12-21-93 856(1)

SANDIA REPORT

SAND93-8576 • UC-401

Unlimited Release

Printed June 1993

Unimolecular Decomposition of Methyltrichlorosilane: RRKM Calculations

Submitted to *The Journal of Physical Chemistry*

T.H. Osterheld, M.D. Allendorf, C.F. Melius

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94551
for the United States Department of Energy
under Contract DE-AC04-76DP00789

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of the contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof or any of their contractors or subcontractors.

This report has been reproduced from the best available copy.

Available to DOE and DOE contractors from:

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge TN 37831

Prices available from (615) 576-8401, FTS 626-8401.

Available to the public from:

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.
Springfield, VA 22161

SAND93-8576
 Unlimited Release
 Printed June 1993

Unimolecular Decomposition of Methyltrichlorosilane: RRKM Calculations*

Thomas H. Osterheld, Mark D. Allendorf, and Carl F. Melius
 Combustion Research Facility
 Sandia National Laboratories/California
 Livermore, CA 94551-0969

Abstract

Based on reaction thermochemistry and estimates of Arrhenius A-factors, it is expected that Si-C bond cleavage, C-H bond cleavage, and HCl elimination will be the primary channels for the unimolecular decomposition of methyltrichlorosilane. Using RRKM theory, we calculated rate constants for these three reactions. The calculations support the conclusion that these three reactions are the major decomposition pathways. Rate constants for each reaction were calculated in the high-pressure limit (800-1500 K) and in the falloff regime (1300-1500 K) for bath gases of both helium and hydrogen. These calculations thus provide branching fractions as well as decomposition rates. We also calculated bimolecular rate constants for the overall decomposition in the low-pressure limit. Interesting and surprising kinetic behavior of this system and the individual reactions is discussed. The reactivity of this chlorinated organosilane is compared to that of other organosilanes.

*This work was supported by the U. S. Department of Energy, Office of Industrial Technologies, Advanced Industrial Concepts Materials Program.

MASTER

I. Introduction

The high-temperature reaction chemistry of chlorinated organosilanes is of intrinsic interest to the field of organosilicon chemistry. Although the thermochemistry^{1,2} and reactions of organosilanes have been studied extensively, particularly with regard to the importance of silylenes,³⁻⁵ comparable investigations of chlorinated organosilicon compounds have not been performed. Methylsilane (CH_3SiH_3) pyrolysis, for example, has been investigated in some detail,⁶⁻⁹ but we are aware of only one study of the pyrolysis of chloromethylsilanes.¹⁰ The reactivity of chlorinated organosilicon compounds differs from simple organosilanes primarily because Si-Cl bonds (in tetravalent compounds) are considerably stronger ($111 - 118 \text{ kcal mol}^{-1}$)¹¹ than either Si-H ($90-95 \text{ kcal mol}^{-1}$)¹ or Si-C ($90-94 \text{ kcal mol}^{-1}$)¹ bonds. These strong bonds contribute to higher activation barriers for the elimination/insertion reactions that are so prevalent⁶⁻⁹ in organosilicon systems. This limits the (unimolecular) reactivity of the silicon functionality and allows access to reactions involving the alkyl group. For example, we will provide evidence that C-H bond cleavage can contribute significantly to chlorinated organosilane pyrolysis. This reaction is not typically expected to play an important role in organosilicon pyrolysis, based on both kinetic and thermochemical arguments.^{2,12,13}

In addition to their fundamental chemical importance, chlorinated organosilanes have widespread industrial applications. They serve, for example, as precursors to polydimethylsiloxanes,¹⁴ which find applications ranging from dielectric media to hydraulic fluids and lubricants. Chlorinated organosilanes are also commonly employed in chemical vapor deposition (CVD) processes used to produce silicon carbide (SiC) coatings, thin films, composites, and powders. Currently, a variety of new methods for depositing SiC are under consideration, operating at both atmospheric^{15,16} and sub-atmospheric pressure.¹⁷⁻¹⁹ One of the most common reactants used in these processes is methyltrichlorosilane (CH_3SiCl_3 ; MTS), which is favored because it is non-pyrophoric and inexpensive. It has been shown that MTS decomposes under typical SiC CVD conditions (atmospheric pressure, deposition temperatures $> 1400 \text{ K}$), producing HCl , SiHCl_3 , SiCl_4 , CH_4 , as well as other silanes and hydrocarbons.^{20,21} These decomposition products result from both primary and secondary reaction pathways. Models used to optimize and scale-up new SiC CVD processes require detailed knowledge of the gas-phase chemistry for two important reasons. First, the high activation energies of MTS unimolecular reactions may make them the rate-limiting step in the deposition, particularly for low-temperature processes. Second, the surface reactivity of the various gas-phase product species, as characterized by a reactive sticking coefficient Γ , varies widely. Saturated molecules such as SiCl_4 react with²² $\Gamma \leq 10^{-3}$, while radicals such as SiH_n ($n=0-3$) are known to react with much higher efficiency,²³⁻²⁶ $\Gamma \sim 0.1-1.0$. Thus, in order to accurately predict deposition rates, the concentrations of the various species present in the gas phase must be known. Unfortunately, we are aware of only one report in the literature that discusses the kinetics of the gas-phase decomposition of MTS.²¹ That paper has been widely cited but contains no data by which the measurements can be critically evaluated.

Recently we reported estimates of thermodynamic properties of molecules in the Si-C-Cl-H system, obtained from *ab initio* calculations using the BAC-MP4(SDTQ) method.¹¹ The structure and energetics of a transition state for the 1,2-elimination of HCl from MTS were also included in that study. These data allow activation energies for several possible MTS decomposition pathways

Figure 1: Potential energy diagram showing potential channels for unimolecular decomposition of MTS. Barrier heights and heats of reaction are relative to MTS and are based on thermodynamic data from Reference 11. The values were calculated for 298 K.

to be estimated (Figure 1). When combined with estimates of reaction A-factors,¹² the results indicate that the three most important processes are the cleavage of the Si-C bond to yield CH₃ and SiCl₃ (Reaction 1), loss of a methyl H-atom (Reaction 2), and the 1,2-elimination of HCl, forming the organosilane Cl₂Si=CH₂ (Reaction 4):

In a previous paper, we reported calculations of the rate coefficient in the limit of high pressures for Reactions (1), (2), and (4); these results were used to estimate the high-pressure branching fraction for the decomposition.²⁷ The calculations in this earlier work used a simplified version²⁸ of the statistical adiabatic channel (SAC) model developed by Quack and Troe²⁹ to estimate k . Rates determined by this method are higher than those obtained from more sophisticated²⁸ treatments, such as Rice-Ramsperger-Kassel-Marcus (RRKM) theory,³⁰ and can thus be considered an upper bound for the MTS decomposition rate. We also estimated the pressure dependence of Reaction (1) using empirical expressions that describe the transition between the high- and low-pressure limiting rates as a function of pressure.³¹ Although this

method is useful for processes in which only a single reaction channel is involved, it will not accurately predict the pressure dependence for systems that involve significant branching.

In this paper, we use statistical theory^{12,30-48} to calculate rate constants for the unimolecular decomposition of MTS in bath gases of helium or hydrogen. We report rate constants in the high- and low-pressure limits, as well as the complete pressure dependence, for the primary unimolecular decomposition pathways available to MTS (Reactions 1, 2, and 4). The results were obtained through the application of RRKM theory. For calculations in the falloff regime and low-pressure limit, we used bath gases of hydrogen or helium since typical CVD processes use a hydrogen bath gas and there is interest in using inert bath gases. We also report branching fractions as a function of temperature and pressure. The branching fractions allow us to evaluate the importance of organosilicon species to the SiC deposition process. The rate coefficients obtained are compared with the earlier experimental measurement²¹ by Burgess and Lewis (BL) of the decomposition of MTS in hydrogen. The calculated rate constant is considerably slower than the BL rate, which was measured at atmospheric pressure in a flow reactor. In a concluding section, we discuss the significance of these calculations to the field of organosilicon chemistry as well as their implications for SiC CVD processes.

