Hydrogen isotope fractionation in the photolysis of formaldehyde

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Abstract. 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 the H₂ produced is 500(±20)%ee with respect to the parent CH₂O. We also observed that complete photolysis of CH₂O under atmospheric conditions produces H₂ that has virtually the same isotope 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)%ee enrichment in D of the remaining CH₂O. When CH₂O is in photochemical steady state, the isotope ratio of the H₂ produced is determined not only by the isotopic fractionation occurring during the photolytical production of H₂ (αₘ) but also by overall fractionation for the removal processes of CH₂O (αᵣ), and is represented by the ratio of αₘ/αᵣ. Applying the isotopic fractionation factors relevant to CH₂O photolysis obtained in the present study to the troposphere, the ratio of αₘ/αᵣ varies from ~0.8 to ~1.2 depending on the fraction of CH₂O that reacts with OH and that produces H₂. This range of αₘ/αᵣ 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 range from sub-ppb levels to ~100 ppb depending largely on local sources (Warneck, 1999). Its turnover is large in the atmosphere and it is a source of molecular hydrogen (H₂), carbon monoxide (CO), and of the hydroperoxyl radical (HO₂), yet limited 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; Troe, 2007).

CH₂O is broken down by photolysis (R1 and R2) and by photochemical oxidation (R3) in the troposphere (Calvert, 1980):

\[ \text{CH}_2\text{O} + h\nu \rightarrow \text{CHO} + \text{H} \]  \hspace{1cm} (R1)
\[ \text{CH}_2\text{O} + h\nu \rightarrow \text{CO} + \text{H}_2 \]  \hspace{1cm} (R2)
\[ \text{CH}_2\text{O} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O} \]  \hspace{1cm} (R3)
Reaction (R1) produces the HO\(_2\) radical by the rapid reaction of hydrogen (H) and formyl (CHO) radicals with atmospheric oxygen (O\(_2\)), which can lead to the formation of the hydroxyl radical (OH) via the reaction with NO or O\(_3\) in the atmosphere. This is an important propagation of the radical chain. Only reaction (R2) yields H\(_2\). All photochemical reactions of CH\(_2\)O do produce CO, while solely reaction (R2) forms H\(_2\), which is the topic of our research. In fact, this photochemically produced H\(_2\) constitutes \(\sim\)50 to \(\sim\)60\% of the total source of tropospheric H\(_2\) (Novelli et al., 1999; Rhee et al., 2006b).

In the stratosphere, H\(_2\) originates both from this in situ photolysis process (R2), albeit under photochemically very different conditions, and 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 (Novelli 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(\(^1\)D), 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(\(^1\)D)) 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 have investigated the isotopic fractionation occurring during the photolysis of CH\(_2\)O 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\(_2\)O has been rarely investigated in the past (Crounse et al., 2003; Feilberg et al., 2005; Feilberg et al., 2007b). Since CH\(_2\)O 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\(_2\)O) was prepared by purifying paraformaldehyde (Merck) in a vacuum system following the method of Spence and Wild (1935). Solid paraformaldehyde was heated at \(\sim\)420 K under vacuum. For purification the evaporating CH\(_2\)O and impurities were forced through a set of glass U-tubes which were partly immersed in an ethanol sludge (\(\sim\)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\(_2\)O (\(\sim\)3 mbar) was released to a 3-L glass bulb and several 0.1-L glass flasks simultaneously, all of which were connected to the same manifold. The pure CH\(_2\)O in the 0.1-L glass flasks were used to determine the D/H ratio of the CH\(_2\)O (see below). Afterwards pressure inside the manifold was read by a capacitance manometer (MKS10, Baratron). CH\(_2\)O-free synthetic air was then introduced into the 3-L glass bulb to reach ambient pressure and the final pressure was read by another capacitance manometer (MKS1000, Baratron) to determine the CH\(_2\)O mixing ratio. Since these pressure readings are essential for determining the CH\(_2\)O mixing ratio in the reactors used for the photolysis experiments, the capacitance manometers were calibrated accurately by an absolute manometer (Digiquartz 740, Paroscientific) whenever necessary. The CH\(_2\)O-air mixture was used as a stock for a series of CH\(_2\)O photolysis experiments. The CH\(_2\)O mixing ratios in the stock air were usually around 0.3\%.

