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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	H ₂	T	OH
			mixing		photo				
			ratio	lysis	ratio	%	ppmv	°C	cm ⁻³
			ppmv	TUV lamp	ppbv				
1&2	25/04/2014	CH ₃ Cl+OH	5, 10	1x 55W	620	65	2000	20.7	2.9 x 10 ⁹
3	03/02/2015	CH ₃ Cl+CH ₄ +OH	10+5	4x 55W	3570	65	2000	20.4	1.6 x 10 ¹⁰
blank	01/02/2015	CH ₄	5			72		20.3	
4	02/02/2015	CH ₄ +OH	6	4x 55W	3570	75 to 72		20.3	1.6 x 10 ¹⁰
control	02/02/2015	CH ₄ +OH	5	4x 55W	5000	72		20.3	2.0 x 10 ¹⁰

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 O₃, the photolysis of O₃ to O(¹D) and O₂ and the subsequent generation of OH in the reaction O(¹D)+H₂O are favoured. One can estimate a photolysis rate of J(O₃) in the range of 10⁻³ s⁻¹ for the first experiment with CH₃Cl. For the CH₄ experiments we had 4 TUV lamps installed around the chamber, which increased the J(O₃) value. This is confirmed by the reduced lifetime of O₃ when the lamps are on and no O₃ is injected (roughly 11 min for the CH₃Cl+OH experiment and 4 min for the CH₄+OH experiment).

During the first two experiments (CH₃Cl+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 (CH₄+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 CH₃Cl and CH₄ in these experiments were 2.9 x 10⁹ cm⁻³ and 1.6 x 10¹⁰ cm⁻³, respectively. The reaction rate constant at 293 K for CH₃Cl+OH (3.3x10⁻¹⁴ cm⁻³, Burkholder et al., 2015) is roughly 6 times higher than that for CH₄ (5.7x10⁻¹⁵ cm⁻³, Burkholder et al., 2015). Considering the adjusted conditions, the lifetime of CH₃Cl in experiment one and two should roughly be the same as that of CH₄ in experiment four. Finally, the third experiment (CH₃Cl+CH₄+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 CH₃Cl and CH₄ in experiment 3 were 10 and 5 ppmv, respectively. Considering the adjusted conditions, the lifetime of CH₃Cl in experiment 3 should roughly be the same as that of CH₄ in experiment 4. Finally the observed loss rate of CH₃Cl was 5.8 times faster than the observed loss rate for CH₄, 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 CH₄ 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 CH₄ and CO₂ and did not take any canister samples. The

mean OH concentration during continuous ozone photolysis in this experiment was $1.7 \times 10^{10} \text{ cm}^{-3}$. We also performed a blank experiment prior to the $\text{CH}_4 + \text{OH}$ experiment to address unaccounted losses such as diffusion of CH_4 through the FEP foil. During all experiments with CH_4 , we used CO_2 as an inert tracer to correct for dilution effects. The CH_4 and CO_2 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^{-1} . The measured mixing ratios were corrected for the respective blanks of the zero air that were $<0.01 \text{ ppmv}$ for methane and $8.2 \pm 0.2 \text{ ppmv}$ for CO_2 . The measured CH_4 and CO_2 mixing ratios as well as the dilution corrected CH_4 mixing ratios are shown in Figure S1. The slope for CH_4 and CO_2 were $-0.00118 \text{ min}^{-1}$ and 0.00117 min^{-1} respectively. This corresponds to a dilution flow of $4.1 \pm 0.1 \text{ L min}^{-1}$, 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_4 changed by less than 0.2%. We can thus safely rule out any unaccounted losses of CH_4 .

The measured CH_4 and CO_2 mixing ratios as well as the dilution corrected mixing ratios from the CH_4 control experiment are shown in Figure S2. The upper panel of figure S3 shows the respective results from the $\text{CH}_4 + \text{OH}$ isotope fractionation experiment (exp.4 in Table S1) and the lower panel shows the corresponding O_3 mixing ratios. For this experiment the dilution flow was reduced initially to 0.6 L min^{-1} . 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_2 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_3Cl 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_4 . 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_2 . 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_2 to generate OH. The reaction rate constants of

