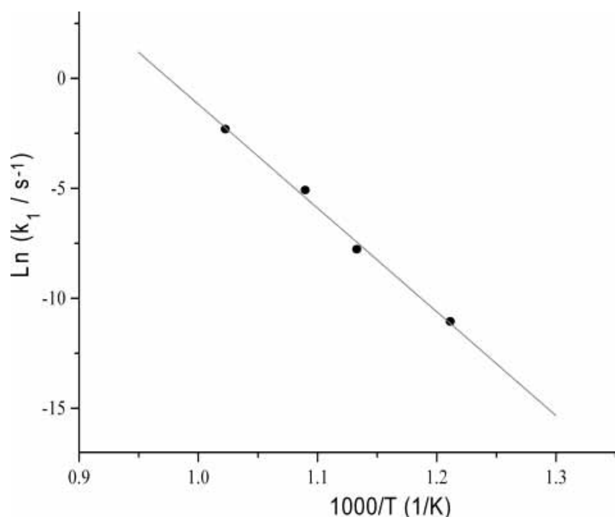


Figure 7. Dependence of the high-pressure limit of k_1 on temperature: ●, experiment; solid line, linear least-squares fit.

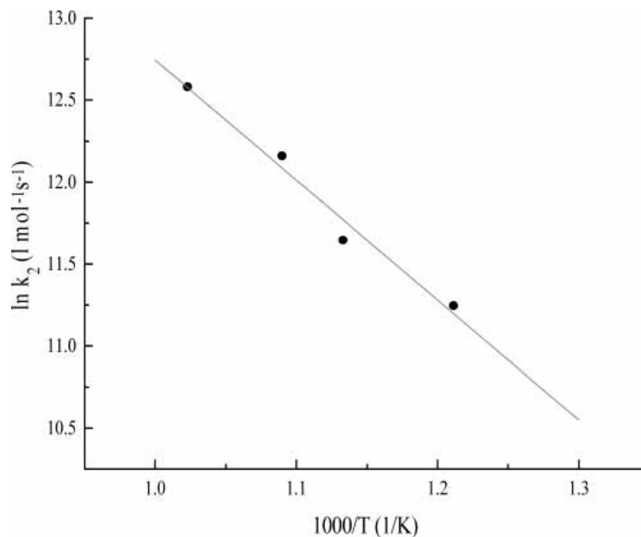


Figure 8. Dependence of k_2 on temperature: ●, experiment; solid line, linear least-squares fit.

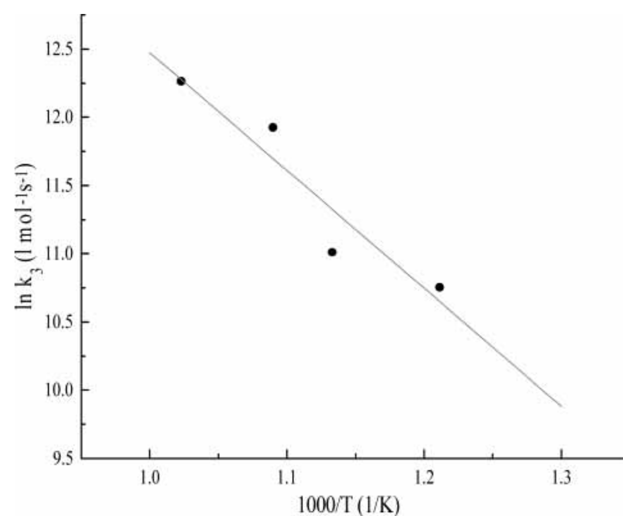


Figure 9. Dependence of k_3 on temperature: ●, experiment; solid line, linear least-squares fit.

of the ratios of $(k_2)^2/k_{10}$ and $(k_3)^2/k_{10}$ at different pressures and temperatures are listed in Table 1. As one expected, k_{10} is pressure dependent while k_2 or k_3 should be independent to the pressure. As shown in Table 1, these ratios are almost independent to the pressure specially, at higher pressures. Therefore, we found it was not necessary to extrapolate these ratios to find their values at infinite pressure.

