Time-Resolved Gas-Phase Kinetic and Quantum Chemical Studies of Reactions of Silylene with Chlorine-Containing Species. 2. CH₃Cl[†]

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Received: October 14, 2005; In Final Form: January 17, 2006

Time-resolved kinetic studies of the reaction of silylene, SiH_2, generated by laser flash photolysis of both silacyclopent-3-ene and phenylsilane, have been carried out to obtain second-order rate constants for its reaction with CH_3Cl. The reaction was studied in the gas phase at six temperatures in the range 294−606 K. The second-order rate constants gave a curved Arrhenius plot with a minimum value at $T \approx 370$ K. The reaction showed no pressure dependence in the presence of up to 100 Torr SF_6. The rate constants, however, showed a weak dependence on laser pulse energy. This suggests an interpretation requiring more than one contributing reaction pathway to SiH_2 removal. Apart from a direct reaction of SiH_2 with CH_3Cl, reaction of SiH_2 with CH_3 (formed by photodissociation of CH_3Cl) seems probable, with contributions of up to 30% to the rates. Ab initio calculations (G3 level) show that the initial step of reaction of SiH_2 with CH_3Cl is formation of a zwitterionic complex (ylid), but a high-energy barrier rules out the subsequent insertion step. On the other hand, the Cl-abstraction reaction leading to $CH_3 + ClSiH_2$ has a low barrier, and therefore, this seems the most likely candidate for the main reaction pathway of SiH_2 with CH_3Cl. RRKM calculations on the abstraction pathway show that this process alone cannot account for the observed temperature dependence of the rate constants. The data are discussed in light of studies of other silylene reactions with haloalkanes.

Introduction

Silylenes are of importance because they are implicated in the thermal and photochemical breakdown mechanisms of silicon hydrides and organosilanes, as well as being key intermediates in chemical vapor deposition (CVD). Time-resolved kinetic studies, carried out in recent years, have shown that the simplest silylene, SiH_2, reacts rapidly and efficiently with many chemical species.[1,2] Examples of its reactions include Si−H bond insertions and C=C and C≡C π-bond additions.[3] SiH_2 also reacts with many small inorganic molecules such as CO,[4] CO_2,[5] N_2O,[6] H_2O (D_2O),[7−9] HCl,[10] NO,[11] and O_2.[12] This class of reactions exhibit significant rate variations, including temperature and pressure dependences, which can be accounted for by a common mechanism involving initial formation of a donor−acceptor complex whose behavior, either continuing rearrangement or redissociation back to reactants, determines the overall rate.[4−12] The particular kinetic study of $SiH_2 + HCl$[10] was also of interest because of the importance of chlorosilanes and routes to their formation in the organosilicon industry.[13] Another chlorine-containing molecule of special interest is CH_3Cl because of its use as the feedstock in the direct process for production of methylchlorosilanes.[13] There is general evidence that silylenes can react with C−Cl bonds.[14] Both insertion[15] and abstraction reactions[16,17] have been found. The reaction between SiH_2 itself and CH_3Cl has not previously been studied

experimentally, but Su[18] has calculated a theoretical value (B3LYP/6-31G* level) of 102 kJ mol⁻¹ for the barrier to the insertion reaction

$$SiH_2 + CH_3Cl \rightarrow CH_3SiH_2Cl$$
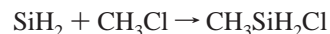
The present study combines an experimental investigation of the kinetics of the gas-phase reaction of SiH_2 with CH_3Cl as a function of both temperature and pressure with a theoretical calculation of the potential energy surface for the reaction.

Experimental Section

Equipment, Chemicals, and Method. The apparatus and equipment for these studies have been described in detail previously.[19,20] Only essential and brief details are therefore included here. SiH_2 was produced by the 193-nm flash photolysis of either silacyclopent-3-ene (SCP) or phenylsilane (PhSiH₃) using a Coherent Compex 100 exciplex laser. Photolysis pulses (beam cross-section 4 cm × 1 cm) were fired into a variable-temperature quartz reaction vessel with demountable windows, at right angles to its main axis. SiH_2 concentrations were monitored in real time by means of a Coherent 699-21 single-mode dye laser pumped by an Innova 90-5 argon ion laser and operating with Rhodamine 6G. The monitoring laser beam was multipassed 36 times along the vessel axis, through the reaction zone, to give an effective path length of 1.5 m. A portion of the monitoring beam was split off before entering the vessel for reference purposes. The monitoring laser was

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[†] Part of the special issue "David M. Golden Festschrift".

