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T. S. Rhee, C. A. M. Brenninkmeijer, T. Röckmann. Hydrogen isotope fractionation in the photolysis of formaldehyde. *Atmospheric Chemistry and Physics Discussions*, 2007, 7 (4), pp.12715-12750. hal-00303076

**HAL Id: hal-00303076**

**<https://hal.science/hal-00303076>**

Submitted on 18 Jun 2008

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**Hydrogen isotope  
fractionation in the  
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formaldehyde**

T. S. Rhee et al.

# Hydrogen isotope fractionation in the photolysis of formaldehyde

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Received: 2 August 2007 – Accepted: 15 August 2007 – Published: 29 August 2007

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Abstract

Experiments investigating the isotopic fractionation in the formation of H<sub>2</sub> by the photolysis of CH<sub>2</sub>O under tropospheric conditions are reported and discussed. The deuterium (D) depletion in H<sub>2</sub> produced is 500(±20)‰ with respect to the parent CH<sub>2</sub>O.

We also observed that complete photolysis of CH<sub>2</sub>O under atmospheric conditions produces H<sub>2</sub> that has virtually the same isotopic ratio as that of the parent CH<sub>2</sub>O. These findings imply that there must be a very strong concomitant isotopic enrichment in the radical channel (CH<sub>2</sub>O + hν → CHO + H) as compared to the molecular channel (CH<sub>2</sub>O + hν → H<sub>2</sub> + CO) of the photolysis of CH<sub>2</sub>O in order to balance the relatively small isotopic fractionation in the competing reaction of CH<sub>2</sub>O with OH. Using a 1-box photochemistry model we calculated the isotopic fractionation factor for the radical channel to be 0.22(±0.08), which is equivalent to a 780(±80)‰ enrichment in D of the remaining CH<sub>2</sub>O. When CH<sub>2</sub>O is in photochemical steady state, the isotopic ratio of the H<sub>2</sub> produced is determined not only by the isotopic fractionation occurring during the photolytical production of H<sub>2</sub> (α<sub>m</sub>) but also by overall fractionation for the removal processes of CH<sub>2</sub>O (α<sub>f</sub>), and is represented by the ratio of α<sub>m</sub>/α<sub>f</sub>. Applying the isotopic fractionation factors relevant to CH<sub>2</sub>O photolysis obtained in the present study to the troposphere, the ratio of α<sub>m</sub>/α<sub>f</sub> varies from ~0.8 to ~1.2 depending on the fraction of CH<sub>2</sub>O that reacts with OH and that produces H<sub>2</sub>. This range of α<sub>m</sub>/α<sub>f</sub> can render the H<sub>2</sub> produced from the photochemical oxidation of CH<sub>4</sub> to be enriched in D (with respect to the original CH<sub>4</sub>) by the factor of 1.2–1.3 as anticipated in the literature.

## 1 Introduction

Formaldehyde (CH<sub>2</sub>O) is a key carbonyl compound in the atmosphere. Its abundance varies over a wide large range from sub-ppb levels to ~100 ppb depending largely on local sources (Warneck, 1999). Its turnover is large and it is a source of molecular hydrogen (H<sub>2</sub>), carbon monoxide (CO), and of the hydroperoxyl radical (HO<sub>2</sub>), yet limited

ACPD

7, 12715–12750, 2007

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Hydrogen isotope  
fractionation in the  
photolysis of  
formaldehyde**

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

measurements are available in various atmospheric regions. Recent satellite observations of CH<sub>2</sub>O make it possible to investigate its distribution on regional and global scales (e.g., Martin et al., 2004; Wittrock et al., 2006). While direct emissions from fossil fuel combustion, biomass burning, and also automotive exhaust contribute significantly to the burden of atmospheric CH<sub>2</sub>O (Carlier et al., 1986; Garcia et al., 2005), in situ production of CH<sub>2</sub>O by photochemical oxidation of volatile organic compounds appears to be the dominant source on a global scale (Carlier et al., 1986; Warneck, 1999). In remote oceanic areas (Wagner et al., 2002; Weller et al., 2000), in the free troposphere (Frost et al., 2002), and in the stratosphere, only the photochemical oxidation of CH<sub>4</sub> serves as the major source. Apart from the importance of the rather simple CH<sub>2</sub>O molecule in the Earth's atmosphere and far beyond, it is also subject to fundamental research regarding for instance the exact processes during its photolysis (e.g., Moore and Weisshaar, 1983; Townsend et al., 2004).

CH<sub>2</sub>O is broken down by photolysis (R1 and R2) and by photochemical oxidation (R3):



“Incomplete” photolysis (R1) produces HO<sub>2</sub> radical by the rapid reaction of hydrogen (H) and formyl (CHO) radicals with atmospheric oxygen (O<sub>2</sub>), which can lead to the formation of hydroxyl radical (OH) via the reaction with NO or O<sub>3</sub> in the atmosphere. This is an important propagation of the radical chain. Only reaction (R2), i.e. the one-step complete photolysis, yields H<sub>2</sub>. All photochemical reactions of CH<sub>2</sub>O do produce CO, while solely reaction (R2) forms H<sub>2</sub>, which is the topic of our research. In fact, this photochemically produced H<sub>2</sub> constitutes ~60% of the total source of tropospheric H<sub>2</sub> (Rhee et al., 2006b).

**Hydrogen isotope fractionation in the photolysis of formaldehyde**

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

In the stratosphere,  $H_2$  originates from this in situ photolysis process (R2), albeit under photochemically very different conditions, and also from tropospheric import. Recently it has been established that stratospheric  $H_2$  is enriched in deuterium (D) along with the decrease of  $CH_4$  mixing ratios whilst the  $H_2$  mixing ratios remain almost constant (Rahn et al., 2003; Rhee et al., 2006a; Röckmann et al., 2003). It appears that the D enrichment of  $H_2$  is much stronger than the concomitant enrichment for  $CH_4$  accompanying its destruction by OH,  $O(^1D)$ , and Cl radicals. This means that the D enrichment of  $H_2$  occurs not only by the fractionation in the reaction of  $H_2$  with oxidizing radicals (OH, Cl,  $O(^1D)$ ) but is also due to the chain reactions leading from  $CH_4$  to  $H_2$  (Rhee et al., 2006a). Gerst and Quay (2001) discussed potential reactions that may lead to the D enrichment along the photochemical chain reactions of  $CH_4$ . However, the detailed mechanism by which the D content of  $H_2$  is accumulated has not yet been elucidated due to the lack of measurements for isotopic fractionation factors at each reaction step and branching, all of which are fundamentally difficult to determine.

To address this question, as a first step we investigated the isotopic fractionation occurring during the photolysis of  $CH_2O$  by which  $H_2$  is produced for the conditions at Earth's surface. In spite of its crucial role in the isotope budget of  $H_2$ , as well as CO, in the atmosphere, the isotopic fractionation occurring during photolysis of  $CH_2O$  has been rarely investigated in the past (Crouse et al., 2003; Feilberg et al., 2005; Feilberg et al., 2007b). Since  $CH_2O$  is a relatively "long-lived" intermediate in the photochemical chain reactions between  $CH_4$  and  $H_2$ , the results will provide essential insight into understanding the accumulation of D in  $H_2$  produced.

## 2 Experiments

Formaldehyde ( $CH_2O$ ) was prepared by purifying para-formaldehyde (Merck) in a vacuum system following the method of Spence and Wild (1935). Solid para-formaldehyde was heated under vacuum at  $\sim 420$  K. For purification the evaporating  $CH_2O$  and impurities were forced through a set of glass U-tubes which were partly immersed in an

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**Hydrogen isotope  
fractionation in the  
photolysis of  
formaldehyde**T. S. Rhee et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

ethanol sludge (~160 K) made with liquid nitrogen. Purified formaldehyde was then collected in a U-tube dipped in liquid nitrogen (77 K). A given amount of pure CH<sub>2</sub>O was released to a 3-L glass bulb and three 0.1-L glass flasks, all of which were connected to the same manifold. Afterwards pressure inside the manifold was read by a capacitance manometer (MKS10, Baratron). We had once monitored the pressure inside the 3-L glass bulb for 2 days and found no change, indicating no absorption or loss of CH<sub>2</sub>O. CH<sub>2</sub>O-free synthetic air was then introduced into the 3-L glass bulb to reach about ambient pressure and the final pressure was read by another capacitance manometer (MKS1000, Baratron) to determine the CH<sub>2</sub>O mixing ratio. Since these pressure readings are essential for determining the CH<sub>2</sub>O mixing ratio in reactors used for the photolysis experiments, the capacitance manometers were calibrated accurately by an absolute manometer (Digiquartz 740, Paroscientific) whenever necessary. The CH<sub>2</sub>O–air mixture was used as a stock for a series of CH<sub>2</sub>O photolysis experiments. The CH<sub>2</sub>O mixing ratios in the stock were usually around 0.3%. All glass used was Duran glass (Schott), thoroughly evacuated and heated prior to use. Glass bulbs were kept in the dark by wrapping them with aluminum foil or with black cloth to avoid any photochemical reactions prior to commencing CH<sub>2</sub>O photolysis experiments.

CH<sub>2</sub>O photolysis experiments in sunlight were carried out on the roof of a 3-story building of the Max Planck Institute for Chemistry, Mainz (50° N, 8.16° E), in August and September of 2003 and in March, May and June of 2004 (Table 1). We conducted also the CH<sub>2</sub>O photolysis experiments using a Xe arc lamp. Aliquots of the CH<sub>2</sub>O stock air were transferred to quartz or glass flasks, diluted to a known mixing ratio with CH<sub>2</sub>O-free synthetic air, and photolyzed for a few hours to ~17 days. The CH<sub>2</sub>O mixing ratios in the reactors were less than ~2 ppm except in the experiments running for few hours, for which ~50 ppm of CH<sub>2</sub>O was used. After photolysis we measured the H<sub>2</sub> mixing ratio and D/H ratio. The δD values and mixing ratios of the H<sub>2</sub> produced were determined by a recently developed technique involving continuous-flow isotope mass spectrometry (Rhee et al., 2004).