II. Theoretical Methods

Thermal reaction rate coefficients were calculated using RRKM transition state theory. Specifically, RRKM theory is used to calculate the microcanonical reaction rate coefficients, $k(E,J)$, which are the rate coefficients for a particular energy (E) and angular momentum state (J) of a molecule. The $k(E,J)$ are then used to calculate thermal rate coefficients which correspond to those measured experimentally. In the high-pressure limit the thermal rate is obtained by averaging the $k(E,J)$ over Boltzmann equilibrium distributions of energy and angular momentum.³⁰ At lower pressures (referred to as the falloff regime) the reactant energy and angular momentum distributions are no longer Boltzmann. In this regime, the $k(E,J)$ are incorporated into a master equation which also accounted for collisions and collisional energy transfer.³⁰ Solution of the master equation provides the thermal rate coefficient. The calculations in this paper were accomplished using the UNIMOL suite of Gilbert, Jordan, and Smith⁴⁹ after making minor modifications to the RRKM program. An excellent description of RRKM theory and the methods used in performing a calculation can be found in the recent book by Gilbert and Smith,³⁰ as well as in many other books and articles.^{12,30-48}

Our calculations involve modeling reactions having both loose and tight transition states. A loose transition state arises in a bond cleavage reaction where the two fragments are separated by large distances in the transition state. Reactions (1), (2), and (3) have loose transition states. Usually the motions of the fragments about axes perpendicular to the breaking bond are relatively unhindered (hence the term loose) and are thus treated as 2-dimensional rotors. These rotors contribute significantly to the entropy of the transition state, giving rise to the large Arrhenius A-factors typical of bond cleavage reactions.¹² On the other hand, a tight transition state is encountered whenever a reaction requires significant atom rearrangement, as in isomerization or elimination/insertion reactions. Usually the transition state has some critical structure (hence the term tight) and even if two products are formed, the transition state does not have the two fragments separated by large distances. Reactions (4)-(6) have tight transition states.

The location of the loose transition state along the reaction coordinate (i.e. on a Morse potential) was determined by canonical variational transition state theory, which means that the transition state was chosen to be the structure that gives the minimum rate in the high-pressure limit.³⁰ This method requires knowledge of how molecular parameters such as vibrational frequencies and rotational constants change along the reaction coordinate. We used the Gorin model to account for this.^{12,30,32-34} The Gorin model assumes that the transition state is very product-like so that each of the two fragments has the structure and vibrational frequencies of the separated products. The separation between the two fragments that gives the minimum rate is then determined using the proper rotational constants for the external and internal rotors at each separation as well as the potential energy at that position on the reaction coordinate.^{12,30,32-34} The two dimensional rotors of the separating fragments were treated as either hindered rotors or sinusoidal hindered rotors.³² Steric hindrance was accounted for by the hard-sphere model of Benson in which the density of states for the two dimensional internal rotors are scaled by a factor that involves the angle through which the fragment can rotate before a steric interaction occurs.^{12,30,32-34} A steric interaction is assumed to occur when hard spheres having radii corresponding to the van der Waals radii of each atom touch. It should be noted that this treatment does not allow for the gradual transition from a free rotor to a sterically hindered rotor and can thus overestimate the steric hindrance.³² Rotational constants of external and internal rotors, for all of the transition states as well as the reactant, were obtained using the GEOM program from the UNIMOL suite.⁴⁹

Structural features and thermodynamic data for the reactant, tight transition states, and for the individual fragments in the simple bond cleavage processes were taken from *ab initio* electronic structure calculations using the BAC-MP4(SDTQ) method.^{1,11,50} When possible, vibrational frequencies were obtained from the literature and used in the calculations (MTS, SiCl₃, and CH₃).^{30,51,52} These frequencies were also compared to the vibrational frequencies from the *ab initio* calculations to account for the systematic overestimation of the calculated frequencies.⁵³ For this system, the *ab initio* calculations appear to overestimate the vibrational frequencies by about 8%. When no literature frequencies were available, as in the case of the HCl loss transition state and the H loss transition state, *ab initio* frequencies were used after scaling by 8%. Reaction thresholds were also determined by *ab initio* calculations. For the discussion in this paper the reaction threshold refers to the critical energy (E_0) of a reaction, which is the minimum energy required for an isolated molecule to undergo reaction (the enthalpy difference between the reactant and transition state at 0 K).

The nature of collisions between reactant molecules and the bath gas contribute to the pressure dependence of the reaction rate. Unfortunately, little data is available on collisional energy transfer between chlorinated or alkylated silanes and He or H₂. We therefore used the semi-empirical biased random walk (BRW) model to estimate parameters for collisional energy transfer into internal modes of the reactant.⁵⁴⁻⁵⁶

Parameters for the RRKM calculations are given in Tables I and II. The parameters include: vibrational frequencies, rotational constants for the external (B_{ext}) and internal (B_{int}) rotors, symmetry and degeneracy factors (σ), critical energies, and in the case of the loose transition states the D_e and β parameters for the Morse potential. The rotational constants in Table II are for the 1200 to 1500 K temperature range which are the temperatures used for the falloff

Table I. RRKM Parameters for Methyltrichlorosilane and the HCl loss transition state^a

CH ₃ SiCl ₃			CH ₂ SiCl ₂ ...HCl [†]		
Vibrational Frequencies			Vibrational Frequencies		
2991 ^b (2) ^c	805 (2)	235 (2)	3154	830	232
2917	762	228	3071	732	202
1411 (2)	572 (2)	164 (2)	1413	630	196
1270	452		1193	487	53
			1186	465	48
			936	406	
B _{ext} (inact), σ _i	0.05800, 1		B _{ext} (inact), σ _i	0.03204, 1	
B _{ext} (act), σ _i	0.04335, 1		B _{ext} (act), σ _i	0.06406, 1	
B _{int} , σ _i , dim	5.436, 3, 1		Critical energy	93.0 kcal/mol	
σ _{sym} /n = 3	σ _{el} = 1		σ _{sym} /n = 1	σ _{el} = 1	

^a Frequencies and rotational constants are in units of cm⁻¹

^b Frequencies from Reference 48

^c Degeneracy of vibration

calculations. We have used the typical treatment for external rotors, in which the molecule or transition state is approximated as a symmetric top. The rotor around the unique axis is treated as active and able to exchange energy with vibrations while, the degenerate 2-dimensional rotor is treated as inactive or uncoupled from the vibrational modes.³⁰

Choosing parameters for the reactant is fairly straightforward, although a question arises over how to deal with the torsional vibration. According to the *ab initio* calculation, this vibration in MTS occurs at 165 cm⁻¹ (the torsion is not observed in the infrared or Raman spectra because of its symmetry). This degree of freedom is treated as a free internal rotor even though the vibrational frequency is fairly high,³⁰ because the reactions are modeled at high temperatures where we would expect that a free rotor is more appropriate.

For the loose transition states (Reactions (1) and (2)), we treated the two dimensional rotors as sinusoidal hindered rotors.³² We also calculated rates without the sinusoidal potential for the 2-dimensional rotors. These rates (in the high-pressure limit) are about 30% faster than those using sinusoidal hindered rotors but the exact values are not reported in this paper. As indicated earlier, steric hindrance was accounted for by the hard sphere model of Benson.¹²

At room temperature it is easy to locate the transition state for Reaction (1) using the techniques described above. As the temperature is raised, the transition state moves to smaller

Table II. RRKM Parameters for Si-C and C-H bond scission transition states^a

CH ₃ ...SiCl ₃ [†]			H...CH ₂ SiCl ₃ [†]		
Vibrational Frequencies			Vibrational Frequencies		
3162 ^b (2) ^c	580	254	3180	601	230
3044	582 ^d (2)	176 (2)	3086	574	227
1396 (2)	470		1429	530	165
			796	448	157
			787	236	
B _{ext} (inact), σ _i	0.03329, 1		B _{ext} (inact), σ _i	0.04742, 1	
B _{ext} (act), σ _i	0.04277, 1		B _{ext} (act), σ _i	0.05914, 1	
B _{int} , σ _i , dim	4.884, 3, 1		B _{int} , σ _i , dim	7.268, 3, 1	
B _{int} , σ _i , dim	0.06897 ^e , 1, 2		B _{int} , σ _i , dim	0.01775, 1, 2	
B _{int} , σ _i , dim	9.681, 2, 2				
D _e	99.9 kcal/mol		D _e	108.9 kcal/mol	
D _o	95.4 kcal/mol		D _o	100.8 kcal/mol	
β	1.82 Å ⁻¹		β	1.86 Å ⁻¹	
σ _{sym} /n = 3	σ _{el} = 4		σ _{sym} /n = 1	σ _{el} = 4	

^a Frequencies and rotational constants are in units of cm⁻¹^b Frequencies for CH₃ from Reference 26^c Degeneracy of vibration^d Frequencies for SiCl₃ from Reference 49^e Average hindrance Θ = 48°

fragment separations.³⁰ However, over the "high" temperature range used for our calculations, the transition state is not as easy to locate. A problem arises because the hard sphere model used to account for steric hindrance causes a discontinuity in the rates for Reaction (1) at fragment separations in which the methyl rotor becomes hindered. The discontinuity is an artifact in the calculation and has been described previously.^{30,32,33} The basic difficulty is that the hindering in the hard sphere model turns on abruptly and strongly so that for Reaction (1), it overestimates the steric hindrance for the methyl rotor.³² We dealt with this by not allowing the methyl rotor to become sterically hindered. This treatment is similar to that of Jordan, Smith, and Gilbert.³² It is possible that we should have included some steric interaction for this rotor but *a priori* we have no criteria for choosing the amount of steric interaction. It should be noted that we did include steric

hindrance for the SiCl_3 rotor in this transition state. We describe below why we believe our treatment is the most appropriate and then we show by calculations with extreme steric hindrance that our treatment appears correct.

