Direct Measurement and Theoretical Calculation of the Rate Coefficient for Cl + CH₃ in the Range from \( T = 202-298 \) K

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The rate coefficient has been measured under pseudo-first-order conditions for the Cl + CH₃ association reaction at \( T = 202, 250, \) and 298 K and \( P = 0.3-2.0 \) Torr helium using the technique of discharge-flow mass spectrometry with low-energy (12-eV) electron-impact ionization and collision-free sampling. Cl and CH₃ were generated rapidly and simultaneously by reaction of F with HCl and CH₄, respectively. Fluorine atoms were produced by microwave discharge in an approximately 1% mixture of F₂ in He. The decay of CH₃ was monitored under pseudo-first-order conditions with the Cl-atom concentration in large excess over the CH₃ concentration \(([\text{Cl}]_0/[\text{CH}_3]_0 = 9-67)\). Small corrections were made for both axial and radial diffusion and minor secondary chemistry. The rate coefficient was found to be in the falloff regime over the range of pressures studied. For example, at \( T = 202 \) K, the rate coefficient increases from \( 8.4 \times 10^{-12} \) at \( P = 0.30 \) Torr He to \( 1.8 \times 10^{-11} \) at \( P = 2.00 \) Torr He, both in units of cm³ molecule⁻¹ s⁻¹. A combination of ab initio quantum chemistry, variational transition-state theory, and master-equation simulations was employed in developing a theoretical model for the temperature and pressure dependence of the rate coefficient. Reasonable empirical representations of energy transfer and of the effect of spin–orbit interactions yield a temperature- and pressure-dependent rate coefficient that is in excellent agreement with the present experimental results. The high-pressure limiting rate coefficient from the RRKM calculations is \( k_2 = 6.0 \times 10^{-11} \) cm³ molecule⁻¹ s⁻¹, independent of temperature in the range from 200 to 300 K.

Introduction

Methane is an important trace species in Earth’s atmosphere.¹ In the stratosphere, it reacts with chlorine atoms to produce HCl and methyl radicals²

\[
\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \quad \text{(R1)}
\]

This is the main process that converts active Cl to the relatively unreactive reservoir species HCl in the stratosphere. It is especially important to have reliable kinetics data for R1, as it is well-established that chlorine atoms catalytically convert ozone to oxygen.³ Despite extensive theoretical and experimental investigations of R1, values of the rate coefficient at low temperatures are uncertain. In the range of 215–220 K, the rate coefficient for R1 has been measured by various groups,⁴⁻¹¹ and the results differ by as much as a factor of 2. A difference of only 27% in the value of the rate coefficient has been shown to have a substantial effect on the calculated abundance of stratospheric HCl.¹²

A suggestion has been made in the literature that methyl radicals formed in R1 can contribute to the observed loss of Cl atoms in experimental kinetics studies of R1.⁸ Therefore, it is desirable to have reliable kinetics data for the reaction

\[
\text{CH}_3 + \text{Cl} + \text{M} \rightarrow \text{CH}_3\text{Cl} + \text{M} \quad \text{(R2)}
\]

so that corrections can be made to the bimolecular rate coefficient of R1, if necessary. To date, there have been no direct measurements of the rate coefficient for R2. The only available data are from a very complex system, the photochlorination of methane.¹³ The experiments were performed at \( P = 50-300 \) Torr CO₂ and \( T = 298-423 \) K and yielded \( k_2 = 3.7 \times 10^{-10} \exp(-185/T) \) cm³ molecule⁻¹ s⁻¹, independent of pressure. The amount of uncertainty in this Arrhenius expression for \( k_2 \) is very large because of the indirect way in which it was derived.

Because of the large uncertainty in the available kinetics data for R2 and its possible role in perturbing laboratory measurements of \( k_1 \), we have undertaken a direct measurement of \( k_2 \) in the ranges \( T = 202-298 \) K and \( P = 0.3-2.0 \) Torr helium. We use the technique of discharge-flow mass spectrometry with low-energy (12-eV) electron-impact ionization and collision-free sampling to follow the CH₃ signal in an excess concentration of chlorine atoms. Helium was chosen as the bath gas in these experiments because most low-temperature kinetics experiments on R1 have been carried out in helium.

We have also developed a theoretical model for the temperature and pressure dependence of \( k_2 \) incorporating a combination...
of multireference configuration-interaction calculations of the interaction potential, variable-reaction-coordinate transition-state-theory calculations of the microcanonical/\(I\)-resolved rate coefficients, and master-equation simulations of the thermal rate coefficient. Excellent agreement with the present experimental results was obtained with reasonable empirical representations of the energy-transfer process and of the effect of spin–orbit interactions. Unfortunately, ambiguities in the appropriate treatment of spin–orbit effects preclude definitive theoretical estimates for the high-pressure-limit rate coefficient. Nevertheless, the modeling process demonstrates that the present experimental observations are incompatible with the high-pressure limit obtained by Timonen et al.\(^\text{13}\) Instead, the present study suggests a high-pressure-limit rate coefficient that is about a factor of 4 lower, i.e., \(\sim 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). Furthermore, these experimental results are consistent with a barrier-free combination of Cl atoms and methyl radicals.

**Experimental Section**

The discharge-flow mass spectrometry apparatus has been described in previous publications.\(^\text{14,15}\) The experiments were performed in a Pyrex flow tube of about 100-cm length and 2.8-cm diameter. The inner surface of the flow tube was lined with Teflon FEP. The flow tube was fitted with a Pyrex movable injector that was positioned between 4 and 44 cm from the sampling pinhole during kinetics experiments. Reactions were studied in He carrier gas with the linear gas velocity (plug flow) in the range of 2400–2700 cm s\(^{-1}\). Flow rates were measured by calibrated MKS flow meters for the following: helium (Air Products, 99.9995%), F\(_2\)/helium mixture (1% F\(_2\) in He; original mixture from Spectra Gases, 5% mixture of F\(_2\) in He, initially 99.0% pure F\(_2\) and 99.995% pure He), the CH\(_3\)/helium mixture (1.3% CH\(_3\), balance helium; CH\(_4\) from MG Industries, 99.9995%), HCl (Air Products, 99.997%), and the Cl\(_2\)/helium mixture (5% Cl\(_2\); Air Products, 99.998% pure in Cl\(_2\)). The Cl\(_2\)/helium mixture was made by diluting pure Cl\(_2\) with helium after a freeze–pump–thaw cycle on pure Cl\(_2\).