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tuned to 17 259.50 cm^{-1}, corresponding to the known $^RQ_{0,J}$ (5) strong rotation transition[21] in the SiH$_2$ Ã^{1}B$_1$(0,2,0) ← X̃^{1}A$_1$-(0,0,0) vibronic absorption band. Light signals were measured by a dual photodiode/differential amplifier combination, and signal decays were stored in a transient recorder (Datalab DL910) interfaced to a BBC microcomputer. This was used to average the decays of between 5 and 25 photolysis laser shots (at a repetition rate of 0.5 or 1 Hz). The averaged decay traces were processed by fitting the data to an exponential form using a nonlinear least-squares package. This analysis provided the values for first-order rate coefficients, k_{obs}, for removal of SiH$_2$ in the presence of known partial pressures of substrate gas.

Gas mixtures for photolysis were made up, containing between 2.0 and 5.7 mTorr of precursor (either SCP or PhSiH$_3$) and 0−35 Torr (1 Torr = 133.3 N m^{-2}) of CH$_3$Cl. In some experiments, inert diluent (SF$_6$) was also added (up to 100 Torr). Pressures were measured by capacitance manometers (MKS, Baratron). All gases used in this work were frozen and rigorously pumped to remove any residual air prior to use. SCP was a gift from the group of Professors Nefedov and Egorov. GC analysis showed it was >99% pure. PhSiH$_3$ (99.9%) was obtained from Ventron-Alfa (Petrarch). CH$_3$Cl (99.8%) was from BDH (Air Products). Sulfur hexafluoride, SF$_6$, (no GC-detectable impurities) was from Cambrian Gases. GC purity checks were carried out with both a 3-m silicone oil column (OV101) operated at 60 °C and with a 3-m Porapak Q operated at 120 °C. N$_2$ was used as carrier gas, and detection was by flame ionization detector (FID). Detection limits for impurity peaks were better than 0.1% of the principal component.

Ab Initio Calculations. The electronic structure calculations were performed with the *Gaussian 98* software package.[22] All structures were determined by energy minimization at the MP2=full/6-31G(d) level. Transition-state structures were characterized as first-order saddle points by calculation of the Hessian matrix. Stable structures, corresponding to energy minima, were identified by possessing no negative eigenvalues of the Hessian, while transition states were identified by having one and only one negative eigenvalue. The standard Gaussian-3 (G3) compound method[23] was employed to determine final energies for all local minima. For transition states, the elements of the G3 method were used, viz., optimization to TS at HF/6-31G(d), frequencies at HF/6-31G(d), optimization to TS at MP2=full/6-31G(d), followed by four single-point energy determinations at the MP2=full/6-31G(d) geometry, viz., QCISD-(T)/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2=full/G3large, and the values were combined according to the G3 procedure.[23] The identities of the transition-state structures were verified by calculation of intrinsic reaction coordinates[24] (IRCs) at the MP2=full/6-31G(d) or B3LYP/6-31G(d) levels. Reaction barriers were calculated as differences in G3 enthalpies at 298.15 K. Where required, harmonic frequencies were obtained from the values calculated at the HF/6-31G(d) level adjusted by the correction factor 0.893 appropriate to this level.[25]

Results

Kinetics. Preliminary experiments established that, for a given reaction mixture, decomposition decay constants, k_{obs}, were not dependent on the exciplex laser energy within the normal routine range of variation (50−70 mJ/pulse). However, there was some variation outside this range (see below). There was no dependence on the number of photolysis laser shots (up to 25 shots). The constancy of k_{obs} (5-shot averages) showed that there was no effective depletion of reactants. Most of the experiments were carried out using SCP as the silylene precursor. A few
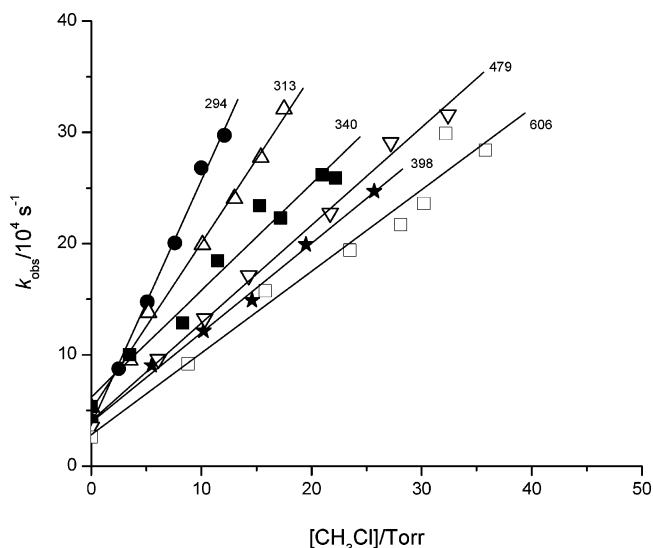

Figure 1. Second-order plots for reaction of SiH$_2$ + CH$_3$Cl: temperatures for each set of data are marked in the figure.

