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Rate Constants for the Reactions of Chlorine Atoms with Deuterated Methanes: Experiment and Theory[†]

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Long-path FTIR spectroscopy and ab initio calculations combined with conventional transition state theory were used to study the kinetics of the reactions of Cl atoms with deuterated methanes. The following experimental relative rate constants for the reaction of Cl atoms at 298 ± 5 K and 760 ± 5 Torr were determined: CH_3D, $(6.5 \pm 0.5) \times 10^{-14}$; CH_2D_2, $(4.2 \pm 0.5) \times 10^{-14}$; CHD_3, $(1.9 \pm 0.3) \times 10^{-14}$; CD_4, $(5.4 \pm 0.4) \times 10^{-15}$. All experimental and theoretical rate constants are in units of cm^3 $molecule^{-1}$ s^{-1} and are relative to the 1.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1} rate constant for the reaction of Cl with CH_4. All experimental uncertainty limits are 2σ. The geometries, energies, and frequencies of the reactants, products, and transition states were calculated at the level of the second-order Møller−Plesset approximation using a 6-311++G-(2d,2p) basis set. The following theoretical relative rate constants were calculated at 298 K using conventional transition state theory combined with an Eckart one-dimensional tunneling correction: CH_3D, 6.8×10^{-14}; CH_2D_2, 4.2×10^{-14}; CHD_3, 2.1×10^{-14}; CD_4, 4.4×10^{-15}. The theoretical rate constants agree well with the experimental results. The curvature in both the experimental and theoretical rate constants as a function of deuteration is due to a secondary kinetic isotope effect, involving mainly the rate constant preexponential factors. The large decrease in Cl atom rate constant in going from CH_4 to CH_3D (i.e., the increase in curvature at CH_3D) is due to the reduced symmetry in the transition state and a mass-dependent effect. The implications for previous studies, atmospheric chemistry, and chemical reactivity are discussed.

Introduction

Methane and atomic chlorine are important constituents of Earth's atmosphere.[1] Methane is a greenhouse gas, and it plays a large role in controlling the OH radical concentration and the oxidizing potential of the atmosphere. Atomic chlorine catalyzes stratospheric ozone destruction and may also be a significant oxidizer in the lower marine troposphere. The reaction of Cl atoms with CH_4 limits Cl atom destruction of ozone in the stratosphere. This reaction proceeds via an abstraction reaction with a well characterized rate constant of 1.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K.[2]

The reactions of Cl atoms with deuterated methanes are of interest for several reasons. Isotopic field studies, both $^{12/13}C$ and H/D, are used to elucidate the sources of methane.[3,4] A necessary criterion for such studies is that the rate constants for the loss of the isotopic species, $^{13}CH_4$ and CH_3D, must be accurately known. In addition, an accurate rate constant for the reaction of Cl atoms with CD_4 is important because it has been used as a reference reaction in a previous relative rate study[5] and because CD_4 has been used as an atmospheric tracer.[6] Moreover, the determination of the rate constants for the reactions of chlorine atoms with the entire series of deuterated methanes provides a test of our knowledge of fundamental chemical kinetics.

Although there have been seven previous experimental studies involving the measurement of one or more of the rate constants for the reactions of Cl atoms with the deuterated methanes, there still is some disagreement over these values. In only one study, by Wallington and Hurley, were all of the rate constants of the reactions of Cl atoms with the deuterated methanes measured.[5] The rate constants decrease as deuteration increases due to a primary kinetic isotope effect (KIE), i.e., the activation energy for the breaking of a C−D bond is greater than that of a C−H bond due to the lower zero-point energy (ZPE) of the more deuterated methane. The KIE is defined as the rate constant for the lighter isotope divided by the rate constant for the heavier isotope. In the last 5 years, there appears to be experimental consensus on the value of the rate constant for the reactions of Cl atoms with CH_3D, due to an adjustment in Wallington and Hurley's value and two recent rate studies that employed two different relative rate methods.[7,8] However, the absolute rate constant measurements of Matsumi et al. cast doubt on this consensus.[9] Their rate constants for Cl + CH_4 and Cl + CD_4 are consistent with past work; however, their rate constant for Cl + CH_2D_2 is 50% larger than that of Wallington and Hurley[5] and is actually larger than the measured rate constants for Cl + CH_3D.[5,7,8] The rate constant for Cl + CHD_3 has been measured once,[5] and a range of values has been obtained for Cl + CD_4 beginning with the study by Chiltz et al. in 1963.[5,9−12]

Theoretical studies of the reactions of Cl atoms with deuterated methanes are limited. Only one ab initio study has been reported, in which the KIE for Cl + CH_4/CH_3D was calculated using transition state theory (TST).[9] Several semiempirical calculations (ab initio calculations with empirical corrections) have been performed using variational transition state theory (VTST).[13−16] Among the ab initio and semiempirical

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methods, significant discrepancies exist for the rate constants for Cl + CH_3D and Cl + CD_4; the rate constant for Cl + CH_2D_2 has only been calculated once; and the rate constant for the reaction of Cl + CHD_3 has not been reported. Empirical bond energy-bond order (BEBO)/TST calculations have also been performed.[9,12,17] Significant contributions were made by Johnston in the 1960s to both the kinetics of Cl + CH_4/CD_4 and to transition state theory.[12,18,19] The recent empirical calculations by Matsumi et al.[9] are the only previous study to calculate the KIE for the reactions of Cl atoms with all of the deuterated methanes; however, their values are systematically lower than the other theoretical calculations and are in disagreement with most experimental values.

Given the importance of the Cl + deuterated methane reactions and the disagreement among the experimental studies, we have conducted a relative rate study of the reaction of Cl atoms with the entire series of deuterated methanes using long-path FTIR spectroscopy. To explain the nonlinear dependence of our experimental rate constants as a function of deuteration and provide the first complete set of ab initio calculations on this system of reactions, we have also calculated the relative rate constants for the reactions of Cl atoms with deuterated methanes using high level ab initio calculations, transition state theory, and Wigner and Eckart one-dimensional tunneling corrections. The experimental work will be discussed first, followed by the theoretical work.

Experimental Section

A. Method. The measurement of Cl atom relative rate constants using an FTIR with a long path cell has been described previously.[20,21] The experimental method will be briefly described here, along with changes specific to this study. A Mattson Instruments Galaxy 7000 Series FTIR with a deuterated triglycine sulfate detector, a spectral resolution of 0.25 cm^{-1}, boxcar apodization, and 12-scan signal averaging was used. The 1 m-, 18 L-borosilicate long path cell (Infrared Analysis) was adjusted for a 24 m path length and coated with halocarbon wax to minimize wall reactions. The photolysis of chlorine was initiated by 8 blacklights (Sylvania, BL350) surrounding the long path cell and encased in a highly reflective aluminum housing.

