



*Supplement of*

## **Mass spectrometric measurement of hydrogen isotope fractionation for the reactions of chloromethane with OH and Cl**

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**Table S1:** Experimental details for the degradation of chloromethane and methane with OH radicals

Exp.	date	reaction	initial	Ozone	steady state	relative humidity	H <sub>2</sub> initial	T	OH
			mixing ratio	photolysis	O <sub>3</sub> mixing ratio				
			ppmv	TUV lamp	ppbv	%	ppmv	°C	cm <sup>-3</sup>
1&2	25/04/2014	CH <sub>3</sub> Cl+OH	5, 10	1x 55W	620	65	2000	20.7	2.9 x 10 <sup>9</sup>
3	03/02/2015	CH <sub>3</sub> Cl+CH <sub>4</sub> +OH	10+5	4x 55W	3570	65	2000	20.4	1.6 x 10 <sup>10</sup>
blank	01/02/2015	CH <sub>4</sub>	5			72		20.3	
4	02/02/2015	CH <sub>4</sub> +OH	6	4x 55W	3570	75 to 72		20.3	1.6 x 10 <sup>10</sup>
control	02/02/2015	CH <sub>4</sub> +OH	5	4x 55W	5000	72		20.3	2.0 x 10 <sup>10</sup>

### Generation of hydroxyl radicals and control measurements for potential loss effects

In our study, OH was generated by UV-photolysis of ozone in the presence of water vapour. This is a well-established efficient method for OH radical generation (Cantrell et al. 1990, DeMore 1992). In order to perform the degradation experiments within a day, the experimental conditions, in particular the radiation intensity and the ozone concentration, were modified for the different experiments as indicated in Table S1. Based on the high radiant efficiency of the TUV lamp at the absorption band of O<sub>3</sub>, the photolysis of O<sub>3</sub> to O(<sup>1</sup>D) and O<sub>2</sub> and the subsequent generation of OH in the reaction O(<sup>1</sup>D)+H<sub>2</sub>O are favoured. One can estimate a photolysis rate of J(O<sub>3</sub>) in the range of 10<sup>-3</sup> s<sup>-1</sup> for the first experiment with CH<sub>3</sub>Cl. For the CH<sub>4</sub> experiments we had 4 TUV lamps installed around the chamber, which increased the J(O<sub>3</sub>) value. This is confirmed by the reduced lifetime of O<sub>3</sub> when the lamps are on and no O<sub>3</sub> is injected (roughly 11 min for the CH<sub>3</sub>Cl+OH experiment and 4 min for the CH<sub>4</sub>+OH experiment).

During the first two experiments (CH<sub>3</sub>Cl+OH), the steady state mixing ratios of ozone during photolysis were about 620 ppbv for 9 h. Ozone photolysis was carried out with one 55W TUV lamp at a relative humidity of 65%. During the fourth experiment (CH<sub>4</sub>+OH) with four TUV lamps, the steady state ozone mixing ratio was 3570 ppbv for 13h and the relative humidity was 75% making a higher OH concentration reasonable. Mean OH concentrations present for the CH<sub>3</sub>Cl and CH<sub>4</sub> in these experiments were 2.9 x 10<sup>9</sup> cm<sup>-3</sup> and 1.6 x 10<sup>10</sup> cm<sup>-3</sup>, respectively. The reaction rate constant at 293 K for CH<sub>3</sub>Cl+OH (3.3x10<sup>-14</sup> cm<sup>-3</sup>, Burkholder et al., 2015) is roughly 6 times higher than that for CH<sub>4</sub> (5.7x10<sup>-15</sup> cm<sup>-3</sup>, Burkholder et al., 2015). Considering the adjusted conditions, the lifetime of CH<sub>3</sub>Cl in experiment one and two should roughly be the same as that of CH<sub>4</sub> in experiment four. Finally, the third experiment (CH<sub>3</sub>Cl+CH<sub>4</sub>+OH) was carried out under similar conditions as the fourth experiment but at a relative humidity of 65% and thus a lower OH yield as compared to the fourth experiment. Moreover, the initial mixing ratios of CH<sub>3</sub>Cl and CH<sub>4</sub> in experiment 3 were 10 and 5 ppmv, respectively. Considering the adjusted conditions, the lifetime of CH<sub>3</sub>Cl in experiment 3 should roughly be the same as that of CH<sub>4</sub> in experiment 4. Finally the observed loss rate of CH<sub>3</sub>Cl was 5.8 times faster than the observed loss rate for CH<sub>4</sub>, being in line with the ratio of the reported rate constants.