The pure CH<sub>2</sub>O in the 0.1-L glass flasks was used to determine the D/H ratio of

the CH<sub>2</sub>O by photolyzing it with light from a mercury arc lamp (HBO102W, OSRAM). The photolysis of pure CH<sub>2</sub>O produces not only CO and H<sub>2</sub> but also H and CHO radicals which further undergo self reactions and reaction with CH<sub>2</sub>O, ending up with the production of CO and H<sub>2</sub>. Thus, the final products of the photolysis are only CO and H<sub>2</sub>. This H<sub>2</sub> has the same isotopic composition as the parent CH<sub>2</sub>O. Complete conversion of the CH<sub>2</sub>O to CO and H<sub>2</sub> was confirmed by measuring the amount of H<sub>2</sub> produced and its isotopic composition. The deuterium content is as usual expressed as  $\delta D = (R_{SPL}/R_{STD}-1) \times 1000(\text{‰})$ , where R<sub>SPL</sub> and R<sub>STD</sub> represent the D/H of H<sub>2</sub> for sample and a reference material, respectively.

### 3 Results

#### 3.1 The yield of H<sub>2</sub> in the photolysis of CH<sub>2</sub>O

As mentioned earlier, photolysis of CH<sub>2</sub>O has one channel that produces CHO and H radicals (R1) and the other that produces CO and H<sub>2</sub> molecules (R2). The CHO radical reacts rapidly with O<sub>2</sub> in the air, also forming CO. Thus, the amount of CO produced should always be the same as that of CH<sub>2</sub>O photolyzed, while the amount of H<sub>2</sub> represents the fraction of CH<sub>2</sub>O that follows the molecular channel (R2). Thereby the yield of the molecular channel, given as  $\Phi(\text{H}_2)$ , can be defined by the ratio of H<sub>2</sub> to CO.

However, a portion of the CH<sub>2</sub>O in the reactor may have reacted with the radicals of H, OH, and HO<sub>2</sub>, as they are produced in the reactor during the photolysis. These reactions produce CO and formic acid (HCOOH) as well. The reaction of CH<sub>2</sub>O with HO<sub>2</sub> produces hydroxymethylperoxy radical (HOCH<sub>2</sub>OO). This radical is so unstable that it immediately dissociates back to CH<sub>2</sub>O. However, a fraction reacts with HO<sub>2</sub> or itself producing HCOOH (Burrows et al., 1989; Su et al., 1979; Veyret et al., 1989) (see Sect. 3.2 for details). In addition, CO and any HCOOH produced can react further with OH to form their oxidized products. These reactions may result in a deficit in the

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

mass balance of CO if only photolysis of CH<sub>2</sub>O is considered. Because of such a non-conservation of CO in the reactor, we did not attempt to measure the ratio of the mixing ratios of H<sub>2</sub> to CO for each photolysis run to obtain the value of  $\Phi(\text{H}_2)$ . But, we tracked the actual fraction of H<sub>2</sub> produced by photolysis of CH<sub>2</sub>O, given as  $\phi(\text{H}_2)$ , which represents the ratio of the H<sub>2</sub> mixing ratio in the reactor to the initial CH<sub>2</sub>O mixing ratio.

Figure 1 shows the evolution of  $\phi(\text{H}_2)$  throughout the periods of photolysis for experiments conducted with different reactor materials or light sources. The period of photolysis is given as number of daylight hours disregarding any parameters that might influence the actual photolysis rates of CH<sub>2</sub>O. For the short periods experiments (<12 h),  $\phi(\text{H}_2)$  increases rapidly with the increase of photolysis time. With long periods of photolysis (>130 h),  $\phi(\text{H}_2)$  converges toward an asymptote. By virtue of negligible production of H<sub>2</sub> through reactions other than the CH<sub>2</sub>O photolysis and little reactivity of H<sub>2</sub> in the reactor for the periods of the CH<sub>2</sub>O photolysis,  $\phi(\text{H}_2)$  approaches an asymptotic value at a function of time. The asymptotic value of  $\phi(\text{H}_2)$  is equivalent to  $\Phi(\text{H}_2)$  when CH<sub>2</sub>O is destroyed only by photolysis.

For the photolysis periods from 50 to 100 h, the measurements are scattered. We suspect that this is due mostly to photolytical effects rather than analytical errors. In particular, changes in radiation occurring over the course of the experiments on the roof (e.g., cloudiness, albedo, solar zenith angle (SZA), light scattering due to aerosol content, etc.) may result in such different values. In addition, since the yield of the molecular channel peaks at longer wavelengths compared to the radical channel (Moortgat et al., 1983),  $\phi(\text{H}_2)$  increases with the increase of SZA. As an indirect support for this speculation, photolysis of CH<sub>2</sub>O performed in the laboratory using Hg and Xe arc lamps shows that the uncertainty of replicate runs is merely about 2% for the yield of H<sub>2</sub> and 3% for the  $\delta\text{D}$  values. Provided that the scatter is due to variations in parameters that influence photolysis rate of CH<sub>2</sub>O, we do not average the values for the same period of photolysis but use individual values for determining the isotopic fractionation occurring in the CH<sub>2</sub>O photolysis.

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The CH<sub>2</sub>O photolysis experiments conducted with a Xe arc lamp give an opportunity to examine a relation between  $\Phi(\text{H}_2)$  and the range of wavelengths by which CH<sub>2</sub>O are photolyzed. As a Xe arc lamp emits photons within a broad range of wavelengths, the effective wavelength for the photolysis of CH<sub>2</sub>O depends on the cut-off wavelength for transmission through quartz which extends down to  $\sim 200$  nm. This is shorter than the lower limit of solar wavelengths at the Earth's surface. Consequently,  $\Phi(\text{H}_2)$  from the Xe arc lamp experiments should be smaller than that obtained with sunlight because of the dominance of the radical channel in CH<sub>2</sub>O photolysis at these short wavelengths (Moortgat et al., 1983). As shown in Fig. 1,  $\phi(\text{H}_2)$  is almost the same for the two different irradiation periods, indicating that it has reached an asymptote. This asymptotic value is smaller than that obtained in sunlight, which reflects a smaller value of  $\Phi(\text{H}_2)$  using the Xe arc lamp.

### 3.2 A box model simulation of the CH<sub>2</sub>O photolysis

To examine the actual photochemistry in the reactor, we constructed a 1-box model composed of 33 photochemical reactions, including photolysis of CH<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> as well as formation of HCOOH (see Appendix A.). The model was run under conditions of standard atmospheric temperature and pressure with the other boundary conditions from the results from the Tropospheric Ultraviolet and Visible (TUV) radiation model (<http://cprm.acd.ucar.edu/Models/TUV>). As shown in Fig. 2, the TUV radiation model predicts that the values of  $\Phi(\text{H}_2)$  range from 0.6 to 0.76 in Mainz. Since SZA at local noon during the experiments were between 27° and 48°, daily averaged photolysis-rate-weighted mean values of  $\Phi(\text{H}_2)$  would be 0.64 to 0.66, which correspond to total CH<sub>2</sub>O photolysis rates for both channels ( $J_{\text{CH}_2\text{O}}$ ) of  $2.4 \times 10^{-5}$  to  $3.8 \times 10^{-5} \text{ s}^{-1}$ . For the same range of SZA, the ratio of the photolysis rates of H<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O,  $J_{\text{H}_2\text{O}_2} / J_{\text{CH}_2\text{O}}$ , varies only from 0.089 to 0.090. The initial mixing ratio of CH<sub>2</sub>O was assumed to be 1 ppm in synthetic air (78% of N<sub>2</sub> and 22% of O<sub>2</sub>). The commercial software package FACIMILE was used to integrate time derivatives of the reactions.

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Hydrogen isotope  
fractionation in the  
photolysis of  
formaldehyde**

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

As shown in Fig. 3, whereas photochemical destruction of  $\text{CH}_2\text{O}$  forms CO and HCOOH, both of which are further oxidized by reacting with the OH radical, the unique source of  $\text{H}_2$  in the reactor is  $\text{CH}_2\text{O}$  photolysis to the molecular channel (R2) and that  $\text{H}_2$  destruction by the OH radical is negligible ( $<0.1\%$  of  $\text{H}_2$  has reacted at 99% of  $\text{CH}_2\text{O}$  being oxidized). Hence, a substantial portion of the initial  $\text{CH}_2\text{O}$  is converted to products other than CO, but the  $\text{H}_2$  produced is accumulated in the reactor reaching an asymptote.

The time evolutions of  $\phi(\text{H}_2)$  were predicted by applying the values of  $\Phi(\text{H}_2)$ ,  $J_{\text{CH}_2\text{O}}$ , and  $J_{\text{H}_2\text{O}_2}$  from the TUV radiation model described above to the 1-box model (see Fig. 1). The results appear comparable to the measurements for photolysis periods of  $<12$  h. However, there are substantial differences between the measurements and the model predictions at longer photolysis periods. In particular, it is difficult to reproduce the asymptote of measurements which substantially differs from the model predictions that are based on most likely values of parameters under photochemical conditions in Mainz, Germany (solid and dashed lines in Fig. 1). As shown in Fig. 3b,  $\sim 10\%$  of  $\text{CH}_2\text{O}$  is destroyed by the reactions with radicals. This leads to the lower asymptotes of  $\phi(\text{H}_2)$  than the value of  $\Phi(\text{H}_2)$  obtained from the TUV radiation model because  $\phi(\text{H}_2)$  is smaller than  $\Phi(\text{H}_2)$  by a factor corresponding to the fraction of  $\text{CH}_2\text{O}$  photolyzed. In order to predict the asymptote of  $\phi(\text{H}_2)$  from measurement, the value of  $\Phi(\text{H}_2)$  would be  $\sim 0.74$ , the value that the TUV radiation model predicts when SZA is near  $85^\circ$  in the location of Mainz.

