

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

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Hydrogen isotope fractionation in the photolysis of formaldehyde

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Experiments investigating the isotopic fractionation in the formation of H₂ by the photolysis of CH₂O under tropospheric conditions are reported and discussed. The deuterium (D) depletion in H₂ produced is 500(±20)‰ with respect to the parent CH₂O.

We also observed that complete photolysis of CH₂O under atmospheric conditions produces H₂ that has virtually the same isotopic ratio as that of the parent CH₂O. These findings imply that there must be a very strong concomitant isotopic enrichment in the radical channel (CH₂O + hν → CHO + H) as compared to the molecular channel (CH₂O + hν → H₂ + CO) of the photolysis of CH₂O in order to balance the relatively small isotopic fractionation in the competing reaction of CH₂O 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 CH₂O. When CH₂O is in photochemical steady state, the isotopic ratio of the H₂ produced is determined not only by the isotopic fractionation occurring during the photolytical production of H₂ (α_m) but also by overall fractionation for the removal processes of CH₂O (α_f), and is represented by the ratio of α_m/α_f. Applying the isotopic fractionation factors relevant to CH₂O photolysis obtained in the present study to the troposphere, the ratio of α_m/α_f varies from ~0.8 to ~1.2 depending on the fraction of CH₂O that reacts with OH and that produces H₂. This range of α_m/α_f can render the H₂ produced from the photochemical oxidation of CH₄ to be enriched in D (with respect to the original CH₄) by the factor of 1.2–1.3 as anticipated in the literature.

1 Introduction

Formaldehyde (CH₂O) 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 (H₂), carbon monoxide (CO), and of the hydroperoxyl radical (HO₂), yet limited

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measurements are available in various atmospheric regions. Recent satellite observations of CH₂O 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 CH₂O (Carlier et al., 1986; Garcia et al., 2005), in situ production of CH₂O 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 CH₄ serves as the major source. Apart from the importance of the rather simple CH₂O 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).

CH₂O is broken down by photolysis (R1 and R2) and by photochemical oxidation (R3):



“Incomplete” photolysis (R1) produces HO₂ radical by the rapid reaction of hydrogen (H) and formyl (CHO) radicals with atmospheric oxygen (O₂), which can lead to the formation of hydroxyl radical (OH) via the reaction with NO or O₃ in the atmosphere. This is an important propagation of the radical chain. Only reaction (R2), i.e. the one-step complete photolysis, yields H₂. All photochemical reactions of CH₂O do produce CO, while solely reaction (R2) forms H₂, which is the topic of our research. In fact, this photochemically produced H₂ constitutes ~60% of the total source of tropospheric H₂ (Rhee et al., 2006b).

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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 ~ 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

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 CH₂O 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 CH₂O. CH₂O-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 CH₂O mixing ratio. Since these pressure readings are essential for determining the CH₂O 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 CH₂O-air mixture was used as a stock for a series of CH₂O photolysis experiments. The CH₂O 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 CH₂O photolysis experiments.

CH₂O 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 CH₂O photolysis experiments using a Xe arc lamp. Aliquots of the CH₂O stock air were transferred to quartz or glass flasks, diluted to a known mixing ratio with CH₂O-free synthetic air, and photolyzed for a few hours to ~17 days. The CH₂O mixing ratios in the reactors were less than ~2 ppm except in the experiments running for few hours, for which ~50 ppm of CH₂O was used. After photolysis we measured the H₂ mixing ratio and D/H ratio. The δD values and mixing ratios of the H₂ produced were determined by a recently developed technique involving continuous-flow isotope mass spectrometry (Rhee et al., 2004).

The pure CH₂O in the 0.1-L glass flasks was used to determine the D/H ratio of

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the CH₂O by photolyzing it with light from a mercury arc lamp (HBO102W, OSRAM). The photolysis of pure CH₂O produces not only CO and H₂ but also H and CHO radicals which further undergo self reactions and reaction with CH₂O, ending up with the production of CO and H₂. Thus, the final products of the photolysis are only CO and H₂. This H₂ has the same isotopic composition as the parent CH₂O. Complete conversion of the CH₂O to CO and H₂ was confirmed by measuring the amount of H₂ 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_{SPL} and R_{STD} represent the D/H of H₂ for sample and a reference material, respectively.

