Development of a new methane tracer: kinetic isotope effect of $^{13}$CH$_3$D + OH from 278 to 313 K

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Abstract

Methane is the second most important long lived greenhouse gas and impacts the oxidative capacity of the Earth’s atmosphere. Nonetheless there are significant uncertainties in its source budget. Analysis of the isotopic composition of atmospheric methane, including doubly substituted species (e.g. $^{13}\text{CH}_3\text{D}$), offers new constraints on the methane source budget as the sources and sinks have distinct isotopic signatures. The most important sink of atmospheric methane is oxidation by OH which accounts for around 90% of methane removal in the troposphere. Here we present experimentally derived methane + OH kinetic isotope effects and their temperature dependence over the range of 278 to 313 K for CH$_3$D and $^{13}$CH$_3$D; the latter is reported here for the first time. We find $k_{\text{CH}_4}/k_{\text{CH}_3\text{D}} = 1.31 \pm 0.01$ and $k_{\text{CH}_4}/k_{^{13}\text{CH}_3\text{D}} = 1.34 \pm 0.03$ at room temperature, implying that the methane + OH kinetic isotope effect is multiplicative such that $(k_{\text{CH}_4}/k_{^{13}\text{CH}_4})(k_{\text{CH}_4}/k_{\text{CH}_3\text{D}}) = k_{\text{CH}_4}/k_{^{13}\text{CH}_3\text{D}}$ to within the experimental uncertainty. In addition the kinetic isotope effect were characterized using transition state theory with tunneling correction. Good agreement between the experimental, quantum chemical and available literature values was obtained. The theoretical calculations show that $^{13}$CH$_3$D isotope effects is the product of D- and $^{13}$C-isotope effect. Based on the results we conclude that the OH reaction at steady-state can produce an atmospheric clumped isotope signal ($\Delta (^{13}\text{CH}_3\text{D}) = \ln([\text{CH}_4][^{13}\text{CH}_3\text{D}]/[^{13}\text{CH}_4][\text{CH}_3\text{D}])$) of $0.02 \pm 0.02$.

1 Introduction

Atmospheric methane is the subject of increasing interest from both the climate research community and the public due its impacts in climate change, as reported by the IPCC (2013). The direct radiative forcing of methane from is $0.64 \text{Wm}^{-2}$. Including feedback mechanisms and secondary effects e.g. increased O$_3$ production, stratospheric water vapor and production of CO$_2$, the radiative forcing becomes...
0.97 W m\(^{-2}\) (i.e. 2/3 of the forcing by CO\(_2\) over the same time period; IPCC, 2013, Fig. 8.15).

Atmospheric methane has both natural and anthropogenic sources and the two categories contribute about equally (Ciais et al., 2013, and references therein). Wetlands are the dominant natural source, and agriculture and waste are the largest anthropogenic sources. Fossil fuels make smaller contributions. A majority (84%) of atmospheric methane is removed in the troposphere by oxidation by OH:

\[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}, \]

oxidation in the troposphere by Cl contributes about 4% of the total:

\[ \text{CH}_4 + \text{Cl} \rightarrow \text{CH}_3 + \text{HCl}. \]

About 8% of methane is removed in the stratosphere by radical oxidation, such as Reactions (R2) and (R3)

\[ \text{CH}_4 + \text{O}^1\text{D} \rightarrow \text{CH}_3 + \text{OH}. \]

The rest (4%) is removed by the soil (Kirschke et al., 2013).

Carbon and hydrogen isotopic analysis are widely used to distinguish microbial and thermal sources of atmospheric methane (e.g., Lowe et al., 1997; Ferretti et al., 2005; Tyler et al., 2007; Lassey et al., 2007). However, Reactions (R1)–(R3) produce relatively large D/H isotope effects (Saueressig et al., 1995, 1996, 2001; Crowley et al., 1999; Feilberg et al., 2005). Thus, the construction of an accurate top-down methane budget by isotopic analysis must take the isotopic signatures of both sources and sinks into account. The interpolation of methane source (and sink) fractionations represent underdetermined systems (e.g., Pohlman et al., 2009). Until recently, isotopic studies have only taken single isotopic substitutions into account. This is due to the technical challenge in measuring the low concentrations of multiply substituted, or “clumped” isotopes (e.g. \(^{13}\text{CH}_3\text{D}\) which has both \(^{13}\text{C}\) and D substitutions). Recent
studies (Stolper et al., 2015; Wang et al., 2015) have shown that the abundance of $^{13}$CH$_3$D gives additional information about methane sources. Analysis of the clumped isotope anomaly in methane will yield unique constraints for the methane budget.