The special treatment of the methyl rotor appears reasonable for several reasons. First, it allows for an unambiguous application of variational transition state theory. Second, error introduced by failing to hinder the rotor should be at least partially offset by including the symmetry of the rotor ($\sigma=2$). Including the symmetry results in a lower sum of states than otherwise but would probably not be appropriate if the rotor were significantly hindered. Third, the use of a sinusoidal potential already provides a lower sum of states than the free rotor potential traditionally used in the past. Fourth, when we hindered the methyl rotor the transition state was located at a position that gave a meaningless rotational constant for the rotor.³⁰ This indicates that strict use of the hard sphere model is inappropriate and results in a significant underestimate of the contribution of these modes to the sum of states in the transition state.³⁰ Finally, test calculations in which we hindered this rotor to any significant degree actually gave rates *slower* than if the two dimensional rotor had been treated as two 300-400 cm^{-1} vibrations. Treating the modes as vibrations of this magnitude is an unrealistically tight treatment in our estimation. Since the high pressure rates calculated in the very hindered extreme of 300-400 cm^{-1} vibrations are only up to a factor of 3 slower than our treatment, we expect that any error introduced from the ambiguity in treating these modes should be minor.

The transition state for HCl elimination (Reaction (4)) has two low-frequency librations. These modes were treated as vibrations and not as a 2-dimensional rotor since an analysis of the hard sphere steric interactions indicated that a rotor would be completely hindered. This view is supported by a normal mode analysis of the *ab initio* force field.⁵⁷ The reason these two modes have such low frequencies is because they are librations involving a relatively heavy HCl group.

III. Results

Before discussing the RRKM results, it is useful to review the thermodynamics of the various MTS decomposition pathways, as determined from our previous *ab initio* calculations.^{1,11,27} Figure 1 shows the potential energy curves and reaction enthalpies of several possible MTS decompositions. All of the possible products are considerably higher in energy than MTS (by an amount ≥ 81.5 kcal/mol). In addition, Reactions (4) and (5), which are the lowest-energy reactions based on product thermodynamics, have potential energy barriers. This results in a minimum reaction threshold for any channel of at least 93.0 kcal/mol. At energies above this, there are 5 possible reactions in an energy range of about 20 kcal/mol. At much higher energies, Reaction (6), which involves breaking strong Si-Cl bonds, also becomes thermodynamically accessible.

We have categorized these reactions as either bond cleavages, having loose transition states with typical Arrhenius A-factors¹² of 10^{16} - 10^{17} s^{-1} , or elimination/insertion reactions, having tight transition states with typical A-factors¹² of 10^{12} - 10^{15} s^{-1} . On the basis of these categories and the thermodynamics discussed above, it is a simple matter to remove reactions from consideration that are so slow that they are unlikely to contribute much to the overall decomposition.

Reaction (6), elimination of Cl_2 , which has both a low A-factor because of a tight transition state and a threshold at least 35 kcal/mol higher than the lowest energy reaction can immediately be removed from consideration.

Reaction (3), loss of Cl, which is the highest energy bond cleavage, can also be eliminated from consideration. We calculated high pressure A-factors using the methods of Benson¹² and found that the A-factor for this reaction was essentially identical to that for Reaction (1) (Si-C bond scission). The much higher threshold (113.4 kcal/mol compared to 95.4 kcal/mol) indicates that it should not contribute significantly to the decomposition. This proposal is further strengthened by the observation that Reaction (2) has a significantly higher A-factor than Reaction (3) (*vide infra*) and as such would be expected to dominate the higher threshold reaction.

Finally, Reaction (5), elimination of CH_3Cl , can be removed from consideration. Although attempts to calculate this transition state using *ab initio* theory were unsuccessful, we estimate that its threshold will be higher than that for Reaction (1) (Si-C bond scission).²⁷ Since Reaction (5) has a much smaller A-factor than Reaction (1), it is not expected to be significant. This conclusion is borne out by the relatively minor contribution of Reaction (4) (the other low-energy elimination) to the overall decomposition (*vide infra*).

We have thus modeled the decomposition of MTS by calculating rates for CH_3 loss, H loss, and HCl elimination (Reactions (1), (2), and (4)). It is expected that these three reactions are the major contributors to the thermal unimolecular decomposition.

A. High Pressure Limit. In the high pressure limit, collisions with the bath gas are sufficiently rapid that energy and angular momentum have equilibrium Boltzmann distributions.³⁰ As a consequence, reaction rate coefficients do not depend on the total pressure and are even independent of each other in the case of multi-channel reactions. Therefore, the high pressure unimolecular rate coefficient, k_{uni}^∞ , is the canonical average of the $k(E, J)$ from RRKM theory and can be calculated without resorting to a master equation.³⁰ For the bond cleavage reactions (Reactions (1) and (2)), k_{uni}^∞ is the rate which is minimized when applying canonical variational transition state theory (the method used in this paper). The high pressure rate coefficients were calculated at temperatures ranging from 800 K to 1500 K for the three reactions of interest. Since these rate constants are for the high-pressure limit they are, of course, independent of bath gas. The calculated high-pressure rate coefficients and reaction parameters are given in Table III. As can be seen from these results, H loss is the most efficient reaction at the higher temperatures. At 1100 K it is about 40% faster than CH_3 loss and as the temperature is increased, H loss becomes even more dominant. At 1500 K it has a rate coefficient that is at least a factor of 5 larger than the other reactions. It should also be noted that according to these calculations, Reaction (4) never contributes significantly to the decomposition; over the 800-1500 K temperature range it contributes less than 0.2% to the overall rate coefficient. These calculations are useful for comparing the efficiency of the various channels especially since they are relatively easy to perform. However, as will be seen below, the high-pressure limit is never achieved in CVD reactors.

Table III. High Pressure Reaction Rates and Parameters for Methyltrichlorosilane

T (K)	Reaction Product	k_{uni}^{∞} (s^{-1})	Log (A^{∞}/s^{-1})	E_a^{∞} (kcal/mol)
800	HCl	9.6×10^{-12}	15.1	95.5
	CH ₃	5.4×10^{-9}	18.3	97.4
	H	1.5×10^{-9}	19.5	103.6
	total	6.9×10^{-9}		
900	HCl	7.6×10^{-9}	15.1	95.7
	CH ₃	4.0×10^{-6}	18.3	97.5
	H	2.1×10^{-6}	19.5	103.7
	total	6.1×10^{-6}		
1000	HCl	1.6×10^{-6}	15.2	96.0
	CH ₃	0.00078	18.2	97.5
	H	0.00068	19.5	103.8
	total	0.0015		
1100	HCl	0.00013	15.2	96.3
	CH ₃	0.057	18.1	97.4
	H	0.078	19.5	103.8
	total	0.135		
1200	HCl	0.0051	15.3	96.5
	CH ₃	2.0	18.0	97.5
	H	4.1	19.5	103.8
	total	6.1		
1300	HCl	0.12	15.3	96.7
	CH ₃	40	18.0	97.5
	H	120	19.5	103.8
	total	160		
1400	HCl	1.7	15.4	96.9
	CH ₃	510	17.9	97.5
	H	2000	19.5	103.8
	total	2500		

Table III. High Pressure Reaction Rates and Parameters for Methyltrichlorosilane (continued)

T (K)	Reaction Product	k_{uni}^{∞} (s^{-1})	Log (A^{∞}/s^{-1})	E_a^{∞} (kcal/mol)
1500	HCl	17	15.4	97.1
	CH ₃	4700	17.9	97.5
	H	24000	19.5	103.8
	total	29000		

B. Falloff Regime. As the pressure is decreased from the high-pressure limit, collisions between reactant and bath gas are no longer sufficiently rapid to maintain Boltzmann energy and angular momentum distributions.³⁰ Thus, reaction drains away population from levels above the critical energy (E_0). To obtain the energy distribution and reaction rate coefficient one must resort to a master equation which also accounts for collisions and collisional energy transfer. In this regime, the thermal reaction rate *does* depend on the total pressure.³⁰ In a multi-channel system the rate of a specific pathway is also influenced by the other reactions. Ultimately, at very low pressures, the reaction reaches the low-pressure limit where conversion of the activated reactant to product is sufficiently faster than collisions that any molecule with $E > E_0$ reacts before it can be deactivated by collisions.³⁰ At this point the reaction becomes first order in bath gas pressure.³⁰ The falloff regime connects the high- and low-pressure limits and is the region where neither collisional energy transfer nor chemical reaction dominate, but both play a contributing role in the overall kinetics. The falloff regime spans several orders of magnitude of pressure and at high temperatures many unimolecular reactions, even at atmospheric pressure, are far from the high-pressure limit. MTS is a large, heavy molecule with many low frequency modes. This means that the high-pressure limit will only occur at extremely high pressures--much higher than atmospheric.³⁰ Thus, from a practical point of view, rates in the falloff regime are very important, since most CVD processes operate in the 10-760 torr region.

