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Isotopic Characterization (^2H , ^{13}C , ^{37}Cl , ^{81}Br) of Abiotic Degradation of Methyl Bromide and Methyl Chloride in Water and Implications for Future Studies

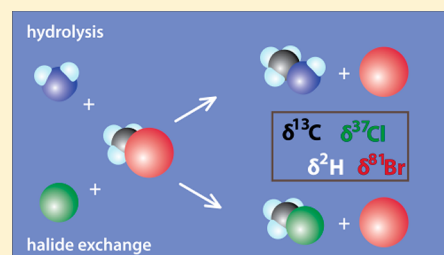
Axel Horst,^{*,†,‡} Magali Bonifacie,[‡] Gérard Bardoux,[‡] and Hans Hermann Richnow^{†,§}

[†]Department of Isotope Biogeochemistry, Helmholtz Centre for Environmental Research – UFZ, Permoserstr.15, 04318 Leipzig, Germany

[‡]Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Université Paris-Diderot, UMR 7154 CNRS, 1 rue Jussieu, F-75005 Paris, France

Supporting Information

ABSTRACT: Methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) significantly contribute to stratospheric ozone depletion. The atmospheric budgets of both compounds are unbalanced with known degradation processes outweighing known emissions. Stable isotope analysis may be capable to identify and quantify emissions and to achieve a balanced budget. Degradation processes do, however, cause isotope fractionation in methyl halides after emission and hence knowledge about these processes is a crucial prerequisite for any isotopic mass balance approach. In the current study, triple-element isotope analysis (^2H , ^{13}C , $^{37}\text{Cl}/^{81}\text{Br}$) was applied to investigate the two main abiotic degradation processes of methyl halides (CH_3X) in fresh and seawater: hydrolysis and halide exchange. For CH_3Br , nucleophilic attack by both H_2O and Cl^- caused significant primary carbon and bromine isotope effects accompanied by a secondary inverse hydrogen isotope effect. For CH_3Cl only nucleophilic substitution by H_2O was observed at significant rates causing large primary carbon and chlorine isotope effects and a secondary inverse hydrogen isotope effect. Observed dual-element isotope ratios differed slightly from literature values for microbial degradation in water and hugely from radical reactions in the troposphere. This bodes well for successfully distinguishing and quantifying degradation processes in atmospheric methyl halides using triple-element isotope analysis.

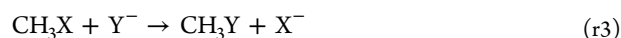
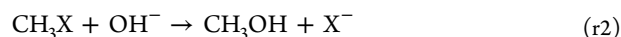
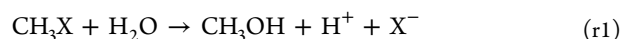


INTRODUCTION

Methyl chloride (CH_3Cl , chloromethane) and methyl bromide (CH_3Br , bromomethane) together contribute about 30% to halogen induced ozone loss even though atmospheric concentrations are very low: 540 pptv and 7 pptv, respectively.¹ CH_3Cl and CH_3Br are emitted by both anthropogenic and natural sources such as fumigation for quarantine and preshipment treatment (for CH_3Br),² marine macroalgae,³ salt marshes,⁴ soils,⁵ biomass burning,⁶ and tropical plants.⁷ Main degradation processes for both of these compounds are reaction with OH and Cl radicals in the troposphere,⁸ degradation in oceans⁹ and soils.¹⁰ The atmospheric budgets of both compounds are unbalanced with known degradation processes exceeding the best estimates of known emissions by approximately 20% for CH_3Cl and 30% for CH_3Br .^{1,11} A better understanding of emission and degradation processes will be necessary in order to better quantify emission and degradation of CH_3X and to improve budget estimates.

Previous studies suggested that degradation in oceans is primarily driven by the abiotic processes hydrolysis and halide exchange as well as microbial degradation.^{9,12,13} To a minor extent, hydrolysis may also contribute to degradation of CH_3Br in soils.¹⁴ Hydrolysis and halide exchange of CH_3X (CH_3Cl

and CH_3Br) are both nucleophilic substitution reactions ($\text{S}_{\text{N}}2$) following second order reaction kinetics. The attacking nucleophiles are either water (H_2O), hydroxide ions (OH^-), or halide ions such as Cl^- and Br^- (Y^-):^{15–17}



In principle, hydrolysis of chlorinated aliphatic compounds may occur due to neutral (R1) and/or alkaline hydrolysis (R2) depending on the pH and the reacting organic compound. For instance, solely neutral hydrolysis (R1) was detected for CCl_4 whereas some chlorinated ethenes only reacted with hydroxide ions (R2).¹⁸ For CH_3X it was shown that alkaline hydrolysis required a hydroxide concentration of more than 0.1 mol L^{-1} ($\text{pH} > 13$) and hence only neutral hydrolysis is considered to be relevant in most environments.¹⁶ Consequently, reactions R1 and R3 were suggested to constitute important degradation

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processes for methyl bromide in the environment.^{19–21} For methyl chloride, microbial degradation seems to be more important, especially in subarctic and arctic ocean waters due to slow degradation rates of abiotic processes.⁹ Still, the overall importance of these reactions compared to microbial degradation of methyl halides in oceans and soils is generally not well understood.

Stable isotope analysis was suggested as a diagnostic tool to overcome the limitations of solely quantifying concentration levels of these compounds.²² Several studies measured the carbon isotope composition of various sources and degradation processes and an overview of these isotopic signatures was published for CH₃Br²³ and CH₃Cl,²⁴ respectively. Isotopic source signatures and existing isotopic enrichment factors for degradation processes were used to calculate an isotopic mass balance which was compared to the measured isotopic composition of tropospheric CH₃X. Both studies revealed that the modeled atmospheric isotopic composition differed considerably from the measured isotopic composition. This discrepancy might be due to several reasons. Unknown sources and their isotopic composition could not be included in the models and also enrichment factors for degradation processes were partly not considered or known. In order to improve future atmospheric budget estimates of CH₃X both emissions and degradation processes need to be characterized more precisely.