During all these degradation experiments, ozone and UV were turned off from time to time to take the canister samples (see Figure S3). In order to estimate the OH yield in this experiment, a further CH<sub>4</sub> degradation experiment was carried out (control experiment Table S1, Figure S2). During this experiment, ozone was photolyzed continuously and we only measured the mixing ratios of CH<sub>4</sub> and CO<sub>2</sub> and did not take any canister samples. The

mean OH concentration during continuous ozone photolysis in this experiment was  $1.7 \times 10^{10}$  cm<sup>-3</sup>. We also performed a blank experiment prior to the CH<sub>4</sub>+OH experiment to address unaccounted losses such as diffusion of CH<sub>4</sub> through the FEP foil. During all experiments with CH<sub>4</sub>, we used CO<sub>2</sub> as an inert tracer to correct for dilution effects. The CH<sub>4</sub> and CO<sub>2</sub> mixing ratios were determined with a Picarro G221i cavity ring down spectrometer. Prior to the experiments, the instrument was calibrated with pressurized air from a tank obtained from the Max-Planck-Institute for Biogeochemistry in Jena/Germany.

The blank experiment was carried out with a dilution flow of 4 L min<sup>-1</sup>. The measured mixing ratios were corrected for the respective blanks of the zero air that were <0.01 ppmv for methane and 8.2±0.2 ppmv for CO<sub>2</sub>. The measured CH<sub>4</sub> and CO<sub>2</sub> mixing ratios as well as the dilution corrected CH<sub>4</sub> mixing ratios are shown in Figure S1. The slope for CH<sub>4</sub> and CO<sub>2</sub> were -0.00118 min<sup>-1</sup> and 0.00117 min<sup>-1</sup> respectively. This corresponds to a dilution flow of 4.1±0.1 L min<sup>-1</sup>, which is in good agreement with the pre-set dilution flow (the major uncertainty in this calculation is the exact volume of the chamber). During this blank experiment, the dilution corrected mixing ratio of CH<sub>4</sub> changed by less than 0.2%. We can thus safely rule out any unaccounted losses of CH<sub>4</sub>.

The measured CH<sub>4</sub> and CO<sub>2</sub> mixing ratios as well as the dilution corrected mixing ratios from the CH<sub>4</sub> control experiment are shown in Figure S2. The upper panel of figure S3 shows the respective results from the CH<sub>4</sub> + OH isotope fractionation experiment (exp.4 in Table S1) and the lower panel shows the corresponding O<sub>3</sub> mixing ratios. For this experiment the dilution flow was reduced initially to 0.6 L min<sup>-1</sup>. During this experiment, it was necessary to stepwise increase the dilution flow for maintaining an overpressure of 0.5 hPa inside the chamber. This resulted in a non-exponential loss due to dilution as shown in the CO<sub>2</sub> mixing ratios.