Reaction rates in the falloff region were calculated at 1300 K, 1400 K, and 1500 K for He and H₂ bath gases. Figure 2 shows the dependence of the overall thermal decomposition rate on temperature and pressure over a 10^{-3} to 10^6 torr pressure range. Based on the calculation discussed in the next section, helium is expected to transfer more energy per collision than hydrogen, which leads to the prediction of slightly higher rates for a helium bath gas at a given temperature and pressure. As can be seen in these plots, even at pressures as high as 10^6 torr the rate constant does not reach its high-pressure limiting value.

C. Collisional Energy Transfer. In the falloff regime and at the low-pressure limit, the energy distribution of reactant molecules (and thus the reaction rate) depends on the energy transfer occurring in collisions between a reactant molecule and bath gas molecule. To include this effect in the determination of a thermal rate coefficient, one must choose a model for energy transfer and obtain the appropriate values for the energy transfer parameters. Usually the best strategy is to find experimentally measured values of the energy transferred per collision, either for the system of interest or similar systems, and apply the appropriate model.

Figure 2: RRKM predictions for the total MTS decomposition rate as a function of temperature and pressure. Dashed lines indicate the high-pressure limit for each temperature. (A) helium bath gas; (B) hydrogen bath gas.

However, as mentioned earlier, little information is available on collisional energy transfer between chlorinated or alkylated silanes and the bath gases of interest. For this reason we used the semi-empirical BRW model for collisional energy transfer.⁵⁴⁻⁵⁶ This model assumes that, during a collision, energy exchange between the internal degrees of freedom of the excited molecule and the bath gas is essentially random but constrained by microscopic reversibility and total-energy conservation. In the BRW model the collisional energy transfer is characterized by the quantity $s=(t_c D_E)^{1/2}$ where t_c is the duration of a collision and D_E is an "energy diffusion coefficient". This model has been tested by comparison with trajectory calculations and incorporates many essential features of the collision dynamics including a temperature dependence. Values of the parameter s calculated for this study are given in Table IV. Equivalent ΔE_{down} (the average downward energy transferred per collision³⁰ in the exponential-down model) are also reported in Table IV. Since the corresponding ΔE_{down} values for helium are fairly large,⁵⁸ we also calculated rate coefficients with the helium s values divided by two. The $s/2$ value should provide a lower bound for the collisional energy transfer. It should be noted, however, that the calculated values in Table IV are not unreasonable when compared to values obtained at intermediate temperatures for alkyl isocyanides.⁵⁹ In the final analysis, calculations of the overall rates as well as branching fractions are fairly insensitive to the collisional energy transfer parameter. This is shown in Figure 3, where, at pressures higher than 10 torr in He, the rates calculated using s and $s/2$ are within about a factor of 2 of each other.

D. Reaction Branching. Figures 4 and 5 show the results of falloff calculations for the rates of the individual reactions at 1300 K and 1500 K respectively. Comparison of the rates in these two plots shows that the reaction branching has only a minor dependence on the temperature or the collisional energy transfer (based on a comparison of helium and hydrogen bath gases). Although we have not included plots at 1400 K or using $s/2$ for helium, they also support these conclusions. Rate constants for the individual reactions at selected pressures are given in Table V.

Table V and Figures 4 and 5 have several interesting features. First, loss of HCl has the lowest threshold by at least a 1.0 kcal/mol but, because of its relatively tight transition state compared to the bond scissions, it only contributes a small fraction to the overall reaction rate at these temperatures and pressures. Second, with increasing temperature, the rate at a given pressure is further from the high-pressure limit (Table V). At atmospheric pressure the total rate at 1300 K in a hydrogen bath gas is expected to be about 6% of the high-pressure rate while at 1500 K it is expected to be about 2% of the high pressure rate. The third and most interesting feature is the fast rate for Reaction (2) at pressures of ca. 10 torr or higher, even though this channel has a threshold at least 5 kcal/mol higher than Reaction (1).

The importance of Reaction (2) arises from its looser transition state relative to Reaction (1), which results in an A-factor an order of magnitude larger than Si-C bond scission (Table III). This larger A-factor is surprising, since atom loss reactions involve transition states with only one 2-dimensional rotor instead of the two associated with polyatomic leaving groups. For bond-cleavage reactions, the 2-dimensional rotors usually contribute the most to the entropy increase between reactant and transition state. This results in bond-cleavage reactions having larger A-factors than tight transition states.¹² Therefore, one would usually expect a transition state with only one 2-dimensional rotor to have a *lower* entropy compared with a transition state having two

Table IV. Methyltrichlorosilane Collisional Energy Transfer Parameters from BRW Model^a

T (K)	He ^b				H ₂	
	S	ΔE_{down}	1/2S	ΔE_{down}	S	ΔE_{down}
1300	614.5	795.6	307.25	369.8	346.2	420.9
1400	663.1	853.2	331.55	398.2	385.2	468
1500	714.4	913.8	357.2	427.8	422.6	512.5

^a s and ΔE_{down} in units of cm^{-1}

^b Collision partner

Figure 3: Comparison of RRKM predictions for the total MTS decomposition rate as a function of pressure for different bath gases and amount of energy transferred per collision (as characterized by the parameter s in the BRW model; see text.)

Table V. Rate Coefficients for Reactions of Methyltrichlorosilane

Bath Gas	T (K)	P (torr)	k_{HCl} (s^{-1})	k_{CH_3} (s^{-1})	k_{H} (s^{-1})	$k_{\text{tot}}/k_{\text{uni}}^\infty$
He	1300	10	0.00307	1.63	0.0967	0.0111
		25	0.0051	2.63	0.262	0.0186
		50	0.00729	3.66	0.522	0.0269
		100	0.0102	4.95	0.985	0.0381
		760	0.0231	10.3	4.73	0.0964
		1000	0.0254	11.2	5.67	0.108
	In low-pressure limit, $k_0=4.63 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$					
	1400	10	0.025	13.1	0.834	0.00547
		25	0.0432	21.9	2.33	0.00953
		50	0.0636	31.3	4.78	0.0142
		100	0.0914	43.6	9.29	0.0208
		760	0.228	98.6	49.0	0.0581
		1000	0.254	108	59.6	0.0661
	In low-pressure limit, $k_0=2.72 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$					
	1500	10	0.145	75.0	5.12	0.00276
		25	0.261	130	14.7	0.00498
		50	0.394	191	30.8	0.00763
		100	0.583	273	61.5	0.0115
		760	1.58	667	353	0.0351
		1000	1.78	740	435	0.0404
	In low-pressure limit, $k_0=1.17 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$					
H ₂	1300	10	0.00169	0.908	0.0227	0.00598
		25	0.00292	1.54	0.0725	0.0103
		50	0.00431	2.22	0.162	0.0153
		100	0.00621	3.13	0.340	0.0223

Table V. Rate Coefficients for Reactions of Methyltrichlorosilane (continued)

Bath Gas	T (K)	P (torr)	k_{HCl} (s^{-1})	k_{CH_3} (s^{-1})	k_{H} (s^{-1})	$k_{\text{tot}}/k_{\text{uni}}^\infty$
		760	0.0157	7.27	2.12	0.0603
		1000	0.0174	8.01	2.62	0.0683
In low-pressure limit, $k_0=2.00 \times 10^8 \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$						
	1400	10	0.0138	7.27	0.202	0.00294
		25	0.0246	12.7	0.660	0.00527
		50	0.0374	18.9	1.51	0.00803
		100	0.0554	27.3	3.23	0.0120
		760	0.152	68.5	21.9	0.0355
		1000	0.171	76.2	27.3	0.0408
In low-pressure limit, $k_0=1.21 \times 10^9 \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$						
	1500	10	0.0796	41.4	1.24	0.00147
		25	0.147	74.7	4.15	0.00271
		50	0.229	114	9.67	0.00424
		100	0.348	168	21.2	0.00652
		760	1.03	454	155	0.0209
		1000	1.18	510	195	0.0243
In low-pressure limit, $k_0=5.29 \times 10^9 \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$						