Chlorine atoms produced by the UV photolysis of Cl_2 reacted with a reactant gas (CH_3D, CH_2D_2, CHD_3, or CD_4) and a reference gas (CH_4 or ^{13}CO):

$$CH_3D + Cl \rightarrow CH_2D + HCl \text{ or } CH_3 + DCl \qquad (1)$$

$$CH_2D_2 + Cl \rightarrow CHD_2 + HCl \text{ or } CH_2D + DCl \qquad (2)$$

$$CHD_3 + Cl \rightarrow CD_3 + HCl \text{ or } CHD_2 + DCl \qquad (3)$$

$$CD_4 + Cl \rightarrow CD_3 + DCl \qquad (4)$$

$$CH_4 + Cl \rightarrow CH_3 + HCl \qquad (5)$$

$$^{13}CO + Cl + M \rightarrow Cl^{13}CO + M \qquad (6)$$

The loss of reactants was monitored as a function of time using an FTIR. The following IR absorbance peaks were monitored for each gas (in cm^{-1}): (CH_4) 3149, 3139, 3131; (CH_3D) 2266, 2259, 2252, 2244, 1329; (CH_2D_2) 1196, 1190; (CHD_3) 2973, 2951, 2912; (CD_4) 2214, 2205, 1009, 1006; and ($^{13}C^{16}O$) 2029, 2016. Total photolysis times ranged from 3 to 10 min depending on initial concentrations of the reactants, with ultraviolet lights on for increments of 20 s to 1 min. Losses of the reactant and reference gases over the course of the reaction ranged from 25% to 80%. The absorbances of the individual reactant and references gases as a function of reactant or reference gas pressure were found to be nonlinear for some of the gases. Consequently, these calibration curves were used to convert measured reactant and reference absorbances into pressures. The growth of the HCl and DCl products, although observable, could not be accurately quantified due to interactions with the halocarbon wax on the walls of reaction cell. Reactions using CH_4 as the reference gas were run in 1 atm of ultrapure nitrogen, while reactions using ^{13}CO as a reference gas were run in 1 atm of ultrapure air. Tests were periodically conducted to check for dark reactions, photolysis of the reactants, and reactions occurring in the absence of Cl_2. No loss of reactants was ever observed.

The relative rate method was employed to determine the Cl + CH_xD_y rate constant values. Provided that the only significant loss processes for the reactant gas, CH_xD_y, and the reference gas, CH_4 or ^{13}CO, is reaction with Cl, and neither the CH_xD_y nor the reference gas is formed during the reaction, it can be shown that[1]

$$\ln\left\{\frac{[\text{react}]_0}{[\text{react}]_t}\right\} = \frac{k_{\text{react}}}{k_{\text{ref}}}\ln\left\{\frac{[\text{ref}]_0}{[\text{ref}]_t}\right\} \qquad (7)$$

where $[\text{react}]_0$ and $[\text{ref}]_0$ are the concentrations of reactant and the reference gas at time $t = 0$, $[\text{react}]_t$ and $[\text{ref}]_t$ are the concentrations at time t, and k_{react} and k_{ref} are the rate constants for the reactions of Cl with the reactant and reference gases. Thus, a plot of $\ln([\text{react}]_0/[\text{react}]_t)$ versus $\ln([\text{ref}]_0/[\text{ref}]_t)$ yields a straight line with a slope of $k_{\text{react}}/k_{\text{ref}}$. From the slope and the literature value for k_{ref}, the value of k_{react} is determined. The rate constant values for the reference gas reactions are 1.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1} for Cl + CH_4[2] and 3.2×10^{-14} cm^3 $molecule^{-1}$ s^{-1} for Cl + ^{13}CO, the observed rate constant for loss of ^{13}CO in the presence of CH_4 and 1 atm of air.[20]

Cl_2 (99.5% purity) and CH_4 (99.97% purity) were obtained from Matheson. CH_3D, CH_2D_2, and CHD_3 (all 98% isotopic purity), CD_4 (>99.6% isotopic purity), and $^{13}C^{16}O$ (99.1% ^{13}C, 99.95% ^{16}O) were obtained from Isotec. Ultrapure air and ultra zero nitrogen were obtained from Scott-Marin. CH_4 and CD_4 were purified three times by the freeze−pump−thaw method using liquid nitrogen. CH_3D, CH_2D_2, and CHD_3 were used as supplied by the manufacturer. ^{13}CO was purified by slowly flowing through a liquid N_2 trap. Ultrapure air was purified by slowly flowing through a methanol/N_2 slush to remove trace amounts of N_2O. The temperature and total pressure were maintained at 298 ± 5 K and 760 ± 5 Torr.

B. Results. Rate constants for the reactions of Cl atoms with the deuterated methanes were determined using the relative rate method. Typical relative rate plots are shown in Figure 1. Rate constants for the reactions of Cl atoms with CH_3D, CH_2D_2, and CHD_3 were determined relative to the rate constant for the reaction of Cl with CH_4 (1.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1}).[2] The rate constant for the reaction of Cl atoms with CD_4 was determined relative to the rate constant for the reaction of Cl atoms with ^{13}CO (3.2×10^{-14} cm^3 $molecule^{-1}$ s^{-1}).[20] The ratio of reactant to reference gas was varied by about a factor of 4 in each case. No trends in the measured rate constants were observed while varying the experimental conditions. Furthermore, the intercepts of the relative rate plots consistently averaged about zero. The Cl atom rate constants were determined to be 6.5 ± 0.5 (CH_3D), 4.2 ± 0.5 (CH_2D_2), 1.9 ± 0.3 (CHD_3), and 0.54 ± 0.04 (CD_4) × 10^{-14} cm^3 $molecule^{-1}$ s^{-1}.

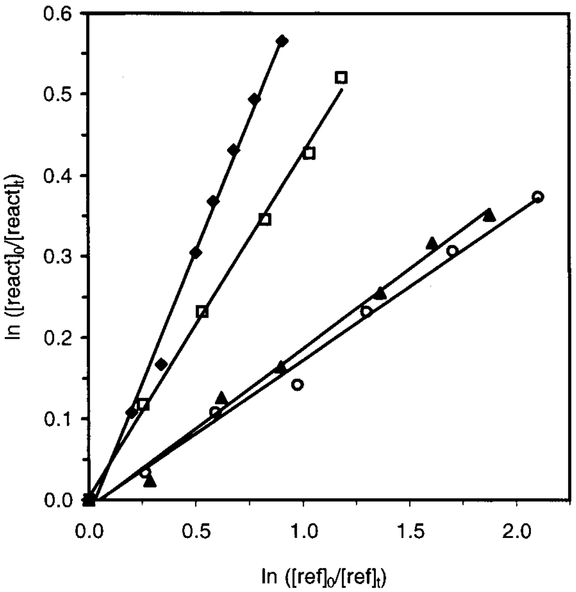

Figure 1. Typical relative rate plots for the reactions of Cl atoms with the deuterated methanes: (a) CH_3D reactant, CH_4 reference, solid diamonds; (b) CH_2D_2 reactant, CH_4 reference, open squares; (c) CHD_3 reactant, CH_4 reference, solid triangles; (d) CD_4 reactant, ^{13}CO reference, open circles. Solid lines are linear least-squares fits to the experimental data.