### **Further discussion regarding the differences between the experimental and analytical design and protocols of the study by Sellevåg et al. (2006) and this study (Keppler et al. 2018)**

One potential source of error is incomplete mixing inside the chamber. Incomplete mixing may result in an underestimation of the KIE due to transport limitation. The experiments of Sellevåg et al. (2006) were carried out in a 250L electropolished stainless steel chamber, whereas our experiments were carried out in a 3500L Teflon-FEP chamber. Hence incomplete mixing might be an issue for our set up. However, the lifetime of CH<sub>3</sub>Cl under the experimental conditions employed in our studies was in the order of 6 to 10h, whereas the turnover of air inside the chamber occurred on time scales of a few minutes, thus making incomplete mixing an unlikely source of error. Incomplete mixing would also have affected the determination of the respective KIEs for CH<sub>4</sub>. Since our reported values are in reasonable agreement with previously reported KIEs we consider incomplete mixing as a potential source of error in our experiments to be highly unlikely.

The chlorine radical generation scheme appears to be quite similar for both studies. Sellevåg et al. (2006) used narrowband photolysis of molecular chlorine employing a Philips TLD-08 fluorescent lamp ( $\lambda_{\text{max}} \sim 370$ ) nm whereas we used broadband photolysis (300 to 700 nm). Both are well established methods.

In the Sellevåg et al. (2006) study, OH was generated under dry conditions from the UV-photolysis of ozone (300 to 500 ppmv) in the presence of 2000 ppmv of H<sub>2</sub>. In our study, ozone was photolyzed at a level of typically 0.5-10 ppmv in the presence of water vapour (RH of about 70%) and 2000 ppmv of H<sub>2</sub> to generate OH. The reaction rate constants of

$O(^1D)$  with  $H_2$  and  $H_2O$  at 298 K are  $1.1 \times 10^{-10}$  and  $2.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , respectively (Burkholder et al., 2015). At a relative humidity of 70% (corresponding to 25000 ppmv of  $H_2O$  at 20°C), the reaction with  $H_2O$  is by far the main pathway to form OH (with the  $H_2$  pathway contributing less than 1% to the OH yield). Thus, in the absence of water vapour, the half-life of  $CH_3Cl$  can be estimated to about 600 h. This is consistent with previous studies, where ozone levels of 500 to 600 ppmv were required for a sufficient OH production from  $H_2$  (Gola et al. 2005, Sellevåg et al. 2006). In our study, photolysis of 2 ppmv ozone in the absence of water vapour (RH<1%) but with 2000 ppmv  $H_2$  resulted in a  $CH_3Cl$  degradation of less than 3% over 10 hours because of the insufficient OH yield. With this, we can safely exclude any measurable effect from potential side reactions on the determination of the KIEs.

Additionally, we monitored the ratio of  $CH_3Cl$  and PFH for at least 2 h prior to each experiment to assess potential side reactions. For the experiments with chlorine, this was done under dark conditions in the presence of 10 ppmv  $Cl_2$ . For the OH experiments, this was either done in the absence of light or ozone. None of these tests revealed any indication of a measurable degradation of  $CH_3Cl$  thus excluding any bias due to side reactions.

Cantrell et al. (1990), who used UV-photolysis in the presence of water as an OH source, estimated that the reaction of  $CH_4$  with  $O(^1D)$  may contribute about 3% to the overall degradation. The higher ozone levels and the less efficient conversion of  $O(^1D)$  to OH in the Sellevåg et al. (2006) study suggest an overall higher transient  $O(^1D)$  concentration as compared to our experiments. However the KIE for the reaction of  $CH_4$  with  $O(^1D)$  is 1.060 (Saueressig et al. 2001) and thus substantially smaller than the respective KIE for the reaction with OH. When assuming a similar trend for the reactions of  $CH_3Cl$ , one would expect an underestimation of the KIE for the reaction of  $CH_3Cl$  with OH in the Sellevåg experiments. Since the KIE reported by Sellevåg et al. (2006) was larger than that determined in our study any side effect from this reaction is unlikely.