In the current study we focused on isotopically characterizing the major abiotic degradation processes in oceans. Isotopic enrichment factors (ϵ) for the isotopes of all three elements in each compound were measured for the two nucleophilic substitution reactions (SN₂) hydrolysis and halide exchange. Significant improvements may be expected if the isotopic compositions of several elements are measured in one compound. Such multielement isotopic approaches have recently become available with improved measurement techniques and were successfully applied to describe, for instance, the fate of organic contaminants in groundwater.^{25,26} For CH₃Cl, hydrogen isotope measurements were presented recently^{27–29} and bromine isotope analysis was demonstrated in two studies for CH₃Br^{30,31} but overall no multielement isotope studies have been published yet for methyl halides. Here we determined the isotope fractionation caused by the two SN₂ reactions for all available stable isotopes in each compound; that is, hydrogen and carbon isotopes in both compounds and chlorine as well as bromine isotopes for methyl chloride and methyl bromide, respectively. To our knowledge, the presented data are the first three-dimensional isotope measurements for each of these substances. The results are compared to isotope fractionation pattern of other potentially important processes and implications toward a future use of multidimensional isotope studies of methyl halides are discussed.

MATERIALS AND METHODS

Chemicals. Methyl chloride and methyl bromide were purchased as compressed gases and with a purity of more than 99%. Methyl chloride was obtained from Linde (Germany) whereas methyl bromide was purchased from Gerling, Holtz & Co (Germany). A commercially available sea salt without any additives (Aquasale, Heilbronn, Germany, major ion composition given in Supporting Information Table S1) was purchased to prepare brines with a concentration of 35 g

kg⁻¹ (psu) which is similar to the average salt content of seawater.

Preparation of Samples and Experiments. Stock solutions with a concentration of 10 mmol L⁻¹ CH₃Br and CH₃Cl were prepared for hydrolysis experiments and 5 mmol L⁻¹ CH₃X for halide exchange experiments by injecting the corresponding amount of gas into the headspace of a 1L crimp-sealed glass bottle filled with distilled water and brine (3.5%), respectively. Additionally, a stock solution of 0.2 mmol L⁻¹ CH₃Br was prepared to carry out a hydrolysis experiment at a lower concentration. The brine was prepared by mixing distilled water with the sea salt and boiling this solution for 10 min. All experiments were carried out in unbuffered solution (see also Results and Discussion for further explanations). After preparation, stock solutions were shaken overnight for equilibration before further usage. For each experiment, 6–10 septum bottles (60 mL) were filled with 40 mL of solution, crimp-sealed and all bottles shaken for at least 3 h. Then, the starting concentration was determined by injecting aliquots of the headspace of all samples. At least three standards were analyzed to quantify the sample concentrations via a three-point calibration (Supporting Information 3). To avoid gas-leakage through the pinched septa, the sample bottles were kept upside-down throughout the entire experiment. Furthermore, samples were kept at a dark place maintaining a temperature of 23 ± 1 °C. Sampling of the bottles took place in different time intervals. For methyl bromide, sampling occurred every 3–5 days whereas for methyl chloride up to two months passed before another sample was collected. After sampling, each bottle was frozen to -18 °C for conservation and stored until the end of the experiment at this temperature. Before analysis, all samples of one experiment were heated simultaneously to 25 °C in a water bath and subsequently shaken for 2 h to ensure equal treatment of all samples and complete equilibration in the sample bottles.

Stable Isotope Analysis of Carbon, Hydrogen, Chlorine, and Bromine. Stable isotope analysis was carried out by injecting aliquots of the headspace gas (50–1000 μL depending on concentration and element) into the injector (split mode) of the gas chromatographic systems (GC) using a gastight syringe with push-button valve (VICI Precision Sampling). The GC was either connected to gas source isotope ratio mass spectrometry (IRMS) for hydrogen and carbon isotope analysis or to multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) for chlorine and bromine isotope analyses. The analytical procedures followed closely the methods described and published in previous studies for carbon,³² hydrogen,³³ chlorine,^{34,35} and bromine³⁶ isotopes. Descriptions of the methods are provided for each method in the Supporting Information 1, including also a cross calibration for bromine isotopes following previously published protocols^{37,38} (Supporting Information 2).

Results from isotopic measurements are reported in delta values (δ) for all isotopes. Delta values are calculated according to the following expression:³⁹

$$\delta^i E(Ur) = \frac{(R)_{\text{sample}}}{(R)_{\text{standard}}} - 1 \quad (1)$$

Here, $^i E$ indicates ²H, ¹³C, ³⁷Cl, and ⁸¹Br, and R is the isotopic ratio ²H/¹H, ¹³C/¹²C, ³⁷Cl/³⁵Cl, and ⁸¹Br/⁷⁹Br for hydrogen, carbon, chlorine, and bromine, respectively. The

delta values are given in Ur (urey) according to recent IUPAC recommendations.⁴⁰ Urey, if expressed in milli-urey (mUr), and the more commonly used permil scale (‰) are interchangeable: 1 mUr = 0.001 = 1‰, but Ur is, in contrast to permil a SI unit and hence common SI prefixes such as milli- and micro- become available. Other terms for the expression of isotopic ratios such as ppm and permeg may also be reported in Ur. Thus, the unit urey provides a single unified approach for the expression of all stable isotope ratios. The overall uncertainties of the analytical procedures, including reproducibility, linearity, and scale normalization are usually better than 5 mUr (hydrogen), 0.5 mUr (carbon), 0.2 mUr (chlorine), and 0.1 mUr (bromine).

Enrichment factors and dual element isotope ratios.