2-dimensional rotors. However, the result can be understood by considering all of the entropy gains and losses in going from ground-state MTS to the different transition states. Table VI compares the various contributions to the total $\Delta S^\ddagger$ for H loss versus CH_3 loss at 1500 K. Although the CH_3 loss transition state has a larger rotational entropy than the transition state for H loss, this comes at a significant loss of vibrational entropy since the Si-C bond has been broken. The low frequency vibrations involving the Si-C bond contribute substantially to the entropy of MTS. In contrast, the H loss transition state has a lower rotational entropy than the CH_3 loss transition state but at a fairly minor cost in vibrational entropy since a C-H bond has been broken. Vibrations involving the C-H bond are much higher in frequency and thus contribute little to the overall entropy. The entropy of the H loss transition state also increases due to the loss of

Figure 4: Reaction branching for MTS decomposition as a function of pressure at 1300 K.
 A): helium bath gas; (B): hydrogen bath gas.

Figure 5: Reaction branching for MTS decomposition as a function of pressure at 1500 K. (A): helium bath gas; (B): hydrogen bath gas.

molecular symmetry. It should be noted that the Cl loss transition state (which also has only one 2-dimensional rotor) involves a greater loss of vibrational entropy because vibrations involving the Si-Cl bond have a much lower frequency than those involving the C-H bond. The result is that the Cl loss transition state has considerably less entropy than the H loss transition state and thus has a much lower A-factor (*vide supra*). To summarize: in the H loss transition state, loose modes are formed from degrees of freedom that do not contribute much to the entropy of MTS; whereas in the other transition states, the loose modes are formed from degrees of freedom that *do* contribute significantly to the entropy of MTS. The result is a larger net entropy *gain* for the H loss transition state.

Table VI. Entropy changes between MTS and H loss or CH₃ loss transition states^{a,b}

reaction	$\Delta S^\ddagger_{\text{vib}}$	$\Delta S^\ddagger_{\text{rot}}$	$\Delta S^\ddagger_{\text{sym}}$	$\Delta S^\ddagger_{\text{tot}}$
CH ₃	-17.0	+35.0 ^c	0	+18.0
H	-3.1	+26.4 ^c	+2.2	+25.5

^a In cal mol⁻¹ K⁻¹

^b At 1500 K

^c Includes contributions from the external rotations

E. Sources of Error. As indicated in the introduction, little experimental or theoretical work has been done on these systems so that a quantitative analysis of the error is not straightforward. However, this section will attempt to provide some indication of the uncertainty. Throughout the discussion of these calculations we have indicated where we had to resort to calculated parameters or simplifications of the dynamic model. In most cases we have attempted to assess the potential for error in our calculations resulting from even gross inaccuracy in a parameter. Most of these assessments are included in the foregoing discussion. Extreme modifications in a given parameter typically changed calculated rate coefficients by less than a factor of two.

One important input to the calculations whose accuracy we have not discussed so far is the reaction threshold, which was determined from *ab initio* calculations due to the paucity of experimental measurements on these systems. Accuracy estimates of the calculations,⁵⁰ which include results from lower level calculations, indicate that the heats of formations of each species are expected to be good to ± 2 kcal/mol, particularly for those involved in the bond cleavages.^{1,11} The accuracy of the threshold for HCl elimination is less easily determined as it involves a calculation using a transition state structure. However, the *calculated* error estimate for the heat of formation of this transition state is still within ± 2 kcal/mol.^{1,11} To assess the importance of changes in reaction thresholds we calculated rate coefficients with each threshold shifted by ± 2 kcal/mol. In the high pressure limit, shifting a threshold down by 2 kcal/mol causes the rate coefficient to increase by about a factor of 2 for each of the reactions. Correspondingly, shifting a threshold up by 2 kcal/mol causes the rate coefficient to drop by about a factor of 2. The same results were observed for calculations at both 1300 K and 1500 K.⁶⁰

To evaluate the magnitude of this effect in the falloff region we also calculated rate coefficients at 100 torr. A change of ± 2 kcal/mol in a given threshold causes a corresponding increase or decrease in the calculated rate coefficient for that reaction of a factor of 2 to 3 at this pressure. Shifting the threshold for HCl elimination has essentially no effect on the rate coefficients for the other reactions because it has such a minor contribution to the overall decomposition. Higher thresholds for the H loss reaction also have little effect on the calculated rate coefficients for the other reactions; a threshold 2 kcal/mol lower for H loss decreases the other rate coefficients by about 20%. The minor dependence of the other reactions on H loss probably occurs because this reaction has a higher threshold to begin with and because it is only the major product at pressures much higher than 100 torr. In other words, at pressures greater than 100 torr, a larger decrease would be observed. Shifting the CH₃ loss threshold, however, has a significant effect on the other reactions. With a 2 kcal/mol lower threshold for CH₃ loss, the rates for both of the other reactions drop by about a factor of 2 while a 2 kcal/mol higher threshold causes a 30% increase in the coefficient for HCl elimination and a factor of 2 increase in the H loss coefficient. Results consistent with these conclusions were observed for calculations at both 1300 K and 1500 K using bath gases of helium or hydrogen.

Thus, in the falloff regime, the overall rate is most sensitive to the threshold for Reaction (1), as is expected.²⁷ Of the 3 channels, thermodynamic data for the products of Reaction (1) should be the most accurate since CH₃ is well characterized and SiCl₃ has fewer empirical corrections¹¹ required to obtain its heat of formation than CH₂SiCl₃. Of course its relative threshold will still depend on the thermodynamic data for the other reactions.

IV. Discussion

A. Significance for organosilicon chemistry. As discussed in the introduction, experimental and theoretical treatments of the chlorinated organosilanes are nearly non-existent. The results of this study thus provide new insight into the characteristic features of chlorinated organosilicon chemistry, in particular the ways in which reactions of these molecules differ from those of species containing no chlorine and from analogous hydrocarbon chemistry.

Our results highlight two factors that have an important influence on the reactions of chlorinated organosilanes. The first is the high strength of the Si-Cl bond, which in MTS¹¹ is 114 kcal mol⁻¹ vs. 92 kcal mol⁻¹ for the Si-H bond in CH₃SiH₃.¹ The effect of this large bond dissociation energy is to make pathways that do not involve breaking the bond, such as CH₃-loss and H-loss, energetically favorable. In addition, the presence of these strong bonds undoubtedly reduces the efficiency of silylene elimination reactions (for example, Reactions 5 and 6), although the magnitude of this effect is difficult to evaluate relative to the reduction in rate caused by the increased electronegativity of chlorine.⁶¹ As discussed earlier, silylene eliminations in MTS (Reactions 5 and 6; see Figure 1) are relatively high-energy pathways for decomposition. In addition, the 1,2-elimination pathway in MTS (96.9 kcal mol⁻¹ at 1400 K in the high-pressure limit) is energetically accessible; its activation barrier is actually lower than the barriers for H loss and CH₃ loss (103.8 kcal mol⁻¹ and 97.5 kcal mol⁻¹ at 1400 K in the high-pressure limit.) This contrasts with the situation in CH₃SiH₃, where the corresponding reaction, 1,2-elimination of H₂, is much higher than other reaction pathways.⁷

The second important factor is the formation of product fragments with large moments of inertia, which leads to large A-factors (and hence, higher reaction rates) for processes that would normally be thought to be relatively slow. In the case of MTS, this is illustrated by the H-loss reaction (Reaction 4), with a high-pressure A-factor at 1400 K that is predicted to be greater than 10^{19} sec^{-1} . This can be compared with the analogous reaction for CH_4 , where the high-pressure A-factor⁶² is $1.0 \times 10^{15} \text{ sec}^{-1}$. (Note that no data are available to make the direct comparison with the analogous H-loss channel in CH_3SiH_3 , due to the availability of lower energy pathways such as H_2 or CH_4 elimination.) Presumably, high A-factors will also be observed in other chlorinated organosilanes. Steric factors may, however, reverse (or at least mitigate) this trend; the bulkiness of groups such as SiCl_3 relative to SiH_3 may tighten the transition state, thus lowering the transition state entropy.

