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Experimentally determined kinetic isotope effects in the reaction of CH_4 with Cl: Implications for atmospheric CH_4

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Abstract. We report experimental values for the carbon and hydrogen kinetic isotope effects (KIEs) in the reaction of CH_4 with Cl at temperatures between 273 and 350 K. Isotope ratio mass spectrometry was utilized to measure $^{13}CH_4/^{12}CH_4$ and CH_3D/CH_4 ratios on samples taken from a 5870- L reaction chamber. At 299 K, k_{c12}/k_{c13} = 1.0621±0.0001 (2σ) and k_h/k_d = 1.474±0.020 (2σ). For both KIEs, the ratio decreased with increasing temperature over the range studied. These results agree well with experimental studies using tunable diode laser absorption spectroscopy and FTIR absorption spectroscopy and with a recent theoretically-calculated set of values.

1. Introduction

Methane (CH_4) is an important radiative trace gas [e.g., *Donner and Ramanathan,* 1980] which also plays an important role in tropospheric and stratospheric chemistry [e.g., *Cicerone and Oremland,* 1988]. Measurements of CH_4 in ice cores indicate that in the past 200 years the mixing ratio has increased from ca. 0.7 ppm to its present value of ca. 1.78 ppm [*Etheridge et al.,* 1998]. The well-documented growth in CH_4 mixing ratio of as much as ca. 1%/yr during the past two decades [e.g, *Dlugokencky et al.,* 1998] concerns researchers and policy makers trying to understand global atmospheric change and its potential impacts on humankind. The exact causes for the increase in CH_4 mixing ratio and the variations in its annual growth rate are not known although studies of CH_4 sources and sink processes are many.

Measurements of CH_4 isotopic composition in ambient air and in CH_4 sources are a useful tool for constraining CH_4 budget estimates. Isotopic fractionation of C and H during CH_4 formation leads to individual CH_4 sources with characteristic ranges of isotopic values. In steady state, the flux-weighted sum of the isotopic signatures from all sources should equal atmospheric values once the atmospheric isotopic value is adjusted to account for isotope fractionation by chemical sink processes [*Rust and Stevens,* 1980].

One such sink process is the reaction of CH_4 with chlorine radicals:

$$CH_4 + Cl \longrightarrow CH_3 + HCl \qquad (1)$$

The rate constant, $k_{Cl} = 1.0\times10^{-13}$ cm^{3}molecules^{-1}s^{-1} at 298 K, for this reaction has been studied extensively with good agreement [*Atkinson et al.,* 1999]. While generally considered only a minor loss process in the troposphere, (1) becomes more important in the stratosphere where it converts Cl atoms into HCl. Its importance in the marine boundary layer (MBL) is not yet established because of uncertainty in MBL Cl radical concentrations. Overall, the effect of Cl has been calculated to account for from 2 to 4% of all atmospheric CH_4 loss [e.g., *Gupta et al.,* 1996].

Both measured and theoretically calculated values for the kinetic isotope effects (KIEs) in (1) are much larger than for a similar reaction involving CH_4 and OH, the principal sink for atmospheric CH_4. This makes (1) of increased importance to researchers using isotopic measurements to study the CH_4 budget. Thus far, studies of KIEs in (1) report a wide range of values, making their use in atmospheric budget calculations somewhat problematic. Here we report an experimental investigation of C and H KIEs in reaction (1) and their temperature dependences with the goal of reaching some consensus values for them.

2. Experimental Methods

Reactions took place in a 5870-L Teflon coated chamber at the Air Pollution Research Center at the University of California, Riverside. A detailed description of the reaction chamber is given in *Winer et al.* [1980]. In brief, light from a 24 kW xenon arc lamp was used to photolyze Cl_2 and thereby initiate the reaction between atomic Cl and CH_4. A pyrex filter eliminated wavelengths <300 nm and prevented the production of $O(^1D)$. Temperature control was achieved by an insulating jacket system located inside the chamber walls. Ethylene glycol was circulated in the jacket to maintain temperature within ±0.6 K over the 273 to 349 K temperature range. Two Teflon coated stirring fans were used to maintain constant temperature and to avoid stratification of air in the chamber. A Nicolet 7199 Fourier transform infrared (FTIR) spectrometer interfaced to a White-type three mirror multiple reflection system was used to monitor changes in CH_4 concentrations.