The isotopic enrichment factor describes the change of the isotopic composition between the substrate and the instantaneous product caused by a reaction or a process.⁴¹ It further characterizes the constant change of the isotopic composition of the substrate reservoir due to the preferential loss of heavy or light isotopes during a reaction or process. In the current study, isotopic enrichment factors (ϵ_{H} , ϵ_{C} , ϵ_{Cl} , ϵ_{Br}) for CH_3Cl and CH_3Br were determined by using the Rayleigh equation:⁴²

$$\ln\left(\frac{\delta^i E + 1000}{\delta^i E_0 + 1000}\right) \approx \ln(f)\epsilon_x \quad (2)$$

where $\delta^i E$ is the isotopic signature ($\delta^2\text{H}$, $\delta^{13}\text{C}$, $\delta^{37}\text{Cl}$, $\delta^{81}\text{Br}$) of the organic after partial degradation, $\delta^i E_0$ indicates the initial delta value ($\delta^2\text{H}_0$, $\delta^{13}\text{C}_0$, $\delta^{37}\text{Cl}_0$, $\delta^{81}\text{Br}_0$), and f is the fraction of organic remaining after partial degradation. The procedure for quantifying f is provided in the [Supporting Information 3](#). The Rayleigh equation is appropriate to derive the isotopic enrichment factors for first-order or pseudo-first-order reactions.⁴³

Λ -values (λ) describe the ratio of the enrichment factors of isotopes of two different elements.⁴³ Λ -values are determined as the slope of a linear regression of isotopic signatures of two elements (e.g., H and C) determined from samples of the same experiment. Λ -values may also be estimated according to the following relationship:⁴³

$$\Lambda_{x/y} \approx \frac{\epsilon_x}{\epsilon_y} \quad (3)$$

where ϵ_x and ϵ_y are the enrichment factors of two different elements determined for the same mechanism in a certain compound.

RESULTS AND DISCUSSIONS

Reaction Rates. Experiments were performed to investigate the abiotic degradation of CH_3Br and CH_3Cl dissolved in water. Experiments in distilled water were carried out to study hydrolysis reactions only. In brines (seawater) degradation may be due to both, hydrolysis and halide exchange. All experiments were performed at a temperature of 23 ± 1 °C. No buffer was added to the stock solutions because buffer catalysis was reported as a complicating factor in previous studies.^{16,44,45} Moreover, hydrolysis of CH_3Cl and CH_3Br is expected to primarily follow reaction R1 in the environment. Theoretically, when taking into account the nucleophilicities of the nucleophiles ([Supporting Information 4](#)), alkaline (R2), and neutral hydrolysis (R1) should be equally important at a pH of 11.6.⁴⁶ Another study showed that alkaline hydrolysis of singly halogenated compounds was

not sustained, if OH^- concentrations dropped below 0.1 mol L^{-1} ¹⁶ (pH 13). Consequently, reaction R2 is supposed to be unimportant at pH 10 and below.⁴⁶ Therefore, all hydrolysis reactions in this study, which were performed at pH values smaller than 7, were assumed to be independent of the pH and to predominantly follow reaction R1. Results for the determined rate constants of the individual experiments are summarized in [Table 1](#) and are compared to previously published values.

Table 1. Rate Constants for Hydrolysis and Halide Exchange of CH_3Br and CH_3Cl

	rate constants ^a [d^{-1}]	rate constants (previous studies) [d^{-1}]
$\text{CH}_3\text{Br} + \text{H}_2\text{O}$	0.013 ± 0.002	0.021 ± 0.002^b
$\text{CH}_3\text{Br} + \text{H}_2\text{O} + \text{Y}^-$	0.115 ± 0.023	0.154 ± 0.06^c
$\text{CH}_3\text{Cl} + \text{H}_2\text{O}$	0.0015 ± 0.0005	0.0014 ± 0.00002^d
$\text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{Y}^-$	0.0012 ± 0.0003	

^aRates constants were determined from linear regressions of $\ln[f]$ versus time and indicate the rate constant at 23 ± 1 °C. The errors are given as the 95% confidence interval. ^bJeffers and Wolfe.¹⁶ ^cKing and Saltzman.¹⁷ ^dElliot and Rowland.⁴⁵

For hydrolysis of CH_3Br two experiments were carried out at different concentrations. Rate constants of both experiments varied between $0.035 \pm 0.008\%$ d^{-1} at 10 mmol L^{-1} CH_3Br and $0.013 \pm 0.002\%$ d^{-1} at 0.2 mmol L^{-1} CH_3Br . The rate constant obtained at high concentrations may, however, be influenced by an additional equilibration effect with Br^- ions in the solution also represented by unusual bromine isotope values (see discussion below). During hydrolytic degradation of CH_3Br , Br^- ions are released into the solution according to reaction R1. Schwarzenbach et al.⁴⁶ summarized previously published relative nucleophilicities of nucleophiles reacting with CH_3Br .⁴⁷ Taking into account these nucleophilicities and the CH_3Br concentration of 10 mmol L^{-1} , released Br^- ions reached indeed a concentration high enough to compete with water as a nucleophile. Both hydrolysis and Br^- exchange are equally important when about 75% of Br^- is released due to transformation of CH_3Br ([Supporting Information 4](#)). A second experiment was run at a lower concentration to avoid any of such additional reactions. At 0.2 mmol L^{-1} CH_3Br the release of Br^- ions due to transformation only reached about 2% of the amount necessary to compete with hydrolysis ([Supporting Information 4](#)) and no additional effect on the Br isotopic composition was detected. Consequently, hydrolysis of methyl bromide at 0.2 mmol L^{-1} CH_3Br followed pseudo first-order kinetics ([Supporting Information Figure S4](#)), a prerequisite to reliably apply the Rayleigh equation for quantification of isotopic enrichment factors. The experimentally determined rate constant of 0.013 ± 0.002 d^{-1} was lower than at high concentrations but the magnitude was close to the rate constant of 0.021 ± 0.002 d^{-1} reported by Jeffers and Wolfe.¹⁶

For experiments with added sea salt the rate constant was about 1 order of magnitude larger (0.115 ± 0.023 d^{-1}) compared to hydrolysis in distilled water and followed pseudo first-order kinetics ([Supporting Information Figure S5](#)). This experimentally determined rate constant agrees, within analytical uncertainty, with 0.154 ± 0.06 d^{-1} published by a previous study.¹⁷ The ten-times higher rate constant due to the