**TABLE 1: Experimental Second-Order Rate Constants for SiH$_2$ + CH$_3$Cl at Several Temperatures**

T/K	k/10^{-13} cm^3 molecule^{-1} s^{-1}
294	6.64 ± 0.17
313	4.72 ± 0.13
340	3.49 ± 0.21
398	2.71 ± 0.09
479	4.40 ± 0.11
606	4.48 ± 0.28

experiments at room temperature were carried out using PhSiH$_3$ as the precursor, and these gave k_{obs} values in good agreement (i.e., within 10%) of the values derived using SCP. Higher pressures of precursor were required at the higher temperatures, because signal intensities decreased with increasing temperature. However, for the purposes of rate constant measurement at a given temperature, the precursor pressure was kept fixed. At each temperature of study, a series of experiments was carried out to investigate the dependence of k_{obs} on CH$_3$Cl pressure (at least 5 different values). The results of these experiments are shown in Figure 1, where good linear fits were obtained, as expected for second-order kinetics. The second-order rate constants derived from the gradients of these plots by least-squares fitting, are shown in Table 1. The error limits (precision) are single standard deviations and are fairly small. It can be seen that, while the rate constants initially decrease with increasing temperature, the trend is reversed at the higher temperatures. This behavior is unusual for silylene reactions, where negative temperature dependences are the norm.[4,6−12,19,26−34]

In addition to these experiments, some runs were carried out at total pressures increased by additions of SF$_6$ up to a total of 100 Torr. This was done at the lowest and second highest temperatures (294 and 479 K, respectively). No effects of increased pressure could be discerned beyond experimental error limits. We therefore assumed that pressure dependence effects were unlikely at any of the other temperatures. Lack of pressure dependence is also confirmed by the linearity of the second-order plots (Figure 1) over a substantial range of CH$_3$Cl pressures. Thus, the rate constants shown in Table 1 should represent the values for the true bimolecular process. However, when the temperature dependence of these rate constants is represented on an Arrhenius plot (Figure 2), the curvature of the fit indicates some complexity to the processes occurring. For discussion purposes, two sets of Arrhenius parameters have
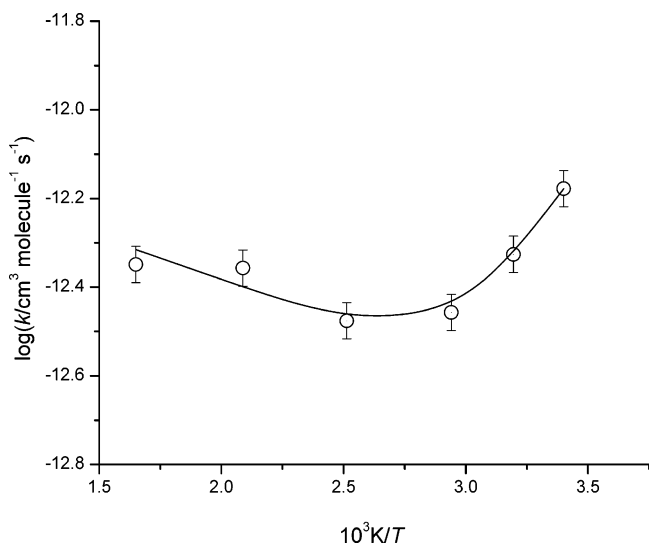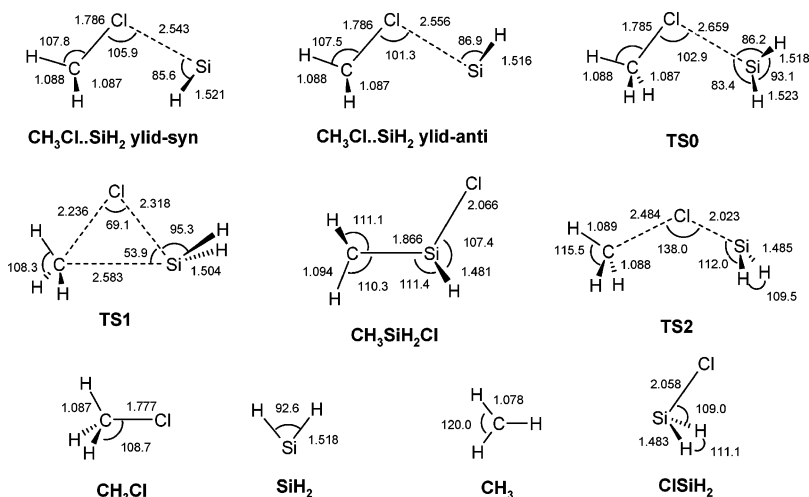
Figure 2. Arrhenius plot of second-order rate constants for SiH_2 + CH_3Cl. Error bars show $\pm 10\%$ uncertainties (accuracy).
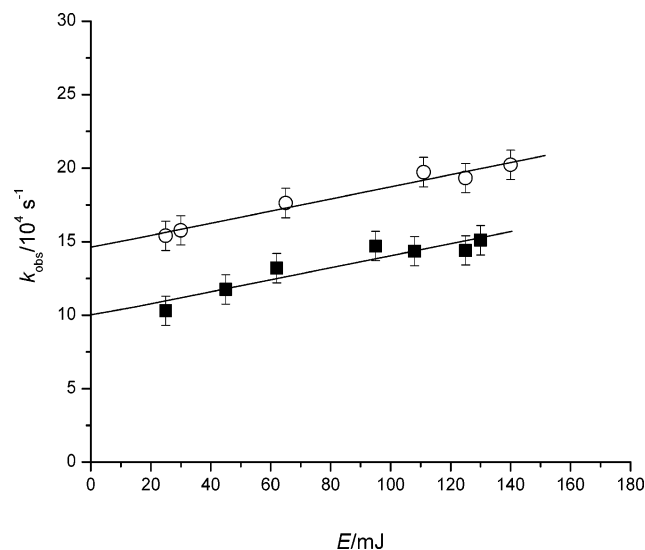
Figure 3. Dependence of decay constants on laser pulse energy. Data points: (○) 294 K; (■) 474 K. Error bars show estimated ± 1 uncertainties (accuracy) in $k_{obs}/10^4$ s^{-1}.