3 Results

3.1 The yield of H₂ in the photolysis of CH₂O

As mentioned earlier, photolysis of CH₂O has one channel that produces CHO and H radicals (R1) and the other that produces CO and H₂ molecules (R2). The CHO radical reacts rapidly with O₂ in the air, also forming CO. Thus, the amount of CO produced should always be the same as that of CH₂O photolyzed, while the amount of H₂ represents the fraction of CH₂O 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 H₂ to CO.

However, a portion of the CH₂O in the reactor may have reacted with the radicals of H, OH, and HO₂, as they are produced in the reactor during the photolysis. These reactions produce CO and formic acid (HCOOH) as well. The reaction of CH₂O with HO₂ produces hydroxymethylperoxy radical (HOCH₂OO). This radical is so unstable that it immediately dissociates back to CH₂O. However, a fraction reacts with HO₂ 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

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mass balance of CO if only photolysis of CH₂O 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 H₂ to CO for each photolysis run to obtain the value of $\Phi(\text{H}_2)$. But, we tracked the actual fraction of H₂ produced by photolysis of CH₂O, given as $\phi(\text{H}_2)$, which represents the ratio of the H₂ mixing ratio in the reactor to the initial CH₂O 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 CH₂O. 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 H₂ through reactions other than the CH₂O photolysis and little reactivity of H₂ in the reactor for the periods of the CH₂O 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 CH₂O 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 CH₂O 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 H₂ and 3% for the δD values. Provided that the scatter is due to variations in parameters that influence photolysis rate of CH₂O, we do not average the values for the same period of photolysis but use individual values for determining the isotopic fractionation occurring in the CH₂O photolysis.

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The CH₂O 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 CH₂O are photolyzed. As a Xe arc lamp emits photons within a broad range of wavelengths, the effective wavelength for the photolysis of CH₂O depends on the cut-off wavelength for transmission through quartz which extends down to ~ 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 CH₂O 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 CH₂O photolysis

To examine the actual photochemistry in the reactor, we constructed a 1-box model composed of 33 photochemical reactions, including photolysis of CH₂O and H₂O₂ 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 CH₂O photolysis rates for both channels ($J_{\text{CH}_2\text{O}}$) of 2.4×10^{-5} to $3.8 \times 10^{-5} \text{ s}^{-1}$. For the same range of SZA, the ratio of the photolysis rates of H₂O₂ and CH₂O, $J_{\text{H}_2\text{O}_2} / J_{\text{CH}_2\text{O}}$, varies only from 0.089 to 0.090. The initial mixing ratio of CH₂O was assumed to be 1 ppm in synthetic air (78% of N₂ and 22% of O₂). The commercial software package FACIMILE was used to integrate time derivatives of the reactions.

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As shown in Fig. 3, whereas photochemical destruction of CH_2O forms CO and HCOOH, both of which are further oxidized by reacting with the OH radical, the unique source of H_2 in the reactor is CH_2O photolysis to the molecular channel (R2) and that H_2 destruction by the OH radical is negligible ($<0.1\%$ of H_2 has reacted at 99% of CH_2O being oxidized). Hence, a substantial portion of the initial CH_2O is converted to products other than CO, but the 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 CH_2O 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 CH_2O photolyzed. In order to predict the asymptote of $\phi(\text{H}_2)$ from measurement, the value of $\Phi(\text{H}_2)$ would be ~ 0.74 , the value that the TUV radiation model predicts when SZA is near 85° in the location of Mainz.

3.3 Isotope effect of the CH_2O photolysis to the molecular channel

Figure 4 shows the variation of the δD value of 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 δD value of the initial CH_2O . Thus, a $\delta\text{D}\text{-H}_2$ value of zero means that the isotopic ratio of the H_2 in sample air is the same as that for the initial CH_2O . 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 CH₂O yields H₂ that has the same isotopic ratios as the initial CH₂O. This observation and the evolution of δD-H₂ as a function of φ(H₂) 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 CH₂O in the reactor is broken down by photolysis (>90%) with the remainder destroyed mostly by reaction with OH (<8%) while HO₂ and H radicals play only a minor role (<2%) (see Fig. 3b). The rate of change of the CH₂O mixing ratio in the reactor can thus be described as:

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

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.