It was not possible to separately determine k_2, k_3, and k_{10} from the present experiments, so a value of $k_{10,\infty}$ was taken from the literature as[17]

$$k_{10,\infty}\ (\mathrm{L\ mol^{-1}\ s^{-1}}) = 9.05 \times 10^{13}\ (T/K)^{-1.18} - \exp(-2.74\ (\mathrm{kJ\ mol^{-1}})/RT)$$

The values of k_2 and k_3 in Table 1 were calculated by substituting these values of $k_{10,\infty}$ into the values of $(k_2)^2/k_{10}$ and $(k_3)^2/k_{10}$ ratios. Arrhenius plots for k_2 and k_3 are shown in Figures8 and 9, respectively. According to the our results, Arrhenius expression for reaction R2 was

$$k_2 = (5.1 \pm 0.4) \times 10^8 \times \exp(-(61 \pm 3)\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{L\ mol^{-1}\ s^{-1}}$$

The Arrhenius expression for the rate constant of reaction R3 from the present work was found by least squares to be

$$k_3 = (1.5 \pm 0.5) \times 10^9 \times \exp(-(72 \pm 6)\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{L\ mol^{-1}\ s^{-1}}$$

Discussion

Thermal decomposition of MTS was studied in the temperature range of 825−977 K and pressure range of 10−120 Torr. As indicated in the suggested mechanism in the present study, the major products are CH_4, CH_3Cl, $SiCl_2$, CH_2SiCl_2, and HCl. As shown in the suggested mechanism, CH_2SiCl_2 could be produced in several steps during the pyrolysis of MTS. Therefore, it was difficult to investigate the role of reaction R13, 1−2 elimination of HCl, for the production of CH_2SiCl_2.

As one expected, reaction R1 is pressure dependent. Values of k_1 at different conditions were calculated from the sum of the rates of the termination reactions R10−R12. We were interested to study the pyrolysis of MTS at low conversion regime, typically between 1 and 3%. Therefore, it was difficult to measure the products with masses heavier than the MTS mass. We calculated the rate of reaction R11 from the results reported by Niiranen and Gutman[16] and the rate of reaction R12 from

geometric mean rule, eq 6. We assumed the contribution of termination reactions R8 and R9 should be small enough to ignore their effect in calculating k_1, especially at higher temperatures, when reaction R5 becomes more important. At the B3LYP/6-311++G(d,p) level of theory, we found a barrier height equal to 295 kJ mol^{-1} for the decomposition of CH_2SiCl_3 to CH_2SiCl_2 and Cl, R5.

As shown in Figure 6, at 825 K the value of k_1 reached its high-pressure limit when the pressure was about 100 Torr, while at higher temperatures the dependency of k_1 to the pressure was stronger.

In the present work, we were able to calculate the ratios of rate constants $(k_2)^2/k_{10}$ and $(k_3)^2/k_{10}$. As shown in Table 1, these ratios are independent to the pressure at higher pressures at different temperatures. We were not able to calculate the value of k_{10} from our experimental results. We used the expression given by Wagner and Wardlaw[17] for the recombination of methyl radical to calculate the values of k_2 and k_3 from our results. As one expected, rate of hydrogen abstraction is higher than the rate of chlorine abstraction from MTS by methyl radicals. As shown in Table 1, the ratio of k_2/k_3 is close to 1.1 at higher temperatures and decreases to a value about 1.6 at lower temperatures. This should be due to the stronger Si---Cl bond relative to C---H bond. We found a value of 61 ± 3 kJ mol^{-1} for the activation energy of reaction R2. Niiranen and Gutman[16] reported a value of 48.1 kJ mol^{-1} for the activation energy of reaction R2 in the temperature range of 378−478 K. As one expected, hydrogen abstraction reaction R2 should have a curved Arrhenius plot because of tunneling effect. Therefore, it is reasonable that this reaction has higher activation energy at higher temperatures.