The kinetic isotope effect $^{i\alpha}E$ is a characteristic property of each process:

$$^{i\alpha}E \equiv \frac{k(iE + OH)}{k(jE + OH)},$$

where $^iE$ is the most abundant (here, the lighter) isotopologue, $^{j\alpha}E$ the rare (heavy) isotopologue, $k(E + OH)$ is the reaction rate coefficient for the reaction E + OH. As a measure of how much of an enrichment of $^{13}$CH$_3$D kinetic reactions produce, the apparent clumpiness, $\gamma$ is used. It is a measure of the effect of the clumped substitution on the reaction rate, as opposed to the combined effect of two single substitutions. It is defined as (Wang et al., 2015):

$$\gamma \equiv \frac{^{13}C,D\alpha}{^{13}C\alpha \times ^D\alpha}$$

A related measure is the $\Delta(^{13}$CH$_3$D) value that quantifies the extent to which rare isotopes clump together to form a multiply substituted species, as opposed to a stochastic distribution (Ono et al., 2014):

$$\Delta(^{13}$CH$_3$D) \equiv \ln \left( \frac{[^{13}$CH$_3$D][^{12}$CH$_4$]}{[^{12}$CH$_3$D][^{13}$CH$_4$]} \right),$$

where $[^{13}$CH$_3$D], $[^{12}$CH$_4$], $[^{12}$CH$_3$D] and $[^{13}$CH$_4$] represent the concentrations of the different isotopologues.

The kinetic isotope effects for the singly substituted species CH$_3$D and $^{13}$CH$_4$ have been studied previously, both experimentally and theoretically, see Tables 1 and 2.
respectively. The kinetic isotope effect $^{13}C,D\alpha$ for the reaction with OH is not described in the existing literature. The related kinetic isotope effect for the $CH_4 + Cl$ reaction was measured at room temperature with the present setup by Joelsson et al. (2014) and found to be $1.60 \pm 0.04$.

In the present study the kinetic isotope effects $D\alpha$ and $^{13}C,D\alpha$ are determined using the relative rate method. Species concentrations in the reaction cell are determined using Fourier Transform Infrared (FTIR) spectroscopy. Further, $D\alpha$, $^{13}C\alpha$, and $^{13}C,D\alpha$ are calculated using quantum chemistry and transition state theory.

2 Experimental procedures

2.1 Relative rate method

The experiment is carried out using the relative rate method on a semi-static gas mixture. The decaying concentrations of reactants are measured as a function of the extent of reaction. Considering two bimolecular reactions with second order rate coefficients $k_A$ and $k_B$,

$$A + OH \xrightarrow{k_A} \text{Products}, \quad \text{(R4)}$$
$$B + OH \xrightarrow{k_B} \text{Products}, \quad \text{(R5)}$$

and assuming there are no other loss processes, the following relation holds:

$$\ln \left( \frac{[A]_0}{[A]_t} \right) = \frac{k_A}{k_B} \ln \left( \frac{[B]_0}{[B]_t} \right). \quad \text{(4)}$$

Here $[A]_0$, $[A]_t$, $[B]_0$ and $[B]_t$ represent the concentrations of compounds A and B at times 0 and $t$ respectively. The slope of $\ln([A]_0/\[A]_t)$ vs. $\ln([B]_0/\[B]_t)$ will give the relative reaction rate coefficient. In these experiments A is $^{12}CH_4$ and B is $^{12}CH_3D$ or $^{13}CH_3D$. 27857
2.2 Photoreactor

Experiments are carried out in the photochemical reactor at the University of Copenhagen, Department of Chemistry. The reactor has been described in detail elsewhere (Nilsson et al., 2009). It consists of a 100 L quartz cell with multi-pass optics surrounded by 16 UV-C florescent Hg lamps in a temperature controlled housing. The cell is coupled to a Bruker IFS 66v/S FTIR spectrometer with either a mercury cadmium telluride (MCT) detector (Experiments 1–4) or an indium antimonide (InSb) (Experiments 5–16). Two thermocouple gauges are placed inside the temperature controlled housing to monitor the temperature and a pressure gauge is connected to the cell to monitor pressure inside the cell. The temperatures and the pressures are logged every 0.5 s.