TABLE 1: Summary of Experimental Conditions and Measured Cl Atom Rate Constants

reactant	[reactant][a]	reference	[reference][a]	[Cl_2][a]	k^b
CH_3D	125−194[c]	CH_4	60−102	145−526	6.5 ± 0.5
	101−133[d]	^{13}CO	131−155	328−388	5.2 ± 0.8
CH_2D_2	173−269[c]	CH_4	54−88	150−555	4.2 ± 0.5
	84−129[d]	^{13}CO	88−134	410−455	3.4 ± 0.5
CHD_3	198−330[c]	CH_4	47−120	195−519	1.9 ± 0.3
	103−124[d]	^{13}CO	88−108	298−485	1.8 ± 0.4
CD_4	81−160[c]	^{13}CO	80−158	213−552	0.54 ± 0.04
	152−216[d]	CH_2D_2	96−201	354−425	0.56 ± 0.16

[a] Units: mTorr. [b] Units: 10^{-14} cm^3 molecule^{-1} s^{-1}. Error limits: $\pm 2\sigma$. [c] First row for each reactant represents the primary data. [d] Second row for each reactant represents the cross check data.

Each rate constant is the average of 10 to 12 relative rate runs. Within each run, the results of the relative rate plots for individual absorbance lines were averaged together. The uncertainties represent 2σ and are derived solely from the scatter in the data.

A small correction was applied to the experimentally measured Cl + CD_4 rate constant to obtain the value quoted in the previous paragraph because, when Cl atom reactions are run in air, OH/OD radicals may be formed and adversely affect the relative rate constant measurement.[20−22] The secondary reaction of the methyl radical with oxygen leads to the production of hydroxyl radicals. If the hydroxyl radical has a significant rate of reaction with the reactant and/or reference gas, then the relative rate measurement may be compromised. In this study, only the rate constants measured relative to Cl + ^{13}CO would be affected because only those experiments were performed in air (there is no net Cl + CO reaction in the absence of oxygen).[20] If the hydroxyl radical interference is significant, a curved relative rate plot will often be observed. Some of our experimental relative rate plots were slightly curved upward while others were slightly curved downward, but there was no consistent trend. However, kinetic modeling studies using ACUCHEM[23] and a modified version of a published reaction scheme[20] predicted a small increase in the net loss of CD_4 due to reaction with OD radicals. The modified scheme assumes that the secondary chemistry rate constants for all deuterated species, unless otherwise known, were identical to that of the corresponding nondeuterated species. Using the results from this model and previous experimental results,[20,21] a −2.4% correction was applied to the experimentally measured Cl + CD_4 rate constant. Note that this correction is much smaller than the precision of the measurements.

The experimentally determined rate constants were also measured relative to a second reference gas to ensure the accuracy of our measurements. The rate constants for the reaction of Cl with CH_3D, CH_2D_2, and CHD_3 were measured relative to Cl + ^{13}CO. The rate constant for the reaction of Cl with CD_4 was measured relative to Cl + CH_2D_2. A summary of the measured rate constants, the cross checks, and experimental conditions is given in Table 1. Each cross check measurement was performed 3−6 times. Using ACUCHEM modeling, the rate constants for the reactions of Cl with CH_3D, CH_2D_2, and CHD_3 were corrected by −4.9%, −4.6%, and −3.6%, respectively, to account for hydroxyl radical interference (these corrections are smaller than the precision of the measurements). The experimental rate constants and cross checks for Cl + CHD_3 and Cl + CD_4 are within 5% of each other. The cross checks for Cl + CH_3D and CH_2D_2 are about 20% slower than the measurements made relative to Cl + CH_4. Although this discrepancy is outside the 2σ uncertainty limits of our measurements, it is within the typical accuracy of rate constant measurements (our uncertainty limits were derived solely from the scatter in our data). Given that the Cl + CH_4 rate constant[2] is probably more accurate than the Cl + ^{13}CO value,[20,24] that the measurements relative to Cl + CH_4 did not involve OH/OD interferences, and that more experiments were performed using CH_4 as a reference gas, we will focus on the rate constants measured relative to Cl + CH_4 in the rest of this article.

To further check the accuracy of our relative rate constant measurements, several additional tests were run. The rate constant of Cl + ^{13}CO relative to Cl + CH_4 in 1 atm of air was determined to be (3.2 ± 0.6) × 10^{-14} cm^3 molecule^{-1} s^{-1}, identical to the previously determined value.[20] In addition, relative rate plots using different absorbance lines of the same gas should yield a slope of 1. An average of 21 of these plots, including plots for each of the deuterated methanes, gave a slope of 1.01 ± 0.14 (2σ). To check for possible interferences due to impurities, the relative rate constants for Cl + CH_2D_2 and Cl + CD_4 were measured with and without purification of the deuterated methane. No significant change in rate constant was observed.

C. Discussion. A comparison of our experimentally measured rate constants with those of other groups is shown in Table 2. Our relative rate constants are in good agreement with the recent relative rate studies of Tyler et al.,[7] Saueressig et al.,[8] and Wallington and Hurley.[5] Only Wallington and Hurley's Cl + CHD_3 rate constant lies outside of our combined error limits; however, it lies just outside the limits. Given our large uncertainty limits, we do not consider our lower rate constant values to be significantly different from the other recent relative rate studies. Tyler et al. measured the CH_4/CH_3D kinetic isotope effect (KIE) by monitoring the change in isotopic composition of CH_4 samples during Cl atom reactions using isotope ratio mass spectrometry and the Rayleigh equation. Saueressig et al. performed similar measurements using tunable diode laser absorption spectroscopy. In addition, they measured the Cl + CH_3D rate constant relative to Cl + CH_4 using an FTIR

TABLE 2: Comparison of Experimental Cl Atom Rate Constants with Literature Values

reactant	k (305 K − 295 K)[a]	technique[b]	reference
CH_3D	$(6.5 \pm 0.5)^c \times 10^{-14}$	FTIR	this work
	$(6.78 \pm 0.09)^c \times 10^{-14}$	IRMS	Tyler et al., 2000[7]
	$(6.72 \pm 0.02)^c \times 10^{-14}$	FTIR	Saueressig et al., 1996[8]
	$(6.63 \pm 0.03)^c \times 10^{-14}$	TDLAS	Saueressig et al., 1996[8]
	$(6.80 \pm 0.03)^{c,d} \times 10^{-14}$	FTIR	Wallington and Hurley, 1992[5]
CH_2D_2	$(4.2 \pm 0.5)^c \times 10^{-14}$	FTIR	this work
	$(7.0 \pm 0.8) \times 10^{-14}$	LIF	Matsumi et al., 1997[9]
	$(4.57 \pm 0.22)^c \times 10^{-14}$	FTIR	Wallington and Hurley, 1992[5]
CHD_3	$(1.9 \pm 0.3)^c \times 10^{-14}$	FTIR	this work
	$(2.32 \pm 0.05)^c \times 10^{-14}$	FTIR	Wallington and Hurley, 1992[5]
CD_4	$(5.4 \pm 0.4)^e \times 10^{-15}$	FTIR	this work
	$(8.2 \pm 1.0) \times 10^{-15}$	LIF	Matsumi et al., 1997[9]
	$(6.1 \pm 0.5)^c \times 10^{-15}$	FTIR	Wallington and Hurley, 1992[5]
	$(6.2 \pm 0.2)^c \times 10^{-15}$	MS	Strunin et al., 1975[10]
	$(7.4 \pm 0.9)^c \times 10^{-15}$	DF-MS	Clyne and Walker, 1973[11]
	$(9.2 \pm 0.9)^c \times 10^{-15}$	MS	Chiltz et al., 1963[12]