### 3.3 Isotope effect of the $\text{CH}_2\text{O}$ photolysis to the molecular channel

Figure 4 shows the variation of the  $\delta\text{D}$  value of  $\text{H}_2$  ( $\delta\text{D}\text{-H}_2$ ) as a function of  $\phi(\text{H}_2)$ . The isotopic ratios are normalized with respect to the  $\delta\text{D}$  value of the initial  $\text{CH}_2\text{O}$ . Thus, a  $\delta\text{D}\text{-H}_2$  value of zero means that the isotopic ratio of the  $\text{H}_2$  in sample air is the same as that for the initial  $\text{CH}_2\text{O}$ . The air samples whose values of  $\phi(\text{H}_2)$  approach the asymptotes at long photolysis times for both the sunlight and Xe arc lamp experiments show near-zero values of  $\delta\text{D}\text{-H}_2$ . This indicates that complete photochemical decomposition

of CH<sub>2</sub>O yields H<sub>2</sub> that has the same isotopic ratios as the initial CH<sub>2</sub>O. This observation and the evolution of δD-H<sub>2</sub> as a function of φ(H<sub>2</sub>) give us crucial information to aid in determining the hydrogen isotopic fractionation processes occurring at (R1) and (R2) as follows.

5 According to the results from the 1-box model described in Sect. 3.2, most of the CH<sub>2</sub>O in the reactor is broken down by photolysis (>90%) with the remainder destroyed mostly by reaction with OH (<8%) while HO<sub>2</sub> and H radicals play only a minor role (<2%) (see Fig. 3b). The rate of change of the CH<sub>2</sub>O mixing ratio in the reactor can thus be described as:

$$10 \quad \frac{d[\text{CH}_2\text{O}]}{dt} = -(J + K)[\text{CH}_2\text{O}] \quad (1)$$

where  $J$  is the sum of photolysis rates of (R1) (i.e.,  $j_r$ ) and (R2) (i.e.,  $j_m$ ) and  $K$  is the sum of the products of the relevant photochemical reaction rate coefficients ( $k_i$ ) and radical concentrations ( $X_i$ ) as follows.

$$J = j_m + j_r \quad (2)$$

$$15 \quad K = \sum_i k_i [X_i] \quad (3)$$

In the same way, for the next abundant isotopologue, CHDO, one obtains:

$$\frac{d[\text{CHDO}]}{dt} = (J' + K')[\text{CHDO}] \quad (4)$$

where  $J'$  and  $K'$  indicate the sums of the photolysis rates and the photochemical reaction rates for CHDO, respectively. In terms of non-equilibrium kinetics, the isotopic fractionation factor is represented as the kinetic isotope effect (or simply isotope effect), which is expressed by the ratio of reaction rates for the different isotopologues, one of which has a rare isotope substituted for the common one (Melander and Saunders, 1980). We define here the isotopic fractionation factor as

**Hydrogen isotope fractionation in the photolysis of formaldehyde**

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

the ratio of photochemical reaction rates or photolysis rates of an isotopologue which has a single deuterium to that for the most abundant isotopologue. For instance, the isotopic fractionation factor for the molecular channel,  $\alpha_m$  is:

$$\alpha_m = \frac{j'_m}{j_m} \quad (5)$$

Hence,  $J'$  and  $K'$  in Eq. (4) have the following relationship with the corresponding rates for  $\text{CH}_2\text{O}$  by means of isotopic fractionation factor,  $\alpha_j$ .

$$J' = j'_r + j'_m = \alpha_r j_r + \alpha_m j_m \quad (6)$$

$$K' = \sum_i k'_i [X_i] = \sum_i \alpha_{k_i} k_i [X_i] = \alpha_K K \quad (7)$$

By definition, the isotopic fractionation factor for  $\text{CH}_2\text{O}$ ,  $\alpha_f$ , is

$$\alpha_f = \frac{J' + K'}{J + K} = \alpha_r \times \frac{j_r}{J} \times \frac{J}{J + K} + \alpha_m \times \frac{j_m}{J} \times \frac{J}{J + K} + \alpha_K \times \frac{K}{J + K} \quad (8a)$$

In Eq. (8a), the ratio of  $j_m$  to  $J$  represents the yield of  $\text{H}_2$  from photolysis of  $\text{CH}_2\text{O}$  ( $\Phi(\text{H}_2)$ ), and the ratio  $J/(J + K)$  is the fraction of  $\text{CH}_2\text{O}$  that is photolyzed. Designating the latter as  $\Gamma$ ,  $\alpha_f$  can be rewritten as:

$$\alpha_f = \alpha_r (1 - \Phi) \Gamma + \alpha_m \Phi \Gamma + \alpha_K (1 - \Gamma) \quad (8b)$$

Or simply,

$$\alpha_f = \alpha_{hv} \Gamma + \alpha_K (1 - \Gamma) \quad (8c)$$

where  $\alpha_{hv}$  represents the isotopic fractionation factor for photolysis of  $\text{CH}_2\text{O}$ . Since the amount of radicals produced along the experiments is not constant,  $\Gamma$  is not a constant but a variable being a function of time. In addition, strictly speaking  $\Phi(\text{H}_2)$  varied during the sunlight experiments as did SZA (Fig. 2b). Accordingly  $\alpha_f$  is changing along with

**Hydrogen isotope fractionation in the photolysis of formaldehyde**

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

the CH<sub>2</sub>O photolysis and photochemical reactions. Nevertheless, assuming that  $\alpha_f$  is constant gives a convenient way to determine the isotopic fractionation factor for the production of H<sub>2</sub>,  $\alpha_m$ . Integrating Eqs. (1) and (4) and then dividing [CHDO] by [CH<sub>2</sub>O] leads to the well-known Rayleigh equation (Rayleigh, 1902):

$$5 \quad \frac{R_Q}{R_o} = f^{\alpha_f} - 1 \quad (9)$$

where  $R_o$  is the isotopic ratio of the initial CH<sub>2</sub>O,  $R_Q$  is that for the remaining CH<sub>2</sub>O during the run of experiment, and  $f$  the fraction of the remaining CH<sub>2</sub>O. Thus, the isotopic ratio of the products ( $R_p$ ) as a function of CH<sub>2</sub>O photochemical destruction can be obtained by mass balance:

$$10 \quad \frac{R_p}{R_o} = \frac{1 - f^{\alpha_f}}{1 - f} \quad (10)$$

Actually  $R_p$  is sum of the isotopic ratios of the products formed by CH<sub>2</sub>O photolysis and its photochemical reactions with radicals. The isotopic ratio of the H<sub>2</sub>,  $R_m$ , which is produced from CH<sub>2</sub>O photolysis to the molecular channel, can be derived from the following derivatives:

$$15 \quad \frac{d[H_2]}{dt} = j_m [CH_2O] \quad (11)$$

and

$$\frac{d[HD]}{dt} = j'_m [CHDO] \quad (12)$$

Solving Eq. (11) and Eq. (12) with inserting the solutions of Eq. (1) and Eq. (4), respectively, and the definition of  $\alpha_m$  in Eq. (5),  $R_m$  has the following relation with  $R_o$ .

$$20 \quad \frac{R_m}{R_o} = \frac{\alpha_m}{\alpha_f} \times \frac{1 - f^{\alpha_f}}{1 - f} \quad (13)$$

**Hydrogen isotope fractionation in the photolysis of formaldehyde**

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

By dividing Eq. (13) by Eq. (10), the ratio of the isotopic ratios of H<sub>2</sub> and all products from CH<sub>2</sub>O photochemistry is the same as the ratios of their isotopic fractionation factors:

$$\frac{R_m}{R_p} = \frac{\alpha_m}{\alpha_f} \quad (14)$$

5 By the same way, the isotopic ratios of the products of the radical channel of CH<sub>2</sub>O photolysis and of photochemical reactions results in a same relations:

$$\frac{R_r}{R_p} = \frac{\alpha_r}{\alpha_f} \quad (15)$$

$$\frac{R_K}{R_p} = \frac{\alpha_K}{\alpha_f} \quad (16)$$

10 From the relations of Eqs. (14), (15), and (16), it is immediately recognized that  $R_p$  is composed of the fractions of the isotopic ratios of the products from two channels of CH<sub>2</sub>O photolysis and its photochemical reactions, which is represented by their reaction rates as the same as for isotopic fractionation factor of CH<sub>2</sub>O in Eq. (8b).

$$R_p = R_r (1 - \Phi) \Gamma + R_m \Phi \Gamma + R_K (1 - \Gamma) \quad (17)$$

15 Since we measured the evolution of  $R_m$  with  $\phi(\text{H}_2)$ ,  $\alpha_m$  can be determined from the relation Eq. (13). As  $f$  approaches 1 (thus,  $\phi(\text{H}_2)$  goes to zero),  $R_m/R_o$  in Eq. (13) becomes the value of  $\alpha_m$ , which is in turn represented by the value of  $\delta\text{D-H}_2$  as follows:

$$\delta\text{D-H}_2 = (\alpha_m - 1) \times 1000(\text{‰}) \quad (18)$$

20 Accordingly, the intercept in Fig. 4 ( $\phi(\text{H}_2)=0$ ) represents the value of  $\alpha_m$  ( $=0.50(\pm 0.02)$ ) and indicates that H<sub>2</sub> produced by photolysis of CH<sub>2</sub>O is 500( $\pm 20$ )‰ depleted with respect to the CH<sub>2</sub>O being photolyzed. Since the experiments for the

**Hydrogen isotope fractionation in the photolysis of formaldehyde**

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

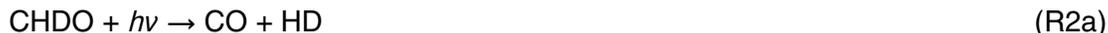
Printer-friendly Version

Interactive Discussion

photolysis of CH<sub>2</sub>O for short periods were conducted with high CH<sub>2</sub>O mixing ratios of 50 ppm, a similar amount of initial CH<sub>2</sub>O, was applied in the 1-box model to determine the value of  $\alpha_m$ . Its uncertainty, 0.02, was determined such that all measurements for the short periods experiments are predicted by the 1-box model within the range of errors (see Fig. 4). The assumption that  $\alpha_f$  is constant should be valid during the initial stage of photolysis of CH<sub>2</sub>O because the amounts of radicals, in particular the OH radical, produced are too small to affect  $\alpha_f$  (see Fig. 3b). Even if  $\alpha_f$  were not constant, it would not interfere with the determination of  $\alpha_m$  because the  $\alpha_f$ 's in (13) cancel for  $f = 1$ .