Aliquots of the CH\(_2\)O stock air were transferred to quartz or glass flasks, diluted to the target mixing ratio with CH\(_2\)O-free synthetic air, and photolyzed for a few hours to \(\sim\)17 days (Table 1). The CH\(_2\)O mixing ratios in the reactors were less than \(\sim\)2 ppm except in the experiments running for few hours, for which \(\sim\)50 ppm of CH\(_2\)O was used. After photolysis we measured the H\(_2\) mixing ratio and D/H ratio. The \(\delta\)D values and mixing ratios of the H\(_2\) produced were determined by a recently developed technique involving continuous-flow isotopic ratio mass spectrometry (Rhee et al., 2004).

In order to test stability of CH\(_2\)O in the reactor, we had once monitored the pressure inside the 3-L glass bulb for 2 days after injecting pure CH\(_2\)O at \(\sim\)3 mbar. No change in pressure inside was found, indicating no absorption or loss of CH\(_2\)O by polymerization or heterogeneous reactions. The same results even at higher pressure of pure CH\(_2\)O air have been reported (e.g., Horowitz and Calvert, 1978).

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\(_2\)O photolysis experiments. CH\(_2\)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 also conducted CH\(_2\)O photolysis experiments using a xenon (Xe) short arc lamp (XBO 75W/2). A characteristic intensity spectrum of the light sources and the transmission of the reactor materials are shown in Fig. 1 together with photolytic properties of CH\(_2\)O.

The D/H ratio of the original CH\(_2\)O in the stock air was determined by analyzing the isotopic composition of the pure CH\(_2\)O in the 0.1-L glass flasks, which originated from the same source of CH\(_2\)O as that in the stock air (see above). The pure CH\(_2\)O sample was photolyzed using a mercury
Table 1. Summary of CH$_2$O photolysis experiments.