The two factors discussed above combine to make bond-scission pathways the most efficient ones for MTS unimolecular decomposition. This indicates that intuition based on the reactivity of organosilanes that do not contain Si-Cl bonds cannot be straightforwardly extended to chlorinated species, since silylene elimination reactions are usually the lowest energy channels for simple organosilanes, especially for compounds containing at least one Si-H bond. Interestingly, the result is that MTS reacts more like methane than silane (at least in the high-pressure limit), since H-atom loss, which is the lowest energy unimolecular decomposition pathway for methane, is more accessible in MTS due to the high activation barriers for other pathways. In fact, the C-H bond dissociation energies in MTS and CH_4 are nearly the same ($102.2 \text{ kcal mol}^{-1}$ in MTS vs. 104.8 in CH_4 at 298 K) and their high-pressure activation barriers are also similar ($103.8 \text{ kcal mol}^{-1}$ for MTS vs. $100.4 \text{ kcal mol}^{-1}$ for CH_4 ⁶²). These characteristics of chlorinated organosilanes, combined with the dominance of other bond scission decomposition paths, lead to the possibility that radical chain processes may occur during the pyrolysis of chlorinated organosilanes, which can complicate experimental measurements of decomposition rates. Mechanisms of this type have been observed for the decomposition of several methylchlorosilanes,¹⁰ although MTS was not among them.

B. Implications for SiC CVD. The results of this study have several important implications for understanding SiC CVD processes that use MTS as a reactant. First, the experimental reaction rates of BL,²¹ which have been widely used in modeling SiC CVD, are substantially higher than those predicted by the RRKM calculations. Figure 6 shows a comparison of the total MTS decomposition rate as determined by BL at a pressure of 760 torr in hydrogen, compared with the RRKM results for the same conditions. The MTS decomposition rate predicted by RRKM ($k_{\text{tot}}(\text{H}_2, 760 \text{ torr}) = 2.08 \times 10^{16} \exp(-90261/RT) \text{ (sec}^{-1}\text{)}$, $T = 950 - 1100 \text{ K}$) is a factor of 5-6 smaller than the experimental result ($k_{\text{tot}}(\text{H}_2, 1 \text{ atm}) = 7.6 \times 10^{14} \exp(-80300/RT) \text{ (sec}^{-1}\text{)}$, $T = 975 - 1025 \text{ K}$). Our evaluation of the uncertainties associated with the RRKM calculations indicates that the rate reported in the BL paper is outside the estimated error of the calculations. In particular, transition state theory is inherently expected to overestimate reaction rates because it does not account for barrier recrossing.³⁰ Barring a gross inaccuracy in a reaction threshold (unlikely, *vide supra*), our calculations would be expected to *overestimate* the decomposition rate. The reasons for this discrepancy are unclear; radical chain processes are a possibility, especially since BL's measurements were made at relatively low temperatures. Unfortunately, the BL paper only reports an Arrhenius expression and no data or error analysis making a critical

Figure 6: Comparison of experimental results of Burgess and Lewis (Ref. 21) with RRKM predictions of the total MTS decomposition rate at 760 torr in hydrogen. Triangles indicate temperatures at which the RRKM calculations were performed; the dashed line is a linear least-squares fit of the Arrhenius rate expression to these points.

comparison difficult. Ironically, extrapolation of the BL results to typical SiC CVD temperatures (1300 - 1500 K) brings them into closer agreement with the RRKM results, a fit to their data yields $k_{tot}(\text{H}_2, 760 \text{ torr}) = 3.72 \times 10^{14} \exp(-80347/RT) \text{ (sec}^{-1}\text{)}$. Further experimental measurements are required to resolve this discrepancy. Based on our evaluation of the uncertainties in the RRKM rate constants, we conclude that these rates are more likely to represent the true unimolecular MTS decomposition rate than the BL experimental result, which was obtained from a complex system in which a large number of reactions may have been occurring.

A second point relevant to SiC CVD is that pressure effects on the decomposition rate of MTS are large. For example, at atmospheric pressure and 1400 K, k/k_∞ is 0.036, while at 25 torr, k/k_∞ is 0.0053. Thus, accurate simulations of SiC CVD processes must take into account the pressure falloff of the reactant pyrolysis reactions. In particular, it should be noted that the results of BL should not be extended to low pressures.

From a mechanistic standpoint, the RRKM results show that at atmospheric pressure the predominant decomposition modes are expected to be loss of H and CH₃. In the presence of hydrogen carrier gas, CH₃ will lead to the production of large quantities of methane. The SiCl₃ radical that is formed can undergo unimolecular decomposition to form SiCl₂ and Cl (ΔH°_{rxn} (298 K) = 68.8 kcal mol⁻¹) or react exothermically with CH₃ to form CH₃Cl and SiCl₂ (ΔH°_{rxn} (298 K) = -15.0 kcal mol⁻¹) or react with H₂ to form SiCl₃H and H (ΔH°_{rxn} (298 K) = 10.9 kcal mol⁻¹). Thus, the gas-phase species in highest concentration during deposition may be SiCl₂, CH₄, and SiCl₃H. The reactivity of SiCl₂ at high temperatures is uncharacterized, pointing again to the need for additional experimentation.

Organosilicon species may play a role in the deposition of SiC, especially if they are radicals. The surface reactivity of organosilicon radicals should be much greater than that of methane, which is likely to be the most abundant hydrocarbon present in the gas-phase and whose reactive sticking coefficient is probably⁶³ 10⁻⁵ - 10⁻⁴. Our results show that two organosilicon radicals⁶⁴ are formed by the initial decomposition of MTS, Cl₂Si=CH₂ and CH₂SiCl₃. The latter species, assuming that its reactivity is similar to methane, will be rapidly reconverted to MTS via reaction with the hydrogen carrier gas. Use of inert carrier gas or high MTS partial pressures favor relatively high concentrations of this molecule, however. The remaining radical, the silaethylene Cl₂Si=CH₂, represents < 0.2% of the products at all pressures examined. The surface reactivity of this molecule is unknown; if it is similar to C₂H₄ (Γ ~0.001 on silicon surfaces⁶³), it could contribute significantly to the deposition of carbon. Thus, the calculations reported here indicate that pathways are available for the production of organosilicon radicals with potentially high surface reactivity. Their concentrations relative to CH₄ must first be known, however, to determine their importance to the deposition process.

Finally, the effect of substituting an inert carrier gas such as helium for hydrogen in a SiC CVD process can be evaluated from the RRKM results. The data shown in Figure 2 indicate that the rates of Reactions (1) and (4) increase by less than a factor of two when the carrier gas is helium instead of hydrogen. The rate of Reaction (2) increases more, about a factor of 3.5 at 25 torr. Such effects are relatively small, however, compared with the change induced by the substitution of a reactive gas such as hydrogen for an unreactive one such as helium. Thus, a different gas-phase product distribution is expected from the two carrier gases, which could alter the deposition SiC deposition rate substantially.

V. Conclusions

Using RRKM theory, we calculated rate constants for the decomposition of MTS in both the high-pressure limit and in the falloff regime. The results show that Si-C bond cleavage, C-H bond cleavage, and HCl elimination (Reactions (1), (2), and (4)) are the predominant thermal decomposition pathways. In the high-pressure limit, Reaction (2) is the most efficient decomposition pathway at the temperatures of interest. However, at atmospheric pressure, both Reaction (1) and Reaction (2) contribute. As the pressure decreases, the rate of Reaction (2) decreases substantially. At the lowest pressures typically accessible to SiC CVD (~0.1 - 1 torr) Reaction (1) dominates the decomposition. HCl elimination, Reaction (4), is never a major

product over the pressure range used in these calculations. Qualitatively, the branching behavior can be understood on the basis of the A-factor and activation energy for each reaction pathway.

The relative importance of the H-atom loss channel (Reaction (2)) is surprising. The large A-factor for this reaction is due to the relatively minor loss of vibrational entropy from breaking the C-H bond. This more than makes up for the lower entropy contribution of only one 2-dimensional rotor in the C-H bond cleavage transition state. We also point out that, in contrast to other organosilanes, this reaction is thermodynamically accessible because the strong Si-Cl bonds in MTS raise the activation barriers for reactions that are normally considerably lower than that for H-loss.

Prior to this work, little information was available on the gas-phase kinetic behavior of chlorinated organosilanes even though they are an important class of compounds of interest in many fields. The results reported here provide new insight into the decomposition reactions of these compounds, which are strongly influenced by the large dissociation energy of the Si-Cl bond. The behavior of these systems is predicted to be very different from the non-chlorinated organosilicon analogs. Along with mechanistic discussions¹⁰ the present study provides a critically needed starting point for future theoretical and experimental investigations of the reactivity of these systems.