The concentrations of the gases in the flow tube were calculated from the flow rates and the total pressure as measured with an MKS Baratron manometer. The pressure in the flow tube was controlled by varying the position of a throttling valve; pressures ranged from \(P = 0.3–2.0\) Torr. The flow tube was used at ambient temperature or cooled by circulating ethanol from a cooled reservoir through the jacket surrounding the tube. At \(T = 202\) K, the temperature profile was flat (±1 K) from 3 to 44 cm. The flow tube was coupled via a two-stage collision-free sampling system to a quadrupole mass spectrometer (ABB Extrel).

Fluorine atoms were produced by microwave discharge (~60 W, 2450 MHz, Optos Instruments) in a 1% mixture of F\(_2\) in He. The discharge region consisted of a \(\frac{3}{4}\)-in. ceramic tube coupled to a glass discharge arm. Fluorine atoms entered the flow tube at \(d \approx 80\) cm upstream from the first pinhole.

During kinetics measurements, HCl and CH\(_3\) were introduced into the system via the movable injector. The reaction time for R2 was then controlled by moving the injector under the condition of constant linear gas velocity. Chlorine atoms and CH\(_3\) radicals were generated rapidly and simultaneously by the reactions\(^\text{16,17}\)

\[\text{F} + \text{CH}_3 \rightarrow \text{CH}_3 + \text{HF} \quad (R3)\]

\[k_3(139–294 \text{ K}) = 6.99 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\]

\[\exp(-9 \text{ K/T})\]

HCl and CH\(_4\) were in large excess over F with the ratio [HCl + CH\(_4\)]/[F] = 33/1–240/1. In separate experiments, the concentration of F atoms was determined by measuring the Cl\(_2\) consumption in the temperature-independent fast “titration reaction”\(^\text{18}\)

\[\text{F} + \text{Cl}_2 \rightarrow \text{FCl} + \text{Cl} \quad (R5)\]

\[k_5(180–360 \text{ K}) = 6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\]

With Cl\(_2\) in excess, the fluorine-atom concentration was determined by measuring the decrease in the Cl\(_2\) signal (\(m/e = 70\)) at an electron energy of 16.8 eV when the discharge was initiated. The dilute Cl\(_2\)/He mixture was admitted via the movable injector. The titration reaction was carried out with the position of the injector (\(d = 20\) cm) chosen to ensure that R5 went to completion and that the injector was at approximately the midpoint of the CH\(_3\) decay. The absolute fluorine-atom concentration is given by

\[\frac{[\text{F}]_0}{[\text{Cl}_2]_{\text{Disc Off}} - [\text{Cl}_2]_{\text{Disc On}}} = \frac{(\Delta \text{Cl}_2 \text{ signal})[\text{Cl}_2]_{\text{Disc Off}}}{(1)}\]

where \(\Delta \text{Cl}_2 \text{ signal}\) is the fractional decrease in the Cl\(_2\) signal, \((S_{\text{Disc Off}} - S_{\text{Disc On}})/S_{\text{Disc Off}}\). The concentration range of fluorine atoms in the experiments was \((2.4–17.0) \times 10^{13}\) atoms cm\(^{-3}\). This yielded initial Cl/CH\(_3\) concentration ratios ([Cl]/[CH\(_3\)]) of 9–67. Previous experience has shown that, in this flow system, the absolute concentration of F is invariant along the flow tube for injector positions of 2–44 cm. HCl and CH\(_3\) concentrations ([HCl] and [CH\(_3\)]) were adjusted to produce the desired initial Cl/CH\(_3\) concentration ratios, \(R\), by using the values given above for \(k_3\) and \(k_5\), as shown in the expression

\[R = \frac{[\text{Cl}]_0}{[\text{CH}_3]_0} = \frac{k_3[\text{HCl}]_0}{k_5[\text{CH}_3]_0} \quad (2)\]

The initial concentrations of Cl and CH\(_3\) ([Cl]\(_0\) and [CH\(_3\)]) were calculated from the measured initial fluorine-atom concentration ([F]\(_0\)) and the ratio \(R\) as given by

\[[\text{Cl}]_0 = \frac{[\text{F}]_0(1 + R)}{R} \quad (3)\]

\[[\text{CH}_3]_0 = [\text{F}]_0 - [\text{Cl}]_0 \quad (4)\]

The range of initial concentrations of HCl in these experiments was \((4.53–6.65) \times 10^{14}\) molecules cm\(^{-3}\), and the range of initial concentrations of CH\(_3\) in these experiments was \((0.97–6.04) \times 10^{12}\) molecules cm\(^{-3}\). Formation of Cl and CH\(_3\) was complete within about 2 ms. A stoichiometry correction of the form

\[[\text{Cl}]_\text{mean} = [\text{Cl}]_0 - [\text{CH}_3]_0/2 \quad (5)\]

was made to the initial chlorine-atom concentration, [Cl]\(_0\). The range of initial Cl concentrations in these experiments was \((2.26–16.7) \times 10^{12}\) atoms cm\(^{-3}\), and the range of initial CH\(_3\) concentrations in these experiments was \((1.25 – 6.79) \times 10^{11}\) molecules cm\(^{-3}\), with all but two experiments having \([\text{CH}_3]_0 < 5 \times 10^{11}\) molecules cm\(^{-3}\).