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

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

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

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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, α_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 CH_2O by means of isotopic fractionation factor, α_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 CH_2O , α_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 H_2 from photolysis of CH_2O ($\Phi(\text{H}_2)$), and the ratio $J/(J + K)$ is the fraction of CH_2O that is photolyzed. Designating the latter as Γ , α_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 α_{hv} represents the isotopic fractionation factor for photolysis of CH_2O . Since the amount of radicals produced along the experiments is not constant, Γ 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 α_f is changing along with

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the CH₂O photolysis and photochemical reactions. Nevertheless, assuming that α_f is constant gives a convenient way to determine the isotopic fractionation factor for the production of H₂, α_m . Integrating Eqs. (1) and (4) and then dividing [CHDO] by [CH₂O] 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 CH₂O, R_Q is that for the remaining CH₂O during the run of experiment, and f the fraction of the remaining CH₂O. Thus, the isotopic ratio of the products (R_p) as a function of CH₂O 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 CH₂O photolysis and its photochemical reactions with radicals. The isotopic ratio of the H₂, R_m , which is produced from CH₂O 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 α_m in Eq. (5), R_m has the following relation with R_o .

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

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By dividing Eq. (13) by Eq. (10), the ratio of the isotopic ratios of H₂ and all products from CH₂O 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 CH₂O 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 CH₂O photolysis and its photochemical reactions, which is represented by their reaction rates as the same as for isotopic fractionation factor of CH₂O 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 $\phi(\text{H}_2)$, α_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 α_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 α_m ($=0.50(\pm 0.02)$) and indicates that H₂ produced by photolysis of CH₂O is 500(± 20)‰ depleted with respect to the CH₂O being photolyzed. Since the experiments for the

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photolysis of CH₂O for short periods were conducted with high CH₂O mixing ratios of 50 ppm, a similar amount of initial CH₂O, was applied in the 1-box model to determine the value of α_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 α_f is constant should be valid during the initial stage of photolysis of CH₂O because the amounts of radicals, in particular the OH radical, produced are too small to affect α_f (see Fig. 3b). Even if α_f were not constant, it would not interfere with the determination of α_m because the α_f 's in (13) cancel for $f = 1$.

3.4 Isotope effect of the CH₂O photolysis to the radical channel

Given that complete photolysis of CH₂O yields H₂ that has the same isotopic ratio as that of the initial CH₂O (Fig. 4), we can also determine the isotopic fractionation factor, α_r , which governs the isotopic fractionation occurring at (R1). However, in this case the Rayleigh model cannot be applied because the value of α_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 α_r as follows:



In Fig. 4 several model runs under different conditions are plotted. As an ideal case, we assume that CH₂O is destroyed exclusively by photolysis. Since in this scenario α_f is constant as the reaction proceeds, the Rayleigh model can be applied to determine α_r . In Eq. (13), as f approaches 0, the ratio of R_m to R_o becomes the ratio of α_m to α_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 CH₂O in the reactor as described above. Introduction of the reactions of H and/or HO₂ with both CH₂O 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 CH₂O photolysis. However, it is apparent that the reaction of OH and CH₂O is critical for determination of α_r , as the $\delta\text{D-H}_2$ value for the final product of H₂ reaches only $\sim -170\text{‰}$. Taking the kinetic isotope effect for the reaction of CH₂O 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 H₂+OH. However, decreasing the value of α_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 H₂ 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 α_r is 0.22 and the isotopic fractionation factor of CH₂O due to photolysis (α_{hv}) results in 0.40 for $\Phi(\text{H}_2) = 0.647$, the yield of H₂ 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 α_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 α_r by varying the values of the various parameters used in the 1-box model. These parameters are the mixing ratio of CH₂O in the reactor, $\Phi(\text{H}_2)$, photolysis rates