[a] Units: cm^3 $molecule^{-1}$ s^{-1}. Error limits: 2σ. [b] FTIR = Fourier transform infrared spectroscopy, IRMS = isotope ratio mass spectrometry, TDLAS = tunable diode laser absorption spectroscopy, LIF = laser-induced fluorescence, DF-MS = discharge flow mass spectrometry, MS = mass spectrometry. [c] Relative to the $Cl + CH_4$ rate constant of 1.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1}. [d] Revised rate constant value reported in ref 8. Original value was $(7.35 \pm 0.02) \times 10^{-14}$. [e] Relative to the $Cl + {}^{13}CO$ rate constant of 3.2×10^{-14} cm^3 $molecule^{-1}$ s^{-1}.

spectrometer. Wallington and Hurley measured all of the $Cl + CH_xD_y$ rate constants relative to $Cl + CH_4$ using an FTIR spectrometer. Recently, Wallington and Hurley adjusted their reported relative rate constant for $Cl + CH_3D$ from 7.4×10^{-14} cm^3 $molecule^{-1}$ s^{-1} to 6.80×10^{-14} cm^3 $molecule^{-1}$ s^{-1},[8] bringing it into better agreement with Tyler et al., Saueressig et al., and the present work. Although the present work also involved measuring relative rate constants using an FTIR spectrometer, the initial concentrations, the absorbance lines monitored, the FTIR resolution (compared to Saueressig et al.), and the reference gas used for $Cl + CD_4$ were different from the previous FTIR relative rate studies.[5,8]

From Table 2 it is clear that the absolute rate constant values reported by Matsumi et al.[9] are not in agreement with the present work nor with the other recent relative rate studies. Matsumi et al. used laser-induced fluorescence (LIF) to measure absolute Cl atom rate constants. Their reported value for $Cl + CH_4$ is in excellent agreement with the JPL/NASA recommended value.[2] However, their value for $Cl + CH_2D_2$ is more than 50% larger than the present work and that of Wallington and Hurley.[5] In addition, if their $Cl + CD_2H_2$ value was correct, then all of the measured rate constants for $Cl + CH_3D$ (see refs 5, 7, and 8 and this work) would have to be incorrect because increasing deuteration should lower the rate constant value for an abstraction reaction due to the kinetic isotope effect (lower zero-point energy leads to a higher activation energy for reaction). This discrepancy is probably due to impurities in the gases used by Matsumi et al. None of their gases were purified. Given the slow rate constant values being measured, even a trace impurity with a large Cl atom rate constant will significantly lower the Cl atom concentration, giving the appearance of a faster rate constant. Gierczak et al. analyzed the impurities in deuterated methane gas bottles supplied by Isotec (the supplier of Matsumi et al.'s deuterated methane) and found significant amounts of ethane, ethene, and propene in CH_2D_2 gas,[25] all of which have large Cl atom rate constants.[24,26] Assuming a $Cl + CH_2D_2$ rate constant of 4.2×10^{-14} cm^3 $molecule^{-1}$ s^{-1}, the level of CH_2D_2 impurities observed by Gierczak et al., and the pressures used by Matsumi et al., an absolute rate constant about 50% higher than the true value would be measured. The $Cl + CH_4$ rate constant value measured by Matsumi et al. was not affected because of the faster $Cl + CH_4$ rate constant and much higher CH_4 purity level. Note that this type of error will not be observed in relative rate studies, because these stable impurities have negligible rates of reaction with the reactant and reference gases and do not lead to the production of the reference and reactant gases. In addition, Matsumi et al.'s rate constant value for $Cl + CD_4$ is more than 30% larger than the present work and that of Wallington and Hurley. Although within the range of all the measured $Cl + CD_4$ rate constant values, this larger rate constant may also be due to impurities (but cannot be accounted for by the impurities found in CD_4 by Gierczak et al.).

In contrast to the other $Cl + CD_4$ relative studies,[5,10−12] we chose not to use CH_4 as the main reference gas because its Cl atom rate constant differs by more than a factor of 15 from that of CD_4. Instead, we used the $Cl + {}^{13}CO$ reaction, with a rate constant about a factor of 5 larger, as our main reference gas. The advantage of doing this was to increase the accuracy and precision of our relative rate measurement. On the other hand, the disadvantage was that the $Cl + {}^{13}CO$ rate constant is not as well characterized as the rate constant for $Cl + CH_4$. However, our $Cl + CD_4$ rate constant value is in good agreement with our cross check experiments which employed CH_2D_2 as the reference gas. Our $Cl + CD_4$ rate constant is also in good agreement with the value of Wallington and Hurley,[5] but significantly lower than the values obtained by Clyne and Walker[11] and by Chiltz et al.[12] Assuming the Cl + HCFC/HFC rate constant ratios measured by Wallington and Hurley relative to $Cl + CD_4$ are correct, we used the NASA/JPL recommended values[24] for the Cl + HCFC/HFC rate constants to calculate an average $Cl + CD_4$ rate constant of $(6.4 \pm 1.4) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}. This comparison suggests that our $Cl + CD_4$ rate constant is reasonable and that the value reported by Chiltz et al. is probably too large.

Our measured rate constants decrease nonlinearly with increasing deuteration (see Figure 2). This is in agreement with Wallington and Hurley's study of the Cl + deuterated methane series (both with and without the adjusted $Cl + CH_3D$ rate constant value)[5,8] and with the recent $Cl + CH_3D$ rate constant measurements which all show more than a 25% drop in the rate constant value in going from CH_4 to CH_3D.[7,8] The rate constant results of Matsumi et al. also show a nonlinear dependence but in the opposite direction (concave downward instead of upward).[9] This discrepancy is probably due to impurities, as discussed previously. Due to the high cost of deuterated gases, it is common practice to measure the rate constants for the reaction of a radical with only the nondeuterated and perdeuterated species, and then calculate the rate constants for reaction with the partially deuterated species assuming a linear dependence of the rate constant with deuteration. As shown in the equation below for the Cl + deuterated methane reactions, this implies that the rate constants for the

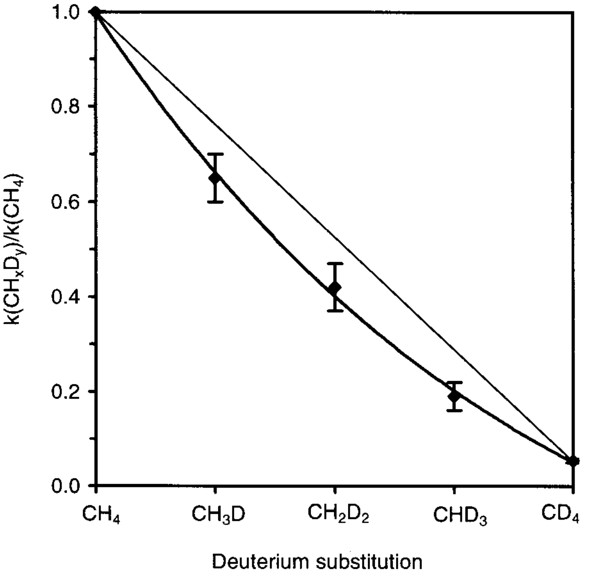

Figure 2. Dependence of the Cl atom rate constant ratio k(CH_xD_y)/k(CH_4) on deuterium substitution. Experimental results are represented by solid diamonds with 2σ error bars. A curved line fit to the data and a straight line between CH_4 and CD_4 are drawn to emphasize the curvature in the experimental data.

abstraction of a H and a D atom do not depend on the extent of deuteration.

$$k(\mathrm{Cl} + \mathrm{CH}_x\mathrm{D}_y) = \frac{x}{4}k_\mathrm{H} + \frac{y}{4}k_\mathrm{D} \tag{8}$$

However, clearly for the Cl + deuterated methane reactions, this is not the case. Thus, one should proceed with caution when making this approximation, especially in cases where the KIE needs to be known to a high degree of accuracy. To better understand the nonlinear dependence of the rate constant with deuteration, ab initio and conventional transition state calculations were performed, as described in the theoretical section.