\[
F + CH_4 \rightarrow CH_3 + HF \quad (R4)
\]

\[k_4(180–410 \text{ K}) = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\]

\[\exp(-215 \text{ K/T})\]
As was the case for fluorine atoms, previous experience\textsuperscript{15c} has consistently demonstrated, using three different methods to determine the chlorine-atom concentration, that first-order wall losses for atomic chlorine in this flow system are small. This was verified for this study by measuring the first-order wall loss for chlorine atoms in a separate set of experiments at $P = 1$ Torr for $T = 202$ and 298 K. The chlorine atoms were generated by reaction R3 with $[\text{HCl}]_0 = 6.3 \times 10^{14}$ molecules cm$^{-3}$ and $[\text{F}]_0 = [\text{Cl}]_0 = 7.9 \times 10^{12}$ or $2.8 \times 10^{12}$ atoms cm$^{-3}$. The chlorine atoms were monitored in a limited m/2 scan range of 34.5–35.2 amu to considerably limit the overlap from the adjacent $\text{HCl}^+$ mass peak. The chlorine-atom signal was measured as the distance from the sampling pinhole to the end of the movable injector both increased (from 5 to 44 cm) and decreased (from 44 to 5 cm). The net signal from the chlorine atoms was obtained by subtraction of the background signal from the total signal. The natural logarithm of the net signal was graphed versus time to yield a pseudo-first-order rate coefficient from the slope. The reaction time was derived from the measured distance between the tip of the movable injector and the pinhole and the linear velocity of the gas, calculated from the measured pressure and gas flow rates. At $T = 202$ K, no loss of chlorine atoms occurred along the flow tube. At $T = 298$ K, the loss of chlorine atoms along the flow tube was negligible, although a small perturbation in the chlorine-atom signal occurred at the position of the side arm to the pressure gauge (approximately 27 cm from the sampling pinhole).

$\text{CH}_3$ radicals were detected at $m/e = 15$ following low-energy ($\sim 12$ eV) electron-impact ionization to minimize any contribution to the $\text{CH}_3$ signal from dissociative ionization of $\text{CH}_4$, which was present in large excess over $\text{CH}_3$ radicals. The observed $\text{CH}_3$ signal was corrected to yield the net signal by subtracting the background signal measured with the microwave discharge off; the background signal includes both the instrument background and a small contribution from the dissociative ionization of $\text{CH}_4$.

**Theoretical Section**

**Potential Energy Surface.** One set of electronic structure calculations was used to characterize the long-range interaction potential between Cl and $\text{CH}_3$, and a second set of electronic structure calculations was used to determine, as accurately as possible, the $\text{C}−\text{Cl}$ bond energy of $\text{CH}_3\text{Cl}$. The former was used to determine the high-pressure limit of the $\text{CH}_3 + \text{Cl}$ combination reaction, the latter for modeling of the pressure dependence. In this section, we describe first the calculation of the potential surface and then the calculation of the bond energy.

Electronic structure calculations of the long-range potential surface were carried out for the lowest three singlet surfaces. For large separations between reactants, the singlet wavefunctions are inherently multireference in character. For this reason, we used multireference configuration-interaction (MR−CI) calculations employing orbitals optimized with a state-averaged, complete-active-space, self-consistent-field (CASSCF) methodology.\textsuperscript{19,20} In these calculations, the CASSCF reference wavefunctions consisted of four active orbitals and six active electrons. The four active orbitals were the $\text{CH}_3$ radical orbital and the three $\text{Cl}$ 3p orbitals. All of the calculations were performed in $C_\text{s}$ symmetry. In this point group, three of the active orbitals are of $A'$ symmetry, and one is of $A''$ symmetry. The orbitals were optimized for an equally weighted average of the $1^1A', 2^1A'$, and $1^1A''$ states. The energies of these three individual states were then obtained using multireference, singles and doubles configuration-interaction calculations,\textsuperscript{21,22} employing the same CAS reference space as described above. The effects of higher-order excitations were tested using a multireference Davidson correction. The basis set used in all of the potential surface calculations was the correlation-consistent, augmented polarized valence triple-$\zeta$ (aug-cc-pvtz) basis set of Dunning.\textsuperscript{23,24}

All three of these states correlate with $\text{CH}_3(1^3A^+)+\text{Cl}(1^3P)$ and at long range are degenerate at this level of theory. Only one of these three states is reactive, and so, to fit the reactive surface, we simply chose the lowest of the three states at each geometry. A more accurate treatment, including spin−orbit coupling, which will split the long-range degeneracy of these states, is planned for the future.

In all of the potential surface calculations, the structure of the $\text{CH}_3$ radical was kept fixed at its equilibrium geometry. The potential surface calculations were done in a single plane, the plane perpendicular to the plane of the $\text{CH}_3$ radical, containing one of the $\text{CH}$ bonds of the $\text{CH}_3$ radical ($\text{CH}_3$) and bisecting the other two $\text{CH}$ bonds. Three coordinates were used to specify a point in this two-dimensional plane. These three coordinates are the $\text{C}−\text{Cl}$ distance, $R$; the angle between the $\text{C}−\text{Cl}$ bond and the $\text{C}_3$ axis of $\text{CH}_3$, $\theta$; and the dihedral angle between the $\text{CH}_3−\text{C}_3$ plane and the $\text{C}−\text{Cl}−\text{C}_3$ plane, $\phi$. Using these three coordinates, $(R, \theta, \phi)$, a $26 \times 10 \times 2$ three-dimensional grid of points was calculated, where $R$ varied from 3.5 to 20.0 au in uneven increments, $\theta$ varied from 0° to 90° in 10° increments, and $\phi$ had a value of either 0° or 180°. A three-dimensional analytic potential was then constructed by fitting the $(R, \theta)$ grids with two-dimensional splines and assuming a cos(3$\phi$) dependence for $\phi$, the coefficient of which was determined to fit the difference between the energies of the points $(R, \theta, 0°)$ and $(R, \theta, 180°)$. This analytic potential is available from the authors upon request. Note that the next nonzero term in the Fourier expansion of the $\phi$ would be cos(6$\phi$). In these calculations, the cos(6$\phi$) and higher terms were neglected.