been calculated, viz., for the lowest three and highest three temperatures, respectively. These are shown in Table 2.

TABLE 2: Partial Arrhenius Parameters for Second-Order Rate Constants for SiH_2 + CH_3Cl

T range/K	$\log(A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	$E_a/\text{kJ mol}^{-1}$
294−340	−14.24 ± 0.18	−11.55 ± 1.11
398−606	−12.09 ± 0.16	2.81 ± 1.45

In light of difficulties in interpreting these results (see discussion), some checks were made of the dependence of k_{obs} on laser pulse energy. These were carried out over the range 25−140 mJ/pulse by varying the laser discharge voltage at each of the two temperatures 294 and 474 K. The data obtained are shown in Figure 3. This indicates a trend of increasing values of k_{obs} with pulse energy at both temperatures. This result is discussed later.

Ab Initio Calculations. Possible species on the $SiCH_5Cl$ potential energy surface (PES) were explored in some detail at the G3 level of theory. A fairly straightforward surface and set of species has been found. This comprises three local minima (i.e., stable intermediates or products), apart from the reactants, SiH_2 + CH_3Cl, and three transition states. The reaction pathway may be described as follows: The initial step forms the donor−acceptor complex (ylid), $CH_3Cl\cdots SiH_2$ (in syn and anti configurations), which, when it does not decompose back to reactants, can then either undergo a chlorine-to-silicon CH_3-group shift via TS1 to form methylchlorosilane, CH_3SiH_2Cl, or decompose by C−Cl bond fission via TS2 to give methyl and chlorosilyl radicals. It is also potentially possible to reach the radical pair via decomposition of CH_3SiH_2Cl (vibrationally excited).

Investigation of the surface between the syn and anti forms of the ylid showed a low maximum (TS0) at 2.5 kJ mol^{-1} above the anti form and 4.1 kJ mol^{-1} above the more stable syn form, which means close to free rotation around the Si$\cdots$Cl bond at ambient temperature. The IRC calculations most readily link the anti form to TS1 and the syn form to TS2, but since the two forms are so readily interconverted, it is clear that either conformer can reach either transition state. The structures of the intermediate species, products, and reaction transition states are shown in Figure 4, and the enthalpy values are listed in Table 3, as well as being represented on the PES in Figure 5.

RRKM Calculations. In view of the ab initio findings of local minima for association complexes with low exit barriers to products via an abstraction channel, the question arises regarding the effects of possible stabilization and redissociation of these complexes prior to continuing reaction by Cl-atom
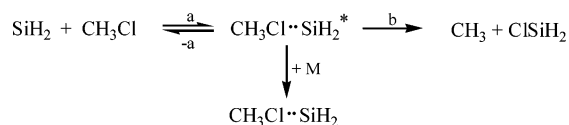

Figure 4. Ab initio MP2=full/6-31G(d) calculated geometries of local-minimum structures and transition states on the SiH_2 + CH_3Cl energy surface. Selected distances are given in Å and angles in degrees.