The partial pressures of CH_4 and Cl_2 were measured into calibrated Pyrex bulbs (5 L and 2 L respectively) with capacitance manometers (MKS Baratron, Boulder, CO) and introduced into the chamber by flushing each bulb in line with zero air (air stripped of all constituents except N_2, O_2, and Ar, Scott-Marin Inc., Riverside, CA) following methods described in *Tuazon et al.* [1992]. Typical chamber concentrations of CH_4 (99.999%, Matheson Gas Products, Inc.) and Cl_2 (>99.5%, Matheson Gas Products, Inc.) were in the range of (2.1-3.8)x10^{15} molecules/cm^3 and 1.5-2.6 x 10^{15} molecules/cm^3, respectively,

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with the balance gas of zero air between 2.2-2.8 x 10^{19} molecules/cm^3. Pressure measurements within the chamber were made with a 0-1000 Torr MKS Baratron capacitance manometer. Initial cell pressures were typically 790 to 800 Torr. The oxygen eliminated CH_3 radical recombination and proton abstraction reactions that might interfere with the desired CH_4 isotope signal by reacting with CH_3 to produce CH_3O_2. Total photolysis time was typically 70 to 90 minutes, consuming 50 to 75% of the initially present CH_4.

To insure that no side reactions were influencing the reaction, a static box model photochemical simulation was run to 83% consumption of CH_4. It used a 20 step mechanism to describe reactions of CH_4 in irradiated Cl_2-CH_4-air mixtures and included reactions of Cl atoms and OH radicals (the latter formed from CH_3OOH) with CH_4 and its products HCHO, CH_3OOH, CH_3OH, HCl, and H_2O_2 [*Atkinson et al.*, 1999]. At the end of the computer simulation less than ~3% of the CH_4 consumption was attributable to reaction with species other than Cl atoms.

Gas samples (12 L STP) were withdrawn from the cell at regular intervals throughout the reaction using a Teflon diaphragm pump (KNF Neuberger, Inc., Princeton, NJ). Gas was collected into evacuated 6-L electropolished stainless steel canisters for analyses. CH_4 mixing ratio was determined using a Hewlett Packard 5880 Gas Chromatograph with flame ionization detector. Samples were measured against reference gas CH_4 prepared by Scott-Marin, Inc. which had been calibrated using a NOAA/CMDL standard [*Lang et al*, 1990]. Measurement uncertainty was 0.25-0.50% over the concentration range of CH_4.

Preparation of the samples for isotopic analysis used either of two combustion vacuum lines designed to separate CH_4 from other reaction constituents and to convert it to CO_2 and H_2O. Vacuum line designs and procedures are described in *Tyler et al.* [1997, 1999]. To analyze D/H ratios, the H_2O from CH_4 was reduced to H_2 by reacting it with zinc shot at 500°C following the method of *Coleman et al.* [1982].

Isotopic measurements were made on a Finnigan-Mat model 252 isotope ratio mass spectrometer. Working C and H isotope standards were from Oztech Gas Company (Dallas, TX). Ratios of $^{13}C/^{12}C$ are reported as $\delta^{13}C$ in per mil (‰) relative to Peedee belemnite (PDB) carbonate. Precision of measurement is ±0.02‰ (1σ) for pure CO_2 reference gases. D/H ratios are reported as δD in per mil (‰) relative to Standard Mean Ocean Water (SMOW) and are measured with a precision of ±1‰ (1σ) for pure H_2 reference gases.