The bond dissociation energy for $\text{CH}_3\text{Cl} \rightarrow \text{CH}_3 + \text{Cl}$ was determined from spin-restricted QCISD(T)\textsuperscript{25} calculations. Results obtained with Dunning’s correlation-consistent polarized valence triple- and quadruple-$\zeta$ basis sets\textsuperscript{26} were extrapolated to the infinite-basis-set limit via the expression\textsuperscript{27,28}

$$E(\infty) = E(l_{\text{max}}) - B/(l_{\text{max}} + 1)^4$$

where $l_{\text{max}}$ is the maximum angular momentum in the basis set. After zero-point and spin−orbit corrections, a bond dissociation energy of 82.1 kcal/mol was obtained. The geometric structures and zero-point energies employed in this analysis were obtained from density functional theory employing the Becke-3 Lee−Yang−Parr (B3LYP) functional\textsuperscript{29} and the 6-311++G(d,p) basis set.\textsuperscript{30} Unrestricted wave functions were employed in these B3LYP optimizations and vibrational analyses.

The MOLPRO quantum chemistry software was employed in all quantum chemistry calculations described here,\textsuperscript{31} except for the B3LYP evaluations, which employed the Gaussian 98 software.\textsuperscript{32}

**Kinetics.** Microcanonical/J-resolved rate coefficients were calculated from variable-reaction-coordinate transition-state theory\textsuperscript{33} employing the above-described CAS+$1^1+2+1$+QC/aug-cc-pvtz analytic potential energy surface. This approach involves the minimization of the transition-state number of states with respect to both the $\text{CH}_3−\cdots\text{Cl}$ separation and the location of a pivot point in the $\text{CH}_3$ fragment. This pivot point specifies the shape of the transition state dividing surface. Various locations of the pivot point along the $C_3$ axis were considered, with the optimal location for this system generally being the $C$ atom. The
of 8 arising from the quartet degeneracy of the $\text{2P}^{3/2}$ state of the

The ground electronic state then has an effective degeneracy

- conserved, and the interaction potential corresponds to the

orbit states in the standard fashion, i.e., as a direct sum over

- effect. For the Cl atom as a reactant, we included the spin–orbit states in the standard fashion, i.e., as a direct sum over

- states with their full spin and orbital degeneracies.

At large separations, the spin–orbit splittings are largely

- conserved, and the interaction potential corresponds to the

-long-range interaction potential plus the spin–orbit splitting.

The ground electronic state then has an effective degeneracy

- of 8 arising from the quartet degeneracy of the $\text{2P}^{3/2}$ state of the

Cl atom and the doublet spin degeneracy of the CH$_3$ radical.

At short separations, only the lowest singlet state is strongly

- attractive.

A proper statistical treatment of the different electronic states

requires some knowledge of the strength and variation in the

spin–orbit interactions in the transition-state region. Unfortu-

nately, this information is not readily available. Thus, we were

forced to resort to certain simplifying assumptions arising from the

observation that, in radical–radical reactions, there are

- two fairly well separated transition-state regions. In the

inner transition-state region, i.e., at short separations, the

spin–orbit splitting is greatly reduced, and we assumed that it

could be ignored. Thus, the interaction potential in the inner

transition-state region was taken to be that from the

CAS$^{+1+2+}$QC evaluations (which ignored the spin–orbit

splitting in defining the interaction) shifted up relative to the

ground state of the product by the base spin–orbit shift of 294

- cm$^{-1}$. In the region of the outer transition state, i.e., at large

separations, we assumed that the spin–orbit splitting was

equivalent to its asymptotic value for the Cl atom. The overall

transition-state number of states was then taken to be the

minimum of the number at large separations employing an

electronic degeneracy of 8 and the number at short separations,

where the electronic degeneracy corresponds to unity, but with

the interaction potential shifted up by the spin–orbit constant

of 294 cm$^{-1}$. A recent article by Schinke and co-workers on

the O + O$_2$ reaction provides further rationale for some of these

assumptions, as does an earlier study of the NCNO dissociation

into CN + NO.

The ambiguity in this approach is that it can depend on the

separation at which we switch from the long-range assumptions to

the short-range assumptions. For our recent study of the

reaction of various hydrocarbon radicals with an O atom, this

dependence was quite weak and yielded uncertainties on the

order of 10%. Here, however, because of the greater spin–orbit

splitting in Cl relative to that in O, this dependence is quite

strong and yields uncertainties of greater than a factor of 2 in

the estimated high-pressure rate coefficient. Here, the transition

from long-range to short-range behavior was presumed to occur

at a C–Cl separation of 4.0 Å. This separation roughly

corresponds to the location at which the bonding interactions

begin to exceed the long-range interactions and the various

electronic states begin to diverge. Furthermore, as demonstrated

below, this value also allowed for accurate modeling of the

present experimental data. However, variation of this location

by just ±0.2 Å yielded variations of nearly a factor of 2 in the

predicted high-pressure rate coefficient. Thus, the present

theoretical results cannot by themselves be taken to provide a

reliable prediction for the high-pressure rate coefficient.

Figure 1. First-order decay plot of the natural logarithm of the net
CH$_3$ signal vs time at $T = 298$ K and $P = 1.00$ Torr. [CH$_3$]$_0 = 2.92 \times 10^{14}$ molecules cm$^{-3}$, [Cl]$_{mean} = 6.21 \times 10^{12}$ atoms cm$^{-3}$, [CH$_4$]$_0 = 2.57 \times 10^{12}$ molecules cm$^{-2}$, [HCl]$_0 = 5.22 \times 10^{14}$ molecules cm$^{-3}$, $k_{corr} = 38.77$ s$^{-1}$.