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of CH₂O and H₂O₂, 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 α_r is most sensitive to the ratio of the photolysis rate of H₂O₂ to that for CH₂O because large production of OH by photolysis of H₂O₂ leads to the increase of the fraction of CH₂O that reacts with OH in the reactor, which in turn forces the value of α_r to be smaller to compensate it (see Eq. 8b). The same effect can be introduced to the variation of α_{OH} for CH₂O + 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 α_r among the parameters because of its large potential error of 40‰, which includes the uncertainty of the δD value of the original CH₂O (=4‰). Overall most of the uncertainty for α_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 CH₂O itself by measuring time evolution of the amount of isotopologues, CH₂O and CD₂O using an optical method (Feilberg et al., 2007a, Feilberg et al., 2005), another experiment examined the same isotopic fractionation but for CH₂O and CHDO using the same technique (Feilberg et al., 2007b), and the other measured the D/H ratio of H₂ produced from the photolysis of CH₂O 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 H₂ ($\phi(\text{H}_2)$) and the δD value of the original CH₂O used for the photolysis experiments, both of which are critical to determine α_m , makes it difficult to infer α_m from this single value of δD . The authors reported that the photolysis of CH₂O produces isotopically light H₂, the

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δD value of which is $\sim -200\text{‰}$. If the authors meant the value to be the degree of enrichment of the H_2 produced, α_m is ~ 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 α_m and α_{hv} as $0.55(\pm 0.02)$ and $0.63(\pm 0.01)$, respectively. The value of α_m is similar to, while that for α_{hv} is far larger than, the values determined in the present study. Actually the large discrepancy of α_{hv} points to a much larger difference in the value of α_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 α_{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 α_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 α_{hv} "directly" by a spectroscopic method and from which α_m was inferred from the isotope-ratio-mass-spectrometric measurements of HD and modeling of the H_2 yield using a

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given quantum yield for CH₂O photolysis. The direct inference of α_{hv} , however, had to be corrected to account for the losses of CH₂O and CHDO by the reaction with OH radical and large leakage of air in the chamber as well as production of CH₂O from the wall. In addition, their values of α_r and α_m depend on which value of the quantum yield for CH₂O photolysis are applied. In our study, performed at the level of natural deuterium abundance, α_m is the “directly” inferred quantity, and α_{hv} follows from the fact that the isotopic compositions of the initial CH₂O and of the H₂ 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 CH₂O between the two studies. More experiments can resolve this issue.

4.2 Atmospheric implication

The determination of α_m and α_r may provide an important insight to comprehend what causes the enrichment in deuterium throughout the photochemical oxidation pathway from CH₄ to H₂. The overall composite of isotopic fractionation factors from CH₄ to H₂, $\alpha_{CH_4-H_2}$, may be defined as:

$$\alpha_{CH_4-H_2} = \frac{R_{H_2}^0}{R_{CH_4}} \quad (19)$$

where $R_{H_2}^0$ represents the hydrogen isotopic ratio of H₂ produced by photochemical oxidation of CH₄ and R_{CH_4} is that for CH₄. Strictly speaking, $\alpha_{CH_4-H_2}$ 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, $\alpha_{CH_4-H_2}$ can be considered as an isotopic fractionation factor. Rhee et al. (2006a) estimated the value of $\alpha_{CH_4-H_2}$ to be 1.3 in the troposphere, meaning that the H₂ produced from CH₄ oxidation is enriched in deuterium 1.3 times as much

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as the initial CH₄. Gerst and Quay (2001) and Price et al. (2007) also expected D in the H₂ from photochemical oxidation of CH₄ 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 CH₄ to H₂. These factors include: (1) isotopic fractionation occurring during the reaction of CH₄ with OH (α_{CH_4}), the rate-determining step of the photochemical chain reactions of CH₄, as well as the subsequent isotopic fractionation processes occurring along the way to CH₂O (α_{Σ}), (2) the branching ratios of deuterated species, e.g., CH₃D, CH₂DOOH, and CH₂DO, (3) the factor of 2 brought up by the reduction of the number of hydrogen atoms from CH₄ to CH₂O, and finally (4) isotopic fractionation occurring during the photolytical production of H₂ from CH₂O. Assuming that CH₂O is in a photochemical steady state, as it has a far shorter chemical lifetime than CH₄ and H₂, point (4) is represented by the ratio of the isotopic fractionation factor of the H₂ produced (α_m) to that for CH₂O (α_f) (Rhee et al., 2006a). Note that α_f differs from α_{hv} by the effect of isotopic fractionation arising from reaction with OH radical (α_{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 β_{CH_4} is the branching ratio for the deuterated product, CH₂D, in the reaction of CH₃D and OH, and β_p is a combined branching ratio for other short-lived intermediates, CH₂DOOH, and CH₂DO.