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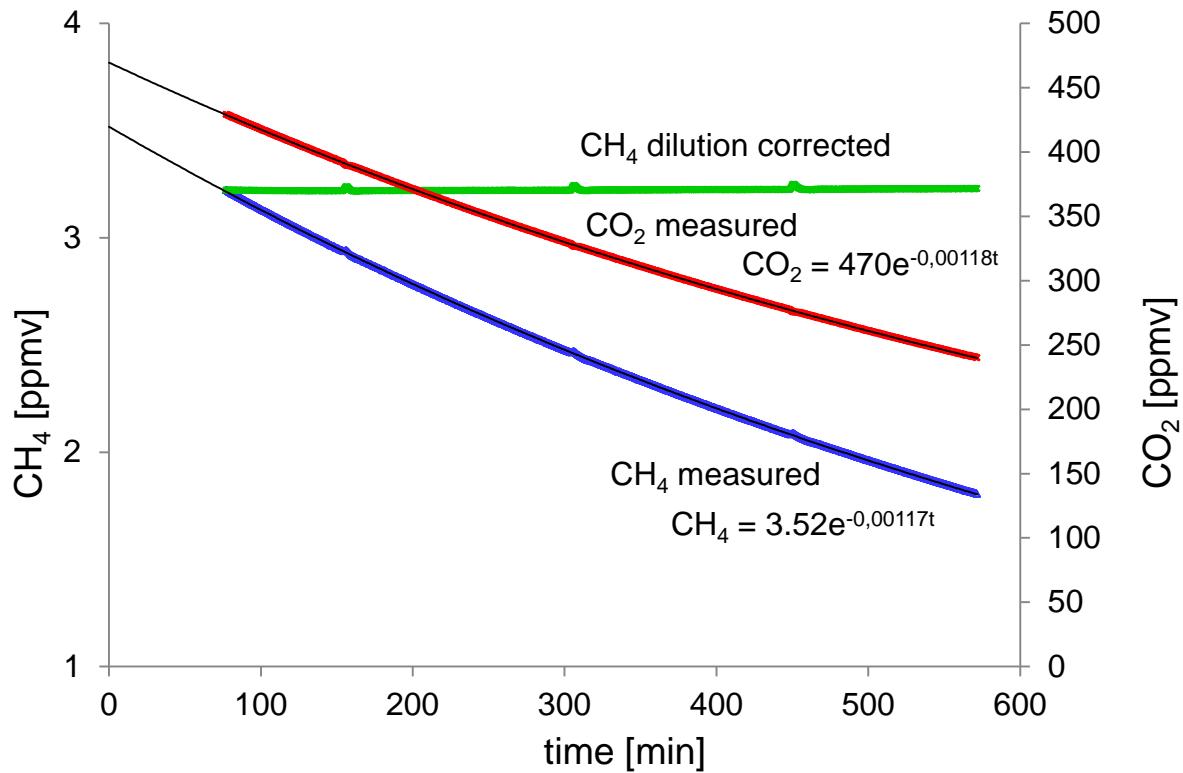
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