The gas mix is prepared by expanding H$_2$O vapor (Milli-Q Ultrapure Water) into the chamber through the glass gas manifold. The two methane isotopologues CH$_3$D (Experiments 1–8) (purity > 98%, Cambridge Isotope Laboratories, Inc.) or $^{13}$CH$_3$D (Experiments 9–16), and CH$_4$ (purity > 99%, Aldrich) and O$_3$ are flushed into the chamber with a N$_2$ buffer (purity 99.998 %, Air Liquide), all at the concentrations given in Table 3. $^{13}$CH$_3$D is synthesized using the Grignard reaction, see Joelsson et al. (2014). O$_3$ is generated from O$_2$ (purity 99.97 %, Air Liquide) using an ozone generator (Model AC-20, O$_3$ Technology), preconcentrated before injection on silica gel cooled with ethanol and dry ice to −67 °C. The desired pressure in the cell (450 hPa) is obtained using N$_2$ as bathgas. The starting pressure is chosen such that the pressure is high enough for the N$_2$ to quench O($^1$D) radicals, but low enough to keep the final pressure below atmospheric pressure. The gas mixture is left to rest for up to 1.5 h while several IR spectra are recorded to ensure that no instability or dark chemistry occurs in the gas mix. The UV-C lamps are lit for up to 5 min photolysing at least 75 % of the O$_3$ according to:

\[ O_3 + h\nu \rightarrow O(^1D) + O_2. \]  

(R6)
Up to 0.2 Pa O$_3$ is flushed with about 20 hPa N$_2$ into the chamber to compensate for the loss of ozone with time, mainly due to O(3 P) + O$_3$. A pressure gradient is established and maintained throughout the filling process such that no gas leaks back from the chamber into the gasoline. Spectra are recorded at each filling step. The procedure is repeated until the mix has a final pressure of 933 hPa. Two experiments are conducted at each of the temperatures 278, 288, 298, and 313 K for each of the two heavy methane isotopologues. Exact temperatures are listed in Table 3. After each experiment a dilution test is performed: 133 hPa is pumped out and the chamber is refilled with 133 hPa N$_2$. This is repeated 5–6 times. Ideally, concentration calculations from the spectral fits (data analysis described below) of the resulting spectra should give a linear fit with the slope of 1. The slope of these dilution tests are presented in Table 3. In an extra experiment with $^{12}$CH$_3$D, N$_2$O (Air Liquide, no purity information available) is added as an O(1 D) tracer. The results from this experiment are used as a spot check to validate a model that was constructed to investigate the extent of O(1 D) chemistry. An example of an experiment plot can be found in Fig. S1 in the Supplement.

2.3 Data analysis

The experimental IR spectra are analyzed using the program MALT, version 5 (Griffith, 1996). The program generates a simulated spectrum from initial estimates of the absorber concentrations and instrument parameters. The residual between the experimental and simulated spectra is reduced through iteration. Simulated line-shapes are generated using HITRAN absorption parameters (version 2008) (Rothman et al., 2009) convolved with an FTIR instrument function simulating the Bruker IFS 66v/S instrument. The InSb detector covers a spectral range from 1800 to 5000 cm$^{-1}$ and the MCT detector covers a spectral range from 400 to 5000 cm$^{-1}$. The concentrations of $^{12}$CH$_3$D and $^{13}$CH$_3$D are calculated from spectral fits in the region 2140–2302 cm$^{-1}$. Concentrations of $^{12}$CH$_4$ are calculated from spectral fits in the region 2838–2997 cm$^{-1}$. As there is no HITRAN data available for $^{13}$CH$_3$D in...
this region, the cross sections from 2000 to 2400 cm\(^{-1}\) for this isotopologue where estimated by shifting the spectrum of \(^{12}\text{CH}_3\text{D}\), see Joelsson et al. (2014). In the region 2850–3009 cm\(^{-1}\), temperature adjusted reference spectra of \(^{13}\text{CH}_3\text{D}\) are used for the fits, together with the simulated spectra of \(^{12}\text{CH}_4\) and \(\text{H}_2\text{O}\). The spectral windows are sometimes adjusted to exclude saturated lines. Examples of spectral fits can be found in Figs. S2, S3, and S4.

After \([x\text{CH}_3\text{D}]\) (where \(x = 12\) or \(x = 13\)) and \([^{12}\text{CH}_4]\) are obtained from the spectral analysis, \(\ln([x\text{CH}_3\text{D}]_0/[x\text{CH}_3\text{D}]_t)\) is plotted against \(\ln([^{12}\text{CH}_4]_0/[^{12}\text{CH}_4]_t)\) as described in Sect. 2.1. A straight line is fitted to these data points using a weighted total least squares routine (York et al., 2004). The fitting procedure takes uncertainties in both dimensions into account. An example of a straight line fit can be found in Fig. S1. In the curve fitting procedure, the parameters \(A\) and \(B\) in the linearized version of the Arrhenius equation:

\[
k = A \cdot \exp(B \cdot T^{-1}) \rightarrow \ln(k) = \ln(A) + B \cdot T^{-1}
\]  

is used. Also here, the method of York et al. (2004) are adjusted to match experiments. The temperature in the cell is taken as the average of the measurements from two thermocouples inside the temperature housing. These averages constitute a combined measurement series. The temperature is defined by the temporal mean of the combined temperature measurements series and the uncertainty of the temperature is the standard deviation of the combined temperature measurement series.