The temperature- and pressure-dependent rate coefficients for

the Cl + CH$_3$ association reaction were computed from a two-

dimensional solution to the master equation involving

multistep vibrational energy transfers for the excited intermediate

(CH$_3$Cl$^*$). A more detailed description of this two-dimensional

solution was provided in our recent study of CH$_4$ dissociation.

A parametrized exponential down model of energy transfer from

CH$_3$Cl$^*$ to He was assumed because there is no suitable

a priori means for obtaining quantitative estimates for the

energy-transfer function. A Lennard-Jones model for the He/

CH$_3$Cl collision frequency was initially employed with $\sigma$ and $\epsilon$

values of 3.36 Å and 62 K, respectively. However, with these

values, the low-pressure rate tended to be too low, even for

quite large values of the average energy transferred in a single

collision. Various trajectory studies have suggested that the

Lennard-Jones model somewhat underestimates the collision

frequency. Thus, in the final analysis, we simply employed a

collision frequency given by 1.3 times that obtained from the

Lennard-Jones model. With this increase, we found, as illustrated

below, that an $\alpha_{down}$ value of 400 cm$^{-1}$ yielded rate coefficients

in best agreement with the experimental data. This value of $\alpha_{down}$

corresponds to a $\langle \Delta E_{down} \rangle$ value of 387 cm$^{-1}$ and $\langle \Delta E_{tot} \rangle$ values

of −248, −264, and −282 cm$^{-1}$ at $T = 298$, 250, and 202 K,

respectively. Notably, the data could have been equally well

modeled by increasing the density of states for CH$_3$Cl at the

dissociation threshold by about a factor of 2, to account for

possible anharmonicity corrections. Because of the small number

of vibrational modes and their high frequencies, increasing the

dissociation energy has only a modest effect on this state density.

The structures, vibrational energies, and rotational constants of

CH$_3$ and CH$_3$Cl, for use in calculating partition functions,

were taken from experimental studies. The electronic

degeneracies and a splitting of the Cl-atom $^2P_{3/2} - ^2P_{1/2}$ levels

of 882.35 cm$^{-1}$ were also used. The

Results

Figure 1 shows a typical temporal profile of the CH$_3$ signal

measured at $m/\ell = 15$ with [Cl]$_{mean} = 6.21 \times 10^{12}$ atoms cm$^{-3}$,

$T = 298$ K, and $P = 1$ Torr. The reaction time was derived
from the measured distance between the tip of the movable
injector and the pinhole and the linear velocity of the gas,
calculated from the measured pressure and gas flow rates. The
decay of CH₃ was pseudo-first-order in all cases and can be
represented by

\[
\ln [\text{CH}_3] = -k_{\text{obs}} t + \ln [\text{CH}_3]_0
\]

However, secondary chemistry effects were not negligible, so
the decays of CH₃ were corrected for these and for the effects
of both axial and radial diffusion. The data analysis for the set
of experiments at each temperature and pressure was a four-
step process. The corrections for secondary chemistry and for
axial and radial diffusion were done in separate steps, because
the computer fitting programs used could not fit the data for
both secondary chemistry and diffusion effects simultaneously.

The set of experiments for each temperature and pressure was
corrected first for secondary chemistry by a one-parameter fitting
of each CH₃ decay curve to a numerical simulation of the
reaction system using the Facsimile program. The reaction
mechanism used in the numerical simulation was the following

\[
\begin{align*}
F + \text{HCl} & \rightarrow \text{Cl} + \text{HF} \\
F + \text{CH}_4 & \rightarrow \text{CH}_3 + \text{HF} \\
\text{CH}_3 + \text{Cl} + \text{M} & \rightarrow \text{CH}_3\text{Cl} + \text{M} \\
\text{Cl} + \text{CH}_4 & \rightarrow \text{HCl} + \text{CH}_3 \\
\text{CH}_3 + \text{F}_2 & \rightarrow \text{CH}_3\text{F} + \text{F} \\
\text{CH}_3 + \text{CH}_3 + \text{M} & \rightarrow \text{C}_2\text{H}_6 + \text{M}
\end{align*}
\]

The temperature-dependent rate coefficients for reaction R1,
where chlorine atoms react with residual methane, were
calculated from the expression

\[
k_1(T) = 9.6 \times 10^{-12} \left(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\right) \exp(-1360 K/T)
\]

The expressions for the temperature-dependent rate coefficient
for reactions R3 and R4 are shown in the Experimental Section.
The rate coefficients used for the reaction of methyl radicals
with residual molecular fluorine (R6) from the microwave
discharge were calculated from the expression

\[
k_6(T) = 7.0 \times 10^{-12} \left(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\right) \exp(-490 K/T)
\]

The methyl radical self-recombination reaction (R7) is both
temperature- and pressure-dependent under the physical condi-
tions of this study. Because experimentally measured rate
coefficients are not available for all of these physical conditions,
the rate coefficients for reaction R7 were calculated using eqs
12 and 14 from ref 15a, which are shown below. The calculated
rate coefficients are listed in Table 1.

\[
k = -(k_{\text{obs}} + k_0 M) + \sqrt{(k_{\text{ obs}} + k_0 M)^2 + 4(J_{5/2} - 1)k_0 k M}
\]

\[
k_0 = 5.822 \times 10^{-28} \exp(564.54/T)
\]

\[
k_w = 4.504 \times 10^{-11} \exp(70.12/T)
\]

The pseudo-first-order rate coefficients \(k_{\text{corr}}\) derived from
the numerical simulations are corrected for secondary chemistry
except for loss of CH₃ at the wall of the flow tube and possibly
by reaction of CH₃ with excess HCl, the concentration of which
was relatively constant for all experiments. These two loss
processes can be represented by the first-order rate coefficient
\(k_w\). The second step of our data analysis determined \(k_w\),
which was needed in the correction for the diffusion effects.
The correction for axial diffusion of the methyl radical along the
flow tube was relatively simple with an analytical equation,
whereas the correction for radial diffusion of the methyl radical
to the wall of the flow tube was complex and required a
numerical solution. For the determination of \(k_w\), the pseudo-
first-order rate coefficients, \(k_{\text{first}}\), for the set of experiments
at each temperature and pressure combination were corrected
for axial diffusion by the equation:

\[
k_{\text{corr}} = k_{\text{first}}[1 + (D_{\text{CH}_3} k_{\text{first}} \nu^2)]
\]