<table>
<thead>
<tr>
<th>Start</th>
<th>End</th>
<th>*Duration (h)</th>
<th>**[CH$_2$O]$_0$ (ppm)</th>
<th>Light source</th>
<th>Reactor material</th>
<th>$\Psi$(H$_2$)</th>
<th>δD-H$_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Sep-03</td>
<td>10-Sep-03</td>
<td>91</td>
<td>2.3</td>
<td>Daylight</td>
<td>Glass</td>
<td>0.47</td>
<td>−247</td>
</tr>
<tr>
<td>4-Sep-03</td>
<td>10-Sep-03</td>
<td>91</td>
<td>2.5</td>
<td>Daylight</td>
<td>Glass</td>
<td>0.52</td>
<td>−190</td>
</tr>
<tr>
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<td>10-Sep-03</td>
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<td>2.6</td>
<td>Daylight</td>
<td>Glass</td>
<td>0.49</td>
<td>−252</td>
</tr>
<tr>
<td>14-Sep-03</td>
<td>17-Sep-03</td>
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<td>0.43</td>
<td>Daylight</td>
<td>Glass</td>
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</tr>
<tr>
<td>14-Sep-03</td>
<td>17-Sep-03</td>
<td>51</td>
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<td>Daylight</td>
<td>Glass</td>
<td>0.66</td>
<td>−46</td>
</tr>
<tr>
<td>14-Sep-03</td>
<td>17-Sep-03</td>
<td>51</td>
<td>0.48</td>
<td>Daylight</td>
<td>Glass</td>
<td>0.56</td>
<td>−205</td>
</tr>
<tr>
<td>29-Mar-04</td>
<td>29-Mar-04</td>
<td>1</td>
<td>53</td>
<td>Daylight</td>
<td>Quartz</td>
<td>0.09</td>
<td>−449</td>
</tr>
<tr>
<td>29-Mar-04</td>
<td>29-Mar-04</td>
<td>2</td>
<td>50</td>
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<td>Quartz</td>
<td>0.18</td>
<td>−459</td>
</tr>
<tr>
<td>29-Mar-04</td>
<td>29-Mar-04</td>
<td>3</td>
<td>34</td>
<td>Daylight</td>
<td>Quartz</td>
<td>0.21</td>
<td>−415</td>
</tr>
<tr>
<td>29-Mar-04</td>
<td>29-Mar-04</td>
<td>7</td>
<td>63</td>
<td>Daylight</td>
<td>Quartz</td>
<td>0.31</td>
<td>−366</td>
</tr>
<tr>
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<td>36</td>
<td>Daylight</td>
<td>Quartz</td>
<td>0.26</td>
<td>−413</td>
</tr>
<tr>
<td>17-May-04</td>
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<td>130</td>
<td>2.1</td>
<td>Daylight</td>
<td>Quartz</td>
<td>0.67</td>
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<tr>
<td>14-Jun-04</td>
<td>18-Jun-04</td>
<td>67</td>
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<td>Daylight</td>
<td>Quartz</td>
<td>0.50</td>
<td>−205</td>
</tr>
<tr>
<td>14-Jun-04</td>
<td>18-Jun-04</td>
<td>67</td>
<td>1.8</td>
<td>Daylight</td>
<td>Quartz</td>
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<td>Quartz</td>
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<td>Quartz</td>
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<td>Daylight</td>
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<td>15</td>
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<tr>
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<td>30-Jun-04</td>
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<td>1.9</td>
<td>Daylight</td>
<td>Quartz</td>
<td>0.66</td>
<td>−65</td>
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<tr>
<td>30-May-04</td>
<td>4-Jun-04</td>
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<td>1.6</td>
<td>Daylight</td>
<td>Glass</td>
<td>0.56</td>
<td>−137</td>
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<tr>
<td>30-May-04</td>
<td>4-Jun-04</td>
<td>80</td>
<td>1.6</td>
<td>Daylight</td>
<td>Glass</td>
<td>0.60</td>
<td>−113</td>
</tr>
<tr>
<td>5-Jun-04</td>
<td>11-Jun-04</td>
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<td>1.6</td>
<td>Daylight</td>
<td>Glass</td>
<td>0.54</td>
<td>−132</td>
</tr>
<tr>
<td>5-Jun-04</td>
<td>11-Jun-04</td>
<td>94</td>
<td>1.5</td>
<td>Daylight</td>
<td>Glass</td>
<td>0.59</td>
<td>−78</td>
</tr>
<tr>
<td>92</td>
<td>1.5</td>
<td>244</td>
<td>1.4</td>
<td>Xe arc lamp</td>
<td>Quartz</td>
<td>0.44</td>
<td>−12</td>
</tr>
<tr>
<td>10</td>
<td>3 mbar</td>
<td>10</td>
<td>3 mbar</td>
<td>Hg arc Lamp</td>
<td>Quartz</td>
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<td>7</td>
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<tr>
<td>10</td>
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<td>13</td>
<td>3 mbar</td>
<td>Hg arc Lamp</td>
<td>Quartz</td>
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<td>1</td>
</tr>
<tr>
<td>13</td>
<td>3.3 mbar</td>
<td>13</td>
<td>3.3 mbar</td>
<td>Hg arc Lamp</td>
<td>Quartz</td>
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<td>3.3 mbar</td>
<td>12</td>
<td>3.3 mbar</td>
<td>Hg arc Lamp</td>
<td>Quartz</td>
<td>0.99</td>
<td>0</td>
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</table>

* 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 CH$_2$O in a reactor prior to photolysis. For the photolysis of pure CH$_2$O, unit of pressure is used.