### 2.4 Kinetic model

The kinetic model, previously described and used by Nilsson et al. (2012), uses the methane reaction subset and associated (\(\text{O}_x\) and \(\text{HO}_x\)) chemistry. The Kintecus software (Ianni, 2003), simulates the photolysis of \(\text{O}_3\) and the following oxidation chain of \(\text{CH}_4\). A primary reason for using the model is to evaluate the influence of \(\text{O}^{(1}\text{D})\), Reaction (R3), which rivals Reaction (R1). To model ozone photolysis accurately, the
modeled O₃ is matched to the measured value, then the model is verified by comparing the decrease of CH₄ and the increase of H₂O with experiment. The model is run for each refill of O₃, the reaction rates of Reactions (R1) and (R3). The model is designed for room temperature; experiments at other temperatures are not modeled. Experiment 2 is thus modeled: 4.4 % of CH₄ is estimated to be lost to Reaction (R3). In an additional experiment N₂O was introduced in the chamber as an O(¹D)-tracer. Since N₂O does not react with OH and is not photolyzed at the wavelengths present (Nilsson et al., 2009), the decrease of N₂O should be only due to Reaction (R7):

$$\text{N}_2\text{O} + \text{O}(¹\text{D}) \rightarrow \text{products.}$$  \hspace{1cm} (R7)

The amount of CH₄ lost by Reaction (R3) can therefore be approximated by:

$$1 - \frac{[\text{CH}_4]_t}{[\text{CH}_4]_0} = 1 - \exp\left(-k_{(R3)}[\text{O}(¹\text{D})]_t\right) = 1 - \frac{[\text{N}_2\text{O}]_t}{[\text{N}_2\text{O}]_0} \left(\frac{k_{(R7)}}{k_{(R3)}}\right),$$  \hspace{1cm} (6)

where $k_{(R7)} = 1.27 \times 10^{-10}$ cm⁻³ s⁻¹ and $k_{(R3)} = 1.75 \times 10^{-10}$ cm⁻³ s⁻¹ (Sander et al., 2010). This gives 2.3 % [CH₄] lost by oxidation of O(¹D), Reaction (R3). The model estimates that 4.7 % [CH₄] was lost by Reaction (R3). Both methods agree that O(¹D) loss is a minor channel.

3 Theoretical procedure

Rate constants and kinetic isotope effects for CH₄ + OH were calculated using a procedure similar to that employed by Joelsson et al. (2014).

3.1 Computational chemistry calculations

The geometries of reactants, products and transition states were determined using a geometry optimization procedure based on the unrestricted MP2 method (Møller and
Plesset, 1934) and the aug-cc-pVQZ orbital basis set (Dunning Jr., 1989; Woon and Dunning Jr., 1993). Harmonic vibrational frequencies for all relevant isotopologues of reactants, products, and transition states were obtained at the same level of theory. The calculations were carried out using the Gaussian 09 program package (Frisch et al., 2009).

The electronic energy of the optimized structures were refined using the CCSD(T) method (Watts et al., 1993; Knowles et al., 1993, 2000) with aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets. The results from the different basis sets were used to extrapolate the electronic energy at the complete basis set limit following the approach of Halkier et al. (1998) as described by Joelsson et al. (2014). Additional information can be found in Supplement.

3.2 Rate constant calculations

The abstraction of a CH₄ hydrogen atom by OH can occur at four different sites. Depending on the methane isotopologue in question, these sites are either distinguishable or indistinguishable. Microscopic rate constants are calculated for hydrogen abstraction at each site using classical transition state theory with a tunneling correction factor,

\[ k^{(i)}_{\text{mikro}} = n^{(i)}_{\text{tun}} \frac{k_b T}{h} \frac{Q^{(i)}_{\text{TS}}}{Q_{\text{reac}}} \exp \left( -\frac{\Delta E^{(i)}}{RT} \right) \]  

(7)

where \( \Delta E^{(i)} \) is the reaction barrier height (including the zero point vibrational energy) for the \( i \)th reaction path. \( n^{(i)}_{\text{tun}} \) is a tunneling correction factor obtained using the Wigner tunneling correction (Wigner, 1932). \( Q^{(i)}_{\text{TS}} \) and \( Q_{\text{reac}} \) are the partition functions for the transition state and reacting pair, respectively. The total rate constant is obtained by summing over the microscopic rate constants.
4 Results and discussion

The results of the 16 individual experiments (eight for each isotopologue) are tabulated in Table 3. The resulting $^D\alpha$, $^{13}C\alpha$, and $^{13}C,D\alpha$ values from the experimental and theoretical studies are tabulated in Tables 1, 2, and 4 along with previous experimental and theoretical results. The results are also shown in Figs. 1 and 2 for reactions of CH$_3$D and $^{13}$CH$_3$D respectively.