In eq 8, \(D_{\text{CH}_3}\) is the diffusion coefficient of CH₃ in He, and
\(\nu\) is the linear velocity of the gas in the flow tube. \(D_{\text{CH}_3}\)
was estimated to be 905 cm² s⁻¹ at \(T = 298\) K and \(P = 1\) Torr
using the method of Lewis et al.\(^1\) A \(T^{3/2}\) dependence was
assumed to estimate \(D_{\text{CH}_3}\) at \(T = 250\) and 202 K, and a 1/P
dependence was assumed for pressure. The axial diffusion
dependence was less than 6% of the observed pseudo-first-order
rate coefficient for \(P = 0.3\) Torr and less than 3% in all other
cases.

The partially corrected pseudo-first-order rate coefficient is
given by

\[
k_{\text{corr}} = k_{\text{corr}} + k_w
\]

where \(k'_{\text{corr}}\) is a second-order rate coefficient for R2 that has been
corrected for secondary chemistry and axial diffusion but not
radial diffusion. The intercepts of graphs of \(k_{\text{corr}}\) versus \([\text{Cl}]\) directly yielded \(k_w\).

The third step of the data analysis corrected \(k_{\text{first}}\) for both
axial and radial diffusion. The pseudo-first-order rate coefficient,
\(k_{\text{first}}\), has been corrected only for secondary chemistry. Reference
52 presents a numerical method and a Fortran program to correct
first-order rate coefficients for both axial diffusion and radial
diffusion. The input parameters from our experiments to the
Fortran program were \(k_{\text{first}}, k_w, D_{\text{CH}_3}\), and an initial value for
the corrected first-order rate coefficient, which was 1.2\(k_{\text{first}}\); these
input parameters were in the required dimensionless format and

<table>
<thead>
<tr>
<th>(T/K)</th>
<th>(P/Torr)</th>
<th>(k_{\text{obs}}) ((\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>202</td>
<td>0.300</td>
<td>4.88</td>
</tr>
<tr>
<td>202</td>
<td>0.500</td>
<td>5.38</td>
</tr>
<tr>
<td>202</td>
<td>1.00</td>
<td>5.83</td>
</tr>
<tr>
<td>202</td>
<td>1.50</td>
<td>6.00</td>
</tr>
<tr>
<td>202</td>
<td>2.00</td>
<td>6.09</td>
</tr>
<tr>
<td>250</td>
<td>0.300</td>
<td>2.89</td>
</tr>
<tr>
<td>250</td>
<td>0.500</td>
<td>3.50</td>
</tr>
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<td>4.27</td>
</tr>
<tr>
<td>250</td>
<td>1.50</td>
<td>4.67</td>
</tr>
<tr>
<td>250</td>
<td>2.00</td>
<td>4.91</td>
</tr>
<tr>
<td>298</td>
<td>0.300</td>
<td>1.78</td>
</tr>
<tr>
<td>298</td>
<td>0.500</td>
<td>2.25</td>
</tr>
<tr>
<td>298</td>
<td>1.00</td>
<td>2.97</td>
</tr>
<tr>
<td>298</td>
<td>1.50</td>
<td>3.40</td>
</tr>
<tr>
<td>298</td>
<td>2.00</td>
<td>3.70</td>
</tr>
</tbody>
</table>
Experimental errors (assumed to be 10% for the concentration were estimated by adding in quadrature the independent in the rate coefficients are given in parentheses. The uncertainties in the rate coefficients are given in parentheses. The uncertainties were estimated by adding in quadrature the independent experimental errors (assumed to be 10% for the concentration

TABLE 2: Measured Rate Coefficients for the Cl + CH₃ Reaction

<table>
<thead>
<tr>
<th>P/ Torr</th>
<th>T/ K</th>
<th>no. of expts</th>
<th>range of [Cl] mean/1012 atoms cm⁻³</th>
<th>range of [Cl]₀/[CH₃]₀</th>
<th>k/10⁻¹² cm³ molecule⁻¹ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>202</td>
<td>9</td>
<td>3.59–16.3</td>
<td>20.4–46.1</td>
<td>8.36 ± 2.07</td>
</tr>
<tr>
<td>0.50</td>
<td>202</td>
<td>6</td>
<td>2.89–9.43</td>
<td>21.8–59.6</td>
<td>13.3 ± 1.9</td>
</tr>
<tr>
<td>1.00</td>
<td>202</td>
<td>5</td>
<td>3.31–9.97</td>
<td>18.3–46.5</td>
<td>16.3 ± 3.0</td>
</tr>
<tr>
<td>1.50</td>
<td>202</td>
<td>7</td>
<td>3.32–14.5</td>
<td>23.9–66.9</td>
<td>16.8 ± 2.7</td>
</tr>
<tr>
<td>2.00</td>
<td>202</td>
<td>6</td>
<td>3.52–8.89</td>
<td>23.4–47.9</td>
<td>17.7 ± 5.7</td>
</tr>
<tr>
<td>0.30</td>
<td>250</td>
<td>8</td>
<td>2.94–12.9</td>
<td>11.4–33.0</td>
<td>4.76 ± 1.23</td>
</tr>
<tr>
<td>0.50</td>
<td>250</td>
<td>5</td>
<td>2.19–8.97</td>
<td>17.6–50.0</td>
<td>8.12 ± 2.42</td>
</tr>
<tr>
<td>1.00</td>
<td>250</td>
<td>5</td>
<td>2.42–9.90</td>
<td>14.0–49.1</td>
<td>9.51 ± 1.34</td>
</tr>
<tr>
<td>1.50</td>
<td>250</td>
<td>6</td>
<td>2.26–10.8</td>
<td>12.1–49.4</td>
<td>13.2 ± 2.7</td>
</tr>
<tr>
<td>2.00</td>
<td>250</td>
<td>5</td>
<td>2.95–11.3</td>
<td>12.7–38.0</td>
<td>10.7 ± 1.9</td>
</tr>
<tr>
<td>0.30</td>
<td>298</td>
<td>6</td>
<td>2.31–11.2</td>
<td>9.4–26.8</td>
<td>0.744 ± 0.445</td>
</tr>
<tr>
<td>0.50</td>
<td>298</td>
<td>6</td>
<td>3.79–14.2</td>
<td>21.2–56.9</td>
<td>2.91 ± 1.34</td>
</tr>
<tr>
<td>1.00</td>
<td>298</td>
<td>14</td>
<td>2.56–14.3</td>
<td>12.1–36.6</td>
<td>4.63 ± 1.24</td>
</tr>
<tr>
<td>1.50</td>
<td>298</td>
<td>5</td>
<td>2.87–10.6</td>
<td>15.7–35.1</td>
<td>5.71 ± 1.15</td>
</tr>
<tr>
<td>2.00</td>
<td>298</td>
<td>8</td>
<td>3.15–16.5</td>
<td>15.7–51.2</td>
<td>5.27 ± 1.55</td>
</tr>
</tbody>
</table>