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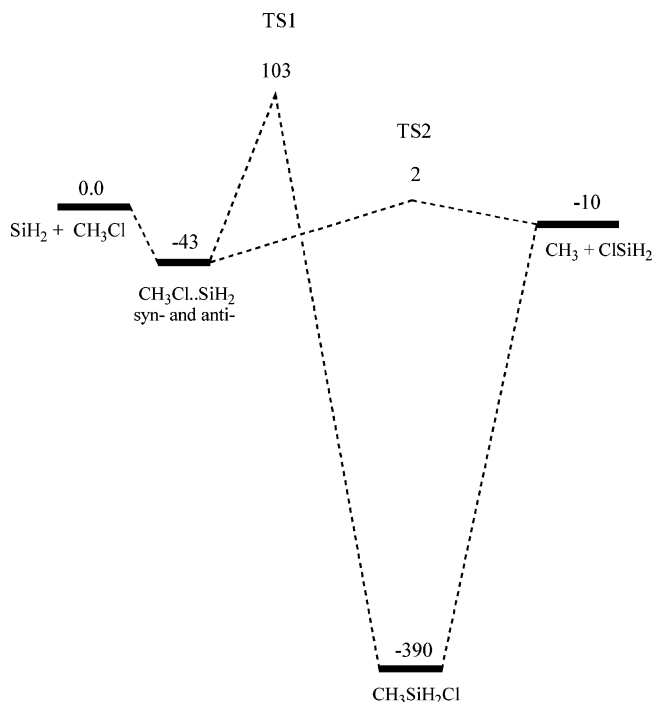
Figure 5. Potential energy (enthalpy) surface for the reaction of SiH$_2$ + CH$_3$Cl. All enthalpies (kJ mol^{-1}) are calculated at the G3 level.

TABLE 3: Ab Initio (G3) Enthalpies for SiCH$_5$Cl Species of Interest in the Reaction of SiH$_2$ with CH$_3$Cl

molecular species	energy/hartree	relative energy/kJ mol^{-1}
SiH$_2$ + CH$_3$Cl	−790.362750	0
CH$_3$Cl··SiH$_2$ ylid-anti	−790.378563	−41.5
TS0	−790.377588	−39.0
CH$_3$Cl··SiH$_2$ ylid-syn	−790.379543	−44.1
TS1	−790.323373	+103.4
CH$_3$SiH$_2$Cl	−790.511164	−389.7
TS2	−790.362028	+1.9
CH$_3$$^{\bullet}$ + ClSiH$_2$$^{\bullet}$	−790.366555	−10.0

transfer (via TS2). With such a low barrier, the populations of energized complexes are likely to lie above the energy threshold, as has indeed been found in earlier studies (e.g., of SiH$_2$ + HCl[10]). To ascertain the effects of this, we have undertaken Rice−Ramsperger−Kassel−Marcus (RRKM) calculations (of chemical activation type[35]) based on the reaction scheme

$$\text{SiH}_2 + \text{CH}_3\text{Cl} \underset{-a}{\overset{a}{\rightleftharpoons}} \text{CH}_3\text{Cl}\cdot\cdot\text{SiH}_2{}^* \overset{b}{\longrightarrow} \text{CH}_3 + \text{ClSiH}_2$$
$$\downarrow {+\text{M}}$$
$$\text{CH}_3\text{Cl}\cdot\cdot\text{SiH}_2$$

For simplicity, only the more stable syn complex was considered. Transition-state models were constructed for the two pathways of dissociation (TSA) and reaction (TSB) of the complex. The assignment of structure and vibrational wavenumbers for the syn adduct and TSB (=TS2) was based on the ab initio values. For TSA, a loose vibrational transition state was constructed by judicious reduction of vibrational wavenumber values for the transitional modes of the syn adduct, similar to that carried out in previous studies.[4,8,11,19,26,27,29,31−33] Details of these assignments are included in Tables 4 and 5. The calculations assumed that the input energy distribution of the CH$_3$Cl···SiH$_2$ adduct, produced by reaction (a) via TSA, was zeroed at the excitation energy corresponding to the dissociation threshold. The calculations employed a weak collisional model (stepladder, $\langle\Delta E\rangle_{\text{down}}$ = 1000 cm^{-1}). The

TABLE 4: Molecular and Transition-State Parameters for RRKM Calculations for the Decomposition of the CH$_3$Cl···SiH$_2$ Adduct^a

parameter	molecule	TS complex	
		TSA	TSB
$\tilde{\nu}$/cm^{-1}	3030(2)	3030(2)	3090(2)
	2930	2930	2945
	1953(2)	1953(2)	2198
	1448(2)	1448(2)	2166
	1370	1370	1402(2)
	1022(2)	1004	935
	1004	676	865
	676	470(2)	658
	532	240	605
	448	190	543
	101	40	449
	92	35	414
	88	32	235
	71		119
			16
A/s^{-1}		2.7 × 10^{14}	7.7 × 10^{12}
E_o/kJ mol^{-1}		44.1	46.0
Z/10^{-10} cm^3 molec^{-1} s^{-1}		5.40	5.40

^{a} Calculated at 294 K.