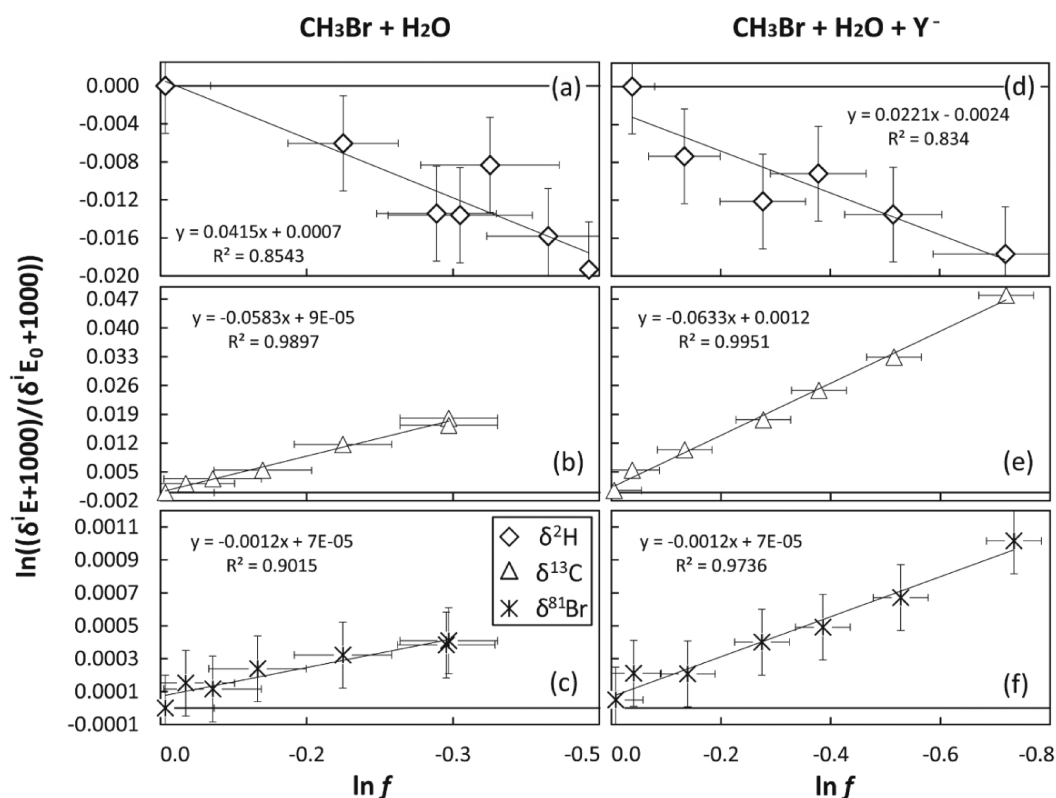


Figure 1. Rayleigh plots for abiotic reactions of CH_3Br in water. Panel (a), (b), and (c) show results of the reaction $\text{CH}_3\text{Br} + \text{H}_2\text{O}$ (hydrolysis). Panel (d), (e), and (f) demonstrate isotope effects due to $\text{CH}_3\text{Br} + \text{H}_2\text{O} + \text{Y}^-$ (hydrolysis and halide exchange combined). The slope of the regression indicates the enrichment factor in Ur. Error bars represent the analytical uncertainty of 5 mUr ($\delta^2\text{H}$), 0.5 mUr ($\delta^{13}\text{C}$), and 0.1 mUr ($\delta^{81}\text{Br}$). For carbon isotopes, error bars are smaller than the used symbols. The quantification was carried out with an uncertainty of usually better than 5%.

Table 2. Isotopic Enrichment Factors (ϵ) and Lambda Values (Λ) of Abiotic Reactions in Water^a

	ϵ_{H} mUr	ϵ_{C} mUr	ϵ_{Cl} mUr	ϵ_{Br} mUr	$\Lambda_{\text{H/C}}$	$\Lambda_{\text{C/Cl}}$	$\Lambda_{\text{C/Br}}$
$\text{CH}_3\text{Br} + \text{H}_2\text{O}$ (10 mmolL ⁻¹)	+42 ± 20	-49.6 ± 5.6		nd			
$\text{CH}_3\text{Br} + \text{H}_2\text{O}$ (0.2 mmol L ⁻¹)	nd	-58.3 ± 6.8		-1.16 ± 0.42	-0.7 ± 0.2*		46.1 ± 16.1
$\text{CH}_3\text{Br} + \text{H}_2\text{O} + \text{Y}^-$	+22 ± 13	-63.3 ± 5.1		-1.22 ± 0.23	-0.3 ± 0.2		48.2 ± 6.5
$\text{CH}_3\text{Cl} + \text{H}_2\text{O}$	+25 ± 6	-41.7 ± 10.2	-5.3 ± 1.3		-0.6 ± 0.3	7.3 ± 0.9	
$\text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{Y}^-$	+24 ± 19	-40.6 ± 13.9	-5.2 ± 1.0		-0.6 ± 0.2	6.9 ± 2.3	

^aEnrichment factors are derived from the Rayleigh plots in Figure 1 and Figure 2. Lambda values are determined graphically from dual-elemental isotope plots (Supporting Information Figure S11–S14). Errors are given as the 95% confidence interval of the regressions. Values in italics indicate that these reactions might not strictly follow pseudo-first-order kinetics and epsilons only serve as an approximation despite acceptable correlation coefficients; nd means “not determined”; * indicates that this value was calculated using eq 3.

nucleophilic strength of Cl (Supporting Information 4) suggests that halide exchange dominates the abiotic degradation of CH_3Br in seawater with hydrolysis only contributing to a minor extent to the overall combined degradation rate.

For hydrolysis of methyl chloride in distilled water the experimentally determined rate constant of $0.0015 \pm 0.0005 \text{ d}^{-1}$ is in good agreement with $0.0014 \pm 0.0002 \text{ d}^{-1}$ reported previously.⁴⁵ The reaction of CH_3Cl with H_2O and salt yielded a rate constant of $0.12 \pm 0.02\% \text{ d}^{-1}$ which is indistinguishable from hydrolysis in distilled water. Data from both reactions of CH_3Cl follow pseudo first-order kinetics (Supporting Information Figures S6 and S7). The similar reaction rate constants obtained from both experiments may indicate that halide exchange of CH_3Cl at ambient temperatures does not have any measurable effect on the combined degradation rate

and hence hydrolysis should be the main abiotic degradation mechanism in natural waters.