were within the range of parameter values which had been tested for convergence in the solutions. The output pseudo-first-order rate coefficients, kcorr, were, at that point, corrected for secondary chemistry and for both axial diffusion and radial diffusion. The correction for radial diffusion was less than 2.5% except at the two highest pressures at T = 202 K, where this correction was less than 3% for P = 1.5 Torr and less than 4% for P = 2 Torr.

These rate coefficients could be represented by the equation

\[ k_{corr} = k_2[Cl]_{mean} \]  \hspace{1cm} (10)

where \( k_2 \) is the second-order rate coefficient for R2.

In the fourth and final step of the data analysis, the slope of the graph of \( k_{corr} \) vs \([Cl]_{mean}\) yielded the bimolecular rate coefficient \( k_2 \) for the reaction of \( CH_3 + Cl \) for a given temperature and pressure. In all cases, the intercept differed from 0 by less than 1.5 s⁻¹. Figure 2 shows a plot of \( k_{corr} \) vs \([Cl]_{mean}\) for \( T = 298 K \) and \( P = 1 \) Torr. The solid line is a linear least-squares fit to the data.

Table 2 summarizes the rate coefficient measurements. The details for each experiment are included in the Supporting Information in Tables S1–S3. The experimental uncertainties in the rate coefficients are given in parentheses. The uncertainties were estimated by adding in quadrature the independent experimental errors (assumed to be 10% for the concentration of Cl, 5% for the total gas flow rate, 2% for the temperature, 2% for the pressure, and 2% for the timing) and the statistical error (1σ) from the plots of \( k_{corr} \) versus \([Cl]_{mean}\).

The CAS+1+2+QC/aug-cc-pvtz-calculated interaction between \( CH_3 \) and Cl in \( C_3v \) symmetry is illustrated in Figure 3 for the three lowest electronic states. The ground electronic state is seen to diverge from the excited electronic states at \( R \approx R\text{eq} = 4.2 \) Å. A contour plot of the interaction energies for the ground electronic state is provided in Figure 4.
This behavior of \( k_2 \) with respect to temperature suggests that the \( \text{Cl} + \text{CH}_3 \) reaction occurs without a significant barrier. This observation is in agreement with the potential energy diagrams of Figures 3 and 4.

The lines of Figure 5 are the theoretical predictions from the variational RRKM-based master-equation calculations. At the three temperatures studied, the RRKM-based rate coefficients either pass through the error bars or come very close to their termini. The experimental results at the lowest pressures approach the low-pressure limit. This low-pressure limit is determined by the density of states at the dissociation threshold, by the collision frequency, and by the collision efficiency. Here, we find that implementation of a collision frequency of 1.3 times the Lennard-Jones value and an \( \alpha_{\text{down}} \) value of 400 cm\(^{-1} \) (both of which are somewhat larger than normal, but not unreasonably so) yields good agreement with the experimental observations.

Similarly enhanced values of \( \alpha_{\text{down}} \) have been encountered in the modeling of other chlorinated reactions.\(^5^3\) Alternatively, the density of states might be somewhat increased by anharmonicities in the vibrational modes or an underestimate of the dissociation threshold.

Figure 6 shows a plot of \( k_2 \) versus the pressure of He over the pressure range 0–50 Torr. At 50 Torr He, the calculated rate coefficients are greater than 70% of the value of \( k_{2,\infty} \) at all three temperatures (\( k_{2,\infty} = 6.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) for all three temperatures). The high level of agreement between the theoretical and experimental rate coefficients over the range of pressure studied suggests that the calculated falloff curves of Figure 5 can be considered to be reasonably reliable extrapolations of the data. It is particularly difficult to reproduce the experimental data with any increase in the high-pressure-limit rate coefficient.

In a previous experimental study\(^1^3\) of the photochlorination of methane, the rate coefficient of the \( \text{Cl} + \text{CH}_3 \) reaction at \( T = 298 \pm 429 \text{ K} \) and \( P = 49 \pm 212 \text{ Torr CO}_2 \) was extracted in an indirect manner. The high-pressure limiting rate coefficient, \( k_{2,\infty} \), was found to be described by the equation \( 3.7 \times 10^{-10} \exp(-185/T) \) for \( T = 298 \pm 429 \text{ K} \). The value of \( k_{2,\infty}(298 \text{ K}) = 2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) is more than a factor of 3 higher than our calculated value (Figure 6). Because of the complex, indirect way in which Timonen et al.\(^1^3\) derived \( k_2 \), we believe the results of Timonen et al. are unreliable and should not be used.