The exponential curve fits yielded the parameters presented in Tables 1 and 4 giving $^D\alpha_{Arr} = 1.32\pm0.13$ and $^{13}C,D\alpha_{Arr} = 1.32\pm0.20$ at $T = 298$K. The mean of results of room temperature experiments Experiments 1 and 2, and Experiments 9 and 10 is $^D\alpha_{exp} = 1.31 \pm 0.01$ and $^{13}C,D\alpha_{exp} = 1.34 \pm 0.01$ respectively. It follows that $\gamma_{exp} = 1.02 \pm 0.02$ at $T = 298$K, using $^{13}C\alpha_{exp} = 1.0039 \pm 0.0002$ (Saueressig et al., 2001), meaning that the clumped isotope might react slower relative to what would be predicted based on the kinetic isotope effects of CH$_3$D and $^{13}$CH$_4$. However, if the Arrhenius parameters are used to calculate the kinetic isotope effects at $T = 298$K, $\gamma_{Arr} = 1.00 \pm 0.18$ (i.e. the reaction has no clumping effect). All uncertainties are given as one standard deviation ($\sigma$). The theoretical results gives $\gamma_{theory} = 1.00$ at $T = 298$K.

The present experimental room temperature results for $^D\alpha$ agree, to within the error bars, with the previous experimental studies, with the exception of DeMore (1993). DeMore (1993) used FTIR spectroscopy with a slow flow setup where the two methane isotopologues were measured separately with a common reference compound. The low $^D\alpha$ value in DeMore (1993) may be explained by interference from O($^1$D) radicals: OH radicals were produced by photolysis of O$_3$ at 254 nm in the presence of H$_2$O, as in the present study. A relatively high rate of Reaction (R3) would reduce the final kinetic isotope effect, since the kinetic isotope effect for oxidation with O($^1$D) is smaller than the kinetic isotope effect for the oxidation of OH (Saueressig et al., 2001). The present experimental results of $^D\alpha$ are also in good agreement with Masgrau et al. (2001) and Sellevåg et al. (2006). The theoretical calculations of $^D\alpha$ give a slightly
higher value than the experimental results, although they are in good agreement with the best Arrhenius curve fit at $T = 298\, K$.

The experimental room temperature result for $^{13}\text{C,D}\alpha$ agrees to within the error bar with both the theoretical value and the best estimate of the Arrhenius curve fit at $T = 298\, K$.

The theoretical calculations show a very small temperature dependence; the variability in the experimental data is large compared to the value of the slope, making a quantification of the temperature dependence uncertain. The $^{D}\alpha$ value of Gordon and Mulac (1975) seems to deviate substantially from an extrapolation of the current Arrhenius expression; it has previously been pointed out that this value includes some inconsistencies (DeMore, 1993).

At steady state, assuming no clumping in emissions, $\Delta^{(13}\text{CH}_3\text{D}) = \ln(\gamma)$. It follows that $\Delta^{(13}\text{CH}_3\text{D}) = 0.02 \pm 0.02$ implying that the clumped isotope effect of the OH reaction is very small.

Furthermore, the theoretical analysis revealed that the primary cause for the kinetic isotope effect is the substantially reduced reactivity of the D atom, which, in turn, can be explained by a significant increase in reaction barrier due to changes in vibrational zero point energy and to a lesser extent tunneling.

### 5 Conclusions

We present experimentally derived CH$_4$ + OH kinetic isotope effects and their temperature dependence for CH$_3$D and $^{13}$CH$_3$D; the latter is reported for the first time. We find $^{D}\alpha = 1.31 \pm 0.01$ and $^{13}\text{C,D}\alpha = 1.34 \pm 0.03$ at room temperature, implying that the kinetic isotope effect is multiplicative such that $\gamma = 1$ to within the experimental uncertainty. We compare our experimental results to theoretical estimates derived using transition state theory with tunneling correction and kinetic isotope effects reported in the literature. We find good agreement with theory and literature values.
Based on these experiments we find that the OH reaction (the main sink of methane) at steady-state has a $\Delta^{13}(\text{CH}_3\text{D}) = 0.02 \pm 0.02$.

The Supplement related to this article is available online at doi:10.5194/acpd-15-27853-2015-supplement.