### 3.4 Isotope effect of the CH<sub>2</sub>O photolysis to the radical channel

Given that complete photolysis of CH<sub>2</sub>O yields H<sub>2</sub> that has the same isotopic ratio as that of the initial CH<sub>2</sub>O (Fig. 4), we can also determine the isotopic fractionation factor,  $\alpha_r$ , which governs the isotopic fractionation occurring at (R1). However, in this case the Rayleigh model cannot be applied because the value of  $\alpha_f$  varies with time due to changes in the amounts of radicals (see below). We ran a photochemical 1-box model instead, which consists of the 33 reactions mentioned in Sect. 3.2 as well as critical reactions of CHDO and HD to determine  $\alpha_r$  as follows:



## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

In Fig. 4 several model runs under different conditions are plotted. As an ideal case, we assume that CH<sub>2</sub>O is destroyed exclusively by photolysis. Since in this scenario  $\alpha_f$  is constant as the reaction proceeds, the Rayleigh model can be applied to determine  $\alpha_r$ . In Eq. (13), as  $f$  approaches 0, the ratio of  $R_m$  to  $R_o$  becomes the ratio of  $\alpha_m$  to  $\alpha_f$ , which is represented by the value of  $\delta\text{D-H}_2$  at the end of photolysis. As the values of  $\delta\text{D-H}_2$  converge at zero,  $\alpha_f = \alpha_m$  and thus  $\alpha_m = \alpha_r$  according to the relation in Eq. (8b) since  $\Gamma=1$ . This scenario is however unlikely considering the substantial production of radicals via the radical channel (R1), which may in turn react with CH<sub>2</sub>O in the reactor as described above. Introduction of the reactions of H and/or HO<sub>2</sub> with both CH<sub>2</sub>O and CHDO with and without kinetic isotope effect do not significantly change the evolution of  $\delta\text{D-H}_2$  compared to the ideal scenario that only accounts for CH<sub>2</sub>O photolysis. However, it is apparent that the reaction of OH and CH<sub>2</sub>O is critical for determination of  $\alpha_r$ , as the  $\delta\text{D-H}_2$  value for the final product of H<sub>2</sub> reaches only  $\sim -170\text{‰}$ . Taking the kinetic isotope effect for the reaction of CH<sub>2</sub>O with OH radicals into account increases the  $\delta\text{D-H}_2$  value for the final product a little to  $\sim -130\text{‰}$ . Applying the kinetic isotope effect for the reaction of HD with OH does not improve the model to simulate the measurements because of too slow reaction rate of H<sub>2</sub>+OH. However, decreasing the value of  $\alpha_r$  from 0.50 to 0.22 (thus larger isotope effect) makes it possible to reach the  $\delta\text{D-H}_2$  value of the final H<sub>2</sub> to zero and significantly improves the predicted evolution of  $\delta\text{D-H}_2$  compared to the measurements. Therefore, providing that the TUV radiation model and the reaction rates applied in the 1-box model are correct, our best estimate of  $\alpha_r$  is 0.22 and the isotopic fractionation factor of CH<sub>2</sub>O due to photolysis ( $\alpha_{hv}$ ) results in 0.40 for  $\Phi(\text{H}_2) = 0.647$ , the yield of H<sub>2</sub> which is the best estimate from the TUV radiation model for the average conditions of Mainz at the times of the experiments (see Fig. 2).

As the value of  $\alpha_r$  in the present study is not determined directly by measurement, but is based on model calculations, we conducted sensitivity runs to estimate the uncertainty of  $\alpha_r$  by varying the values of the various parameters used in the 1-box model. These parameters are the mixing ratio of CH<sub>2</sub>O in the reactor,  $\Phi(\text{H}_2)$ , photolysis rates

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

of CH<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>, kinetic isotope effects for the reaction of CHDO with the radicals, and the uncertainty of  $\delta\text{D-H}_2$  for the final product (Table 2). Among them  $\alpha_r$  is most sensitive to the ratio of the photolysis rate of H<sub>2</sub>O<sub>2</sub> to that for CH<sub>2</sub>O because large production of OH by photolysis of H<sub>2</sub>O<sub>2</sub> leads to the increase of the fraction of CH<sub>2</sub>O that reacts with OH in the reactor, which in turn forces the value of  $\alpha_r$  to be smaller to compensate it (see Eq. 8b). The same effect can be introduced to the variation of  $\alpha_{\text{OH}}$  for CH<sub>2</sub>O + OH and of  $\Phi(\text{H}_2)$ . Sensitivity runs for the potential error in the  $\delta\text{D-H}_2$  value of final product shows the largest impact to  $\alpha_r$  among the parameters because of its large potential error of 40‰, which includes the uncertainty of the  $\delta\text{D}$  value of the original CH<sub>2</sub>O (=4‰). Overall most of the uncertainty for  $\alpha_r$  originates from the uncertainties in  $\Phi(\text{H}_2)$  and the  $\delta\text{D-H}_2$  of final products. Quadratic sum of the errors incurred by these parameters are 0.08.

## 4 Discussions

### 4.1 Comparison with previous research

To our knowledge three experiments have been done in sunlight (Table 3): One experiment investigated the isotopic fractionation of CH<sub>2</sub>O itself by measuring time evolution of the amount of isotopologues, CH<sub>2</sub>O and CD<sub>2</sub>O using an optical method (Feilberg et al., 2007a, Feilberg et al., 2005), another experiment examined the same isotopic fractionation but for CH<sub>2</sub>O and CHDO using the same technique (Feilberg et al., 2007b), and the other measured the D/H ratio of H<sub>2</sub> produced from the photolysis of CH<sub>2</sub>O which is reported in a conference proceeding abstract (Crouse et al., 2003). In the latter study a similar procedure as in the present study was apparently applied. However, the lack of details of the experiment, in particular the fraction of H<sub>2</sub> ( $\phi(\text{H}_2)$ ) and the  $\delta\text{D}$  value of the original CH<sub>2</sub>O used for the photolysis experiments, both of which are critical to determine  $\alpha_m$ , makes it difficult to infer  $\alpha_m$  from this single value of  $\delta\text{D}$ . The authors reported that the photolysis of CH<sub>2</sub>O produces isotopically light H<sub>2</sub>, the

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

$\delta D$  value of which is  $\sim -200\text{‰}$ . If the authors meant the value to be the degree of enrichment of the  $H_2$  produced,  $\alpha_m$  is  $\sim 0.8$ , which is far larger (so less isotopically fractionated) than what we obtained in this study.

In the case of Feilberg et al. (2005)'s experiments, the ratio of photolysis rate of the two isotopologues,  $J_{CD_2O}/J_{CH_2O}$ , was determined as  $0.333(\pm 0.056)$  (Feilberg et al., 2007a) using an optical technique. This value is smaller than the value for  $J_{CHDO}/J_{CH_2O}(= \alpha_{hv})$  of  $0.40(\pm 0.03)$  determined in the present study as expected from the convention that double-deuterated formaldehyde is more stable than the single-deuterated one in view of zero point energy.

Recent work reported by the same group (Feilberg et al., 2007b) has a particular interest as the goal of the experiment is the same as the present study, but approaches it in a different way. In this experiment, the authors determined the values of  $\alpha_m$  and  $\alpha_{hv}$  as  $0.55(\pm 0.02)$  and  $0.63(\pm 0.01)$ , respectively. The value of  $\alpha_m$  is similar to, while that for  $\alpha_{hv}$  is far larger than, the values determined in the present study. Actually the large discrepancy of  $\alpha_{hv}$  points to a much larger difference in the value of  $\alpha_r$  between Feilberg et al. (2007b)'s and the present study:  $0.91(\pm 0.05)$  versus  $0.22(\pm 0.08)$ . Unlike the previous work (Feilberg et al., 2005), Feilberg et al. (2007b) took into account the  $CH_2O$  production in the chamber of the facility in determination of  $\alpha_{hv}$  in addition to leakage of the experimental chamber. Notwithstanding, there is still such a large discrepancy in the isotopic fractionation factors of  $CH_2O$  between the two studies. Besides the discrepancy in the magnitude of  $\alpha_r$ , an interesting result of Feilberg et al. (2007b) is that the degree of the isotopic fractionation in  $CH_2O$  photolysis to the molecular channel is larger than that for the radical channel, being opposite to the results from the present study and from early results by McQuigg and Calvert (1969).