The measurement of isotopic abundances of atmospheric species can be used to differentiate between different sources and to quantitate source strength. Budget studies of the greenhouse gas methane involve measuring the abundances of $^{13}CH_4$ and/or CH_3D. The KIE value at 298 K for OH radicals reacting with CH_4/CH_3D is 1.2[25,27] and with $^{12/13}CH_4$ is 1.0054.[28] The KIE value at 298 K for Cl atoms reacting with CH_4/CH_3D is 1.5 (see refs 5, 7, and 8 and this work) and with $^{12/13}CH_4$ is 1.06.[7,29,30] The H/D KIE is much larger than the $^{12/13}C$ KIE because primary KIEs are larger than secondary KIEs. Thus, the reaction of Cl with CH_4/CH_3D has the potential for larger fractionation (depletion of the lighter methane isotope) in the troposphere and should be distinguishable from OH induced fractionation. However, given the long lifetime of methane (~10 years) and the small Cl to OH concentration ratio in the troposphere,[1,24] the CH_4/CH_3D fractionation of methane in the troposphere will probably not be significantly affected by the reaction of Cl atoms with methane. The converse situation arises in the stratosphere. At the coldest temperatures, about 225 K in the lower stratosphere, the Cl KIE (1.59)[8] is similar to the OH KIE (1.57).[25] Consequently, differences in CH_4/CH_3D fractionation due to Cl atom versus OH radical reaction will become more difficult to distinguish. On the other hand, given the increased Cl atom KIE at colder temperatures and the larger Cl to OH concentration ratio,[24] a significant portion of the CH_4/CH_3D fractionation in the stratosphere will be due to Cl atom reactions. In addition, Cl atom fractionation of CH_4/CH_3D will also affect the fractionation of H_2O/HDO and H_2/HD in the stratosphere,[31] as has already been observed in the case of Cl atom fractionation of $^{12/13}CH_4$ affecting $^{12/13}CO$ fractionation in the stratosphere.[32-34]

Theoretical Section

A. Method. Ground-state equilibrium geometries, energies, and vibrational frequencies of the reactants, products, and transition states of the reaction of chlorine atoms with methane were calculated using ab initio methods. The corresponding harmonic frequencies were calculated for the deuterated methane reactions. The following basis sets were used to confirm the convergence of the calculated results: 6-311G(d,p), 6-311++G(d,p), and 6-311++G(2d,2p). The results from the 6-311++G(2d,2p) basis set are reported here. Electron correlation was taken into account by using second-order Møller−Plesset (MP2) perturbation theory. Higher level electron correlation was also considered in some calculations using quadratic configuration interaction including single and double excitations, QCISD. Spin contamination was found to be negligible in all calculations, as the calculated value of $\langle s^2 \rangle$ was within the range 0.750−0.785 compared to the expected value of 0.75. Density functional theory calculations were also attempted. However, we were unable to find stable transition state structures using this method, consistent with the report by Duncan and Truong on the Cl + CH_4 system.[35] All ab initio calculations were carried out using Gaussian 94.[36]

The rate constants for the reactions of Cl atoms with deuterated methanes were calculated relative to the rate constant for the reaction of Cl atoms with methane using conventional transition state theory (TST). The rate constant k is given by the following expression:[18,37-39]

$$k = \Gamma \frac{k_\mathrm{B}T}{h} \frac{Q^\ddagger}{Q_\mathrm{A}Q_\mathrm{B}} e^{-E_\mathrm{a}/k_\mathrm{B}T} \tag{9}$$

where Γ is a tunneling correction factor, k_B is Boltzmann's constant, T is the temperature, h is Planck's constant, Q and $Q^\ddagger$ represent the total partition functions for the reactants and transition state, respectively, and E_a is the activation energy including zero-point energy. The total partition function Q can be written as the product of the electronic, vibrational, rotational, and translational partition functions. The rigid rotor and harmonic oscillator approximations were used to calculate the rotational and vibrational partition functions, respectively (since the smallest vibrational frequency was 275 cm^{-1}, none of the vibrational frequencies were treated as hindered rotors). Two different one-dimensional tunneling corrections were applied to the TST results. The Wigner tunneling correction factors were calculated using the following equation:[40]

$$\Gamma = 1 + \frac{1}{24}\left|\frac{\mathrm{h}\nu^\ddagger}{k_\mathrm{B}T}\right|^2 \tag{10}$$

where $\nu^\ddagger$ is the imaginary frequency of the transition state. The Eckart tunneling correction factors were calculated using the imaginary frequency of the transition state, an unsymmetrical Eckart barrier function characterized by the zero-point corrected activation energies in the forward and reverse directions, and a composite Newton−Cotes quadrature (Boole's law) numerical analysis.[18,19,41-44] For each partially deuterated methane, rate constants for the abstraction of a H atom, k_H, and the abstraction of a D atom, k_D, were calculated separately and then combined to determine the overall rate constant for the reaction using a statistical factor to represent the number of abstractable atoms

TABLE 3: Optimized Structures of the Reactants, Products, and Transition State Using MP2/and QCISD/6-311++G(2d,2p)

molecule	parameter	MP2[a]	QCISD[a]	exptl[a]
HCl ($C_{\infty v}$)	r(HCl)	1.270	1.272	1.275[45]
CH_3 (D_{3h})	r(CH)	1.073	1.077	1.079[46]
CH_4 (T_d)	r(CH)	1.084	1.087	1.091[46]
H_3C-H_x-Cl (C_{3v})	$r(CH_x)$	1.377	1.412	
	$r(H_xCl)$	1.450	1.450	
	r(CH)	1.079	1.081	
	$\angle(HCH_x)$	101.4	101.4	

[a] Bond lengths in angstroms, bond angles in degrees.