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Table 1. Experimental and theoretical studies of $^D\alpha$. The temperature dependence studies are presented in the Arrhenius form $^D\alpha(T) = A(T/298\text{K})^n \exp(BT^{-1})$, where $A$, $n$, and $B$ are tabulated, $T$ is the given temperature range, and $^D\alpha(T = 298\text{K})$ is the resulting kinetic isotope effect at $T = 298\text{K}$. Where no $B$ coefficient is presented $A$ can be taken as $^D\alpha(T)$ for the given temperature range. All uncertainties are given as one standard deviation ($\sigma$).

<table>
<thead>
<tr>
<th>Study</th>
<th>$A$</th>
<th>$n$</th>
<th>$B$ (K)</th>
<th>$T$ (K)</th>
<th>$^D\alpha(T = 298\text{K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental studies</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present study$^a$</td>
<td>1.23 ± 0.08</td>
<td>0</td>
<td>21 ± 21</td>
<td>[278, 313]</td>
<td>1.31 ± 0.01$^h$</td>
</tr>
<tr>
<td>Saueressig et al. (2001)$^b$</td>
<td>1.294 ± 0.009</td>
<td>–</td>
<td>–</td>
<td>296</td>
<td>–</td>
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<tr>
<td>Gierczak et al. (1997)$^c$</td>
<td>1.09 ± 0.05</td>
<td>0</td>
<td>49 ± 11</td>
<td>[220, 415]</td>
<td>1.25 ± 0.07</td>
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<tr>
<td>DeMore (1993)$^a$</td>
<td>0.91</td>
<td>0</td>
<td>75</td>
<td>[298, 360]</td>
<td>1.17</td>
</tr>
<tr>
<td>Gordon and Mulac (1975)$^d$</td>
<td>1.50</td>
<td>–</td>
<td>–</td>
<td>416</td>
<td>–</td>
</tr>
<tr>
<td>Gordon and Mulac (1975)$^d,i$</td>
<td>1.06</td>
<td>–</td>
<td>–</td>
<td>416</td>
<td>–</td>
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<tr>
<td><strong>Theoretical studies</strong></td>
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<tr>
<td>Present study$^e$</td>
<td>1.314</td>
<td>0</td>
<td>6.354</td>
<td>[200, 300]</td>
<td>1.339</td>
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<tr>
<td>Sellevåg et al. (2006)$^f$</td>
<td>[1.30, 1.00]</td>
<td>–</td>
<td>–</td>
<td>[200, 300]</td>
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<tr>
<td>Masgrau et al. (2001)$^g,j$</td>
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<td>–0.02</td>
<td>50.5</td>
<td>[200, 1500]</td>
<td>1.25</td>
</tr>
</tbody>
</table>

$^a$ Fourier transform infrared spectroscopy – relative rate.
$^b$ Tunable Diode Laser Absorption Spectroscopy – isotope ratio mass spectrometry.
$^c$ Pulsed photolysis – pulsed laser-induced flourescence.
$^d$ Pulse radiolysis.
$^e$ Transition state theory with Wigner tunneling correction.
$^f$ Canonical unified statistical theory.
$^g$ Multicoefficient correlation method.
$^h$ Average room temperature value, not obtained from curve fit.
$^i$ Re-evaluated by DeMore (1993).
Table 2. Experimental and theoretical studies of $^{13}$C $\alpha$. The temperature dependence studies are presented in the Arrhenius form $^{13}$C $\alpha(T) = A \exp(BT^{-1})$, where $A$ and $B$ are tabulated, $T$ is the given temperature range, and $^{13}$C $\alpha(T = 298 \text{ K})$ is the resulting kinetic isotope effect at $T = 298 \text{ K}$. Where no $B$ coefficient is presented $A$ can be taken as $^{13}$C $\alpha(T)$ for the given temperature range. All uncertainties are given as one standard deviation ($\sigma$).

<table>
<thead>
<tr>
<th>Study</th>
<th>$A$</th>
<th>$B$</th>
<th>$T$</th>
<th>$^{13}$C $\alpha(T = 298 \text{ K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental studies</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saueressig et al. (2001) $^a$</td>
<td>1.0039 ± 0.0002</td>
<td>–</td>
<td>296</td>
<td>–</td>
</tr>
<tr>
<td>Cantrell et al. (1990) $^c$</td>
<td>1.0054 ± 0.0005</td>
<td>–</td>
<td>[273, 353]</td>
<td>1.0054 ± 0.0005</td>
</tr>
<tr>
<td>Rust and Stevens (1980) $^d,i$</td>
<td>1.003</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Theoretical studies</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present study $^b$</td>
<td>1.0137</td>
<td>–1.219</td>
<td>[200, 300]</td>
<td>1.0094</td>
</tr>
<tr>
<td>Sellevåg et al. (2006) $^e$</td>
<td>[1.014, 1.00]</td>
<td>–</td>
<td>[200, 1500]</td>
<td>1.003</td>
</tr>
<tr>
<td>Gupta et al. (1997) $^f$</td>
<td>1.010</td>
<td>–</td>
<td>300</td>
<td>–</td>
</tr>
<tr>
<td>Melissas and Truhlar (1993) $^g$</td>
<td>[1.005, 1.001]</td>
<td>–</td>
<td>[223, 416]</td>
<td>1.005</td>
</tr>
</tbody>
</table>