TABLE 5: Vibrational Wavenumbers Used to Assign TSA at Different Temperatures in RRKM Calculations of CH$_3$Cl···SiH$_2$ Decomposition (E_0 = 44.1 kJ mol^{-1})

T/K	294	313	340	398	479	606
$\tilde{\nu}$(TS)/cm^{-1}	470(2)	470(2)	490(2)	510(2)	540(2)	570(2)
	240	240	250	260	280	300
	190	190	210	220	240	260
	40	42	44	47	50	55
	35	37	37	40	44	48
	32	33	33	37	38	42

TABLE 6: RRKM Calculated Values for the Average Rate Constants for Decomposition and Abstraction of CH$_3$Cl···SiH$_2$* under Experimental Conditions

T/K	$\langle k_{-a}\rangle^a$/s^{-1}	$\langle k_b\rangle^a$/s^{-1}	$\langle k_{-a}\rangle/\langle k_b\rangle$
294	7.34 × 10^{10}	2.62 × 10^9	28.0
313	8.30 × 10^{10}	3.25 × 10^9	25.6
340	9.06 × 10^{10}	4.22 × 10^9	21.2
398	1.19 × 10^{11}	7.68 × 10^9	15.5
479	1.55 × 10^{11}	1.40 × 10^{10}	11.1
606	2.34 × 10^{11}	3.31 × 10^{10}	7.06

^{a} Average values over the molecular energy distribution.

results of these calculations show, importantly, that the extent of pressure stabilization of the energized complexes (CH$_3$Cl···SiH$_2$*) was very small. The maximum value was 10% (at 294 K, 100 Torr). The values for $\langle k_{-a}\rangle$ and $\langle k_b\rangle$, the chemical activation rate constants under average pressure conditions (negligible stabilization), were obtained at each temperature. These are shown in Table 6. It can clearly be seen that $\langle k_{-a}\rangle \gg \langle k_b\rangle$, i.e., redissociation of excited complexes is significantly faster than reaction.

The effective rate constant for overall reaction, k_{eff}, in the absence of pressure stabilization of complexes is given by the stationary-state expression

$$k_{\text{eff}} = k_{a}/(1 + \langle k_{-a}\rangle/\langle k_b\rangle)$$

An Arrhenius plot of the factor $1 + \langle k_{-a}\rangle/\langle k_b\rangle$ yields the equation

$$\log(1 + \langle k_{-a}\rangle/\langle k_b\rangle) =$$
$$(+0.40 \pm 0.04) + (6.08 \pm 0.27 \text{ kJ mol}^{-1})/RT \ln 10$$

The Arrhenius parameters for k_a are, of course, unknown, but

an estimate based on previous experience of SiH$_2$ reactions[19,20,26,27,32,33] and consistent with the RRKM model for TSA would suggest $A_a \approx 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $E_a \approx -3$ kJ mol^{-1}. This implies that overall $A_{eff} \approx 10^{-10.40}$ cm^3 molecule^{-1} s^{-1} and $E_{eff} \approx 3.08$ kJ mol^{-1}.

Discussion

Kinetic Considerations and Comparison with Theory. The main experimental purpose of the present work was to study the kinetics of the reaction of SiH$_2$ with CH$_3$Cl for the first time and to investigate the temperature and pressure dependences of the second-order rate constants. This has been accomplished. The reaction is found to be pressure independent and to have a temperature dependence in which rate constants both decrease and subsequently increase with temperature with a minimum value occurring at ca. 370 K. There is no previous work on this reaction system with which to compare these results, nor is there, to our knowledge, any previous example of a silylene reaction displaying this kind of kinetic behavior. It seems likely that the observed behavior corresponds to a change of mechanism with increasing temperature. The most obvious suggestion would appear to be that at lower temperatures reaction is occurring via an insertion mechanism while at higher temperatures an abstraction process is taking place. This interpretation is apparently reinforced by our knowledge that SiH$_2$ insertion reactions almost invariably have negative temperature dependences,[1,2,10,19,30] while abstraction reactions (although not experimentally known for SiH$_2$) usually have positive temperature dependences (i.e., positive activation barriers). The latter is supported by the ab initio calculations carried out here. However, there are several difficulties with this simple interpretation.