Reproducibility of isotopic measurements was established by processing and measuring replicate samples taken out of the reaction chamber. When taking into account all possible errors associated with sampling, processing, and measuring, precision for $\delta^{13}C$-CH_4 and δD-CH_4 were determined to be ±0.03‰ and ±5‰ (1σ) respectively. To insure that CH_4 isotope fractionation did not take place when gas was introduced or extracted from the reaction chamber, a comparison of $\delta^{13}C$-CH_4 and δD-CH_4 values in unreacted air sample aliquots both before and after they were introduced to the chamber was made. There were no differences in either C or H isotope ratios outside of measurement error.

Where reaction with atomic chlorine is the only loss process for CH_4, the KIE can be expressed as a competitive reaction for Cl between two isotopomers [*Melander and Saunders*, 1980]. Therefore the KIE can be determined from easily measurable quantities related by the Rayleigh equation as in (2),

$$\ln\left(\frac{[CH_4]_t}{[CH_4]_0}\right)=\frac{\alpha}{1-\alpha}\ln\left(\frac{\delta_t+1000}{\delta_0+1000}\right) \qquad (2)$$

where α refers to the ratio of the two rate constants.

Equation (2) holds for either the carbon or hydrogen KIE. For C, $\alpha = k_{c12}/k_{c13}$, and δ_0 and δ_t refer to $\delta^{13}C$-CH_4 at time 0 and t respectively, while for H, α is the ratio of the two rate constants, k_h/k_d, where k_h and k_d are the rate constants for CH_4 and CH_3D respectively. In this case δ_o and δ_t refer to δD-CH_4. There is one notable difference, however. In the reaction of CH_3D with Cl there are two reactions that contribute to the decay of the reactants. One reaction is the direct abstraction of deuterium resulting in DCl and CH_3 as products, while the other reaction is an abstraction of a proton resulting in the products HCl and CH_2D. The rate constant, k_d, determined in this study is in fact the sum of these two rate constants.

3. Results and Discussion

Results of the first room temperature (299 K) carbon KIE experiment are displayed in Figure 1. Following the form of equation (2), the fraction of remaining CH_4 is plotted against the logarithm of the ratio of the two $\delta^{13}C$-CH_4 terms for a reaction run to 76% completion. A curve fit to the data using a least squares regression method with residual sum of squares uncertainty analysis results in a calculated carbon KIE of k_{c12}/k_{c13} = 1.0621±0.0004 (2σ, R^2 = 0.99999). We repeated this experiment in a reaction run only to 48% completion to check the reproducibilty of our experimental methods. In the second carbon KIE experiment at T = 299 K, a similar curve fit resulted in a calculated KIE of k_{c12}/k_{c13} = 1.0621±0.0007 (2σ, R^2 = 0.99991). Based on these results, subsequent reactions were run only until approximately 50% of CH_4 was reacted in order to keep experiments relatively short.

In every experimental reaction run except the first one, both the carbon and hydrogen KIEs were studied simultaneously. Figure 2 displays the hydrogen KIE results at room temperature from the second experimental reaction run (48% completion run). Least squares regression of the curve resulted in a hydrogen KIE of k_h/k_d = 1.47±0.02 (2σ, R^2 = 0.993).

Additional determinations were made at 273 K, 323 K, and 349 K. The results from these experiments are listed in Table 1. Both KIEs show decreasing isotope effects as temperature increases over the range studied. Figure 3 shows Arrhenius plots of the natural logarithm of the isotope effect versus inverse temperature developed from the results of all experiments for both carbon and hydrogen isotopes. Error bars represent the 95% confidence intervals in each individual determination while

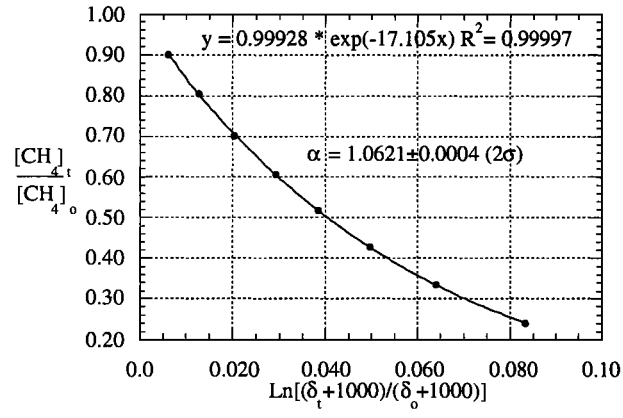

Figure 1. Carbon kinetic isotope effect in the reaction of CH_4 + Cl determined from fraction of CH_4 remaining versus logarithm of the ratio (δ_t +1000) / (δ_0 +1000) at 299 K.