Regarding the right-hand side of Eq. (20), the value of α_{CH_4} is 0.78(±0.07) at 298 K (Gierczak et al., 1997) and decreases with the decrease of temperature, that for β_{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 β_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 α_{Σ} may not be larger than unity. The last two parameters in Eq. (20), α_f and α_m , are what we are concerned with here: since

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α_f is a combined isotopic fractionation factor due to photolysis and photochemical reactions of CH_2O 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 α_m and α_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 α_{OH} as $0.781(\pm 0.006)$. The optimal values of $\Phi(\text{H}_2)$ and Γ 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° (see Fig. 2). In order to determine Γ , we calculated OH radical concentrations and their uncertainties from the relationship between the photolysis rate of 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 α_f is $0.51(\pm 0.11)$. Most of its uncertainty is carried over from the uncertainty of OH. The ratio of α_m/α_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 CH_2O photolysis could lead to a depletion or enrichment of D in the H_2 produced with respect to the parent CH_2O . When using the values of isotopic fractionation factors determined by Feilberg et al. (2007b), the CH_2O photolysis leads to the depletion of D in the H_2 , however, even taking into account the uncertainty of α_m/α_f (see Table 3).

We extend the calculation of the ratio of α_m/α_f to a range of values of $\Phi(\text{H}_2)$ and Γ , assuming that the values of α_m , α_r , and α_{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 Γ 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 cm^{-3}

(e.g., Berresheim et al., 2003), leading to $\Gamma \sim 0.45$. Thus, the range of Γ is likely to be between 0.4 and 1 in the troposphere. As shown in Fig. 5, the ratios of α_m/α_f vary from ~ 0.8 to ~ 1.2 , which suggests that, depending on the values of Γ and $\Phi(\text{H}_2)$ in the troposphere, the H_2 produced from the CH_2O photolysis would be either enriched or depleted in D. For instance, at the Earth's surface the values of α_m/α_f along the track of the sun are likely to be lower than unity, thus yielding the depleted H_2 in D with respect to the parent CH_2O .

Finally, we examine the range of α_m/α_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 α_{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 α_m/α_f will be ~ 0.8 when the branching ratio for deuterated compounds (β_{CH_4} and β_p) and α_Σ unity. When these three values follow Gerst and Quay (2001)'s speculation ($\beta_{\text{CH}_4} \times \alpha_\Sigma \times \beta_p = 0.96 \times 0.77 \times 0.96$), α_m/α_f is 1.15. These two values of α_m/α_f bound the range which was estimated for the typical values of Γ and $\Phi(\text{H}_2)$ in the troposphere (Fig. 5). This suggests that even if α_m/α_f is smaller than unity it is still possible that H_2 formed from the photochemical oxidation of CH_4 is enriched in D with respect to the original 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 CH_2DO reacting with O_2 to be $0.88(\pm 0.01)$, suggesting β_p to be lower than unity and that α_m/α_f is likely to be larger than unity.

5 Conclusions

The CH_2O 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 H_2 produced is depleted in D by $500(\pm 20)\%$.

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with respect to the initial CH₂O. The radical channel (R1) appears to have a much stronger isotopic fractionation than the molecular channel (R2), resulting in D enrichment of the remaining CH₂O 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, CH₂O photolysis may produce the H₂ that is slightly depleted in D. However, the large uncertainty in the combined isotopic effects of photochemical reactions of CH₂O, which primarily originates from the uncertainty of OH concentration, makes it impossible to precisely define the role of CH₂O photolysis in the D enrichment of H₂. In the troposphere, CH₂O photolysis may produce the H₂ either enriched or depleted in D with respect to the parent CH₂O depending on the fraction of CH₂O that reacts with OH or that is photolyzed to H₂. Nonetheless, our estimated range of α_m/α_f (~0.8 to ~1.2) in the troposphere, the ratio of isotopic fractionation factors which determines the degree of D enrichment of H₂ at steady state of CH₂O mixing ratio, can meet the production of the H₂ enriched in D with respect to the original CH₄ 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 N₂ and 22% of O₂. Unless otherwise mentioned, the yield of H₂ in the photolysis of CH₂O 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.