O(¹D) with H₂ and H₂O at 298 K are 1.1×10^{-10} and 2.2×10^{-10} cm³ s⁻¹, respectively (Burkholder et al., 2015). At a relative humidity of 70% (corresponding to 25000 ppmv of H₂O at 20°C), the reaction with H₂O is by far the main pathway to form OH (with the H₂ pathway contributing less than 1% to the OH yield). Thus, in the absence of water vapour, the half-life of CH₃Cl 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 H₂ (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 H₂ resulted in a CH₃Cl 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 CH₃Cl 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 Cl₂. 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 CH₃Cl 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 CH₄ 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 CH₄ 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 CH₃Cl, one would expect an underestimation of the KIE for the reaction of CH₃Cl 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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Figures S1-S3

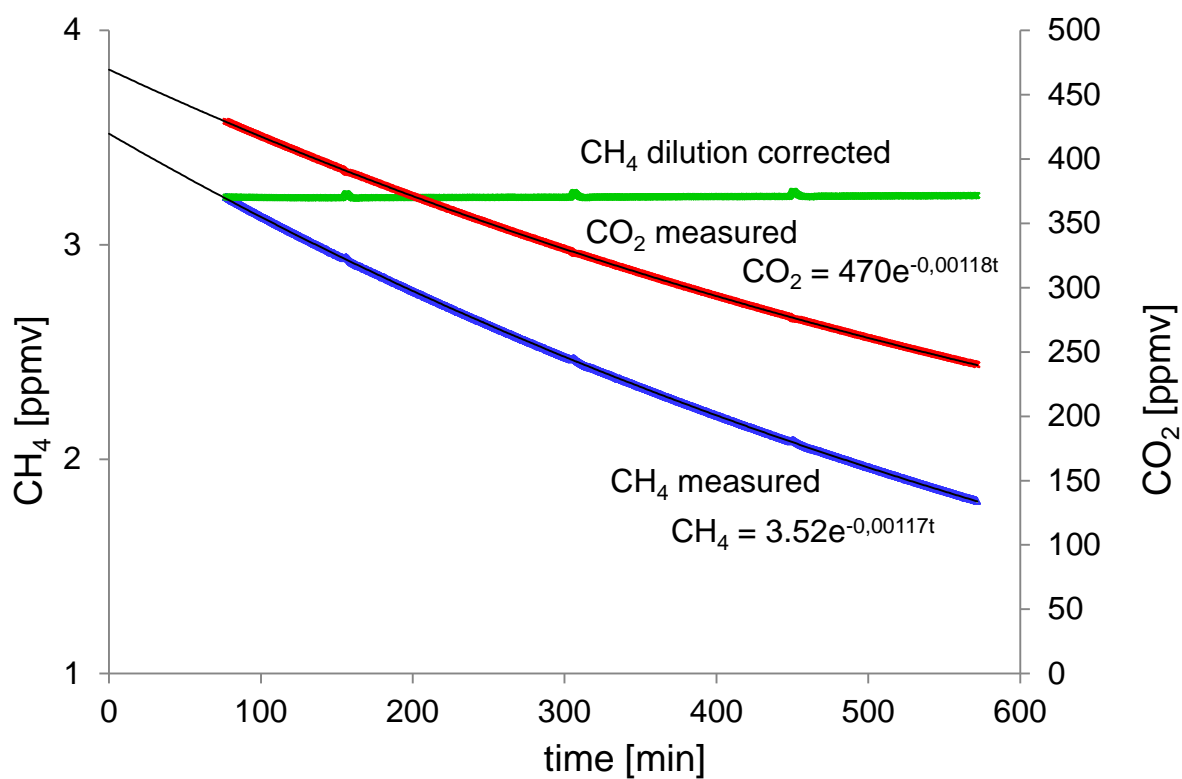


Figure S1: Methane blank experiment without ozone and OH. The blue and red lines show the measured CH₄ and CO₂ mixing ratios, respectively. The green line shows the dilution corrected CH₄ mixing ratios using CO₂ as inert tracer. The dilution corrected CH₄ mixing ratio changed from 3.22 ppmv at the beginning to 3.23 ppmv at the end of the experiment.