TABLE 4: Harmonic Vibrational Frequencies for HCl, CH_3, CH_4, and the $H_3C-H-Cl$ Transition State Using MP2/6-311++G(2d,2p)

molecule	mode	calculated (cm^{-1})	exptl (cm^{-1})
HCl	σ	3004	2991[45]
CH_3	a_1'	3178	3002[46]
	a_2''	470	580
	e'	3368	3184
	e'	1453	1383
CH_4	a_1	3084	2917[46]
	e	1595	1534
	t_2	3212	3019
	t_2	1370	1306
$H_3C-H-Cl$	e	385	
	a'	512	
	e	971	
	a'	1212	
	e	1458	
	a'	3134	
	e	3302	
	a'	1274i	

TABLE 5: Zero-Point Energy-Corrected Activation Energies(E_a) and Reaction Energies (ΔH_0) for the Cl + CH_xD_y Reactions Using MP2/6-311++G(2d,2p)

reaction	E_a[a]	ΔH_0[a]
CH_4 + Cl → CH_3-H−Cl → CH_3 + HCl	5.152	1.258
CH_3D + Cl → CH_2D-H−Cl → CH_2D + HCl	5.155	1.471
CH_2D_2 + Cl → CHD_2-H−Cl → CHD_2 + HCl	5.163	1.688
CHD_3 + Cl → CD_3−H−Cl → CD_3 + HCl	5.177	1.911
CH_3D + Cl → CH_3−D−Cl → CH_3 + DCl	6.299	1.909
CH_2D_2 + Cl → CH_2D-D−Cl → CH_2D + DCl	6.328	2.152
CHD_3 + Cl → CHD_2-D−Cl → CHD_2 + DCl	6.361	2.398
CD_4 + Cl → CD_3−D−Cl → CD_3 + DCl	6.400	2.649

[a] Units: kcal/mol. $V^{\ddagger}$ = 9.3 kcal/mol. ΔE = 6.6 kcal/mol.

TABLE 6: Calculated Kinetic Isotope Effect and Corresponding Rate Constants at 298 K Using Conventional Transition State Theory Both with and without Tunneling Corrections

	no tunneling		Wigner		Eckart	
reaction	KIE	k[a]	KIE	k[a]	KIE	k[a]
Cl + CH_3D	1.41	7.1×10^{-14}	1.43	7.0×10^{-14}	1.48	6.8×10^{-14}
Cl + CH_2D_2	2.16	4.6×10^{-14}	2.24	4.5×10^{-14}	2.40	4.2×10^{-14}
Cl + CHD_3	3.93	2.5×10^{-14}	4.28	2.3×10^{-14}	4.83	2.1×10^{-14}
Cl + CD_4	12.3	8.1×10^{-15}	16.8	6.0×10^{-15}	22.6	4.4×10^{-15}

[a] Units: cm^3 $molecule^{-1}$ s^{-1}.

(see eq 8).[13,37] Given the inaccuracies in the calculation of absolute rate constant values and to be consistent with our experimentally measured relative rate constants, all calculated rate constant values reported here are relative to the rate constant for the reaction of Cl atoms with CH_4. The calculated rate constant ratios, $k(Cl + CH_xD_y)/k(Cl + CH_4)$, were multiplied by the NASA/JPL recommended value for the $k(Cl + CH_4)$, 1.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1} to determine $k(Cl + CH_xD_y)$.[2]

B. Results. Optimized geometries and energies were calculated for the Cl + CH_4 reaction system at several levels of theory. The optimized values of geometrical parameters, using the 6-311++G(2d,2p) basis set, are shown in Table 3. The MP2 values for the reactant and product structures differ from experimental values[45,46] by no more than 0.8%. The QCISD values differ by no more than 0.4%. Using the MP2 geometries, total electronic energies were calculated at the MP2 level. The energies without zero-point correction, in hartrees, were −40.39378, CH_4; −459.60397, Cl; −39.72041, CH_3; −460.26683, HCl; and −499.98285, CH_3-H-Cl. The activation energy without zero-point correction $V^{\ddagger}$ was calculated to be 9.3 kcal/mol and the corresponding reaction energy ΔE, 6.6 kcal/mol.

The harmonic vibrational frequencies and zero-point energies (ZPEs) were calculated for the Cl + CH_xD_y reactants, products, and transition states. The calculated harmonic vibrational frequencies for Cl + CH_4 are shown in Table 4 (see Table 1S and 2S in Supporting Information for the calculated harmonic vibrational frequencies for Cl + deuterated methanes). The frequencies for HCl, CH_4, and CH_3 are in good agreement with experimental values,[45,46] within 6% of experimental values except for the a_2'' out-of-plane bending mode of CH_3 which deviates by 19%. The calculated harmonic frequencies were used to obtain ZPEs. The HCl, CH_4, and CH_3 ZPEs are within about 0.1%, 0.1%, and 5% of the experimental values. For the partially deuterated methanes, two transition states are possible: one involving H atom abstraction and one involving D atom abstraction. The ZPE-corrected activation energy, E_a, and reaction energy, ΔH_0, were determined for each reaction using the calculated electronic energies and ZPEs (see Table 5). Upon inclusion of ZPEs, both the activation and reaction energies were significantly reduced. The lower activation energies correspond to H atom abstraction as would be expected from a simple ZPE/activation energy argument. The activation energy E_a also depends on the number of D atoms on the methyl group. The calculated activation energy with ZPE correction for the Cl + CH_4 reaction, 5.2 kcal/mol, is significantly larger than the experimental values of 2.4−3.6 kcal/mol,[24] but it is within the 3.6−5.5 kcal/mol range of previous ab initio calculations.[13]

The ab initio results were employed to calculate the rate constants for the reactions of Cl atoms with the deuterated methanes using conventional transition state theory (TST). The calculated rate constants, relative to the Cl + CH_4 rate constant of 1.0×10^{-13} cm^{-3} $molecule^{-1}$ s^{-1},[2] and calculated kinetic isotope effects (KIEs) are shown in Table 6 for three cases: without tunneling correction, with Wigner tunneling correction, and with Eckart tunneling correction. As expected, the rate constants decrease with deuteration. Since we are always calculating a ratio of rate constants, the activation energy $V^{\ddagger}$ is canceled out. Only the ZPEs, which are in much better agreement with experimental values, remain in the exponential part of the TST calculation. However, the activation energy does play a role in the Eckart tunneling correction term. Given the importance of the KIE to isotopic field studies, the calculated temperature dependence of the Cl + CH_4/CH_3D KIE is presented in Table 7. As the temperature increases, the rate constants increase; however, the KIE decreases with increasing temperature because tunneling becomes less important.

C. Discussion. Our theoretical rate constant ratios $k(CH_xD_y)$/$k(CH_4)$ are compared to our experimental results in Figure 3. As expected, transition state theory (TST) without tunneling overestimates the rate constant ratios. The Wigner tunneling corrected rate constant ratios are in better agreement with the experimental data, with two calculated points falling within the

TABLE 7: Temperature Dependence of the Kinetic Isotope Effect for Cl + CH_4 versus Cl + CH_3D Using Conventional Transition State Theory Both with and without Tunneling Corrections

T (K)	KIE (no tunneling)	KIE (Wigner)	KIE (Eckart)	exptl
200	1.50	1.51	1.58	
225	1.47	1.49	1.54	1.59[8]
250	1.45	1.47	1.51	1.58[8]
275	1.43	1.44	1.48	
298	1.41	1.43	1.48	1.47−1.54 (refs 5, 7, and 8 and this work)
350	1.36	1.39	1.45	1.35[7]
400	1.33	1.36	1.44	
450	1.30	1.33	1.43	
500	1.27	1.31	1.43	
1000	1.14	1.19	1.41	