It is useful to recall the different experimental conditions in both studies. Feilberg et al. (2007b) performed an isotope tracer study using similar amounts of  $CH_2O$  and  $CHDO$  in the EUPHORE reactor in Valencia, Spain, which allowed them to infer  $\alpha_{hv}$  "directly" by a spectroscopic method and from which  $\alpha_m$  was inferred from the isotope-ratio-mass-spectrometric measurements of HD and modeling of the  $H_2$  yield using a

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

given quantum yield for CH<sub>2</sub>O photolysis. The direct inference of  $\alpha_{hv}$ , however, had to be corrected to account for the losses of CH<sub>2</sub>O and CHDO by the reaction with OH radical and large leakage of air in the chamber as well as production of CH<sub>2</sub>O from the wall. In addition, their values of  $\alpha_r$  and  $\alpha_m$  depend on which value of the quantum yield for CH<sub>2</sub>O photolysis are applied. In our study, performed at the level of natural deuterium abundance,  $\alpha_m$  is the “directly” inferred quantity, and  $\alpha_{hv}$  follows from the fact that the isotopic compositions of the initial CH<sub>2</sub>O and of the H<sub>2</sub> that are formed from complete photolysis are identical. At present we are not able to pinpoint why there is such a large discrepancy in the isotopic fractionation factors of CH<sub>2</sub>O between the two studies. More experiments can resolve this issue.

### 4.2 Atmospheric implication

The determination of  $\alpha_m$  and  $\alpha_r$  may provide an important insight to comprehend what causes the enrichment in deuterium throughout the photochemical oxidation pathway from CH<sub>4</sub> to H<sub>2</sub>. The overall composite of isotopic fractionation factors from CH<sub>4</sub> to H<sub>2</sub>,  $\alpha_{\text{CH}_4-\text{H}_2}$ , may be defined as:

$$\alpha_{\text{CH}_4-\text{H}_2} = \frac{R_{\text{H}_2}^0}{R_{\text{CH}_4}} \quad (19)$$

where  $R_{\text{H}_2}^0$  represents the hydrogen isotopic ratio of H<sub>2</sub> produced by photochemical oxidation of CH<sub>4</sub> and  $R_{\text{CH}_4}$  is that for CH<sub>4</sub>. Strictly speaking,  $\alpha_{\text{CH}_4-\text{H}_2}$  differs from the general definition of isotopic fractionation factor in that it is a function of not only thermodynamic conditions but also environmental parameters such as radiation, radical species and their concentrations in the atmosphere. Nonetheless, given a system with these parameters,  $\alpha_{\text{CH}_4-\text{H}_2}$  can be considered as an isotopic fractionation factor. Rhee et al. (2006a) estimated the value of  $\alpha_{\text{CH}_4-\text{H}_2}$  to be 1.3 in the troposphere, meaning that the H<sub>2</sub> produced from CH<sub>4</sub> oxidation is enriched in deuterium 1.3 times as much

as the initial CH<sub>4</sub>. Gerst and Quay (2001) and Price et al. (2007) also expected D in the H<sub>2</sub> from photochemical oxidation of CH<sub>4</sub> to be enriched by a factor of 1.2–1.3.

As Gerst and Quay (2001) described in detail,  $\alpha_{\text{CH}_4-\text{H}_2}$  represents the results from the combination of several factors that are associated with photochemical chain reactions from CH<sub>4</sub> to H<sub>2</sub>. These factors include: (1) isotopic fractionation occurring during the reaction of CH<sub>4</sub> with OH ( $\alpha_{\text{CH}_4}$ ), the rate-determining step of the photochemical chain reactions of CH<sub>4</sub>, as well as the subsequent isotopic fractionation processes occurring along the way to CH<sub>2</sub>O ( $\alpha_{\Sigma}$ ), (2) the branching ratios of deuterated species, e.g., CH<sub>3</sub>D, CH<sub>2</sub>DOOH, and CH<sub>2</sub>DO, (3) the factor of 2 brought up by the reduction of the number of hydrogen atoms from CH<sub>4</sub> to CH<sub>2</sub>O, and finally (4) isotopic fractionation occurring during the photolytical production of H<sub>2</sub> from CH<sub>2</sub>O. Assuming that CH<sub>2</sub>O is in a photochemical steady state, as it has a far shorter chemical lifetime than CH<sub>4</sub> and H<sub>2</sub>, point (4) is represented by the ratio of the isotopic fractionation factor of the H<sub>2</sub> produced ( $\alpha_m$ ) to that for CH<sub>2</sub>O ( $\alpha_f$ ) (Rhee et al., 2006a). Note that  $\alpha_f$  differs from  $\alpha_{\text{hv}}$  by the effect of isotopic fractionation arising from reaction with OH radical ( $\alpha_{\text{OH}}$ ) in the troposphere. Combining all these factors yields:

$$\alpha_{\text{CH}_4-\text{H}_2} = 2 \times \alpha_{\text{CH}_4} \times \beta_{\text{CH}_4} \times \alpha_{\Sigma} \times \beta_p \times \frac{\alpha_m}{\alpha_f} \quad (20)$$

where  $\beta_{\text{CH}_4}$  is the branching ratio for the deuterated product, CH<sub>2</sub>D, in the reaction of CH<sub>3</sub>D and OH, and  $\beta_p$  is a combined branching ratio for other short-lived intermediates, CH<sub>2</sub>DOOH, and CH<sub>2</sub>DO.

Regarding the right-hand side of Eq. (20), the value of  $\alpha_{\text{CH}_4}$  is 0.78(±0.07) at 298 K (Gierczak et al., 1997) and decreases with the decrease of temperature, that for  $\beta_{\text{CH}_4}$  is at most unity but most likely is less than unity as Gerst and Quay (2001) speculated, and the same is expected for  $\beta_p$ . In the subsequent reactions, there is no compelling rationale that the more deuterated isotopologues react faster than the lighter ones considering the theoretical view of lower zero point energy for the isotopically heavier isotopologues. Thus, the value of  $\alpha_{\Sigma}$  may not be larger than unity. The last two parameters in Eq. (20),  $\alpha_f$  and  $\alpha_m$ , are what we are concerned with here: since

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Hydrogen isotope fractionation in the photolysis of formaldehyde**

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

$\alpha_f$  is a combined isotopic fractionation factor due to photolysis and photochemical reactions of  $\text{CH}_2\text{O}$  by the fraction of the reaction routes as shown in Eq. (8), the value is the weighted mean of the isotopic fractionation factors involved in the reactions. As listed in Table 3 under the radiation conditions of Mainz, the best values of  $\alpha_m$  and  $\alpha_r$  were estimated as  $0.50(\pm 0.02)$  and  $0.22(\pm 0.08)$ , respectively, from the present study. Feilberg et al. (2004) determined the value of  $\alpha_{\text{OH}}$  as  $0.781(\pm 0.006)$ . The optimal values of  $\Phi(\text{H}_2)$  and  $\Gamma$  in Mainz were calculated as  $0.647(\pm 0.039)$  and  $0.69(\pm 0.28)$ , respectively, for the periods of experiments using the TUV radiation model at a weighted mean SZA of  $62.7^\circ$  (see Fig. 2). In order to determine  $\Gamma$ , we calculated OH radical concentrations and their uncertainties from the relationship between the photolysis rate of  $\text{O}_3$  ( $\text{J}(\text{O}^1\text{D})$ ) and OH concentration by Rohrer and Berresheim (2006) (i.e.,  $[\text{OH}] = 2.4 \times \text{J}(\text{O}^1\text{D}) + 0.13$  and  $\sigma = 0.07 \times 10^6 + 0.33 \times [\text{OH}]$ ). By inserting these values to (8b) the resulting value for  $\alpha_f$  is  $0.51(\pm 0.11)$ . Most of its uncertainty is carried over from the uncertainty of OH. The ratio of  $\alpha_m/\alpha_f$  ( $=0.97(\pm 0.21)$ ) results slightly smaller than unity, but because of its large uncertainty, coming from the uncertainty of OH concentration, it is not possible to judge whether the  $\text{CH}_2\text{O}$  photolysis could lead to a depletion or enrichment of D in the  $\text{H}_2$  produced with respect to the parent  $\text{CH}_2\text{O}$ . When using the values of isotopic fractionation factors determined by Feilberg et al. (2007b), the  $\text{CH}_2\text{O}$  photolysis leads to the depletion of D in the  $\text{H}_2$ , however, even taking into account the uncertainty of  $\alpha_m/\alpha_f$  (see Table 3).

We extend the calculation of the ratio of  $\alpha_m/\alpha_f$  to a range of values of  $\Phi(\text{H}_2)$  and  $\Gamma$ , assuming that the values of  $\alpha_m$ ,  $\alpha_r$ , and  $\alpha_{\text{OH}}$  determined from the present study and Feilberg et al. (2004) are applicable to the entire troposphere. The potential ranges of  $\Phi(\text{H}_2)$  for the troposphere were estimated using the TUV radiation model with varying SZA at the altitudes of the US standard air. In order to estimate  $\Gamma$  for the troposphere, it is necessary to know the reaction rate of  $\text{CH}_2\text{O} + \text{OH}$  at a given time and place. The reaction rate coefficient varies  $\sim 15\%$  in the troposphere due to change in temperature, while the OH concentration varies in the order of magnitude with its peak occurring at local noon. The peak values are well above  $10^7$  molecules  $\text{cm}^{-3}$

(e.g., Berresheim et al., 2003), leading to  $\Gamma \sim 0.45$ . Thus, the range of  $\Gamma$  is likely to be between 0.4 and 1 in the troposphere. As shown in Fig. 5, the ratios of  $\alpha_m/\alpha_f$  vary from  $\sim 0.8$  to  $\sim 1.2$ , which suggests that, depending on the values of  $\Gamma$  and  $\Phi(\text{H}_2)$  in the troposphere, the  $\text{H}_2$  produced from the  $\text{CH}_2\text{O}$  photolysis would be either enriched or depleted in D. For instance, at the Earth's surface the values of  $\alpha_m/\alpha_f$  along the track of the sun are likely to be lower than unity, thus yielding the depleted  $\text{H}_2$  in D with respect to the parent  $\text{CH}_2\text{O}$ .