(Hg) short arc lamp (HBO 103W/2, OSRAM). The photolysis of pure CH$_2$O produces not only CO and H$_2$ but also H and CHO radicals which further undergo self reactions and reaction with CH$_2$O, ending up with the production of CO and H$_2$ (e.g., Calvert, 1980). Thus, the final products of the photolysis are only CO and H$_2$. Isotopic mass balance requires that for complete conversion the product H$_2$ has the same isotopic composition as the parent CH$_2$O. Complete conversion of the CH$_2$O to CO and H$_2$ was confirmed by measuring the amount of H$_2$ produced and its isotopic composition. The deuterium content is as usual expressed as $\delta$D=(R$_{SPL}$/R$_{STD}$−1)×1000 (‰), where R$_{SPL}$ and R$_{STD}$ represent the D/H of H$_2$ for sample and a reference material, respectively. For convenience, we express the $\delta$D values relative to the isotopic composition of the parent CH$_2$O.

3 Results

3.1 The yield of H$_2$ in the photolysis of CH$_2$O

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

However, a portion of the CH$_2$O in the reactor may react with the radicals, H, OH, and HO$_2$, as they are produced in the reactor during the photolysis. These reactions produce CO and formic acid (HCOOH). The reaction of
CH$_2$O with HO$_2$ produces the hydroxymethylperoxy radical (HOC$_2$OO). This radical is so unstable that it immediately dissociates back to CH$_2$O. However, a fraction reacts with HO$_2$ 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 mass balance of CO if only photolysis of CH$_2$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$_2$ to CO for each photolysis run to obtain the value of $\Phi$(CH$_2$O). But, we tracked the actual fraction of H$_2$ produced by photolysis of CH$_2$O, given as $\Psi$(H$_2$), which represents the ratio of the H$_2$ mixing ratio in the reactor to the initial CH$_2$O mixing ratio.

Figure 2 shows the evolution of $\Psi$(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$_2$O. For the short periods experiments (<12 h), $\Psi$(H$_2$) increases rapidly with the increase of photolysis time. At long periods of photolysis (>130 h), $\Psi$(H$_2$) converges toward an asymptotic value. By virtue of negligible production of H$_2$ (<10$^{-5}$ per CH$_2$O according to the model described below) through reactions other than the CH$_2$O photolysis and of little reactivity of H$_2$ in the reactor for the periods of the CH$_2$O photolysis, $\Psi$(H$_2$) approaches an asymptotic value as a function of time. This asymptotic value of $\Psi$(H$_2$) is equivalent to $\Phi$(H$_2$) when CH$_2$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 quantum yield of the molecular channel peaks at longer wavelengths compared to the radical channel (Moortgat et al., 1983), $\Psi$(H$_2$) increases with the increase of SZA. As an indirect support for this speculation, photolysis of CH$_2$O performed in the laboratory using Hg and Xe short arc lamps shows that the uncertainty of replicate runs is merely about 2% for the yield of H$_2$. Provided that the scatter is due to variabilities of the parameters that influence photolysis rate of CH$_2$O, we did not average the values of $\Psi$(H$_2$) for the same period of photolysis, but the individual values were used to determine the isotopic fractionation factors for the CH$_2$O photolysis.

The CH$_2$O photolysis experiments conducted with a Xe short arc lamp give an opportunity to qualitatively examine a relation between $\Phi$(H$_2$) and the range of wavelengths by which CH$_2$O is photolyzed. As a Xe short arc lamp emits photons within a broad range of wavelengths, the effective wavelength for the photolysis of CH$_2$O depends on the cut-off wavelength for transmission through quartz which extends down to $\sim$200 nm (see Fig. 1). This is shorter than the lower limit of solar wavelengths at the Earth’s surface.
Consequently, $\Phi(H_2)$ from the Xe short arc lamp experiments should be smaller than that obtained with sunlight because of the dominance of the radical channel in CH$_2$O photolysis at these short wavelengths (Moortgat et al., 1983). As shown in Fig. 2, $\Psi(H_2)$ 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, as expected, reflects a smaller value of $\Phi(H_2)$ using the Xe short arc lamp.