Osterheld and co-workers[12] have suggested three different unimolecular decomposition paths for MTS as R1, R13, and C−H bond cleavage R16.

$$CH_3SiCl_3 \rightarrow CH_2SiCl_3 + H \quad (R16)$$

In their study, they reported the rate of reaction R16 is almost 100 times lower than the rate of reaction R1 and activation energy for R16 is higher than that for reaction R1 by 26 kJ mol^{-1} and has a lower preexponential factor. They reported their results as the following Arrhenius expressions in the temperature range of 800−1000 K.

$$k_1 = 2.0 \times 10^{18} \exp(-407.1 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$$

$$k_{13} = 1.3 \times 10^{15} \exp(-399.2 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$$

$$k_{16} = 5.0 \times 10^{17} \exp(-433.0 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$$

It was difficult to verify the role of reactions R13 and R16 in production of CH_2SiCl_2 or CH_2SiCl_3 because we expected other reactions such as reactions R5 (directly) and R6 (indirectly) to produce the same products. As listed in Table 1, the average rate of formation of CH_2SiCl_2 is smaller than the rate of formation of methane. Therefore, we can conclude from these results that the role of reactions R13 and R16 could not be very important in the pyrolysis of MTS.

According to ref 10, $\Delta_f H°$ for MTS, CH_3, $SiCl_3$, CH_2SiCl_3, H, and CH_2SiCl_2 are reported as −576 ± 4, 146 ± 5, −318 ± 7, −367 ± 6, 217 ± 0.0, −143 ± 5 kJ mol^{-1} at 298 K, respectively, and for HCl −92.31 ± 0.10 kJ at 298 K from ref 18. According to these data, ΔH^0_{298} for reactions R1, R13, and R16 equaled 404 ± 16, 341 ± 9, and 426 ± 10 kJ mol^{-1}, respectively.

According to our suggested mechanism, the concentration of $SiCl_2$ should be almost equal to the sum of the concentrations of methane and chloromethane. The effect of presence of $SiCl_2$ on the rate of deposition of SiC is considered by different researchers. Sachdev and Scheid[19] have studied the formation of SiC by rf-plasma CVD. They suggested the formation of silicon halides results in a loss of silicon needed for the correct stoichiometry of the SiC deposits. Thus, the deposits become carbon-rich because of different reaction kinetics of the silicon- and carbon-containing species. Kaneko and co-workers[20] have studied the growth process of SiC from MTS by rf-plasma. From the compositional analysis of the film, they suggested that the competitive decomposition of $SiCl_3$ and CH_3 fragments is rate-determining in an electron collision process. They believe the existence of $SiCl_2$ instead of $SiCl_3$ supports their conclusion. They detected $SiCl_2$ by IR adsorption. They suggested that the precursor of SiC is $SiCl_2$. Josiek and Langlais[21] have studied the residence-time-dependent kinetics of CVD growth of SiC in the MTS/H_2 system. They suggested the simplest precursors $SiCl_3$ and CH_3 which are directly formed by MTS decomposition and adsorb on surfaces site cannot fulfill their experimental results. They suggested $SiCl_2$, C_2H_2, or C_2H_4 are the dominant reactive intermediate source species in the intermediate. $SiCl_3$ adsorbed more strongly on surface site than $SiCl_2$. They concluded, at low residence time and temperature, the gas-phase concentration of $SiCl_2$ should be lower than that of $SiCl_3$. $SiCl_2$ must adsorb on two surface sites to play a more important role for the growth kinetics than $SiCl_3$. At higher residence times, it is possible for $SiCl_2$ to react with H_2 [22] or CH_4 [23] in gas phase to produce SiH_2Cl_2 or CH_3SiHCl_2, respectively.

From the previous paragraph, it is difficult to suggest a reliable mechanism for the formation of SiC film on the surfaces. According to the suggested mechanism in the present study, it is expected that a large amount of $SiCl_2$ produces during the initial steps of the thermal decomposition of MTS. $SiCl_2$ produces in a loop that consists of reactions R2, R3, R4, R7, and R15. If we accept a key role for $SiCl_2$ in the formation of SiC film, therefore, further studies are necessary to investigate this role of $SiCl_2$. According to our suggested mechanism, we do not expect $SiCl_3$ produces in a large amount during the initial steps in the pyrolysis of MTS.

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