$^a$ Tunable Diode Laser Absorption Spectroscopy – isotope ratio mass spectrometry
$^b$ Transition state theory with Wigner tunneling correction.
$^c$ Gas chromatography – mass spectrometry.
$^d$ Isotope ratio mass spectrometry.
$^e$ Canonical variational transition state theory.
$^f$ Conventional transition state theory.
$^g$ Interpolated variational transition state theory with centrifugal-dominant, small-curvature tunneling coefficients.
$^h$ Ab initio calculations.

$^i$ No temperature information available.
Table 3. List of experiments. The experiment numbers are listed in column Exp., the detector in the column Detector, the heavy CH\(_4\) isotopologue included in the experiments are listed in column Isotop., the mean measured temperatures in the photoreactor are listed in column \(T\), the H\(_2\)O-vapour concentrations at the start of the experiments (\(t = 0\)) as obtain from spectral fitting are listed in column \([\text{H}_2\text{O}])_{t=0}\); the mean O\(_3\) concentration after refill (i.e. the “top”-values) as obtained from spectral fitting are listed in column \([\text{O}_3]_{\text{top}}\); the kinetic isotope effect corresponding to the isotopologue are listed in column \(\alpha\), and the result of the dilution experiments are listed in column \(k_{\text{dil}}\).

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Detector</th>
<th>Isotop.</th>
<th>(T) (K)</th>
<th>([\text{H}<em>2\text{O}])</em>{t=0}) (hPa)</th>
<th>([\text{O}<em>3]</em>{\text{top}}) (hPa)</th>
<th>(\alpha)</th>
<th>(k_{\text{dil}}) (hPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MCT</td>
<td>CH(_3)D</td>
<td>298.2 ± 1.2</td>
<td>7.1</td>
<td>(-^a)</td>
<td>1.302 ± 0.038</td>
<td>1.011 ± 0.048</td>
</tr>
<tr>
<td>2</td>
<td>MCT</td>
<td>CH(_3)D</td>
<td>297.6 ± 0.8</td>
<td>5.6</td>
<td>0.19</td>
<td>1.314 ± 0.020</td>
<td>(-^b)</td>
</tr>
<tr>
<td>3</td>
<td>MCT</td>
<td>CH(_3)D</td>
<td>277.2 ± 0.2</td>
<td>5.2</td>
<td>0.29</td>
<td>1.294 ± 0.017</td>
<td>0.962 ± 0.037</td>
</tr>
<tr>
<td>4</td>
<td>MCT</td>
<td>CH(_3)D</td>
<td>277.0 ± 0.2</td>
<td>5.1</td>
<td>0.16</td>
<td>1.335 ± 0.017</td>
<td>(-^b)</td>
</tr>
<tr>
<td>5</td>
<td>InSb</td>
<td>CH(_3)D</td>
<td>284.5 ± 0.1</td>
<td>7.2</td>
<td>0.26</td>
<td>1.334 ± 0.012</td>
<td>0.999 ± 0.009</td>
</tr>
<tr>
<td>6</td>
<td>InSb</td>
<td>CH(_3)D</td>
<td>291.1 ± 0.2</td>
<td>7.4</td>
<td>(-^a)</td>
<td>1.323 ± 0.010</td>
<td>0.998 ± 0.010</td>
</tr>
<tr>
<td>7</td>
<td>InSb</td>
<td>CH(_3)D</td>
<td>313.5 ± 1.3</td>
<td>7.1</td>
<td>0.17</td>
<td>1.301 ± 0.007</td>
<td>1.006 ± 0.031</td>
</tr>
<tr>
<td>8</td>
<td>InSb</td>
<td>CH(_3)D</td>
<td>312.4 ± 0.9</td>
<td>4.3</td>
<td>(-^a)</td>
<td>1.338 ± 0.010</td>
<td>(-^b)</td>
</tr>
<tr>
<td>9</td>
<td>InSb</td>
<td>(^{13})CH(_3)D</td>
<td>298.5 ± 0.1</td>
<td>5.1</td>
<td>(-^a)</td>
<td>1.359 ± 0.022</td>
<td>1.000 ± 0.029</td>
</tr>
<tr>
<td>10</td>
<td>InSb</td>
<td>(^{13})CH(_3)D</td>
<td>297.6 ± 0.6</td>
<td>6.4</td>
<td>0.13</td>
<td>1.314 ± 0.007</td>
<td>0.990 ± 0.064</td>
</tr>
<tr>
<td>11</td>
<td>InSb</td>
<td>(^{13})CH(_3)D</td>
<td>276.8 ± 0.8</td>
<td>5.4</td>
<td>(-^a)</td>
<td>1.357 ± 0.046</td>
<td>1.016 ± 0.031</td>
</tr>
<tr>
<td>12</td>
<td>InSb</td>
<td>(^{13})CH(_3)D</td>
<td>277.2 ± 1.3</td>
<td>5.1</td>
<td>(-^a)</td>
<td>1.344 ± 0.013</td>
<td>1.008 ± 0.030</td>
</tr>
<tr>
<td>13</td>
<td>InSb</td>
<td>(^{13})CH(_3)D</td>
<td>287.4 ± 1.2</td>
<td>5.4</td>
<td>(-^a)</td>
<td>1.346 ± 0.025</td>
<td>1.009 ± 0.022</td>
</tr>
<tr>
<td>14</td>
<td>InSb</td>
<td>(^{13})CH(_3)D</td>
<td>287.4 ± 0.4</td>
<td>4.5</td>
<td>(-^a)</td>
<td>1.342 ± 0.015</td>
<td>1.011 ± 0.019</td>
</tr>
<tr>
<td>15</td>
<td>InSb</td>
<td>(^{13})CH(_3)D</td>
<td>314.4 ± 1.0</td>
<td>5.2</td>
<td>0.26</td>
<td>1.316 ± 0.016</td>
<td>1.003 ± 0.038</td>
</tr>
<tr>
<td>16</td>
<td>InSb</td>
<td>(^{13})CH(_3)D</td>
<td>313.8 ± 0.8</td>
<td>8.3</td>
<td>0.17</td>
<td>1.331 ± 0.033</td>
<td>1.001 ± 0.034</td>
</tr>
</tbody>
</table>