References

- (1) Allendorf, M. D.; Melius, C. F. *J. Phys. Chem.* **1992**, *96*, 428.
- (2) Walsh, R. In *The Chemistry of Organic Silicon Compounds*; S. Patai and Z. Rappoport, Ed.; John Wiley and Sons: New York, 1989; pp 371-391.
- (3) Safarik, I.; Sandhu, V.; Lown, E. M.; Strausz, O. P.; Bell, T. N. *Res. Chem. Intermed.* **1990**, *14*, 105-131.
- (4) Gaspar, P. P. In *Reactive Intermediates*; M. Jones Jr. and R. A. Moss, Ed.; Wiley: New York, 1985; Vol. 3; pp 333-427.
- (5) Tang, Y.-N. In *Reactive Intermediates*; R. A. Abramovitch, Ed.; Plenum: New York, 1982; Vol. 2; pp 297-367.
- (6) Gordon, M. S.; Gano, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 5421.
- (7) Gordon, M. S.; Truong, T. N. *Chem. Phys. Lett.* **1987**, *142*, 110.
- (8) Neudorfl, P. S.; Lown, E. M.; Safarik, I.; Jodhan, A.; Strausz, O. P. *J. Am. Chem. Soc.* **1987**, *109*, 5780.
- (9) Sawrey, B. A.; O'Neal, H. E.; Ring, M. A.; Coffey Jr., D. *Int. J. Chem. Kinetics* **1984**, *16*, 31.

- (10) Davidson, I. M. T.; Dean, C. E. *Organometallics* **1987**, 6, 966.
- (11) Allendorf, M. D.; Melius, C. F. *J. Phys. Chem.* **1993**, 97, 720.
- (12) Benson, S. W. *Thermochemical Kinetics*; 2nd ed.; J. Wiley and Sons: New York, 1976.
- (13) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, 33, 493.
- (14) Voorhoeve, R. J. H. *Organohalosilanes: Precursors to Silicones*; Elsevier: New York, 1967.
- (15) Besmann, T. M.; Sheldon, B. W.; Kaster, M. D. *Surface and Coatings Technol.* **1990**, 43/44, 167.
- (16) Motojima, S.; Hasegawa, M. *J. Vac. Sci. Technol. A* **1990**, 8, 3763.
- (17) Cheng, D. J.; Shyy, W. J.; Kuo, D. H.; Hon, M. H. *J. Electrochem. Soc.* **1987**, 134, 3145.
- (18) Kuo, D. H.; Cheng, D. J.; Shyy, W. J.; Hon, M. H. *J. Electrochem. Soc.* **1990**, 137, 3688.
- (19) So, M. G.; Chun, J. S. *J. Vac. Sci. Technol. A* **1988**, 6, 5.
- (20) Yeheskel, J.; Agam, S.; Dariel, M. S. *Chemical Vapor Deposition 1990*; K. E. Spear and G. W. Cullen, Eds. The Electrochemical Society Softbound Proceedings Series, Seattle, **1990**.
- (21) Burgess, J. N.; Lewis, T. J. *Chemistry and Industry* **1974**, 76.
- (22) Whitman, L. J.; Joyce, S. A.; Yarmoff, J. A.; Mcfeely, F. R.; Terminello, L. J. *Surf. Sci.* **1990**, 232, 297.
- (23) NoorBatcha, I.; Raff, L. M.; Thompson, D. L. *J. Chem. Phys.* **1984**, 81, 3715.
- (24) He, P.; Breiland, W. G.; Buss, R. J. *J. Chem. Phys.* **1989**, 91, 2627.
- (25) Robertson, R. M.; Rossi, M. J. *Appl. Phys. Lett.* **1989**, 54, 185.
- (26) Perrin, J.; Broekhuizen, T. *Appl. Phys. Lett.* **1987**, 50, 433.
- (27) Allendorf, M. D.; Melius, C. F.; Osterheld, T. H. accepted for publication in *Chemical Vapor Deposition 1993 Softbound Proceedings Series*; G. W. Cullen and K. Jenson, Eds. The Electrochemical Society, Pennington, NJ, **1993**.

- (28) This simplified version of the statistical adiabatic channel model uses the maximum free energy criterion to determine the location of the transition state. The model uses a single adjustable parameter to determine the reaction coordinate potential energy curve, the value of which is determined empirically, using data from known reactions. Reaction rates can then be determined from spectroscopic and thermodynamic data for the reactants and products only. It should be noted that the *full* statistical adiabatic channel model is not considered less sophisticated than RRKM theory.
- (29) Quack, M.; Troe, J. *Ber. Bunsen Gesell. Phys. Chem.* **1977**, *81*, 329.
- (30) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell Scientific Publications: Oxford, 1990.
- (31) Gardiner Jr., W. C.; Troe, J. In *Combustion Chemistry*; W. C. Gardiner Jr., Ed.; Springer-Verlag: New York, 1984; pp 173-196.
- (32) Jordan, M. J. T.; Smith, S. C.; Gilbert, R. G. *J. Phys. Chem.* **1991**, *95*, 8685.
- (33) Pitt, I. G.; Gilbert, R. G.; Ryan, K. R. *Aust. J. Chem.* **1990**, *43*, 169.
- (34) Greenhill, P. G.; Gilbert, R. G. *J. Phys. Chem.* **1986**, *90*, 3104.
- (35) Berne, B. J.; Borkovec, M.; Straub, J. E. *J. Phys. Chem.* **1988**, *92*, 3711.
- (36) Forst, W. *Theory of Unimolecular Reactions*; Academic Press: New York, NY, 1973.
- (37) Karas, A. J.; Gilbert, R. G. *J. Phys. Chem.* **1992**, *96*, 10893.
- (38) Klippenstein, S. J.; Marcus, R. A. *J. Chem. Phys.* **1989**, *91*, 2280.
- (39) Klippenstein, S. J. *J. Chem. Phys.* **1990**, *93*, 2418.
- (40) Klippenstein, S. J. *J. Chem. Phys.* **1991**, *94*, 6469.
- (41) Marcus, R. A. *Science* **1992**, *256*, 1523.
- (42) Miller, W. H. *J. Chem. Phys.* **1976**, *65*, 2216.
- (43) Ravi, R.; Takoudis, C. G. *J. Electrochem. Soc.* **1992**, *139*, 1994.
- (44) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; John Wiley and Sons Ltd.: New York, NY, 1972.
- (45) Smith, S. C.; Gilbert, R. G. *Int. J. Chem. Kinet.* **1988**, *20*, 307.
- (46) Troe, J. *J. Chem. Phys.* **1977**, *66*, 4745.

- (47) Troe, J. *J. Chem. Phys.* **1977**, *66*, 4758.
- (48) Wardlaw, D. M.; Marcus, R. A. *Adv. Chem. Phys.* **1987**, *70*, 231.
- (49) Gilbert, R. G.; Jordan, M. J. T.; Smith, S. C. UNIMOL program suite, 1992
- (50) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1990**, *94*, 5120.
- (51) Soliman, M. S.; Khattab, M. A.; El-Kourashy, A. G. *Spectrochim. Acta* **1983**, *39A*, 621.
- (52) Chase, M. W. J.; Davies, C. A.; Downey, J. R. J.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, 860.
- (53) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, NY, 1986.
- (54) Gilbert, R. G. *J. Chem. Phys.* **1984**, *80*, 5501.
- (55) Lim, K. F.; Gilbert, R. G. *J. Chem. Phys.* **1986**, *84*, 6129.
- (56) Lim, K. F.; Gilbert, R. G. *J. Chem. Phys.* **1990**, *92*, 1819.
- (57) Melius, C. F., personal communication.
- (58) Both the BRW model and trajectory calculations can overestimate energy transfer values for collisions with He. For a discussion see References 30 and 54-56.
- (59) Quack, M.; Troe, J. In *A Specialist Periodical Report. Gas Kinetics and Energy Transfer*; P. G. Ashmore and R. J. Donovan, Ed.; The Chemical Society: London, 1977; Vol. 2.
- (60) The ratio describing the change in the calculated rate resulting from a different reaction threshold is simply $\exp[(E_1 - E_2)/RT]$. This ratio is essentially 2 in all cases since E_1 is nominally 100 kcal/mol for all of the reactions considered and the temperature increase from 1300 K to 1500 K is relatively minor.
- (61) Sosa, C.; Schlegel, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 5847.
- (62) Warnatz, J. In *Combustion Chemistry*; W. C. Gardiner Jr., Ed.; Springer-Verlag: New York, 1984.
- (63) Stinespring, C. D.; Wormhoudt, J. C. *J. Appl. Phys.* **1989**, *65*, 1733.
- (64) In this paper we use the term "radical" to refer to any unsaturated species.