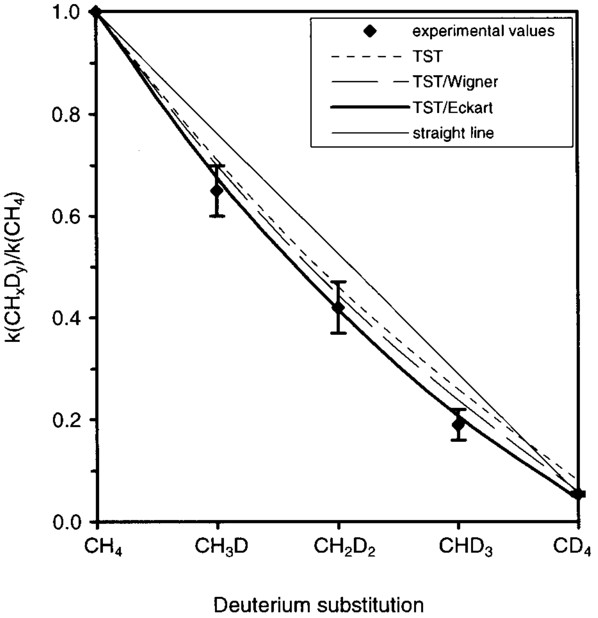

Figure 3. Dependence of the Cl atom rate constant ratio k(CH_xD_y)/k(CH_4) on deuterium substitution: dotted, dashed, and solid lines represent the results of ab initio/transition state calculations without tunneling, including Wigner tunneling, and including Eckart tunneling, respectively. Experimental results of the present study are given by solid diamonds with 2σ error bars. A straight line drawn from CH_4 to CD_4 is included to emphasize the curvature in the theoretical and experimental data.

TABLE 8: Comparison of Theoretical Rate Constants and Kinetic Isotope Effects with Literature Values

reaction	$k^{a,b}$	KIE^a	method	ref
CH_3D +Cl	6.8×10^{-14c}	1.48	ab initio	this work
	6.8×10^{-14c}	1.47	ab initio	Matsumi et al., 1997[9]
	5.1×10^{-14}	1.94	semiempirical	Corchado et al., 2000[13]
	6.9×10^{-14}	1.45	semiempirical	Roberto-Neto et al., 1998[15]
	8.0×10^{-14c}	1.25	empirical	Matsumi et al., 1997[9]
CH_2D_2 + Cl	4.2×10^{-14c}	2.40	ab initio	this work
	3.4×10^{-14}	2.93	semiempirical	Corchado et al., 2000[13]
	5.9×10^{-14c}	1.7	empirical	Matsumi et al., 1997[9]
CHD_3 + Cl	2.1×10^{-14c}	4.83	ab initio	this work
	3.8×10^{-14c}	2.6	empirical	Matsumi et al., 1997[9]
CD_4 +Cl	4.4×10^{-15c}	22.6	ab initio	this work
	6.9×10^{-15}	14.3	semiempirical	Corchado et al., 2000[13]
	8.8×10^{-15}	7.7	semiempirical	Yu & Nyman, 1999[14]
	9.1×10^{-15}	11	semiempirical	Roberto-Neto et al., 1998[15]
	2.3×10^{-15}	42.7	semiempirical	Espinosa-Garcia and Corchado, 1996[16]
	17.9×10^{-15c}	5.6	empirical	Matsumi et al., 1997[9]
	4.9×10^{-14c}	20.5	empirical	Whytock et al., 1977[17]

[a] T = 298−300 K. [b] Units: cm^3 molecule^{-1} s^{-1}. [c] Relative to the Cl + CH_4 rate constant of 1.0×10^{-13} cm^3 molecule^{-1} s^{-1}.

2σ experimental uncertainty limits. The Eckart tunneling corrected rate constant ratios are in the best agreement with our experimental data, three out of four values being within the experimental uncertainty limits. In addition, the temperature dependence of our Eckart tunneling corrected kinetic isotope effect (KIE) for Cl + CH_4/CH_3D (see Table 7) is in good agreement with experimental values at 298 K and below, the temperature range of atmospheric importance (see refs 5, 7, and 8 and this work). However, at 350 K, our KIE without tunneling correction is in the best agreement with experiment.[7] It is expected that tunneling will be important even at 350 K.[13,15,16] The Wigner tunneling correction should be less accurate since it only depends on the imaginary frequency at the saddle point.[40] The shape of the barrier should be more accurately approximated with Eckart's approach which relies on the imaginary frequency and the activation energies in the forward and reverse directions.[18,19,44] In an MP2/6-311G(3d,2p)/TST study of the Cl + $^{12/13}CH_4$ system, it was found that the absolute rate constants were better approximated using an Eckart tunneling correction, whereas the KIE was better approximated using a Wigner tunneling correction.[47] A more detailed study of one-dimensional tunneling corrections and the temperature dependence of the rate constants for Cl + $^{12/13}CH_4$ and Cl + CH_xD_y will be the focus of a future publication.[41]

Our ab initio/TST rate constants and KIEs with Eckart tunneling corrections are compared to previous theoretical calculations in Table 8. Previous theoretical methods are divided into three groups: ab initio (ab initio/TST), semiempirical (ab initio with empirical corrections/variational transition state theory, VTST), and empirical(bond energy-bond order/TST). The present work reports for the first time ab initio/TST calculated rate constants for the reactions of Cl atoms with the entire series of deuterated methanes. One previous ab initio/TST calculation has been reported for the Cl + CH_3D reaction.[9] The only previous theoretical study of the reaction of Cl atoms with the entire series of deuterated methanes was the empirical work by Matsumi et al.;[9] however, their results significantly underestimated the experimental and theoretical KIEs obtained in this work and by other groups.[5,7−17] It is difficult to reconcile this discrepancy given that the details of the empirical calculations were not published.

Our theoretical results are in the middle of the range of theoretical values for the CH_3D and CD_4 KIEs[9,13−17] and in good agreement with the semiempirical CH_2D_2 KIE value.[13] However, the range of theoretical CH_3D and CD_4 KIE values is large. In fact, it is larger than the range of experimental values (see Table 2),[5,7−12] even when only considering theoretical results from the last four years and excluding the empirical calculations of Matsumi et al.[9] The CH_3D KIE result of the one other recent ab initio/TST study is in very good agreement with our result, as would be expected given that they used a very similar theoretical method, MP2/6-311G(2d,3p)/TST with Wigner and Eckart tunneling corrections.[9] The other recent theoretical studies all involve semiempirical/VTST studies.[13−15] On one hand, variational TST is superior to conventional TST in terms of determining the bottleneck, calculating tunneling corrections, and taking into account the multidimensionality of the potential energy surface. On the other hand, VTST requires detailed and accurate knowledge of the multidimensional potential energy surface that is usually not available. Consequently, a range of KIE values have been calculated recently as VTST and the semiempirical potential energy surfaces are refined. Similarly, for the smaller Cl + $^{12/13}CH_4$ KIE, a significant range of theoretical values have been determined from ab initio/TST and semiempirical/VTST calculations.[13,15,47,48]

As shown in Figure 3, our theoretical calculations reproduce the nonlinearity in our experimental rate constant ratios as a function of deuteration. This curvature can also be seen in the semiempirical/VTST results of Corchado et al.[13] for CH_4, CH_3D, CH_2D_2, and CD_4, as well as in the large CH_3D KIE reported in the ab initio/TST calculation by Matsumi et al.[9] and the semiempirical/VTST study by Roberto-Neto et al.[15] The empirical results by Matsumi et al. are linear with deuteration;[9] however, as noted before, these values disagree with most other experimental and theoretical studies. The curvature in Figure 3 is similar for the TST results both with and without tunneling correction, indicating that tunneling is not the main contributor to the observed nonlinearity.