The first and most obvious one is the discrepancy with the calculations. The ab initio barrier for insertion is 103.4 kJ mol^{-1}, which effectively rules out this pathway as a contributing process. Unless there is some error in the G3 calculations, insertion of SiH$_2$ into the C−Cl bond of CH$_3$Cl should not occur. Since the G3 (and previously G2) calculations have been in good agreeent with experiment for other SiH$_2$ reactions,[4,5,8,10–12,32,33] there is little reason to believe there could be a serious error here. It should also be mentioned that the calculation on this reaction system by Su[18] at the B3LYP/6-31G* level of theory gave a value of 102.4 kJ mol^{-1} for the energy of TS1, in excellent agreement with our result.

Second, there is a probable discrepancy with the measured A factor for the low-temperature process. As previously,[10] we may use transition-state theory (TST) to estimate the A factor for the insertion pathway ($A = e^2(kT/h) \exp(\Delta S^{\ddagger}/R)$).[36] The required $\Delta S^{\ddagger}$ value is calculated from the S values for TS1, SiH$_2$, and CH$_3$Cl obtained as part of the output of the ab initio calculations and shown in Table 7. This yields a value for log-(A/cm^3 molecule^{-1} s^{-1}) of -12.34 (at the mean T of 315 K), which is significantly different from the measured value for the lower-temperature process (Table 2).

The situation is not quite so bad for the proposed abstraction process. The ab initio calculated barrier is 1.9 kJ mol^{-1}, which is in reasonable agreement with the measured activation energy of 2.8 kJ mol^{-1} for the higher-temperature process. The simple TST calculation, using the ab initio derived entropy values shown in Table 7, gives the value of -11.10 for log(A/cm^3 molecule^{-1} s^{-1}). While this is in better agreement with experiment, it is still about an order of magnitude larger than the measured higher-temperature A factor (Table 2).

The RRKM calculations do not resolve the situation. While they support the lack of an observed pressure dependence, they

TABLE 7: Ab Initio (MP2=full/6-31G(d)) Entropy Values for Species of Interest in SiH$_2$ + CH$_3$Cl Reaction

species	SiH$_2$	CH$_3$Cl	TS1	TS2
$S°$/J K^{-1} mol^{-1}	206.9	233.5	312.2	329.6

predict rate constants for abstraction, k_{eff}, which are larger than those observed. As presented in Arrhenius form, the A factor, A_{eff}, is more than 1 order of magnitude higher than the measured higher-temperature A factor (Table 2), but E_{eff}, at 3.1 kJ mol^{-1}, is close to the measured high-temperature activation energy. Both the TST (canonical) and RRKM (microcanonical) calculations overestimate the rate constant for abstraction. It is worth noting that if the ab initio calculations have underestimated the energy of the abstraction process (viz., the energy of TS2) by a small amount (ca. 10 kJ mol^{-1}) then the TST calculations (both versions) will come close to the correct order of magnitude of the observed rate constants in the higher temperature range. However, neither calculation can explain the experimental finding of a curved Arrhenius plot.

Potential Complications and the Reactions of Silylenes with Chloroalkanes in General. The discrepancies between the above proposed mechanism and theoretical calculations led us to consider other possible explanations. One of the problems with a relatively unreactive substrate such as CH$_3$Cl is that the results can be vitiated by relatively small amounts of a reactive impurity. The specified purity of our CH$_3$Cl sample was 99.8%. A GC analytical check showed no detectable impurities. If the 0.2% possible impurity were the sole source of reaction, it would have to react with SiH$_2$ with a rate constant of 3.3×10^{-10} cm^3 molecule^{-1} s^{-1} at 294 K. While this cannot be totally ruled out, possible impurities such as O$_2$ or HCl have much lower rate constants than this, and organic (unsaturated) molecules which could react with this rate constant are ruled out by lack of a GC (FID) signal. We therefore wondered whether photo-decomposition of CH$_3$Cl could be the source of a reactive impurity. At 193 nm, CH$_3$Cl has a weak n → s* transition, with an absorption cross-section of ca. 5×10^{-20} cm^2 molecule[37] (which we verified by measurement). The primary photodissociation of CH$_3$Cl at 193 nm is the bond fission process,[37] which proceeds with unit quantum efficiency

$$CH_3Cl + h\nu \rightarrow CH_3 + Cl$$
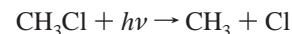
The formation of radicals such as CH$_3$ and Cl offers potential reactive partners for SiH$_2$ which could react at collisional rates (although there is, as yet, no specific rate information about these processes). To test this possibility, we undertook some further experiments in which the photolysis laser intensity was varied, the reasoning being that the concentrations of any radicals formed would be affected by this, and therefore, if the radicals were reacting with SiH$_2$, the decays of the latter would be likewise affected. Figure 3 shows the results of these experiments (see Results section). While the effects are not dramatic, it is clear that the values of k_{obs}, the decay constants, increase with increasing intensity. A nearly sixfold increase in intensity causes increases of ca. 30% at 294 K and 40% at 474 K. Thus, it seems likely that there is a contribution to the SiH$_2$ decays from reaction with radicals (probably CH$_3$). Within experimental error, the dependence of k_{obs} on intensity looks to be approximately linear. With this assumption, under working experimental conditions, the true second-order rate constants for reaction of SiH$_2$ with CH$_3$Cl would be overestimated by 18% at 294 K and 30% at 474 K. Although these are fairly

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substantial contributions, it seems unlikely that reactions of SiH$_2$ with radicals could account for the whole of our observations.