Finally, we examine the range of  $\alpha_m/\alpha_f$  that can be reconciled with the values of  $\alpha_{\text{CH}_4-\text{H}_2}$  inferred for the tropospheric conditions. In the literature it is reported that  $\alpha_{\text{CH}_4-\text{H}_2}$  would be between 1.2 and 1.3 in the troposphere (Gerst and Quay, 2001; Price et al., 2007; Rhee et al., 2006a). According to Gierczak et al. (1997), the value of  $\alpha_{\text{CH}_4}$  at the tropospheric mean temperature of 272 K is  $0.77(\pm 0.08)$ . Inserting these values into Eq. (20), the lowermost value for  $\alpha_m/\alpha_f$  will be  $\sim 0.8$  when the branching ratio for deuterated compounds ( $\beta_{\text{CH}_4}$  and  $\beta_p$ ) and  $\alpha_\Sigma$  unity. When these three values follow Gerst and Quay (2001)'s speculation ( $\beta_{\text{CH}_4} \times \alpha_\Sigma \times \beta_p = 0.96 \times 0.77 \times 0.96$ ),  $\alpha_m/\alpha_f$  is 1.15. These two values of  $\alpha_m/\alpha_f$  bound the range which was estimated for the typical values of  $\Gamma$  and  $\Phi(\text{H}_2)$  in the troposphere (Fig. 5). This suggests that even if  $\alpha_m/\alpha_f$  is smaller than unity it is still possible that  $\text{H}_2$  formed from the photochemical oxidation of  $\text{CH}_4$  is enriched in D with respect to the original  $\text{CH}_4$  due to the factor of 2 that arises from the reduction of the number of hydrogen atom. Recent laboratory experiment (Nilsson et al., 2007) reports the branching ratio for  $\text{CH}_2\text{DO}$  reacting with  $\text{O}_2$  to be  $0.88(\pm 0.01)$ , suggesting  $\beta_p$  to be lower than unity and that  $\alpha_m/\alpha_f$  is likely to be larger than unity.

## 5 Conclusions

The  $\text{CH}_2\text{O}$  photolysis experiments conducted in sunlight under ambient conditions allowed us to determine the isotopic fractionation factors for both the radical (R1) and molecular (R2) channels. The  $\text{H}_2$  produced is depleted in D by  $500(\pm 20)\%$ .

### Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

with respect to the initial CH<sub>2</sub>O. The radical channel (R1) appears to have a much stronger isotopic fractionation than the molecular channel (R2), resulting in D enrichment of the remaining CH<sub>2</sub>O by 780(±80)‰. This isotope effect is significantly larger than the result obtained from the experiments in the EUPHORE reaction chamber by Feilberg et al. (2007b), a difference we do not understand at present.

Applying the isotopic fractionation factors obtained from the present study to the conditions of Mainz, CH<sub>2</sub>O photolysis may produce the H<sub>2</sub> that is slightly depleted in D. However, the large uncertainty in the combined isotopic effects of photochemical reactions of CH<sub>2</sub>O, which primarily originates from the uncertainty of OH concentration, makes it impossible to precisely define the role of CH<sub>2</sub>O photolysis in the D enrichment of H<sub>2</sub>. In the troposphere, CH<sub>2</sub>O photolysis may produce the H<sub>2</sub> either enriched or depleted in D with respect to the parent CH<sub>2</sub>O depending on the fraction of CH<sub>2</sub>O that reacts with OH or that is photolyzed to H<sub>2</sub>. Nonetheless, our estimated range of  $\alpha_m/\alpha_f$  (~0.8 to ~1.2) in the troposphere, the ratio of isotopic fractionation factors which determines the degree of D enrichment of H<sub>2</sub> at steady state of CH<sub>2</sub>O mixing ratio, can meet the production of the H<sub>2</sub> enriched in D with respect to the original CH<sub>4</sub> by the factor reported in the literature.

## Appendix A

### 1-box photochemistry model

The 1-box model is composed of 33 reactions (Table A1) running at 25°C and 1 bar of air which is composed of 78% of N<sub>2</sub> and 22% of O<sub>2</sub>. Unless otherwise mentioned, the yield of H<sub>2</sub> in the photolysis of CH<sub>2</sub>O and the ratio of  $J_{\text{H}_2\text{O}_2} / J_{\text{CH}_2\text{O}}$  are assumed to be 0.647 and 0.0896, respectively, following the result from the TUV radiation model in Mainz.

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

*Acknowledgements.* We gratefully acknowledge support of this research from the Max Planck Society. We thank J. Crowley for advice concerning photochemistry and his suggestion to conduct a simple experiment and K. Boering for useful comments to the earlier version. This work was partially supported by the Korea Meteorological Administration Research and Development Program under Grant CATER 2007-4405.

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## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Hydrogen isotope fractionation in the photolysis of formaldehyde**

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Hydrogen isotope  
fractionation in the  
photolysis of  
formaldehyde**

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Hydrogen isotope  
fractionation in the  
photolysis of  
formaldehyde**

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Hydrogen isotope  
fractionation in the  
photolysis of  
formaldehyde**

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Table 1.** Summary of CH<sub>2</sub>O photolysis experiments.

Photolysis							
Start	End	*Duration (hr)	<sup>§</sup> [CH <sub>2</sub> O] <sub>0</sub> (ppm)	Light source	Reactor material	φ(H <sub>2</sub> )	δD-H <sub>2</sub> (‰)
4-Sep-03	10-Sep-03	91	2.3	Daylight	Glass	0.47	-247
4-Sep-03	10-Sep-03	91	2.5	Daylight	Glass	0.52	-190
4-Sep-03	10-Sep-03	91	2.6	Daylight	Glass	0.49	-252
14-Sep-03	17-Sep-03	51	0.43	Daylight	Glass	0.52	-214
14-Sep-03	17-Sep-03	51	0.46	Daylight	Glass	0.66	-46
14-Sep-03	17-Sep-03	51	0.48	Daylight	Glass	0.56	-205
29-Mar-04	29-Mar-04	1	53	Daylight	Quartz	0.09	-449
29-Mar-04	29-Mar-04	2	50	Daylight	Quartz	0.18	-459
29-Mar-04	29-Mar-04	3	34	Daylight	Quartz	0.21	-415
29-Mar-04	29-Mar-04	7	63	Daylight	Quartz	0.31	-366
29-Mar-04	29-Mar-04	7	36	Daylight	Quartz	0.26	-413
17-May-04	25-May-04	130	2.1	Daylight	Quartz	0.67	3
17-May-04	31-May-04	230	2.0	Daylight	Quartz	0.68	-4
14-Jun-04	18-Jun-04	67	1.4	Daylight	Quartz	0.50	-205
14-Jun-04	18-Jun-04	67	1.8	Daylight	Quartz	0.61	-38
14-Jun-04	18-Jun-04	67	1.8	Daylight	Quartz	0.61	-77
14-Jun-04	18-Jun-04	67	1.1	Daylight	Quartz	0.39	-256
14-Jun-04	30-Jun-04	277	2.1	Daylight	Quartz	0.71	15
14-Jun-04	30-Jun-04	277	1.9	Daylight	Quartz	0.66	-65
30-May-04	4-Jun-04	80	1.6	Daylight	Glass	0.56	-137
30-May-04	4-Jun-04	80	1.6	Daylight	Glass	0.60	-113
5-Jun-04	11-Jun-04	94	1.6	Daylight	Glass	0.54	-132
5-Jun-04	11-Jun-04	94	1.5	Daylight	Glass	0.59	-78
31-May-04	4-Jun-04	92	1.5	Xe arc lamp	Quartz	0.44	-12
5-Jun-04	11-Jun-04	244	1.4	Xe arc lamp	Quartz	0.43	5

\* This is simply a sum of daylight hours calculated using astronomical parameters from the internet ([http://aa.usno.navy.mil/data/docs/RS\\_OneDay.html](http://aa.usno.navy.mil/data/docs/RS_OneDay.html)).

<sup>§</sup> Initial mixing ratios of CH<sub>2</sub>O in a reactor prior to photolysis.

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

**Table 2.** Sensitivity test of the  $\alpha_r$  at a given range of the parameters.

	Prescribed value ( $Z_i$ )	Uncertainty of parameter ( $\Delta Z_i$ )	Sensitivity ( $\Delta\alpha_r/\Delta Z_i$ )	Uncertainty of $\alpha_r$ ( $\Delta\alpha_r$ )
$[\text{CH}_2\text{O}]_0$ (ppm)	1	$\pm 1$	0.0027 <sup>§</sup>	$\pm 0.003$
$J_{\text{CH}_2\text{O}}$ ( $\text{s}^{-1}$ )	$3.143 \times 10^{-5}$	$\pm 4.4 \times 10^{-5}$	0.0026 <sup>§</sup>	$\pm 0.004$
$\Phi(\text{H}_2)$	0.647	$\pm 0.039$	-0.476	$\mp 0.019$
$J_{\text{H}_2\text{O}_2}/J_{\text{CH}_2\text{O}}$	0.0896	$\pm 0.0036$	-2.48	$\mp 0.009$
$\alpha_{\text{H}}$ for $\text{CH}_2\text{O} + \text{H}$	0.781	$\pm 0.25$	$\sim 0$	$\sim 0$
$\alpha_{\text{OH}}$ for $\text{CH}_2\text{O} + \text{OH}$	0.781	$\pm 0.0061$	-0.45	$\mp 0.003$
$\alpha_{\text{HO}_2}$ for $\text{CH}_2\text{O} + \text{HO}_2$	0.781	$\pm 0.25$	-0.036	$\mp 0.009$
$\delta\text{D-H}_2$ of final product (‰)	0	$\pm 40$	-0.0019	$\mp 0.076$
Sum*				0.079

<sup>§</sup>Sensitivity is calculated by the ratio of a parameter to the prescribed value.