Fig. 3. (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$_2$ ($\Phi(H_2)$) and photolysis rate of CH$_2$O ($J_{\text{CH}_2\text{O}}$) at a given solar zenith angle calculated with the TUV radiation model. The gray-shaded area indicates a range of $\Phi(H_2)$ 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 $\Phi(H_2)$ 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 $\Phi(H_2)$. These two values of $J_{\text{CH}_2\text{O}}$ and $\Phi(H_2)$ were then used in the 1-box photochemistry model.

Fig. 4. A 1-box model simulation of CH$_2$O photochemistry in the reactor. Details of the reactions are given in Appendix A. (a) Time evolution of the relative abundances of CH$_2$O and its photochemical products. “OH\text{+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$_2$O that is photolyzed or reacts with radicals.

3.2 A box model simulation of CH$_2$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$_2$O and H$_2$O$_2$ as well as formation of HCOOH (see Appendix A). The model was run under conditions of standard ambient temperature (25°C) and pressure (10$^5$ Pa) 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. 3, the TUV radiation model predicts that the values of $\Phi(H_2)$ 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-weighted mean values of $\Phi(H_2)$ would be 0.64 to 0.66, which correspond to total CH$_2$O photolysis rates for both channels ($J_{\text{CH}_2\text{O}}$) of 2.4×10$^{-5}$ to 3.8×10$^{-5}$ s$^{-1}$. For the same range of SZA, the ratio of the photolysis rates of H$_2$O$_2$...
and CH$_2$O. $J_{\text{H}_2O}/J_{\text{CH}_2O}$, varies only from 0.089 to 0.090. The initial mixing ratio of CH$_2$O was assumed to be 1 ppm in synthetic air (78% of N$_2$ and 22% of O$_2$). The commercial software package FACSIMILE (MCPA Software, UK) was used to integrate time derivatives of the chemical species in the reactions.

As shown in Fig. 4, while photochemical destruction of CH$_2$O forms CO and HCOOH, both of which are further oxidized by reacting with the OH radical, H$_2$ in the reactor is almost entirely produced by CH$_2$O photolysis to the molecular channel (R2) and is little oxidized by the OH radical within the time periods of the experiments (<0.1% of H$_2$ has reacted at 99% of CH$_2$O being oxidized). Hence, a substantial portion of the initial CH$_2$O is converted to products other than CO, but the H$_2$ produced is accumulated in the reactor reaching an asymptotic value at full conversion.

The time evolutions of $\Psi$(H$_2$) were predicted by applying the values of $\Phi$(H$_2$), $J_{\text{CH}_2O}$, and $J_{\text{H}_2O}$ from the TUV radiation model described above to the 1-box model (Fig. 2). 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, the asymptotic value of the measurements differs from the model predictions when the most likely values of parameters under photochemical conditions in Mainz, Germany, are applied (solid and dashed lines in Fig. 2). As shown in Fig. 4b, ~10% of CH$_2$O is destroyed by the reactions with radicals. This leads to the lower asymptote of $\Psi$(H$_2$) than the value of $\Phi$(H$_2$) obtained from the TUV radiation model because this asymptotic value of $\Psi$(H$_2$) is smaller than $\Phi$(H$_2$) by a factor corresponding to the fraction of CH$_2$O photolyzed. In order to reproduce the asymptote of $\Psi$(H$_2$) from the measurements in the model, a value of $\Phi$(H$_2$)$\approx$0.74 is necessary, the value that the TUV radiation model predicts when SZA is near 85° in the location of Mainz. This SZA is larger than the weighted-mean value of 63° predicted by the model. This discrepancy could be associated with feeding the parameters relevant to photochemical reactions in the model without accounting for their variation along the change in radiation as mentioned above.