INITIAL DISTRIBUTION
UNLIMITED RELEASE

Dr. Peter Angelini
Bldg. 4515
Oak Ridge National Laboratories
P.O. Box 2008, 1 Bethel Valley Road
Oak Ridge, TN 37831-6065

Dr. Charles A. Sorrell
Adv. Industrial Concepts Div., CE-232
U.S. DOE - CE
Forrestal Building, 1000 Independence Ave.
Washington, DC 20585

Dr. K.B. Alexander
Metals and Ceramics Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6068

Dr. Theodore M. Besmann
Oak Ridge National Laboratories
P.O. Box 2008
Oak Ridge, TN 37831-6063

Dr. R.P. Currier
C348
Los Alamos National Laboratory
P.O. Box 1663
Los Alamos, NM 87545

Dr. D.J. Devlin
K762
Los Alamos National Laboratory
P.O. Box 1663
Los Alamos, NM 87545

Dr. Greg Glaitzmaier
NREL
1617 Cole Blvd.
Golden, CO 80401

Dr. Suleyman A. Gokoglu
NASA Lewis Research Center
Mail Stop 106-1
Cleveland, OH 44135

Dr. John H. Kinney
Mail Stop L-356
Lawrence Livermore National Laboratory
Livermore, CA 94550

Dr. Gerd M. Rosenblatt
Building 50A, Room 4119
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720

Dr. Michael Zachariah
National Institute of Standards and Technologies
Building 221, Rm. B312
Gaithersburgh, MD 20899

Prof. Peter B. Armentrout
Department of Chemistry
University of Utah
Henry Eyring Building
Salt Lake City, Utah 84112

Prof. Dieter Baeuerle
Johannes-Kepler-Universitat Linz
Institut fur Angewandte Physik
A-4040 Linz
Austria

Prof. C. Bernard
Laboratoire de Thermodynamique
ENSEEG
Bp.75, 28402
St. Martin d'Hères
France

Dr. Ken Brezinsky
Department of Mechanical & Aerospace Engineering
Princeton University
Engineering Quadrangle, D329
Princeton, NJ 08544

Prof. Jan-Otto Carlsson
Uppsala University
Chemistry Department
Box 531
S-75121 Uppsala
Sweden

Prof. David S. Dandy
Dept. of Agricultural and Chemical Engineering
Colorado State University
Fort Collins, CO 80523

Prof. James Edgar
Department of Chemical Engineering
Kansas State University
Manhattan, Kansas 66506-5102

Prof. James W. Evans
Dept. of Materials Science and Mineral
Engineering
University of California
Berkeley, CA 94720

Prof. Richard C. Flagan
Environmental Engineering
California Institute of Technology
138-78
Pasadena, CA 91125

Prof. Michael Frenklach
Dept. of Materials Science and
Engineering
202 Academic Projects Building
Pennsylvania State University
University Park, PA 16802

Prof. Bernard Gallois
Dept. of Materials Science
Stevens Institute of Technology
Castle Point on the Hudson
Hoboken, NJ 07030

Prof. Steven M. George
Department of Chemistry
University of Colorado
Boulder, CO 80309

Prof. Irvin Glassman
Dept. of Mechanical & Aerospace
Engineering
Princeton University
Princeton, NJ 08544

Prof. Mark S. Gordon
Department of Chemistry
North Dakota State University
Fargo, ND 58105

Prof. David Gutman
Department of Chemistry
Catholic University of America
Washington, DC 20064

Prof. John Haggerty
Department of Materials Sciences
Massachusetts Institute of Technology
12-009
Cambridge, MA 02139

Professor D. Lynn Johnson, Chairman
Dept. of Materials Science & Engineering
Northwestern University
The Technology Institute
Evanston, IL 60201

Dr. Sean King
Dept. of Materials Science and Engineering
North Carolina State University
Route 229
Rayleigh, NC 27695

Prof. M.C. Lin
Department of Chemistry
Emory University
Atlanta, GA 30322

Prof. Paul Marshall
Department of Chemistry
University of North Texas
P.O. Box 5068
Denton, TX 76203-5068

Dr. Roger Naslain
Laboratoire des Composites
Thermostructuraux
Domaine Universitaire
33600 Pessac
France

Prof. H. Edward O'Neal
Department of Chemistry
San Diego State University
San Diego, CA 92182-0328

Prof. Emil Pfender
Institute of Technology
244 Mechanical Engineering Building
111 Church Street S.E. Univ. of Minnesota
Minneapolis, MN 55455

Prof. S.E. Pratsinis
Chemical & Nuclear Engineering
University of Cincinnati
627 Rhodes Hall, Mail Loc. 171
Cincinnati, OH 45221-0171

Prof. Robert J. Santoro
Department of Mechanical Engineering
Pennsylvania State University
313A Mechanical Engineering Building
University Park, PA 16802

Dr. Daniel J. Skamser
Dept. of Materials Science and Engineering
Northwestern University
MLSF 2036 2225 N. Campus Drive
Evanston, IL 60208-3108

Prof. Karl E. Spear
Dept. of Ceramic Science and Engineering
Pennsylvania State University
201 Steidle Building
University Park, PA 16802

Prof. Thomas L. Starr
Room 113
Baker Building
Georgia Institute of Technology
Atlanta, GA 30332-0245

Prof. Robin Walsh
Department of Chemistry
University of Reading
Whiteknights
Reading RG62AD
England

Dr. Thomas H. Baum
IBM Almaden Research Center
650 Harry Rd.
San Jose, CA 95120

Dr. H.F. Calcote
Director of Research
Aerochem Research Laboratories
P.O. Box 1
Princeton, NJ 08542

Dr. Stephan de la Veaux
Experimental Station, E304/C216
E.I. DuPont
Wilmington, DE 19880-0304

Dr. William Felder
Aerochem Research Laboratories
P.O. Box 1
Princeton, NJ 08542

Dr. Stephen O. Hay
United Technologies Research Center
MS-90 Propulsion Science
Silverlane
East Hartford, CT 06108

Dr. John A. Mucha
Room 1D-357
AT&T Bell Laboratories
600 Mountain Avenue
Murray Hill, NJ 07974-2070

Dr. Bruce R. Palmer
Manager, Exploratory Research
Kerr-McGee Corporation
P.O. Box 25861
Oklahoma City, OK 73125

Dr. Michel Pons
Laboratoire de Science des Surfaces et
Matériaux Carbonés
Institut National Polytechnique de Grenoble
ENSEEG
38402 Saint-Martin-D'Heres Cedex
France

Mr. Peter Reagan
Project Manager, CVD Composites
Thermo Trex Corporation
74 West Street, P.O. Box 9046
Waltham, MA 02254-9046

Dr. Andrew J. Sherman
Ultramet
12173 Montague Street
Pacoima, CA 91331

Dr. Richard Silberglitt
Technology Assessment and Transfer, Inc.
133 Defense Highway, #212
Annapolis, MD 21401

Dr. Richard G. Tave
Day and Zimmermann, Inc.
1818 Market Street
Philadelphia, PA 19103

Dr. Jody Wormhoudt
Aerodyne Research Inc.
45 Manning Road
Billerica, MA 01821

1112 S.T. Picraux

1126 W.G. Breiland

1126 M.E. Coltrin

1126 P. Ho

1700 R.J. Eagan
 Attn: 1703 D.W. Schaefer
 1708 R.E. Loehman

6200 D.E. Arvizu

6211 G.A. Carlson

8000 J.C. Crawford
 Attn: 8100 E.E. Ives
 8200 R.J. Detry

8300 W.J. McLean
 Attn: 8302 W. Bauer 8351 L.A. Rahn
 8341 W.G. Wolfer 8355 G.A. Fisk
 8342 R.H. Stulen 8362 R.W. Carling
 8347 A. Pontau 8366 C.M. Hartwig

8347 D.A. Outka

8353 C.F. Melius (3)

8353 F.P. Tully
 Attn: R.J. Behrens
 D.W. Chandler
 J.L. Durant Jr.
 J.A. Miller

8361 M.D. Allendorf (10)

8745 R.J. Kee
 Attn: W.G. Houf
 R.S. Larson
 E. Meeks

8535 Publications for OSTI (10)

8535 Publications/Technical Library Processes, 7141

7141 Technical Library Processes Department (3)

8523-2 Central Technical Files (3)

END

DATE
FILMED
9 / 10 / 93