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Clumped isotope effects during OH and Cl oxidation of methane

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Abstract

A series of experiments were carried out to determine the clumped ($^{13}CH_3D$) methane kinetic isotope effects during oxidation of methane by OH and Cl radicals, the major sink reactions for atmospheric methane. Experiments were performed in a 100 L quartz photochemical reactor, in which OH was produced from the reaction of $O(^1D)$ (from O_3 photolysis) with H_2O, and Cl was from photolysis of Cl_2. Samples were taken from the reaction cell and analyzed for methane ($^{12}CH_4$, $^{12}CH_3D$, $^{13}CH_4$, $^{13}CH_3D$) isotopologue ratios using tunable infrared laser direct absorption spectroscopy. Measured kinetic isotope effects for singly substituted species were consistent with previous experimental studies. For doubly substituted methane, $^{13}CH_3D$, the observed kinetic isotope effects closely follow the product of the kinetic isotope effects for the ^{13}C and deuterium substituted species (i.e., $^{13,2}KIE = {}^{13}KIE \times {}^{2}KIE$). The deviation from this relationship is $0.3‰ \pm 1.2‰$ and $3.5‰ \pm 0.7‰$ for OH and Cl oxidation, respectively. This is consistent with model calculations performed using quantum chemistry and transition state theory. The OH and Cl reactions enrich the residual methane in the clumped isotopologue in open system reactions. In a closed system, however, this effect is overtaken by the large D/H isotope effect, which causes the residual methane to become anti-clumped relative to the initial methane. Based on these results, we demonstrate that oxidation of methane by OH, the predominant oxidant for tropospheric methane, will only have a minor ($\sim 0.3‰$) impact on the clumped isotope signature ($\Delta^{13}CH_3D$, measured as a deviation from a stochastic distribution of isotopes) of tropospheric methane. This paper shows that $\Delta^{13}CH_3D$ will provide constraints on methane source strengths, and predicts that $\Delta^{12}CH_2D_2$ can provide information on methane sink strengths.

Keywords: Clumped isotopes; Kinetic isotope effect; Methane

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1. INTRODUCTION

Atmospheric methane is the second most important long-lived greenhouse gas behind carbon dioxide (CO_2), and is a much stronger greenhouse gas than CO_2 on a molecule-per-molecule basis (e.g. Lelieveld et al., 1998). Atmospheric methane has more than doubled from preindustrial levels below 800 parts per billion by volume (ppbv) (Craig and Chou, 1982; Khalil and Rasmussen, 1982; Rasmussen and Khalil, 1984) to current atmospheric concentrations of over 1800 ppbv. Methane also plays a central role in the chemistry of the troposphere and stratosphere (Harnung and Johnson, 2012). In the troposphere, methane oxidation moderates hydroxyl radical concentrations (OH) and is the main photochemical precursor for carbon monoxide (CO), in addition to forming formaldehyde (CH_2O) and ozone (O_3). In the stratosphere, oxidation of methane results in the formation of stratospheric water vapor (e.g. Rosenlog et al., 2001) and has an impact on stratospheric HO_x (OH and HO_2), ClO_x, and ozone concentrations.

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The dominant sink of tropospheric methane is oxidation by OH, which is responsible for about 90% of methane oxidation. Due to the strong temperature dependence of the $CH_4 + OH$ reaction, as well as the global distribution of OH radicals, methane oxidation by OH occurs predominantly in the lower to middle tropical troposphere (e.g. Fung et al., 1991; Dlugokencky et al., 2011) during high sunlight conditions. Minor oxidation pathways include oxidation by Cl in the marine boundary layer (Allen et al., 2007) and uptake by soil microbes. In the stratosphere, oxidation by OH, Cl, and $O(^1D)$ are all sinks of methane. Natural sources of methane include wetlands, termites, and oceans. Anthropogenic methane sources include fossil fuels, ruminant agriculture, rice agriculture, and biomass burning. The budgets of different sources and the balance of sources and sinks, both on a regional and a global level, still have high uncertainties (Dlugokencky et al., 2011; Kirschke et al., 2013).

One contentious issue in methane biogeochemistry is the cause of decadal variability in methane mixing ratios. Methane concentrations were rising steadily from the industrial revolution until the 1980's (Stauffer et al., 1985; Etheridge et al., 1992; Dlugokencky et al., 1994), when methane growth rates began to decline (Steele et al., 1992; Dlugokencky et al., 1994) and eventually methane concentrations stabilized (Dlugokencky et al., 2003). However, starting around 2007, methane growth rates have increased again (Rigby et al., 2008; Bousquet et al., 2011). A number of theories have been proposed to explain this variability in methane growth rates, including changes in microbial sources (Mikaloff Fletcher et al., 2004; Bousquet et al., 2006; Kai et al., 2011), changes in fossil fuel emissions (Aydin et al., 2011; Simpson et al., 2012), or changes in the OH sink (Bekki et al., 1994). Reducing the uncertainties in methane biogeochemistry is key to understanding and constraining the global methane cycle and predicting future changes in the methane cycle in a changing world.