\*Quadratic sum of errors.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

**Table 3.** Comparison of the isotope effects determined from CH<sub>2</sub>O photolysis experiments.

Source	Minor isotopologue	$\alpha_m$	$\alpha_r$	$^*\alpha_{\text{OH}}$	$\Phi(\text{H}_2)$	$^{\&}\Gamma$	$\alpha_{h\nu}$	$\alpha_f$	$\alpha_m/\alpha_f$
This study	[CHDO]	0.50(±0.02)	0.22(±0.08)	0.781(±0.006)	0.65(±0.04)	0.69(±0.28)	0.40(±0.03)	0.51(±0.11)	0.97(±0.21)
Feilberg et al. (2007b)	[CHDO]	0.55(±0.02)	0.91(±0.05)	0.781(±0.006)	$^{\S}0.77(\pm 0.06)$	0.69(±0.28)	0.63(±0.01)	0.68(±0.04)	0.81(±0.06)
Crouse et al. (2003)	[CHDO]	0.8							
Feilberg et al. (2007a)	[CD <sub>2</sub> O]						0.333(±0.056)		

\* Kinetic isotope effect for CH<sub>2</sub>O + OH from Feilberg et al. (2004).

& The value is calculated for the Mainz conditions for the periods of experiments.

$^{\S}$  The value was calculated by the relation  $\alpha_{h\nu} = \alpha_m \times \Phi(\text{H}_2) + \alpha_r \times (1 - \Phi(\text{H}_2))$ .

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table A1. Photochemical reactions in the model.

No.*	Reaction	Rate coefficient <sup>§</sup>	Notes
(R1)	CH <sub>2</sub> O + hν → CHO + H	1.109E-5	1
(R2)	CH <sub>2</sub> O + hν → CO + H <sub>2</sub>	2.033E-5	1
(R3)	CH <sub>2</sub> O + OH → CHO + H <sub>2</sub> O	8.6E-12 × exp(166/RT)	2
(R3')	CH <sub>2</sub> O + OH → HCOOH + H	2.01E-13	9
(R4)	CH <sub>2</sub> O + H → CHO + H <sub>2</sub>	2.14E-12 × exp(-9063/RT) × (T/298) <sup>1.62</sup>	8
(R5)	CH <sub>2</sub> O + HO <sub>2</sub> → HOCH <sub>2</sub> OO	6.71E-15 × exp(4989/RT)	3
(R6)	H <sub>2</sub> + OH → H + H <sub>2</sub> O	5.5E-12 × exp(-16629/RT)	3
(R7)	H <sub>2</sub> O <sub>2</sub> + hν → 2OH	2.816E-6	1
(R8)	O <sub>2</sub> + CHO → CO + HO <sub>2</sub>	3.5E-12 × exp(1164/RT)	3
(R9)	CHO + CHO → CH <sub>2</sub> O + CO	5.0E-11	4
(R9')	CHO + CHO → (CHO) <sub>2</sub>	5.0E-11	5
(R10)	CHO + H → CO + H <sub>2</sub>	1.13E-10	6
(R11)	CHO + OH → CO + H <sub>2</sub> O	1.69E-10	4
(R12)	CHO + HO <sub>2</sub> → product	5.0E-11	4
(R13)	H <sub>2</sub> O + CHO → CH <sub>2</sub> O + OH	8.54E-13 × exp(-108920/RT)	7
(R14)	H <sub>2</sub> O <sub>2</sub> + CHO → CH <sub>2</sub> O + HO <sub>2</sub>	1.69E-13 × exp(-29018/RT)	7
(R15)	O <sub>2</sub> + H → HO <sub>2</sub>	M × 5.71E-32 × (T/298) <sup>-1.6</sup>	3
(R16)	H + H → H <sub>2</sub>	M × 8.85E-33 × (T/298) <sup>-0.6</sup>	4
(R17)	OH + H → H <sub>2</sub> O	M × 4.38E-30 × (T/298) <sup>-2.0</sup>	4
(R18)	(CHO) <sub>2</sub> + OH → product	1.1E-11	2
(R19)	HCOOH + OH → product	4.0E-13	3
(R20)	CO + OH → CO <sub>2</sub> + H	1.5E-13 × (1 + 0.6*P/1013.25)	3
(R21)	CO + HO <sub>2</sub> → CO <sub>2</sub> + OH	5.96E-11 × exp(-95616/RT) × (T/298) <sup>0.5</sup>	10
(R22)	OH + OH → H <sub>2</sub> O <sub>2</sub>	M × 6.20E-31 × (T/298) <sup>-1</sup>	3
(R23)	HO <sub>2</sub> + H → product	8.10E-11	3
(R24)	HO <sub>2</sub> + OH → H <sub>2</sub> O + O <sub>2</sub>	4.8E-11 × exp(2079/RT)	3
(R25)	HO <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	M × 1.7E-33 × exp(8314/RT)	3
(R26)	H <sub>2</sub> O <sub>2</sub> + OH → HO <sub>2</sub> + H <sub>2</sub> O	2.91E-12 × exp(-1330/RT)	3
(R27)	HOCH <sub>2</sub> OO → HO <sub>2</sub> + CH <sub>2</sub> O	2.4E12 × exp(-58201/RT)	2
(R28)	HOCH <sub>2</sub> OO + HO <sub>2</sub> → HCOOH + H <sub>2</sub> O + O <sub>2</sub>	5.6E-15 × exp(19123/RT)	2
(R29)	2HOCH <sub>2</sub> OO → 2HOCH <sub>2</sub> O + O <sub>2</sub>	5.5E-12	11
(R29')	2HOCH <sub>2</sub> OO → HCOOH + CH <sub>2</sub> (OH) <sub>2</sub> + O <sub>2</sub>	5.71E-14 × exp(6236/RT)	11
(R30)	O <sub>2</sub> + HOCH <sub>2</sub> O → HCOOH + HO <sub>2</sub>	3.5E-14	12

Notes: 1, TUV radiation model; 2, Atkinson et al. (1997); 3, DeMore et al. (1997); 4, Baulch et al. (1992); 5, Stoeckel et al. (1985); 6, Ziemer et al. (1998); 7, Tang and Hampson (1986); 8, Baulch et al. (1994); 9, Yetter et al. (1989); 10, Volman (1996); 11, Atkinson et al. (1992); 12, Veyret et al. (1982)

\* Prime (') designates the second reaction.

§ R and T in rate constant designate gas constant and absolute temperature, respectively. M indicates air concentration in termolecular reaction.

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

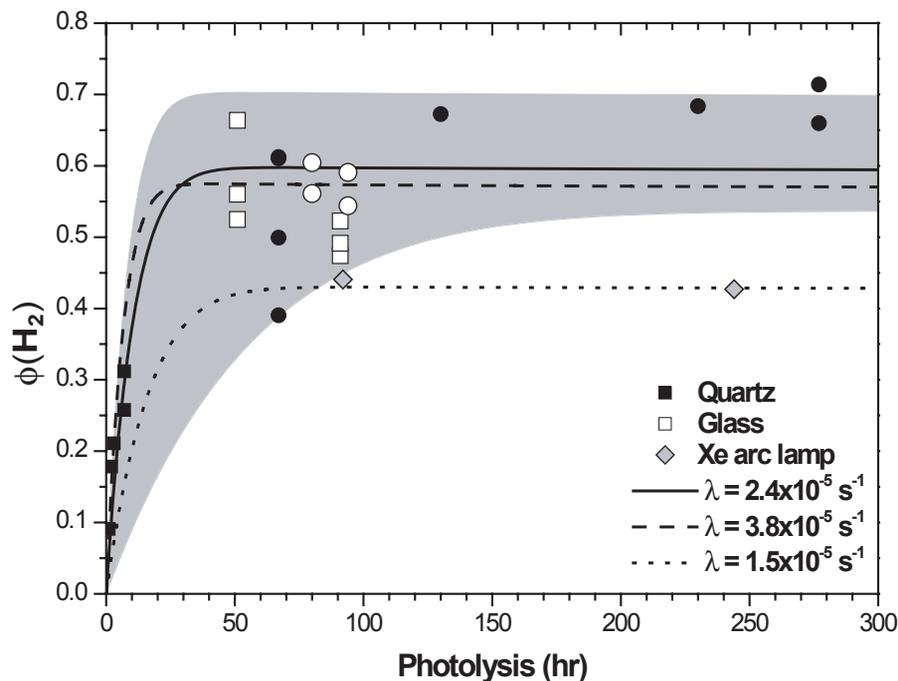
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Printer-friendly Version

Interactive Discussion

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.