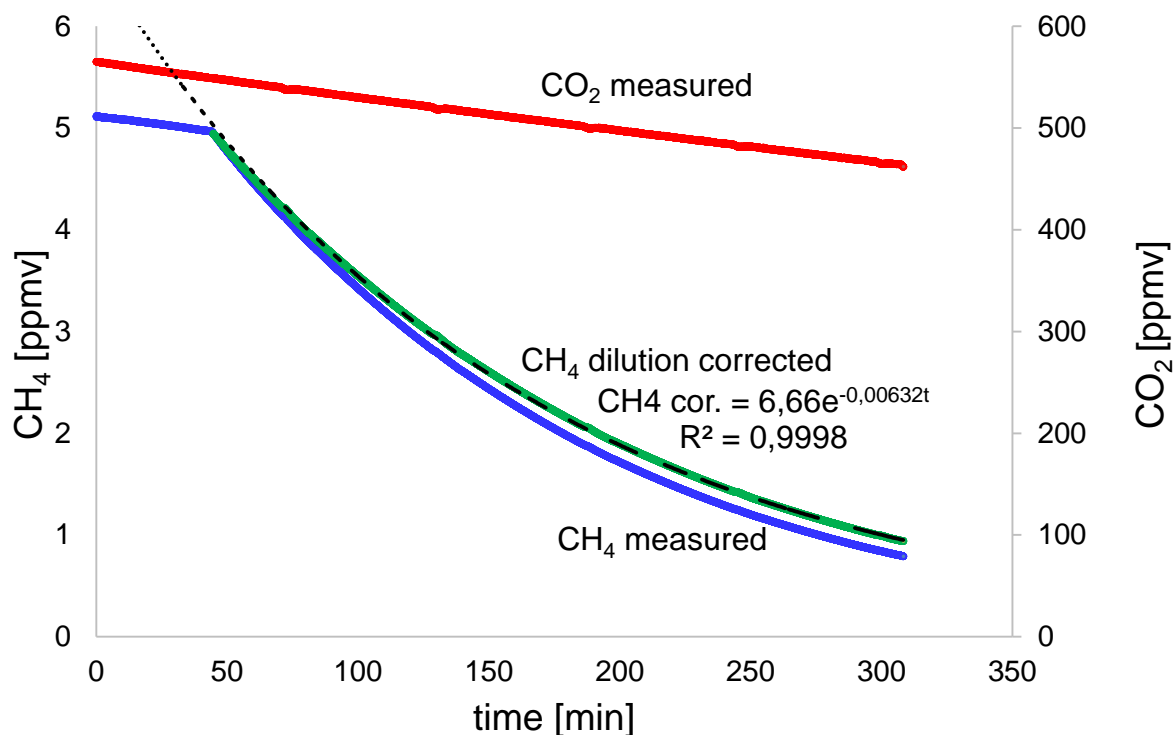


Figure S2: CH₄ + OH control experiment without canister sampling where ozone was continuously photolysed. The steady state ozone mixing ratio was about 5000 ppbv. The observed degradation rate of CH₄ of 0.00632 min⁻¹ = 1.05 e⁻⁴ s⁻¹ corresponds to a level of 1.7x10¹⁰ cm³ s⁻¹ for OH, using a rate constant of 5.7x10⁻¹⁵ cm³ at 293 K (taken from Burkholder et al., 2015). The blue and red lines show the measured CH₄ and CO₂ mixing ratios, respectively. The green line shows the dilution corrected CH₄ mixing ratios using CO₂ as inert tracer.