A few experiments have also probed the dissociation of \( \text{CH}_2\text{Cl} \), but at higher temperatures (1200–2100 K).\(^5^4−5^6\) Figure 7 provides a comparison of predictions from the present theoretical model with the data from these experimental studies. The theoretical predictions for a pressure of 760 Torr are based on a \( \text{CH}_4 \) bath gas, whereas those for the other pressures are for an \( \text{Ar} \) bath gas, in keeping with the related experimental studies. In each case, a collision frequency equal to 1.3 times the Lennard-Jones values was employed for consistency with the low-temperature model. \( \alpha_{\text{down}} \) was treated as a fitting parameter, with the form \( 400[T(\text{K})/298]^{-0.5} \text{ cm}^{-1} \) providing a satisfactory reproduction of the experimental results from both refs 54 and 56. In contrast, the data from ref 55 could not be reproduced. The prediction of an increase in \( \alpha_{\text{down}} \) with temperature is in keeping with the observations from a number of related studies;\(^5^7−6^1\) however, the exponent has been closer to unity in
studies on the value of $k_1$ concluded that Cl.

Our prior studies. It is unclear whether the small magnitude of this exponent is a meaningful result or whether there is simply insufficient information to accurately determine $a_{low}$ in either the low-temperature or the high-temperature limit.

The present predictions for the CH$_3$ + Cl association rate coefficients over the 200−2000 K temperature range and the (1.0 × 10$^{-5}$)−(1.0 × 10$^{5}$) Torr pressure range were fit to the Troe form. The high-pressure limit was reproduced to within 2% by the modified Arrhenius expression

$$k_0(T) = 5.09 \times 10^{-11} \frac{(T/298)^{0.300}}{\exp(54.6/T)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where $T$ was in Kelvin for each case. The low-pressure limit was reproduced to within about 15% by the modified Arrhenius expression

$$k_0(T) = 6.27 \times 10^{-27} \frac{(T/298)^{-4.67}}{\exp(-846/T)} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

The pressure dependence was reproduced to within about 20% by the modified Arrhenius form

$$F_{cent}(T) = 0.674(T/298)^{-0.414} \exp(-38.7/T)$$

for the central broadening factor.

An experimental determination of the rate coefficient for the reaction CH$_3$ + Cl → HCl + CH$_2$ was carried out to test the discharge-flow resonance fluorescence technique for possible effects of secondary chemistry (i.e., Cl + CH$_3$ + M → ClCH$_3$ + M) below $T = 300$ K, where disagreement among previous studies on the value of $k_1$ is greatest. Wang and Keyser concluded that Cl + CH$_3$ was most likely interfering in their measurements of the rate coefficient of Cl + CH$_4$ and further stated that $k_1$(298 K, 1 Torr He) must be greater than or equal to $5 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ to interfere in measurements of $k_1$. We measured $k_1$(298 K, 1 Torr He) = 4.5 × 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Therefore, Cl + CH$_3$ + M cannot be interfering in the laboratory measurements of the Cl + CH$_4$ rate coefficient; some other explanation must be sought to reconcile the disparate low-temperature rate coefficient data for R1.

A suggestion was made recently in the literature that resonance fluorescence detection of Cl might be a deficient experimental method for measuring $k_1.$

Penson stated that Cl promoted to the 3s Rydberg state (by absorption of Cl resonance radiation near $\lambda = 139$ nm) is much more likely to dissociate than to relax to a lower electronic state, yielding CH$_3$, CH$_2$, H, and H$_2$. They concluded that reaction of Cl with these fragments would yield rate coefficients of R1 that were too large and that studies using alternative detection techniques should be carried out for a proper evaluation of $k_1$.

However, a reasonable estimate of the CH$_3$ concentration formed via photolysis of CH$_4$ by vacuum-UV radiation from a typical Cl resonance lamp (not a Cl photolysis lamp) is [CH$_3$] $\leq 3 \times 10^{10}$ molecule cm$^{-3}$. This is 5 orders of magnitude less than the typical CH$_3$ concentration employed in either photolysis or flow-tube studies. The ratio of the low-temperature rate coefficients for the two reactions is $k_1$(CH + CH$_3$)/$k_1$(Cl + CH$_3$) $\approx 10^{-3}$. Thus, the contribution of Cl + CH$_3$ (where CH$_3$ is formed via photolysis of CH$_4$ by a Cl resonance lamp) to the loss of Cl via Cl + CH$_3$ is on the order of 1% and is negligibly small.

Finally, we assess the results of an experimental study of the measurement of rate coefficients for the related reaction CH$_3$ + Br + He → CH$_3$Br + He at $T = 297$ K over the pressure range of 1−100 bar helium. Using the relative-rate method (relative to CH$_3$ + CH$_4$) and the laser photolysis−transient UV spectroscopy technique, the authors found that the rate coefficient is in the falloff regime over this very large and very high pressure range. They found that the high-pressure limiting rate coefficient is $1.19 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at $T = 297$ K. The observation of a pressure dependence above 1 bar for this analogous reaction is very different from our theoretical results (and not consistent with our experimental results) for CH$_3$ + Cl. From our theoretical results, $k_2$(298 K) is 70% of the value of $k_{2,w}$ at 50 Torr and $k_2 = 0.99k_{2,w}$ at 1 bar. The large difference in the pressure dependence of the rate coefficient for these two reactions is difficult to reconcile. The very large pressures required to stabilize the CH$_3$Br$^+$ adduct imply that this species is formed with much more internal energy than CH$_3$-Cl$^+$. For this to be true, the potential energy surface for CH$_3$ + Br and/or the location of the transition state on the reaction coordinate would have to be very different from those for the CH$_3$ + Cl reaction. We recommend additional experimental and theoretical studies for CH$_3$ + Br + M → CH$_3$Br + M.

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**Supporting Information Available:** For each experiment, the concentration of each reactant and the corrected first-order