Hydrolysis and Associated Isotope Effects. Isotopic enrichment factors derived from hydrolysis experiments were determined for stable carbon, hydrogen, and bromine isotopes of CH_3Br . At high concentrations (10 mmol L⁻¹ CH_3Br) additional equilibration with Br^- influenced the reaction rate constant and the Rayleigh equation may only possess a limited validity for this experiment. Despite this limitation, the carbon isotopic data followed a linear regression with an ϵ_{C} of $-49.6 \pm 5.6 \text{ mUr}$ (Supporting Information Figure S9). This value is close to $-58.3 \pm 6.8 \text{ mUr}$ (Figure 1b) which was determined for the low-concentration experiment (0.2 mmol L⁻¹ CH_3Br) where no significant Br^- exchange occurred. Both ϵ_{C} are consistent with a published carbon isotope enrichment factor of $-51.0 \pm 6.0 \text{ mUr}$.⁴⁸ The same authors investigated the pH

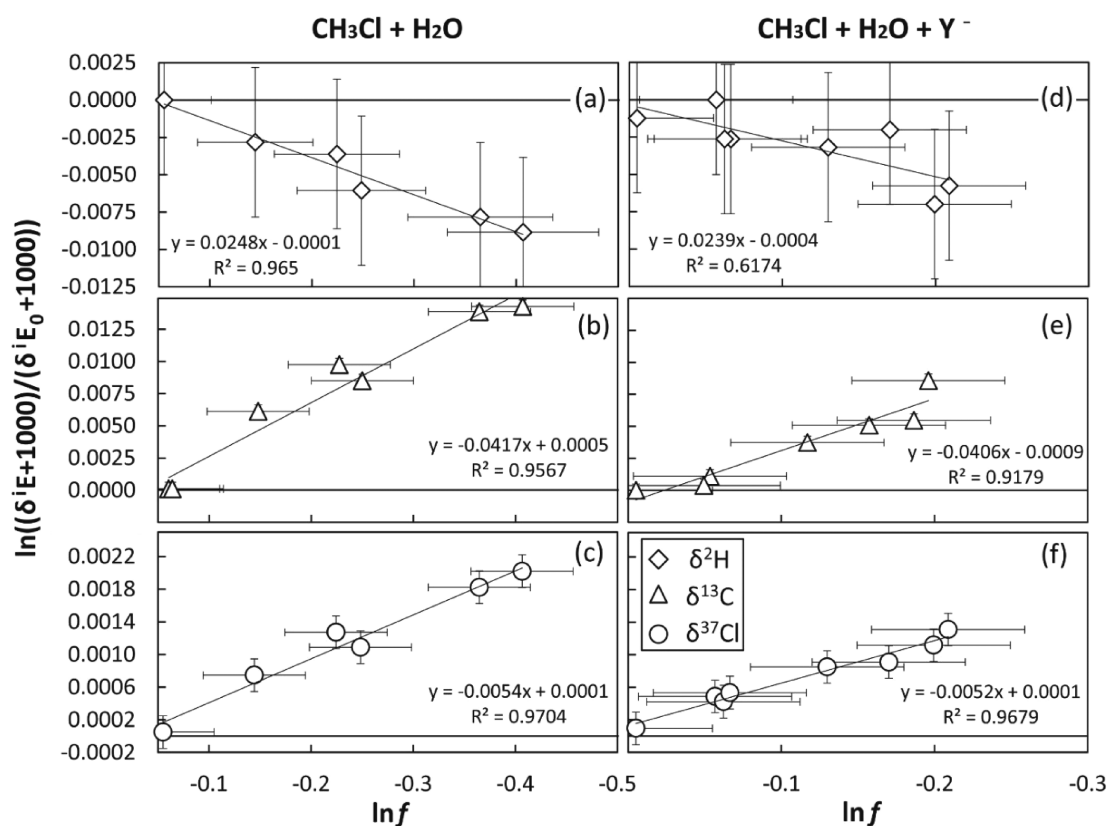


Figure 2. Rayleigh plots for reactions of CH_3Cl . Panel (a), (b), and (c) show results of the reaction $\text{CH}_3\text{Cl} + \text{H}_2\text{O}$ (hydrolysis). Panel (d), (e), and (f) represent isotope effects due to $\text{CH}_3\text{Cl} + \text{H}_2\text{O} + \text{Y}^-$ (combined hydrolysis and halide exchange). The slope of the regression indicates the enrichment factor in Ur. Error bars represent the analytical uncertainty of 5 mUr ($\delta^2\text{H}$), 0.5 mUr ($\delta^{13}\text{C}$), and 0.2 mUr ($\delta^{37}\text{Cl}$). For carbon isotopes, error bars are smaller than the used symbols. The quantification was carried out with an uncertainty of usually better than 5%.

independence of carbon isotope fractionation by carrying out experiments at different pH (4.6, 7.3, and 8.8) and additionally in unbuffered solutions (pH 3.6–6.0). No significant difference was observed in that study for isotopic enrichment factors obtained from unbuffered solutions compared to those with a fixed pH confirming that hydrolysis primarily occurs via one reaction (R1). Hence enrichment factors obtained in the current study should be valid for the conditions found in relevant environmental compartments such as surface waters and soils.

Hydrogen isotope enrichment factors could only be measured for samples at high concentrations. CH_3Br concentrations of 0.2 mmol L^{-1} were too low to meet the isotopic detection limit for hydrogen isotope measurements. Despite the mentioned uncertainties regarding the rate law, the enrichment factor of $+42 \pm 20 \text{ mUr}$ is consistent with a secondary isotope effect resulting from reaction R1 (Figure 1a, Table 2). Secondary effects are usually smaller than primary isotope effects and occur in elements located adjacent to a reactive position due to the changing structure of the molecule or influences of bond vibrations, for example.⁴⁹ Furthermore, the positive ϵ_{H} indicates an inverse isotope effect. The remaining CH_3Br in water becomes successively depleted in deuterium throughout the reaction. Secondary inverse isotope effects of hydrogen are in fact a common feature for nucleophilic substitution reactions of methyl derivatives and this was investigated in several experimental studies in the gas phase as well as in computational studies.^{50–53} Accordingly, the inverse isotope effects may be explained with transition state theory. During $\text{S}_{\text{N}}2$ reactions the nucleophile (H_2O , Y^-)

approaches the carbon atom from the side opposite to the halogen atom. In the transition state both the nucleophile and the leaving halogen atom are partly bound to the carbon atom. The tetrahedral geometry of the methyl halide molecule changes to a trigonal bipyramidal geometry in the transition state where the hydrogen atoms are located in a single plane.⁴⁶ This structural change is associated with an increase of the bending and stretching force constants, the latter caused by a tightening of the C–H bonds.⁵² This increase is represented by a symmetric excitation of the stretching vibration which increases the reaction probability of the molecules containing a C–D bond to a larger extent than for molecules containing a C–H bond.⁵³ As a result, CH_3Br in the solution becomes enriched in ^{13}C and ^{81}Br (see below) but depleted in ^2H . Even though our measured enrichment factor of $+42 \text{ mUr}$ was smaller than those in the cited articles (up to $+200 \text{ mUr}$ in gas phase experiments), it qualitatively confirms these inverse effects for different nucleophiles (see also discussion further below) reacting with methyl halides dissolved in water.