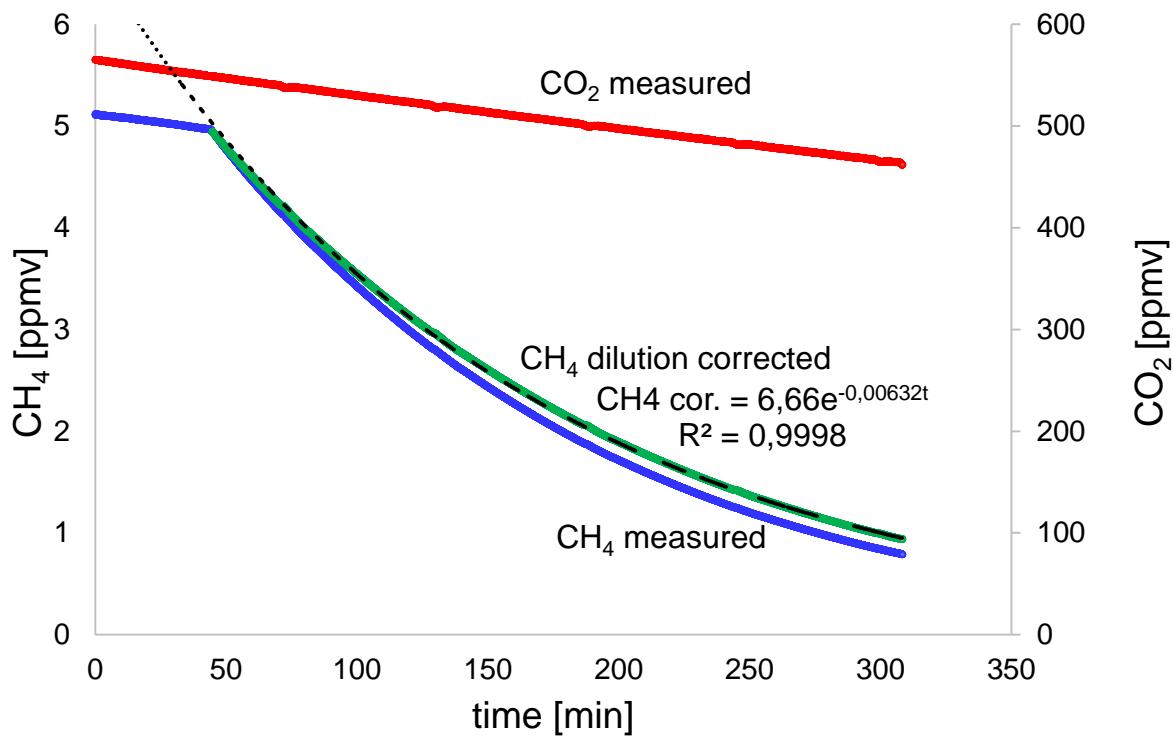
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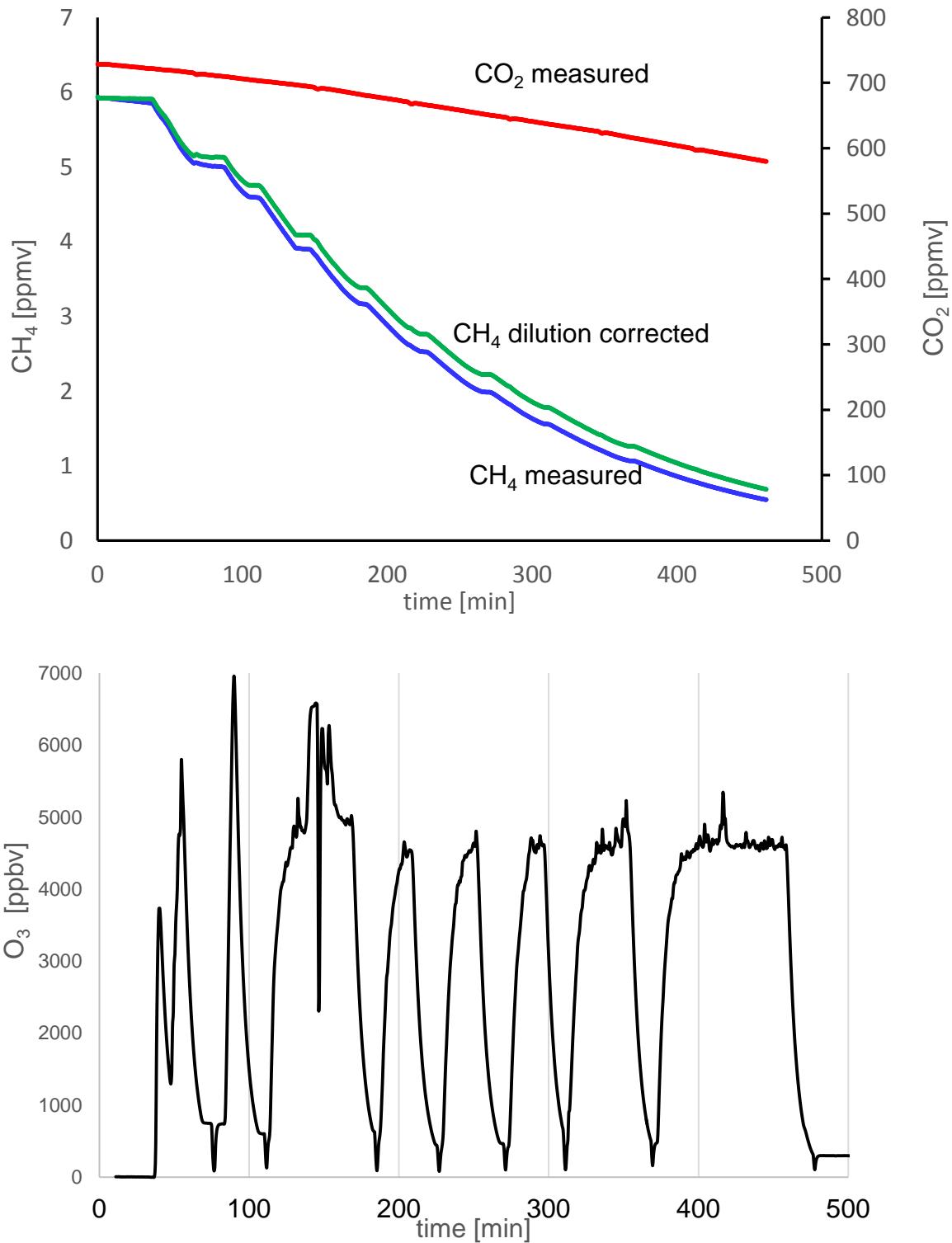
## Figures S1-S3