High-precision measurements of global, hemispheric, and regional methane mixing ratios and bulk isotope ratios ($\delta^{13}C$ and δD) have provided significant insight into the seasonal, decadal, and interhemispheric variability in methane concentrations (e.g. Quay et al., 1999; Lassey et al., 2000; Miler et al., 2002). In particular, measurements and modeling of $\delta^{13}C$ values of atmospheric methane, as well as the interhemispheric variability in $\delta^{13}C$ and its changes over time, have provided additional constraints on the global methane cycle (Allen et al., 2007). Seasonal covariation between methane concentration and isotope ratios ($\delta^{13}C$ and δD) suggest that seasonal changes in methane are due to changes in both source and sink concentrations over the course of the year (Bergamaschi et al., 2000; Allan et al., 2001). Despite these efforts, the methane budget has significant uncertainties (Fung et al., 1991; Dlugokencky et al., 2011).

Most stable isotope work on methane to date has focused on the measurement of bulk isotope ratios ($\delta^{13}C$, δD) rather than isotopologue ratios ($\delta^{13}CH_4$, $\delta^{12}CH_3D$), generally by conversion of methane to CO_2 and H_2 and subsequent analysis by isotope ratio mass spectrometry (e.g. Miler et al., 2002). Recent developments in near-infrared and mid-infrared laser spectroscopy instruments have allowed direct measurement of intact methane isotopologues (i.e. $\delta^{13}CH_4$, $\delta^{12}CH_3D$), both with preconcentration (e.g. Eyer et al., 2016) and at atmospheric abundance (e.g. Santoni et al., 2012). High-precision and high temporal resolution measurements of atmospheric methane (e.g. Röckmann et al., 2016), once widely deployed, promise modest reductions in uncertainties for different methane sources and sinks (Rigby et al., 2012).

Alongside technological improvements in the measurement of traditional (singly-substituted) isotopologues of methane, recent advances in isotope ratio mass spectrometry (Eiler et al., 2013; Stolper et al., 2014) and quantitative infrared laser spectroscopy (Ono et al., 2014; Wang et al., 2015) are facilitating the ability to measure the rare doubly-substituted methane isotopologues (i.e. $^{13}CH_3D$, and $^{12}CH_2D_2$) at natural abundance. To first order, the abundance of these "clumped" (doubly-substituted) isotopologues follow a stochastic distribution of isotopologues (i.e. $[^{12}CH_4][^{13}CH_3D] = [^{13}CH_4][^{12}CH_3D]$). However, small (per mil level) deviations from this stochastic distribution are observed due to thermodynamic (Ma et al., 2008; Stolper et al., 2014; Liu and Liu, 2016), kinetic (Wang et al., 2015), photolytic (Schmidt et al., 2013; Schmidt and Johnson, 2015), and combinatorial (Yeung, 2016) effects. Stolper et al. (2014) hypothesize that there could be significant clumped kinetic isotope effects during the photochemical methane sink reactions. If this were the case, doubly-substituted isotopologues of methane could be used as tracers for atmospheric sink reactions.

Kinetic isotope effects have been measured experimentally for both OH and Cl oxidation of methane for $^{13}CH_3D$ (Joelsson et al., 2014, 2016). The uncertainties in the measurements, however, are too large to resolve per mil level deviations from a stochastic distribution during these sink reactions. One recent study (Joelsson et al., 2016) suggests that the impact of OH oxidation of atmospheric methane was $\Delta^{13}CH_3D = 20‰ \pm 20‰$ (measured as a deviation from a stochastic distribution of isotopes). The uncertainty is larger than the range of measured $\Delta^{13}CH_3D$ values of methane sources ($-4‰$ to $6‰$, Wang et al., 2015).

In this study, a series of methane oxidation experiments were carried out using both OH and Cl. At several points during the experiment, residual methane was sampled and measured for abundance of isotopologues of methane ($^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$, $^{13}CH_3D$) by using tunable mid-infrared laser direct absorption spectroscopy (TILDAS, Ono et al., 2014). Experimental results are compared with a model constructed using quantum chemistry and transition state theory. We will discuss our results using a simple box model (Tans, 1997) to provide a first estimate the $\Delta^{13}CH_3D$ value of tropospheric methane, as well as its seasonal variability.

2. METHODS

2.1. Terminology and notation

Isotopologue ratios (R values) express the ratio of a particular minor isotopologue ($^{13}CH_4$, $^{12}CH_3D$, $^{13}CH_3D$) to the major isotopologue ($^{12}CH_4$). For example,