Before reaching final conclusions, it is worthwhile reviewing existing evidence for the mechanism of reaction of silylenes with chloroalkanes. There have been no studies with SiH$_2$ nor of any other silylene with alkyl chlorides in the gas phase. However, there have been several solution studies involving other silylenes. All these studies involved end-product analysis. Kumada's group,[15] using trimethylsilyl phenylsilylene, Me$_3$-SiSiPh (in dry hexane solution), obtained the direct products of C−Cl insertion with octyl chloride, cyclopropylcarbinyl chloride and *s*-butyl chloride. In the case of *s*-butyl chloride, as well as *tert*-butyl chloride (for which no insertion product was found), the product Me$_3$SiSiHClPh (trimethylsilylchlorophenylsilane) was also obtained. This apparent "HCl abstraction" was explained by the formation of an initial silylene−chloroalkane zwitterionic adduct (i.e., an ylid), which could either proceed to the formal insertion product or undergo β-H-transfer to give the chlorosilane (+alkene). It is worth noting that yields of these products were rather small.

Nakao et al.[16] found strong evidence for the abstraction reaction

$$SiMe_2 + CCl_4 \rightarrow ClSiMe_2 + CCl_3$$
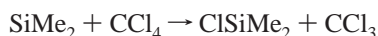
by the detection of C$_2$Cl$_6$ among the reaction products of SiMe$_2$ with CCl$_4$ in cyclohexane solution. Further studies by Oka and Nakao[17] using the silylene Me$_3$SiSiPh in reaction with several chloro- and alkylchloromethanes showed that products derived from all three types of reaction processes (insertion, Cl abstraction, and "HCl" abstraction) could be observed. Most recently, Kira's group[14] found evidence for Cl abstraction by their stabilized (isolable) dialkyl silylene, SiR$_2$. Interestingly, this did not undergo C−Cl insertion reactions with either CH$_2$-Cl$_2$ or cyclopropylcarbinyl chloride, but rather gave the products of double insertion, incorporating two units of SiR$_2$ into the substrate molecules. This was explained as a reaction of the initial zwitterionic complex with a second molecule of SiR$_2$ (present in high concentration because of its stability), occurring before the complex had time to react further on its own. Thus, it appears that there is considerable complexity to these reactions in solution.

At the present time, the best explanation of our own results seems to be that, at least at the higher temperatures, Cl abstraction by SiH$_2$ is occurring. There is some contribution to the rates by reaction of SiH$_2$ with radicals (probably CH$_3$) formed by photodissociation of CH$_3$Cl. This contribution is temperature dependent, so precise Arrhenius parameters for the abstraction reaction cannot be obtained. Direct insertion, even via the ylid complex, seems to be ruled out by theory. The well depth of the CH$_3$Cl···SiH$_2$ complex, although greater than that of HCl···SiH$_2$, is still insufficient to trap any of these species as products in the gas phase via collisional quenching. Thus, there are no pressure dependences. This contrasts with the reaction of SiH$_2$ with CH$_3$OH,[7] where effectively the CH$_3$O-(H)···SiH$_2$ adduct, with a well depth of 83 kJ mol^{-1}, is the final product. (No abstraction occurs, and the barriers to insertion, into both O−H and O−CH$_3$, are too high.) Thus, SiH$_2$ + CH$_3$-OH is a pressure-dependent association reaction, unlike SiH$_2$ + CH$_3$Cl.

As for the solution reactions, strict comparisons have to be made with caution, because they involve both different silylenes and different chloroalkanes. However, on the basis of theoretical calculations, it appears to us that C−Cl insertion, even via the ylid complex, is an unlikely process. It seems to

us much more likely that the insertion products observed are the result of Cl abstraction followed by radical recombination within the solvent cage. The abstraction process, having a low barrier and small exothermicity, is probably quite sensitive to structural features of the molecules and will vary in importance on a case-by-case basis. In solution also, the zwitterionic complex will be stabilized and could well live long enough to undergo other processes such as β-H-transfer or reaction with other reactive molecules.

There is strong evidence that silylenes are involved in the direct synthesis of methylchlorosilanes.[38] In the present work, although we do not have a complete explanation for our rate measurements, the results help to set a frame of reference for further studies of silylenes with chloroalkanes.

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