For bromine isotopes in CH_3Br an ϵ_{Br} of $-1.2 \pm 0.4 \text{ mUr}$ was measured for the experiment carried out at 0.2 mmol L^{-1} CH_3Br (Figure 1c). At high concentrations (10 mmol L^{-1} CH_3Br) a nonlinear behavior of the $\delta^{81}\text{Br}$ values could be observed which was not in agreement with the Rayleigh equation (Supporting Information Figure S8). At first, the $\delta^{81}\text{Br}$ of the substrate became more enriched but then started to converge toward the starting value again. Apparently, the rising concentrations of bromine ions released into the solution started to equilibrate with the CH_3Br substrate. At low concentrations no such effect was observed because Br^-

concentrations in solution were too low to compete with H₂O as a nucleophile (Supporting Information 4). Hence, this equilibration is unlikely to occur in most freshwaters and soils, environments where CH₃Br and Br⁻ concentrations are low and where hydrolysis may contribute to degradation. Even in ocean waters the Br⁻ content only reaches 25% of the concentration required to compete with H₂O (1.8 mmol L⁻¹, Supporting Information 4), which might explain why no indications of such an equilibration effect were observed in experiments with brines, as discussed further below.

For hydrolysis of CH₃Cl, stable hydrogen, carbon, and chlorine isotope enrichment factors were determined. The degradation experiment of CH₃Cl in distilled water (hydrolysis) was carried out over 232 days and sampling occurred in time steps of 1–3 months. Isotopic enrichment factors of +25 ± 6 mUr (²H), -41.7 ± 10.2 mUr (¹³C), and -5.3 ± 1.3 mUr (³⁷Cl) were derived from the Rayleigh plots (Figure 2a-c). No equivalent data is available in the literature for comparison. Compared to hydrolysis of CH₃Br, enrichment factors for hydrogen and carbon showed a similar magnitude and direction; that is, carbon isotope effects were relatively large and normal whereas hydrogen isotope effects were small and inverse due to a secondary isotope effect caused by the nucleophilic substitution reaction. The chlorine isotope enrichment factor is about 3 times larger than the measured bromine isotope effect in CH₃Br which is consistent with a previous estimate based on theoretical calculations for primary kinetic isotope effects for halogens.⁵⁴

Isotope Effects Caused by Halide Exchange Reactions. The nucleophilic substitution reaction of halide ions was the second abiotic degradation process investigated in this study. The enrichment factors obtained from experiments with CH₃Br dissolved in brine were +22 ± 13 mUr, -63.3 ± 5.1 mUr, and -1.2 ± 0.2 mUr for ²H, ¹³C, and ⁸¹Br, respectively (Figure 1d-f and Table 2). The measured carbon isotope enrichment factor (-63.3 ± 5.1 mUr) agrees well with -57.0 ± 5.0 mUr reported by Baesman and Miller.⁴⁸ Another study published an ϵ_C of -41.2 mUr for this reaction which is by about 20 mUr smaller.⁵⁵ Compared to the hydrolysis experiments carried out in the current study, enrichment factors for halide exchange are indistinguishable if the analytical uncertainty is taken into account (Table 2). Chlorine ions dominated the exchange reaction with CH₃Br because Cl⁻ concentrations were about nine times higher than necessary to compete with water as a nucleophile (Supporting Information 4). The product of this reaction was CH₃Cl which could be identified during $\delta^{13}\text{C}-\text{CH}_3\text{Br}$ measurements (Supporting Information 5). The measured $\delta^{13}\text{C}$ values of the generated CH₃Cl were indistinguishable from the $\delta^{13}\text{C}$ predicted by the Rayleigh equation for the cumulative product (Supporting Information Table S3, Figure S10) and CH₃Cl is considered the major product of this reaction.

Exchange of chlorine with bromine is a degradation process for CH₃Br but simultaneously constitutes a source for CH₃Cl. Still, oceanic concentrations of CH₃Br are very low compared to CH₃Cl. Hu et al.⁵⁶ reported average concentrations of 2 pM which is much lower than the 88 pM found for CH₃Cl during the same cruise in the Atlantic Ocean. Thus, the transformation of CH₃Br would only marginally (<2%) increase the total CH₃Cl concentration in seawater even if all CH₃Br were completely transformed to CH₃Cl. Chlorine exchange in CH₃Br is therefore not a significant source of CH₃Cl despite its importance as an abiotic degradation process for CH₃Br.

The degradation of CH₃Cl dissolved in brine generated similar enrichment factors as for hydrolysis of CH₃Cl in distilled water: +24 ± 19 mUr for hydrogen, -40.6 ± 13.9 mUr for carbon and -5.2 ± 1.0 mUr for chlorine (Figure 2d-f, Table 1). In contrast to CH₃Br, the addition of sea salt did not increase the degradation rates of CH₃Cl (see discussion above) and it can be assumed that only hydrolysis took place. Furthermore, chlorine isotope measurements did not deliver any evidence for equilibrium exchange of Cl⁻ with CH₃Cl. The CH₃Cl dissolved in the brine had a starting $\delta^{37}\text{Cl}$ of +6.02 mUr SMOC³⁴ whereas Cl⁻ in the added sea salt should be close to 0.0 mUr SMOC.⁵⁷ In our experiments we observed a shift of $\delta^{37}\text{Cl}$ toward more enriched values following clearly pseudo first-order kinetics (Supporting Information Figure S7). In contrast, exchange of CH₃Cl with Cl⁻, if occurring at ambient temperatures, should have caused a shift of $\delta^{37}\text{Cl}$ in the direction of the lighter values of the added sea salt. Thus, halide exchange in CH₃Cl may be considered negligible at ambient temperatures and should not affect the $\delta^{37}\text{Cl}$ of methyl chloride in most environments.