**Figure S1:** Methane blank experiment without ozone and OH. The blue and red lines show the measured CH<sub>4</sub> and CO<sub>2</sub> mixing ratios, respectively. The green line shows the dilution corrected CH<sub>4</sub> mixing ratios using CO<sub>2</sub> as inert tracer. The dilution corrected CH<sub>4</sub> mixing ratio changed from 3.22 ppmv at the beginning to 3.23 ppmv at the end of the experiment.



**Figure S2:** CH<sub>4</sub> + OH control experiment without canister sampling where ozone was continuously photolysed. The steady state ozone mixing ratio was about 5000 ppbv. The observed degradation rate of CH<sub>4</sub> of  $0.00632 \text{ min}^{-1} = 1.05 \text{ e}^{-4} \text{ s}^{-1}$  corresponds to a level of  $1.7 \times 10^{10} \text{ cm}^3 \text{ s}^{-1}$  for OH, using a rate constant of  $5.7 \times 10^{-15} \text{ cm}^3$  at 293 K (taken from Burkholder et al., 2015). The blue and red lines show the measured CH<sub>4</sub> and CO<sub>2</sub> mixing ratios, respectively. The green line shows the dilution corrected CH<sub>4</sub> mixing ratios using CO<sub>2</sub> as inert tracer.



**Figure S3:** Upper row panel:  $\text{CH}_4+\text{OH}$  degradation experiment for stable hydrogen isotope measurements. The measured  $\text{CH}_4$  mixing ratios (blue line) were corrected (green line) for dilution using  $\text{CO}_2$  (red line) as an inert tracer. We noted a small spectral interference (<0.1%) in the  $\text{CO}_2$  signal arising from ozone. The lower row panel shows the corresponding steady state mixing ratios of ozone. Ozone and the TUV lamps were switched off from time to time to collect the canister samples. This interrupts the degradation of  $\text{CH}_4$  as shown in the upper panel. Mean ozone mixing ratios during photolysis were 4600 ppbv and 3570 ppbv on average over the entire experiment.