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Table 1. Summary of CH₂O photolysis experiments.

Photolysis							
Start	End	*Duration (hr)	[§] [CH ₂ O] ₀ (ppm)	Light source	Reactor material	φ(H ₂)	δD-H ₂ (‰)
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).

[§] Initial mixing ratios of CH₂O in a reactor prior to photolysis.

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Table 2. Sensitivity test of the α_r at a given range of the parameters.

	Prescribed value (Z_i)	Uncertainty of parameter (ΔZ_i)	Sensitivity ($\Delta\alpha_r/\Delta Z_i$)	Uncertainty of α_r ($\Delta\alpha_r$)
$[\text{CH}_2\text{O}]_0$ (ppm)	1	± 1	0.0027 [§]	± 0.003
$J_{\text{CH}_2\text{O}}$ (s^{-1})	3.143×10^{-5}	$\pm 4.4 \times 10^{-5}$	0.0026 [§]	± 0.004
$\Phi(\text{H}_2)$	0.647	± 0.039	-0.476	∓ 0.019
$J_{\text{H}_2\text{O}_2}/J_{\text{CH}_2\text{O}}$	0.0896	± 0.0036	-2.48	∓ 0.009
α_{H} for $\text{CH}_2\text{O} + \text{H}$	0.781	± 0.25	~ 0	~ 0
α_{OH} for $\text{CH}_2\text{O} + \text{OH}$	0.781	± 0.0061	-0.45	∓ 0.003
α_{HO_2} for $\text{CH}_2\text{O} + \text{HO}_2$	0.781	± 0.25	-0.036	∓ 0.009
$\delta\text{D}-\text{H}_2$ of final product (‰)	0	± 40	-0.0019	∓ 0.076
Sum*				0.079

[§]Sensitivity is calculated by the ratio of a parameter to the prescribed value.

*Quadratic sum of errors.

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Table 3. Comparison of the isotope effects determined from CH₂O photolysis experiments.

Source	Minor isotopologue	α_m	α_r	$^* \alpha_{\text{OH}}$	$\Phi(\text{H}_2)$	$^{\&} \Gamma$	α_{hv}	α_f	α_m/α_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 ₂ O]						0.333(±0.056)		

* Kinetic isotope effect for CH₂O + OH from Feilberg et al. (2004).

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

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

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Table A1. Photochemical reactions in the model.

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

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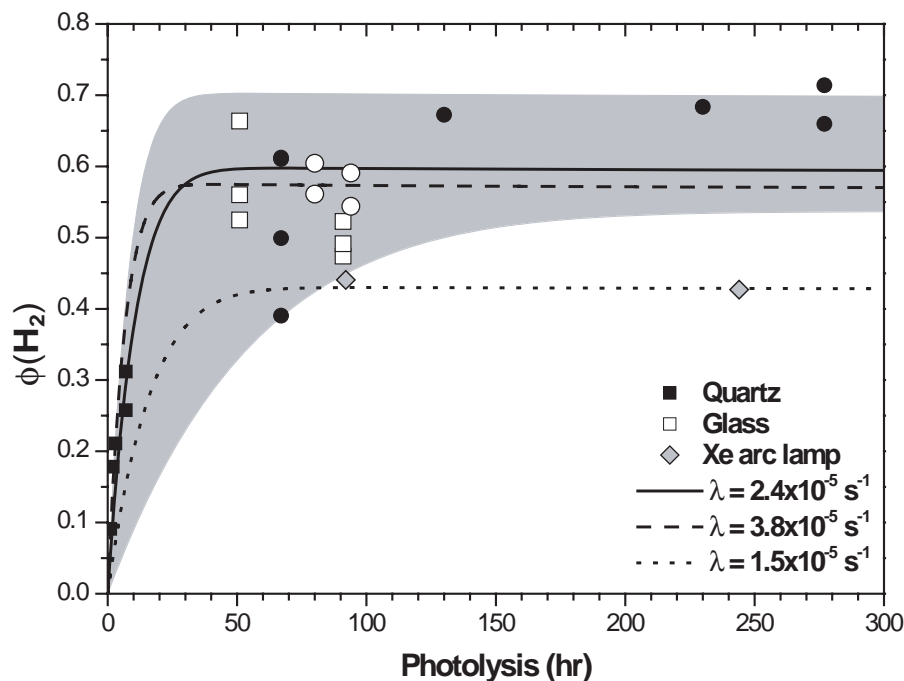