### 3.3 Isotope effect of the CH$_2$O photolysis to the molecular channel

Figure 5 shows the variation of the $\delta$D value of H$_2$ ($\delta$D-H$_2$) as a function of $\Psi$(H$_2$). As the isotope ratios are normalized with respect to the $\delta$D value of the initial CH$_2$O, a $\delta$D-H$_2$ value of zero means that the isotope ratio of the H$_2$ in sample air is the same as that for the initial CH$_2$O. The air samples whose values of $\Psi$(H$_2$) approach the asymptotic values at long photolysis times for both the sunlight and Xe short arc lamp experiments show near-zero values of $\delta$D-H$_2$. This indicates that complete photochemical decomposition of CH$_2$O yields H$_2$ that has the same isotope ratios as the initial CH$_2$O. This observation and the evolution of $\delta$D-H$_2$ as a function of $\Psi$(H$_2$) give us crucial information to aid in determining the hydrogen isotopic fractionation processes occurring in (R1) and (R2) as follows.

According to the results from the 1-box model described in Sect. 3.2, most of the CH$_2$O in the reactor is broken down by photolysis (>90%) with the remainder being destroyed mostly by reaction with OH (<8%) while HO$_2$ and H radicals play only a minor role (<2%) (see Fig. 4b). The rate of change of the CH$_2$O mixing ratio in the reactor can thus be described as:

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

where $J$ is the sum of photolysis rates of (R1) (i.e., $j_m$) 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.

\[
J = j_m + j_r \tag{2}
\]

\[
K = \sum_i k_i [X_i] \tag{3}
\]

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

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

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 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:

\[
\alpha_m = \frac{j_m}{j_f} \tag{5}
\]

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

\[
J' = j_r + j_m = \alpha_r j_r + \alpha_m j_m \tag{6}
\]

\[
K' = \sum_i k_i' [X_i] = \sum_i \alpha_i k_i [X_i] = \alpha K \tag{7}
\]

By definition, the isotopic fractionation factor for CH$_2$O, \(\alpha_f\), is

\[
\alpha_f = \frac{J' + K'}{J + K} = \frac{j_r}{J + K} + \alpha_m \frac{j_m}{J + K} + \alpha_K \frac{K}{J + K} \tag{8a}
\]

In Eq. (8a), the ratio of \(j_m\) to \(J\) represents the yield of H$_2$ from photolysis of CH$_2$O (\(\Phi(H_2)\)), and the ratio \(J/(J+K)\) is the fraction of CH$_2$O that is photolyzed. Designating the latter as \(\Gamma\), \(\alpha_f\) can be rewritten as

\[
\alpha_f = \alpha_r (1 - \Phi) \Gamma + \alpha_m \Phi \Gamma + \alpha_K (1 - \Gamma) \tag{8b}
\]

Or simply,

\[
\alpha_f = \alpha_{hv} \Gamma + \alpha_K (1 - \Gamma) \tag{8c}
\]

where \(\alpha_{hv}\) represents the isotopic fractionation factor for photolysis of CH$_2$O. Since the amount of radicals produced along the experiments is not constant, \(\Gamma\) is not a constant but varies as a function of time. In addition, strictly speaking, \(\Phi(H_2)\) varied during the sunlight experiments as did SZA (Fig. 3b). Accordingly \(\alpha_f\) is changing along with the CH$_2$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$_2$, \(\alpha_m\).

Integrating Eqs. (1) and (4) and then dividing [CHDO] by [CH$_2$O] leads to the well-known Rayleigh equation (Rayleigh, 1902):

\[
\frac{R_Q}{R_o} = f^{\alpha_f - 1} \tag{9}
\]

where \(R_o\) is the isotope ratio of the initial CH$_2$O, \(R_Q\) is that for the remaining CH$_2$O along the course of experiment, and \(f\) the fraction of the remaining CH$_2$O. Thus, the isotope ratio of the products \(R_p\) as a function of CH$_2$O photochemical destruction can be obtained by mass balance:

\[
\frac{R_p}{R_o} = \frac{1 - f^{\alpha_f}}{1 - f} \tag{10}
\]

Actually \(R_p\) is the sum of the isotope ratios of the products formed by CH$_2$O photolysis and its photochemical reactions with radicals. The isotope ratio of the H$_2$, \(R_m\), which is produced from CH$_2$O photolysis to the molecular channel, can be derived from the following derivatives:

\[
\frac{d [H_2]}{dt} = j_m [CH_2O] \tag{11}
\]

and

\[
\frac{d [HD]}{dt} = j_m' [CHDO] \tag{12}
\]