To further elucidate the origin of this nonlinearity, the rate constant ratio was factored into contributions from each part of the transition state calculation in eq 9 (see Table 3S in Supporting Information for the numerical values for each factor). The effect of each factor was determined by calculating the Cl + CH_xD_y/CH_4 rate constant ratios, with one of the factors in the calculation removed. These ratios were then plotted versus deuteration, and the curvature Δ^2(rate constant ratio)/Δ(deuteration)^2 was calculated at CH_3D, CH_2D_2, and CHD_3. The largest contributor to the observed nonlinearity is the rotational partition function factor. The second largest contributor is the translational partition function factor; however, its effect on the curvature is offset by the vibrational partition function factor which is curved in the opposite direction. The effect of the rotational, translational, and vibrational partition function factors on the nonlinearity are illustrated in Figure 4. The Eckart and Wigner tunneling factors and the exponential term enhance the observed curvature to a smaller extent. Consequently, the observed nonlinearity is due predominantly to the preexponential portion of the rate constant. Although the exponential factor plays only a minor role in the overall nonlinearity, it is the largest contributor to the rate constant ratios being less than unity. All of the individual factors for H atom abstraction and for D atom abstraction in the TST calculation vary with deuteration; however, when k_H and k_D are combined to calculate the overall rate constant (eq 8), this variation with deuteration is not necessarily evident in the overall rate constant.

One way of interpreting this curvature is that, in addition to the primary KIE, there is a secondary KIE: the individual rate constant k_H, for abstraction of a H atom (or k_D for abstraction of a D atom), depends on the total number of deuterium atoms on the methane molecule. Saueressig et al. have suggested that the unusually large KIE for CH_3D is due not to a decrease in reactivity of the C−H bonds with deuteration, but to the loss in symmetry in going from CH_4 to CH_3D which will lift the vibrational degeneracies in the transition state.[8] This hypothesis would explain the larger change in rate constant in going from CH_4 to CH_3D that we have observed both experimentally and theoretically, as well as the absence of an unusually large drop in the experimental OH rate constant value in going from CH_4 to CH_3D[25] because of the already reduced symmetry of the transition state (C_s for OH + CH_4 vs C_{3v} for Cl + CH_4). However, from the factor analysis of our TST calculations, it appears that the increase in curvature at CH_3D is manifested predominantly in the following TST factors: the translational and rotational partition functions (the only variables in these two factors that change with deuteration are the masses), the Eckart tunneling correction, and the exponential term. The vibrational partition function factor reduces the curvature, particularly at CH_3D. There also appears to be significant curvature (about 50% of that at CH_3D) in both our experimental and theoretical results at CH_2D_2 and CHD_3 (see Figure 3). This smaller curvature is also observed in the OH + deuterated methane reaction system.[25] We attribute this curvature to a secondary KIE, and the increase in curvature at CH_3D to the reduced symmetry of the transition state and a mass-dependent effect.

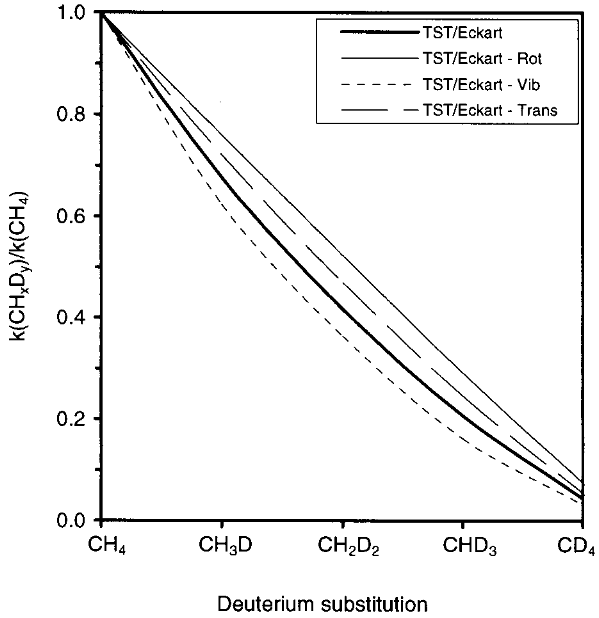

Figure 4. Effect of the rotational, translational, and vibrational partition function factors on calculated Cl atom rate constant ratio: bold solid line, transition state theory with Eckart tunneling correction (TST/Eckart); narrow solid line, TST/Eckart calculation without rotational partition function factor; large dashed line, TST/Eckart calculation without translational partition function factor; small dashed line, TST/Eckart calculation without vibrational partition function factor.

Although ab initio theory does not provide chemically accurate energies and vibrational frequencies, our results suggest that ab initio methods, with no scaling factors, combined with TST can be used to determine accurate KIE values. Our theoretical results reproduce the nonlinear dependence of the KIE values with deuteration as well as the magnitude of the KIE values. This agreement is due, in part, to the following factors: 1) our calculated $V^\ddagger$ value cancels out of the KIE ratio, 2) the calculated ZPEs for the stable species are in good agreement with experiment, 3) most of the vibrational frequencies do not contribute significantly to the vibrational partition function, and 4) two of the largest TST factors involved in the nonlinear dependence of the KIE are the translational and rotational partition functions which do not depend on the ab initio calculations of the energies and vibrational frequencies.

Conclusions

The rate constants for the reactions of Cl atoms with deuterated methanes have been experimentally measured and theoretically calculated. Our FTIR relative rate measurements are in agreement with the majority of previous rate constant measurements. Our MP2/6-311++G(2d,2p)/conventional transition state theory calculations with one-dimensional tunneling corrections are in agreement with our experimental results and some of the previous theoretical calculations. We have observed that the effect of deuteration on the Cl atom rate constant is nonlinear. Our theoretical calculations show that the observed nonlinearity is due mainly to several preexponential factors, with the largest contribution coming from the rotational partition function factor. This nonlinearity in rate constant with deuteration can be thought of as being due to a secondary kinetic isotope effect. The increase in curvature at CH_3D is due to the loss of transition state symmetry upon deuteration and a mass-dependent effect. Given the nonlinearity in our rate constant results, if accurate kinetic isotope effect values are needed, one should not a priori assume that isotopic substitution will affect the reaction rate constant in a linear manner. The large $Cl + CH_4/CH_3D$ kinetic isotope effect should play a significant role in methane fractionation in the stratosphere.

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Supporting Information Available: Tables of calculated harmonic vibrational frequencies for Cl + deuterated methanes (Tables 1S and 2S) and calculated TST factors in the $Cl + CH_xD_y/CH_4$ rate constant ratios (Table 3S). This material is available free of charge via the Internet at http://pubs.acs.org.

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