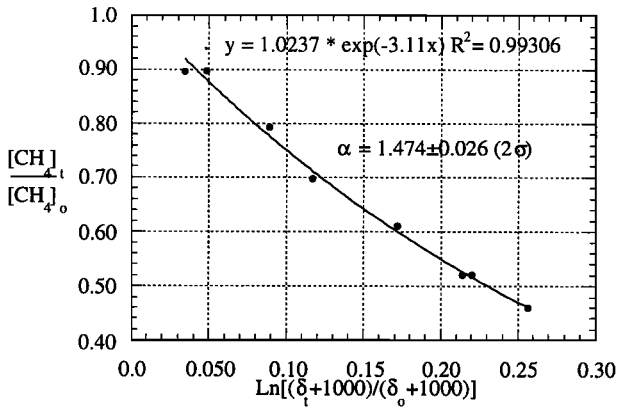

Figure 2. Hydrogen kinetic isotope effect in the reaction of CH_4 + Cl determined from fraction of CH_4 remaining versus logarithm of the ratio $(\delta_t + 1000) / (\delta_0 + 1000)$ at 299 K.

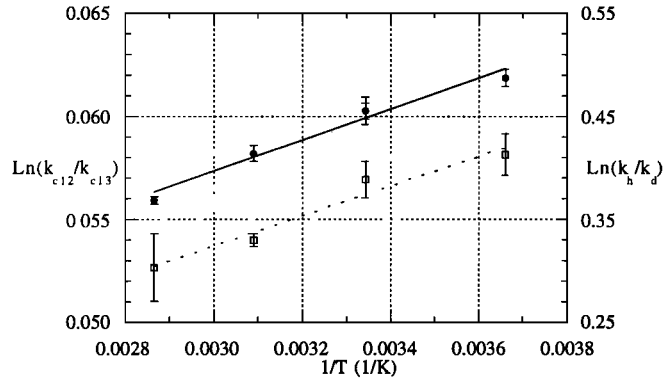

Figure 3. Temperature dependence of the carbon KIE (—●—) and the hydrogen KIE (- ⊡ -) in the reaction of CH_4 + Cl between 273 and 350 K determined from natural logarithm of the isotope effect versus inverse temperature (Arrhenius plot).

overall error in the slope is calculated by the residual sum of squares method. For the carbon KIE the temperature dependence was found to be $k_{c12}/k_{c13} = 1.035\exp(7.55\pm1.64/T)$ (2σ, $R^2 = 0.971$) over the range 273 to 349 K. The temperature dependence of the hydrogen isotope effect was found to be $k_h/k_d = 0.894\exp(145\pm42/T)$ (2σ, $R^2 = 0.959$) over the same temperature range.

Table 2 compares our results with other recent theoretical and experimental determinations of the carbon KIE near room temperature. Our determination is in good agreement with the experimental values reported by *Saueressig et al.* [1995] and *Crowley et al.* [1999] measured using tunable diode laser absorption spectroscopy and FTIR spectroscopy, respectively, and with a theoretical determination made by *Roberto-Neto et al.* [1998] that utilized variational transition state theory and a multidimensional tunneling approach with semi-empirical potential energy surfaces (PESs). Previous theoretical work by *Tanaka et al.* [1996], using conventional transition state theory with *ab initio* calculated PESs, and by *Gupta et al.* [1997], also using conventional transition state theory with *ab initio* calculated PESs and a Wigner tunneling correction but with a higher level of electronic structure calculations, are in qualitative agreement with each other. However, both theoretical studies indicate a fractionation effect roughly a factor of two lower than our experimental determination. An additional experimental determination at room temperature by *Tanaka et al.* [1997] is also a factor of three to five lower than ours.