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

\[
\frac{R_m}{R_o} = \frac{\alpha_m}{\alpha_f} \times \frac{1 - f^{\alpha_f}}{1 - f} \tag{13}
\]

By dividing (13) by (10), the ratio of the isotope ratios of H$_2$ \((R_m)\) and all products from CH$_2$O photochemistry \((R_p)\) is the same as the ratios of their isotopic fractionation factors:

\[
\frac{R_m}{R_p} = \frac{\alpha_m}{\alpha_f} \tag{14}
\]

Similar expressions can be derived for the radical channel of CH$_2$O photolysis (15) and for the photochemical reactions (16):

\[
\frac{R_r}{R_p} = \frac{\alpha_r}{\alpha_f} \tag{15}
\]
Table 2. Sensitivity test of the $\alpha_f$ at a given range of the parameters.

<table>
<thead>
<tr>
<th>Prescribed value (Z_i)</th>
<th>Uncertainty of parameter (ΔZ_i)</th>
<th>Sensitivity (Δα_f/ΔZ_i)</th>
<th>Uncertainty of α_f (Δα_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH_2O)_0 (ppm)</td>
<td>1</td>
<td>±1</td>
<td>0.0027*</td>
</tr>
<tr>
<td>J_{CH_2O} (s^{-1})</td>
<td>3.143×10^{-5}</td>
<td>+4.53×10^{-5}</td>
<td>0.0026*</td>
</tr>
<tr>
<td>Φ(H_2)</td>
<td>0.647</td>
<td>±0.039</td>
<td>−0.476</td>
</tr>
<tr>
<td>J_{H_2O}/J_{CH_2O}</td>
<td>0.0896</td>
<td>±0.0036</td>
<td>−2.48</td>
</tr>
<tr>
<td>α_H for CH_2O+H</td>
<td>0.781</td>
<td>±0.25</td>
<td>~0</td>
</tr>
<tr>
<td>α_OH for CH_2O+OH</td>
<td>0.781</td>
<td>±0.0061</td>
<td>−0.45</td>
</tr>
<tr>
<td>α_HO for CH_2O+HO_2</td>
<td>0.781</td>
<td>±0.25</td>
<td>−0.036</td>
</tr>
<tr>
<td>δD-H_2 of final product (‰)</td>
<td>0</td>
<td>±40</td>
<td>−0.0019</td>
</tr>
<tr>
<td>Sum**</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Sensitivity is calculated by the ratio of a parameter to the prescribed value.
** Quadratic sum of errors.

\[
\frac{R_K}{R_p} = \frac{\alpha_K}{\alpha_f} \tag{16}
\]

From the relations of Eqs. (14), (15), and (16), it is immediately recognized that $R_p$ is the weighted sum of the isotope ratios of the products from two channels of CH_2O photolysis and its photochemical reactions, similar to the isotopic fractionation factor of CH_2O in Eq. (8b).

\[
R_p = R_f (1 - \Phi) \Gamma + R_m \Phi \Gamma + R_K (1 - \Gamma) \tag{17}
\]

Since we measured the evolution of $R_m$ with $\Psi(H_2)$, $\alpha_m$ can be determined from Eq. (13). As $f$ approaches 1 (thus, $\Psi(H_2)$ goes to zero), $R_m/R_p$ in Eq. (13) becomes the value of $\alpha_m$, which is in turn represented by the value of δD-H_2 as follows:

\[
\delta D - H_2 = (\alpha_m - 1) \times 1000 \ (‰) \tag{18}
\]

Accordingly, the intercept in Fig. 5 ($\Psi(H_2)=0$) represents the value of $\alpha_m$ (=0.50(±0.02)) and indicates that H_2 produced by photolysis of CH_2O is 500(±20)% depleted with respect to the initial CH_2O. Since the experiments for the photolysis of CH_2O for short periods were conducted with high CH_2O mixing ratios of 50 ppm, a similar amount of initial CH_2O 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. 5). The assumption that $\alpha_f$ is constant should be valid during the initial stage of photolysis of CH_2O because the amounts of radicals, in particular the OH radical, produced are too small to affect $\alpha_f$ (see Fig. 4b). Even if $\alpha_f$ were not constant, it would not interfere with the determination of $\alpha_m$ because the $\alpha_f$’s in Eq. (13) cancel for $f$ approaching 1.