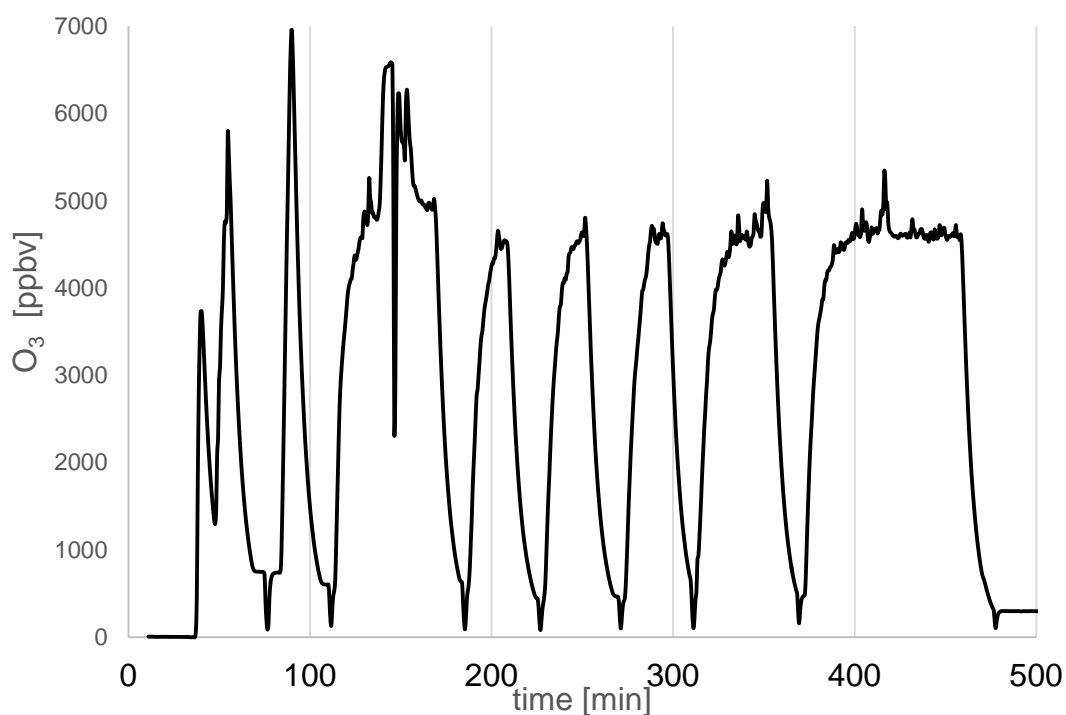
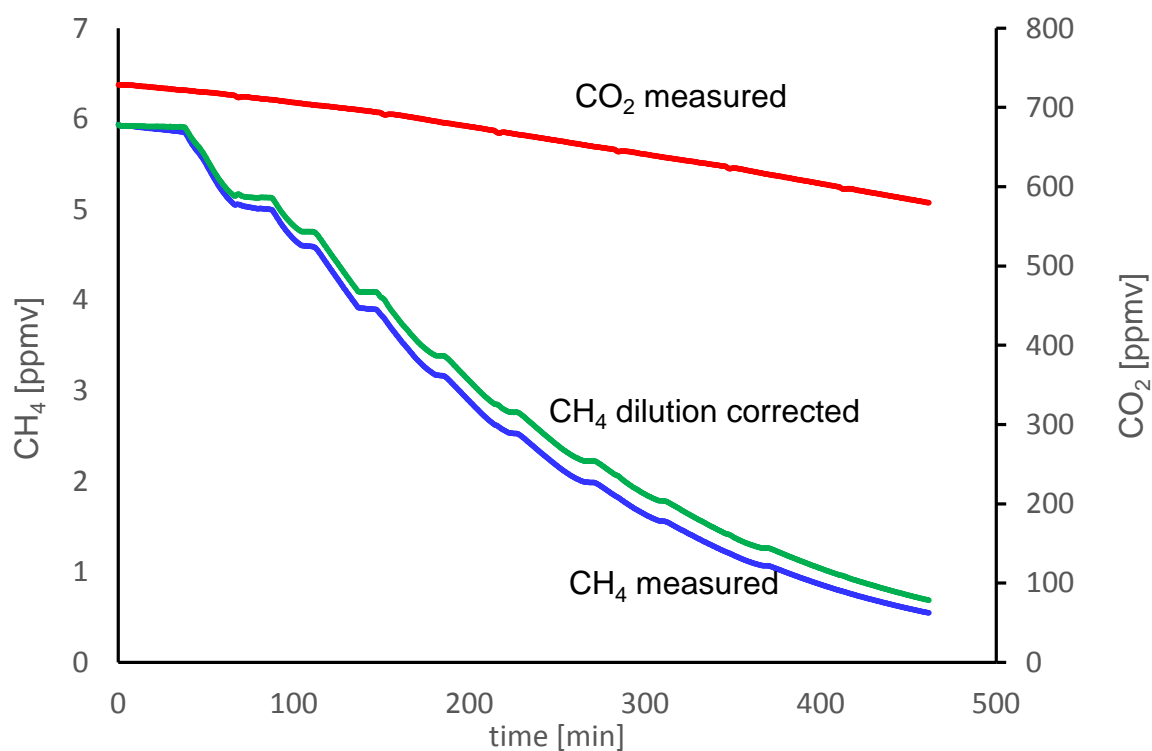


Figure S3: Upper row panel: CH_4+OH degradation experiment for stable hydrogen isotope measurements. The measured CH_4 mixing ratios (blue line) were corrected (green line) for dilution using CO_2 (red line) as an inert tracer. We noted a small spectral interference ($<0.1\%$) in the CO_2 signal arising 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 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.