Overall, the results of the current study give further insights into the importance of these two reactions for degradation of CH₃X in water and provide first isotopic enrichment factors for hydrogen and halogens. For CH₃Br, halide exchange should be the dominant abiotic degradation mechanism in seawater which confirms the findings of previous studies.^{15,48,58} Hydrolysis may have a rather minor role in degrading CH₃Br in freshwaters and soils. Hydrolysis of CH₃Br also occurs in oceans at a 10 times slower rate and isotopic enrichment factors are similar to those obtained from halide exchange reactions due to the same reaction mechanism (S_N2 reaction). Consequently, the two processes cannot be individually characterized and quantified with isotopic methods and both reactions may be included as a combined abiotic degradation process in future isotope-based budget estimates. Still, if necessary, degradation by the individual processes can be estimated from the relative rate difference of these abiotic processes which should be constant at relevant temperatures in seawater. For CH₃Cl, only hydrolysis may occur as an abiotic mechanism in most environments with degradation rates being 1 order of magnitude lower than for hydrolysis of CH₃Br. Consequently, hydrolysis should only marginally contribute to degradation of CH₃Cl in oceans, freshwater, and soils as confirmed by previous studies.^{45,59}

Dual-Element Isotope Ratios. Λ -values provide a more precise parameter than ϵ values to characterize and compare reaction mechanisms because these ratios are insensitive to masking and rate limitation by additional processes.⁶⁰ For the current study, lambda values were derived from dual-element isotope plots provided in Supporting Information Figures S11–S14. The resulting $\Lambda_{\text{H/C}}$, $\Lambda_{\text{C/Cl}}$, and $\Lambda_{\text{C/Br}}$ are given in Table 2. $\Lambda_{\text{H/C}}$ values ranged from -0.3 to -0.7 for both compounds and both reaction pathways. The $\Lambda_{\text{C/Cl}}$ for CH₃Cl ranged from 6.9 to 7.3 and the $\Lambda_{\text{C/Br}}$ of CH₃Br ranged from 46.1 to 48.2. No other lambda values have been reported yet for both CH₃Cl and CH₃Br. Some $\Lambda_{\text{H/C}}$ for reactions of CH₃Cl could be calculated from published ϵ_{H} and ϵ_{C} according to eq 3 because these enrichment factors were derived from the same experiment. The resulting $\Lambda_{\text{H/C}}$ are given in SI Table S4. For CH₃Br no dual-element isotope studies are available yet and therefore lambda values of other reaction pathways could not be calculated.

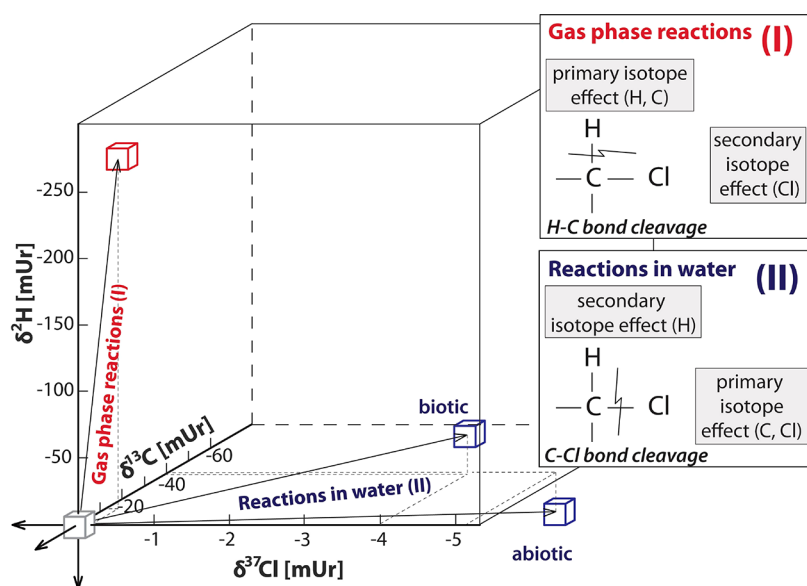


Figure 3. Illustration of fractionation effects of CH_3Cl in water and in the gas phase (troposphere). The $\delta^2\text{H}$, $\delta^{13}\text{C}$, and $\delta^{37}\text{Cl}$ are expressed as the relative difference from $\delta^2\text{H}_0$, $\delta^{13}\text{C}_0$, and $\delta^{37}\text{Cl}_0$ of the undegraded sample. All isotopic values for abiotic reactions in water are taken from the current study whereas carbon and hydrogen isotope values are taken from the literature (SI Table S4). Fractionation for chlorine isotopes in biotic reactions has been estimated assuming a minimum isotope effect of -4 mUr based on previous studies on chlorinated alkanes as described in the text (average of aerobic/anaerobic reactions). For gas phase reactions an insignificant secondary chlorine isotope effect was assumed being smaller than analytical uncertainty of 0.2 mUr. The figure demonstrates a clear distinction between isotope fractionation in the gas phase (troposphere) and fractionation in water.

The $\Lambda_{\text{H/C}}$ of -0.6 for hydrolysis of CH_3Cl shows a similarly small absolute value as degradation by methylotrophic bacteria²⁷ ($\Lambda_{\text{H/C}} = 0.7$, SI Table S4), differing by the algebraic sign due to an inverse ϵ_{H} for hydrolysis. Consortia of soil microbes showed slightly larger $\Lambda_{\text{H/C}}$ which ranged from 1.3 up to 4.6 due to a decreasing ϵ_{C} with decreasing CH_3Cl concentrations.⁶¹ These small lambdas for abiotic and biotic reactions in water are the result of relatively small secondary hydrogen isotope effects (< -50 mUr) due to rupture of the C-X bond. Abiotic and biotic reactions in water are, however, still distinguishable by opposing positive and negative $\Lambda_{\text{H/C}}$.