**Fig. 1.** Evolution of the fraction of  $\text{H}_2$  ( $\phi(\text{H}_2)$ ) produced by photolysis of  $\text{CH}_2\text{O}$  in daylight or using a Xe arc lamp. The squares are for the experiments in March, May and June, and the circles for August and September. Solid symbols indicate a quartz reactor and open symbols a glass reactor. The gray-shaded area and lines represent model calculations for a given  $\text{CH}_2\text{O}$  photolysis rate and yield of  $\text{H}_2$ ,  $\Phi(\text{H}_2)$ . Solid and dashed lines are the bounds of the most probable evolution of  $\phi(\text{H}_2)$  in Mainz using the results from the Tropospheric Ultraviolet and Visible (TUV) radiation model as described in Fig. 2. For photolysis with the Xe lamp, the photolysis rate of  $1.5 \times 10^{-5} \text{ s}^{-1}$  and  $\Phi(\text{H}_2) = 0.49$  are arbitrarily forced to fit the measurements.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

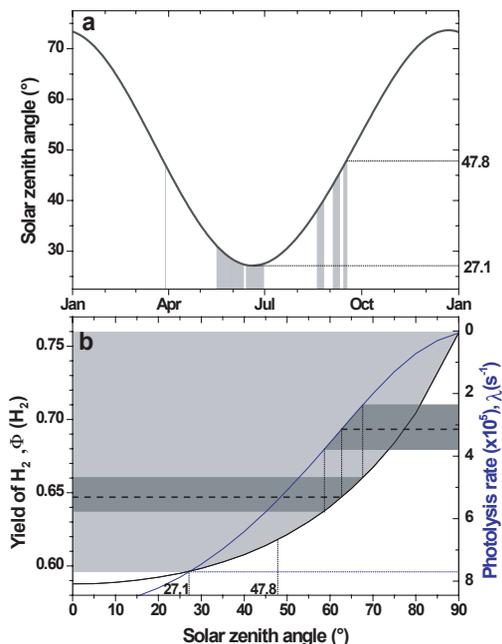
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Printer-friendly Version

Interactive Discussion

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.



**Fig. 2.** (a) Solar zenith angle (SZA) at local noon in Mainz (11:00 GMT) in 2004. Gray shaded areas indicate the dates when experiments were conducted. SZA at local noon ranges from 27.1° to 47.8° for the periods of experiment. (b) Photolytic yield of H<sub>2</sub> ( $\Phi(\text{H}_2)$ ) and photolysis rate of CH<sub>2</sub>O ( $J_{\text{CH}_2\text{O}}$ ) at a given solar zenith angle calculated with the Tropospheric Ultraviolet and Visible radiation model. The gray-shaded area indicates a range of  $\Phi(\text{H}_2)$  for the situation of Mainz, and the blue line represents the photolysis rates at a given SZA. The dark gray area represents daily mean values of  $\Phi(\text{H}_2)$  and their corresponding values of  $J_{\text{CH}_2\text{O}}$  obtained by weighting the photolysis rates over the range of SZA for the experimental periods. The dashed line indicates the arithmetic mean of minimum and maximum values of these mean values of  $J_{\text{CH}_2\text{O}}$  and its mapping onto values for  $\Phi(\text{H}_2)$ . These two values of  $J_{\text{CH}_2\text{O}}$  and  $\Phi(\text{H}_2)$  were then used in the 1-box photochemistry model.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

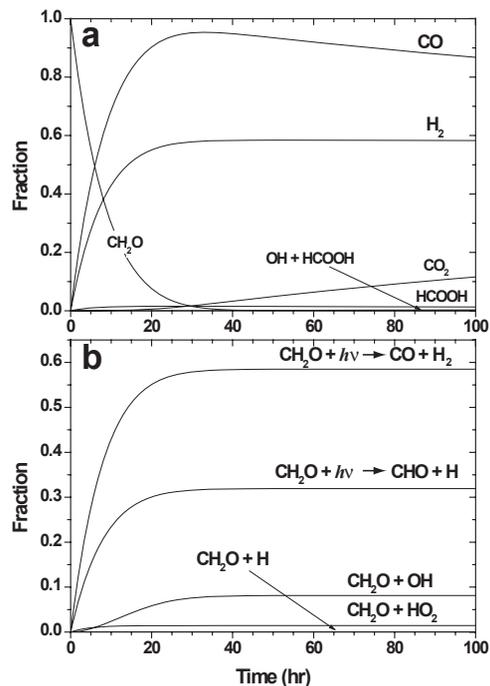
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Printer-friendly Version

Interactive Discussion

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

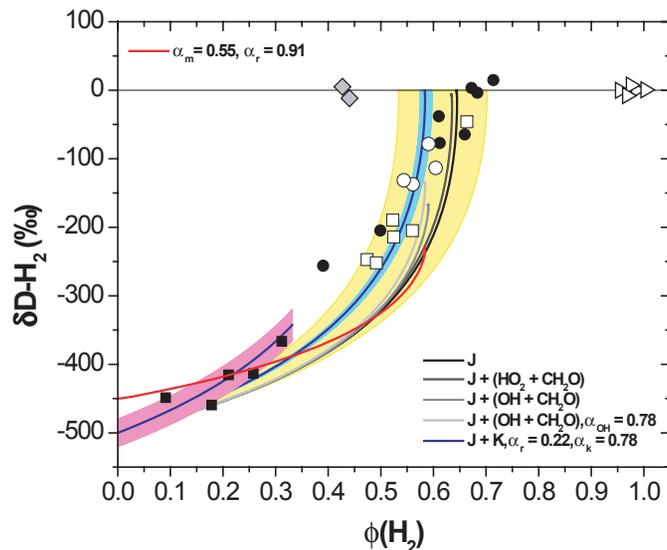


**Fig. 3.** A 1-box model simulation of CH<sub>2</sub>O photochemistry in the reactor. Details of the reactions are given in Appendix A. **(a)** Time evolution of the relative abundances of CH<sub>2</sub>O and its photochemical products. “OH + HCOOH” represents the sum of the amounts of any compounds produced by the reaction of formic acid and OH radical. **(b)** Time evolution of the fraction of CH<sub>2</sub>O that is photolyzed or reacts with radicals.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.

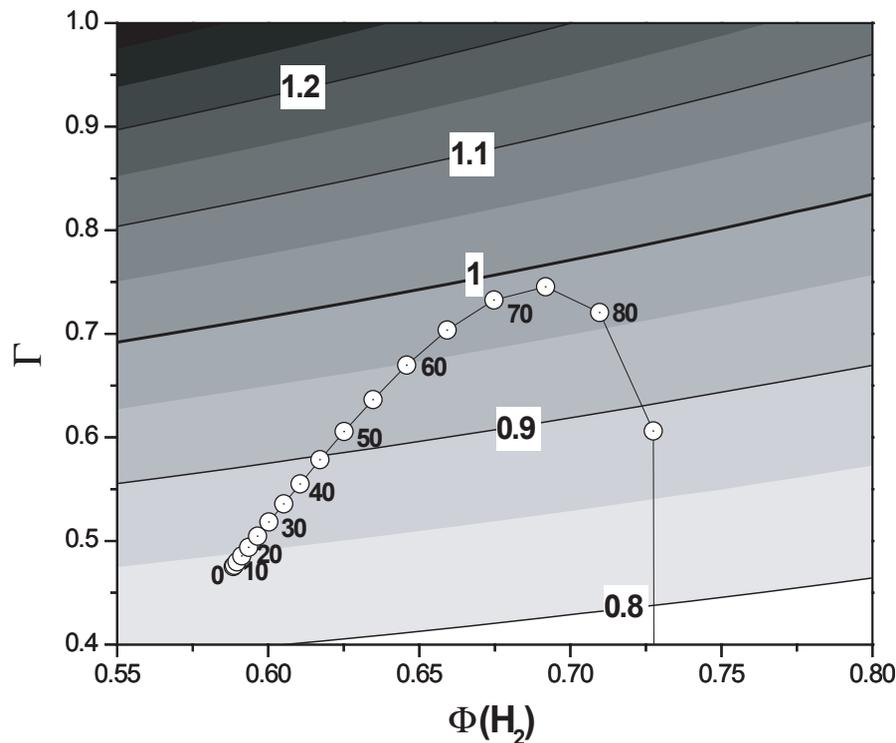


**Fig. 4.** Evolution of  $\delta\text{D-H}_2$  as a function of the fraction of  $\text{H}_2$  produced by photolysis of  $\text{CH}_2\text{O}$ . Symbol keys are the same as in Fig. 1. Several model sensitivity runs are shown with solid lines. Yellow shading indicates potential isotopic fractionation evolutions for various ranges of  $\Phi(\text{H}_2)$  for the location of Mainz, and cyan shading represents the isotopic fractionation evolutions using the daily-mean value of  $\Phi(\text{H}_2)$  during the experiments according to the TUV radiation model described in Fig. 2. For the short duration experiments, we assumed that the initial mixing ratio of  $\text{CH}_2\text{O}$  in the 1-box model was 50 ppm, represented by magenta shading. When calculating the evolution of  $\delta\text{D-H}_2$  using the 1-box model, we constrain the model such that the values of  $\alpha_m$  and  $\alpha_K$  (see text) are always 0.50 and 0.78, respectively, and that the complete photolysis of  $\text{CH}_2\text{O}$  yields  $\text{H}_2$  with a  $\delta\text{D}$  value that is the same as that of the initial  $\text{CH}_2\text{O}$ . For comparison, the evolutions of  $\delta\text{D-H}_2$  using the isotopic fractionation factors determined by Feilberg et al. (2007b) is shown as red solid line on the premise that the values of other parameters are the same as those in the present study (see Appendix A).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

## Hydrogen isotope fractionation in the photolysis of formaldehyde

T. S. Rhee et al.



**Fig. 5.** Contour plot of the ratio  $\alpha_m/\alpha_f$  for potential ranges of the yield of  $\text{H}_2$  from  $\text{CH}_2\text{O}$  photolysis ( $\Phi(\text{H}_2)$ ) and of the fraction of  $\text{CH}_2\text{O}$  that is decomposed by photolysis ( $\Gamma$ ) in the troposphere. The symbols track the values of  $\Phi(\text{H}_2)$  and  $\Gamma$  calculated by the TUV radiation model and Rohrer and Berresheim (2006)'s parameterization of OH concentration at the indicated solar zenith angle from  $0^\circ$  to  $90^\circ$  in  $5^\circ$  steps at Earth's surface.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)