Fig. 1. Evolution of the fraction of H_2 ($\phi(\text{H}_2)$) produced by photolysis of CH_2O in daylight or using a Xe arc lamp. The squares are for the experiments in March, May and June, and the circles for August and September. Solid symbols indicate a quartz reactor and open symbols a glass reactor. The gray-shaded area and lines represent model calculations for a given CH_2O photolysis rate and yield of 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.

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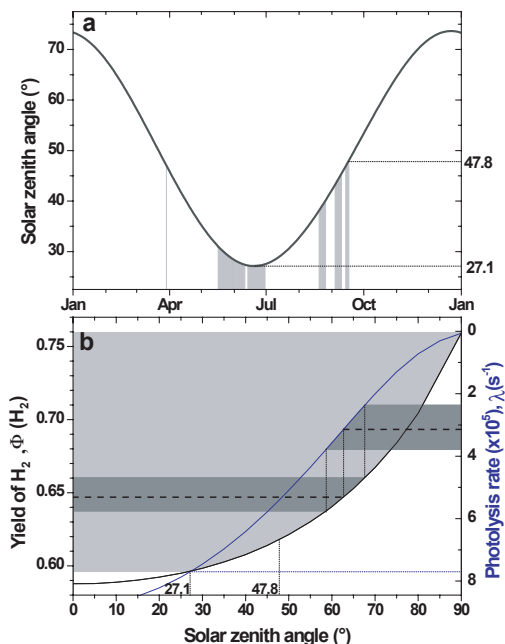


Fig. 2. (a) Solar zenith angle (SZA) at local noon in Mainz (11:00 GMT) in 2004. Gray shaded areas indicate the dates when experiments were conducted. SZA at local noon ranges from 27.1° to 47.8° for the periods of experiment. **(b)** Photolytic yield of H_2 ($\Phi(\text{H}_2)$) and photolysis rate of CH_2O ($J_{\text{CH}_2\text{O}}$) 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.

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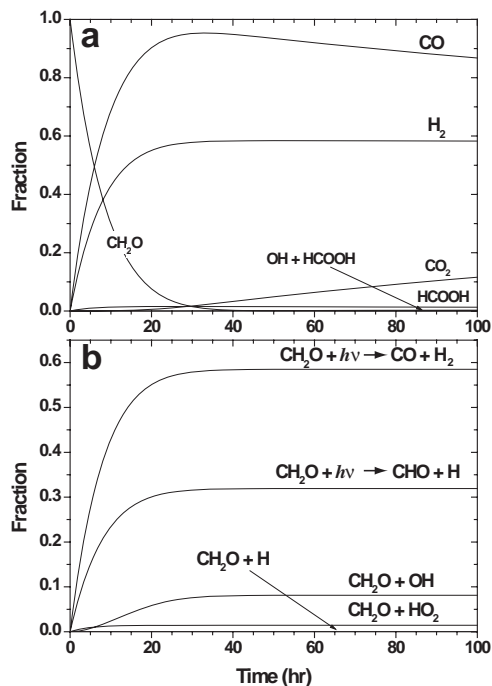


Fig. 3. A 1-box model simulation of CH₂O photochemistry in the reactor. Details of the reactions are given in Appendix A. **(a)** Time evolution of the relative abundances of CH₂O and its photochemical products. “OH + HCOOH” represents the sum of the amounts of any compounds produced by the reaction of formic acid and OH radical. **(b)** Time evolution of the fraction of CH₂O that is photolyzed or reacts with radicals.