Considerably better agreement exists among all the reports of the hydrogen KIE in reaction (1) at room temperature. Our value of $k_h/k_d = 1.474\pm0.026$ (2σ) is in good agreement with a relative rate FTIR determination of $k_h/k_d = 1.47\pm0.09$ (2σ) at 295 K by *Wallington and Hurley* [1992] (reported as $k_h/k_d = 1.361\pm0.004$ by *Wallington and Hurley* [1992] but later revised to $k_h/k_d = 1.47\pm0.09$ as reported in Saueressig et al. [1996]), and a combined TDLAS and FTIR determination of $k_h/k_d = 1.508\pm0.041$ at 296 K by Saueressig et al. [1996]. We are also in good agreement with the only published theoretical calculation of the hydrogen KIE, $k_h/k_d = 1.45$, by *Roberto-Neto et al.* [1998].

Table 1 Temperature Dependence of KIEs

Temperature	$k_{c12}/k_{c13} \pm 2\sigma$	$k_h/k_d \pm 2\sigma$
273 K	1.0638 ± 0.0004	1.511 ± 0.031
299 K	1.0621 ± 0.0004	1.474 ± 0.026
323 K	1.0599 ± 0.0004	1.390 ± 0.008
349 K	1.0575 ± 0.0002	1.354 ± 0.044

4. Conclusion

Our results and those of several others listed in Table 2 indicate convergence toward consensus values for both KIEs in reaction 1. This is important because the sensitivity of isotope modeling studies to the magnitude of KIEs is well demonstrated in *Gupta et al.* [1996]. In their two dimensional global tropospheric model they examined the vertical gradient of $\delta^{13}C$-CH_4 using results from both the *Tanaka et al.* [1996] and *Saueressig et al.* [1995] studies of reaction (1). With a KIE of $k_{c12}/k_{c13} = 1.026$ the difference in $\delta^{13}C$-CH_4 between the surface and 18.25 km was found to be 0.51‰ as compared with 0.95‰ when a KIE of $k_{c12}/k_{c13} = 1.043\exp(6.455/T)$ (1.066 at 298 K) is used.

There is a need for more direct studies of all the KIEs in atmospheric CH_4 loss processes (including OH, $O(^1D)$, and soil

Table 2 Comparison of room temperature (296-300 K) Kinetic Isotope Effects for the Reaction of CH_4 with Cl

Determination	Type	α
CARBON KINETIC ISOTOPE EFFECT		
Saueressig *et al.* [1995]	Experimental	1.066±0.002
Tanaka *et al.* [1996]	Theoretical	1.026
Tanaka *et al.* [1997]	Experimental	1.013-1.020
Gupta *et al.* [1997]	Theoretical	1.04
Roberto-Neto *et al.* [1998]	Theoretical	1.06
Crowley *et al.*. [1999]	Experimental	1.066±0.002
This Work	**Experimental**	**1.0621±0.0004**
HYDROGEN KINETIC ISOTOPE EFFECT		
Wallington and Hurley *	Experimental	1.47±0.09
Saueressig *et al.* [1995]	Experimental	1.508±0.041
Roberto-Neto *et al.* [1998]	Theoretical	1.45
This Work	**Experimental**	**1.474±0.026**

*Remeasurement of earlier result reported in *Wallington and Hurley* [1992]

uptake) reported by various investigators to determine consensus values for them. Studies such as these will help resolve the discrepancy between observed and calculated $\delta^{13}C$-CH_4 values in the upper atmosphere. Recent measurements of $^{13}C/^{12}C$ ratios in CH_4 from air collected in the upper troposphere and lower stratosphere indicate significant enrichment in ^{13}C when compared to surface measurements [e.g., *Wahlen et al.*, 1989; *Brenninkmeijer et al.*, 1995; *Tyler et al.*, 1999]. However, modeling studies which use currently accepted values of KIEs in CH_4 sinks, are unable to fully account for these enrichments [*Bergamaschi et al.*, 1996; *Gupta et al.*, 1996; *Tyler et al.*, 1999].

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