\(^a\) Spectra recorded during or after photolysis, \([\text{O}_3]_{\text{top}}\) not available.
\(^b\) No dilution test performed.
Table 4. Experimental and theoretical studies of \( ^{13}\text{C}_2\text{D} \alpha \). The temperature dependencies are presented in the Arrhenius form \( ^{13}\text{C}_2\text{D} \alpha(T) = A \exp(BT^{-1}) \), where \( A \) and \( B \) are tabulated, \( T \) is the given temperature range, and \( ^{13}\text{C}_2\text{D} \alpha(T = 298\text{K}) \) is the resulting kinetic isotope effect at \( T = 298\text{K} \). All uncertainties are given as one standard deviation (\( \sigma \)).

<table>
<thead>
<tr>
<th>Study</th>
<th>( A ) (K)</th>
<th>( B ) (K)</th>
<th>( T ) (K)</th>
<th>( D^\alpha(T = 298\text{K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental study(^a)</td>
<td>1.18 ± 0.10</td>
<td>38 ± 26</td>
<td>[278, 313]</td>
<td>1.34 ± 0.03(^c)</td>
</tr>
<tr>
<td>Theoretical study(^b)</td>
<td>1.328</td>
<td>5.301</td>
<td>[200, 300]</td>
<td>1.349</td>
</tr>
</tbody>
</table>

\(^a\)Fourier transform infrared spectroscopy – relative rate.

\(^b\) Transition state theory with Wigner tunneling correction.

\(^c\) Average room temperature value, not obtained from curve fit.
Figure 1. The individual measurements of $D\alpha$, are represented by points; the accompanying individual error bars are represented by thin black solid lines; the experimental Arrhenius curve fit is represented by a dashed line; the theoretical Arrhenius curve fit is represented by a dashed-dotted line; the mean of the room temperature measurements are represented by a gray solid circle; the uncertainty of the room temperature measurements are represented by a thick gray solid line; the result from Gierczak et al. (1997) (which is included for comparison) are represented by a dotted line. All uncertainties are given as one standard deviation ($\sigma$).
Figure 2. The individual measurements of $^{13}\text{C,D}\alpha$, are represented by points; the accompanying individual error bars are represented by thin black solid lines; the experimental Arrhenius curve fit is represented by a dashed line; the theoretical Arrhenius curve fit is represented by a dashed-dotted line; the mean of the room temperature measurements are represented by a gray solid circle; the uncertainty of the room temperature measurements are represented by a thick gray solid line. All uncertainties are given as one standard deviation ($\sigma$).