In contrast, the main abiotic degradation pathways of CH_3Cl in the gas phase ($\text{OH}\cdot$, $\text{Cl}\cdot$ radical reactions) are characterized by larger $\Lambda_{\text{H/C}}$ of 23.6 to 27.5 (SI Table S4) based on the enrichment factors published by two recent studies.^{28,62} Radical reactions cleave the C-H bond and therefore primary isotope effects for both C and H can be observed causing an overall larger $\Lambda_{\text{H/C}}$ which is clearly distinguishable from reactions in water, even though only two isotopic systems are used.

Implications for Future Isotope-Based Studies of CH_3X . The results presented in this paper provide a first glimpse of the capabilities of triple-element isotope analysis of CH_3X for identification and characterization of degradation processes of methyl halides. Specifically, the pattern of isotopic shifts defined by enrichment factors and lambda values will be a useful tool to distinguish abiotic degradation processes from other removal processes of CH_3X . A comparison of isotope effects measured for degradation mechanisms of CH_3Cl demonstrates that basically all known relevant abiotic and biotic degradation mechanisms in water (and soils) are due to a C-Cl bond cleavage in CH_3Cl (Figure 3). Resulting $\Lambda_{\text{C/Cl}}$ are relatively similar for all these reactions but $\Lambda_{\text{H/C}}$ may still be used to distinguish abiotic from biotic degradation due to opposing inverse and normal hydrogen isotope fractionation,

respectively (Table 2, SI Table S4). Methylotrophic bacteria, for instance, were identified as the main biotic degraders in water and soils because these organisms are capable of consuming considerable amounts of methyl halides.⁶³ Large carbon isotope enrichment factors (-38 to -41 mUr) were reported for this biotic reaction but rather small secondary hydrogen isotope enrichment factors (-27 to -29 mUr) due to cleavage of the C-Cl bond.²⁷ Halogen isotope effects for aerobic microbial degradation of CH_3Cl (or CH_3Br) have not been published yet but it is conceivable that they show a similarly large isotope fractionation as reported for other halogenated alkanes. Aerobic microbial degradation of 1,2-dichloroethane, for instance, caused an ϵ_{Cl} of at least -3.8 mUr⁶⁴ which was similar to the ϵ_{Cl} reported for anaerobic microbial degradation (-4.2 mUr).²⁶

In contrast, CH_3X in the troposphere mainly degrades via OH and Cl radical reactions¹ which cause a C-H bond dissociation. Consequently, reported hydrogen isotope effects for CH_3Cl were large²⁸ (> -264 to -280 mUr) and carbon isotope effects were moderate (-10.2 to -11.2 mUr).⁶² Halogens present in CH_3X should only show small secondary isotope effects because they are not involved in radical reactions.⁴⁹ Consequently, gas phase reactions of CH_3Cl show a completely different pattern of isotopic shifts compared to reactions in water and soils (Figure 3). This separation of fractionation patterns of aqueous and gas phase reactions may also be conceivable for CH_3Br because biotic and abiotic degradation mechanisms are largely the same.¹ The possibility to clearly distinguish degradation in water from degradation in the gas phase may considerably simplify the characterization and probably even allow for quantification of degradation processes of methyl halides when applying triple-element isotope analysis.

In order to fully benefit from the advantages of triple-element isotope analysis in the future, however, it will be

necessary to determine three-dimensional isotopic fingerprints of atmospheric samples and of the largest sources (macroalgae, salt marshes, biomass burning, plants, soils). Moreover, full sets of isotopic enrichment factors and lambda values for the main removal processes (OH radical reactions, microbial degradation in oceans and soils) must be determined. Once these tasks are completed, the isotopic data can be fed into models. Previous models relied exclusively on upscaled emission data, used together with the corresponding stable carbon isotopic signatures of the sources to create a weighted mean isotopic source signature for CH₃Cl and CH₃Br, respectively.^{24,62,65} This weighted mean does however not reflect the atmospheric isotopic composition because degradation processes induce isotope fractionation in methyl halides during or shortly after emission (e.g., in oceans or soils) or in the well-mixed atmosphere. Previous models often only partly included the isotopic shifts induced by degradation processes or relied on estimates because enrichment factors were not available for each assumed degradation process.^{23,24,65} A recent study provided a more refined carbon isotope mass balance which accounted for the effect of degradation in atmospheric CH₃X and simultaneous mixing of continuous emissions of CH₃X from sources.⁶² The calculated budget, however, suggested an even larger imbalance between emissions and loss processes than previously thought.

The future use of two additional isotopic systems for each compound may substantially improve such mass balance approaches because of the different sensitivity of hydrogen and halogen isotopes for radical reactions in the atmosphere and degradation in water/soil respectively (Figure 3). Hence, three different isotopic mass balances may be created which have to yield matching results for emissions and degradation rates derived from isotope enrichment factors thus providing a tool for verification of such a mass balance approach. Apart from these bottom-up approaches, inverse top-down models using isotopic data might be appropriate methods for source apportionment of atmospheric compounds.⁶⁶ These inverse models estimate emissions and degradation from variations in the atmospheric composition but require long-term monitoring using a relatively dense network of sampling stations.⁶⁷ Inverse models may, however, provide an alternative route to calculate the atmospheric budget, but for CH₃X the application of these models is currently still out of reach because of the challenges to regularly measure the isotopic composition of atmospheric CH₃X. Once these challenges are overcome, triple-element isotope analysis may provide a realistic chance to better quantify the unbalanced atmospheric budgets of CH₃X and to identify the putatively missing sources.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.9b02165](https://doi.org/10.1021/acs.est.9b02165).

Additional information on analytical methods (isotope analysis, quantification), cross-calibration of standards for bromine isotope analysis, relative nucleophilicities of halogens and water, graphical determination of the rate laws of the different reactions, isotopic measurements of carbon and bromine for hydrolysis of CH₃Br at high concentrations, determination of lambda values from the current and previous studies, and isotopic information on product-CH₃Cl (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: axel.horst@ufz.de.

ORCID

Axel Horst: 0000-0002-3475-2425

Hans Hermann Richnow: 0000-0002-6144-4129

Notes

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