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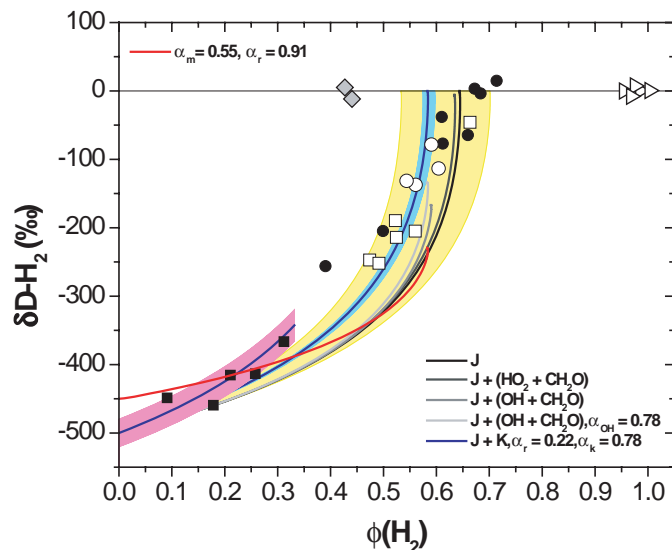


Fig. 4. Evolution of $\delta\text{D-H}_2$ as a function of the fraction of H_2 produced by photolysis of CH_2O . Symbol keys are the same as in Fig. 1. Several model sensitivity runs are shown with solid lines. Yellow shading indicates potential isotopic fractionation evolutions for various ranges of $\Phi(\text{H}_2)$ 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 CH_2O 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 α_m and α_K (see text) are always 0.50 and 0.78, respectively, and that the complete photolysis of CH_2O yields H_2 with a δD value that is the same as that of the initial CH_2O . 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).

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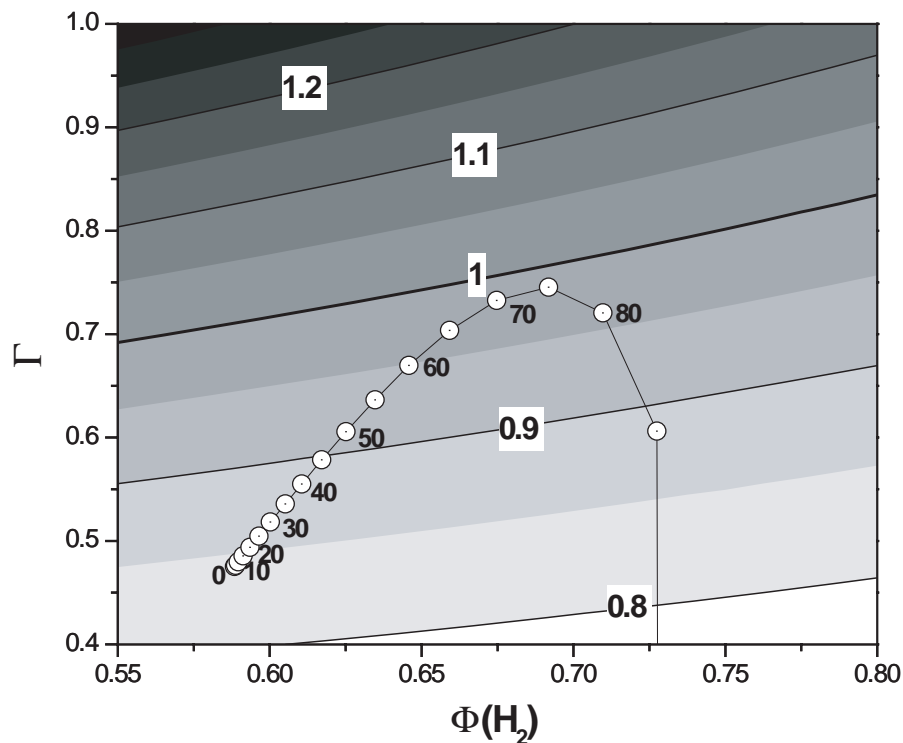


Fig. 5. Contour plot of the ratio α_m/α_f for potential ranges of the yield of H₂ from CH₂O photolysis ($\Phi(\text{H}_2)$) and of the fraction of CH₂O that is decomposed by photolysis (Γ) in the troposphere. The symbols track the values of $\Phi(\text{H}_2)$ and Γ calculated by the TUV radiation model and Rohrer and Berresheim (2006)'s parameterization of OH concentration at the indicated solar zenith angle from 0° to 90° in 5° steps at Earth's surface.

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