3.4 Isotope effect of CH_2O photolysis to the radical channel

Provided that complete photolysis of CH_2O yields H_2 that has the same isotopic ratio as that of the initial CH_2O (Fig. 5), we can also determine the isotopic fractionation factor, $\alpha_f$, which governs the isotopic fractionation occurring in (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 $\alpha_f$ as follows:

CHDO $+ h\nu \rightarrow$ products \quad (R1a)

CHDO $+ h\nu \rightarrow$ CO + HD \quad (R2a)

CHDO $+ OH \rightarrow$ products \quad (R3a)

CHDO $+ H \rightarrow$ products \quad (R4a)

CHDO $+ HO_2 \rightarrow$ HOCHDOO \quad (R5a)

HD $+ OH \rightarrow$ products \quad (R6a)

HOCHDOO $\rightarrow$ CHDO $+ HO_2$ \quad (R27a)

HOCHDOO $+ HO_2 \rightarrow$ products \quad (R28a)

In Fig. 5 several model runs under different conditions are plotted. As an ideal case, we assume that CH_2O 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 $\alpha_f$. In Eq. (13), as $f$ approaches 0, the ratio of $R_m$ to $R_p$ becomes the ratio of $\alpha_m$ to $\alpha_f$, which is represented by the value of δD-H_2 at the end of photolysis. As the values of δD-H_2 converge at zero, $\alpha_f=\alpha_m$ and thus $\alpha_m=\alpha_f$. 

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

<table>
<thead>
<tr>
<th>Source</th>
<th>Minor isotologue</th>
<th>α₀</th>
<th>αᵣ</th>
<th>α₀/αᵣ</th>
<th>Φ(H₂)</th>
<th><strong>Γ</strong></th>
<th>αᵣ/H₂</th>
<th>αₒ/αᵣ</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>CHDO</td>
<td>0.95 (+0.02)</td>
<td>0.22 (+0.08)</td>
<td>0.781 (+0.006)</td>
<td>0.65 (+0.04)</td>
<td>0.69 (+0.28)</td>
<td>0.40 (+0.03)</td>
<td>0.51 (+0.11)</td>
</tr>
<tr>
<td>Feilberg et al. (2007b)</td>
<td>CHDO</td>
<td>0.55 (+0.02)</td>
<td>0.91 (+0.05)</td>
<td>0.781 (+0.006)</td>
<td>**Φ(Φ) = 0.77 (+0.06)</td>
<td>0.69 (+0.28)</td>
<td>0.63 (+0.01)</td>
<td>0.68 (+0.04)</td>
</tr>
<tr>
<td>Crounse et al. (2003)</td>
<td>CHDO</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feilberg et al. (2007a)</td>
<td>CD₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 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 \( \alpha₀ = \alphaᵣ \times \Phi \left( \frac{1}{\Phi} \right) \).

Table 3 shows that the isotope effects determined from CH₂O photolysis experiments varied significantly depending on the source and conditions. The values of α₀/αᵣ, Φ(H₂), and **Γ** were used to compare the results with previous studies. The quadratic sum of the errors incurred by these parameters amounts to 0.08.

4 Discussions

4.1 Comparison with previous research

To our knowledge, three experiments have been done in sunlight to determine the isotopic fractionation factor for formaldehyde photolysis (Table 3). One experiment investigated the isotopic fractionation of CH₂O itself by measuring the 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 and the D/H ratio of H₂ produced by mass spectrometry (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 proceedings abstract (Crounse 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 (Φ(H₂)) and the δD value of the original CH₂O used for the photolysis experiments, both of which are critical to determine αᵣ, makes it difficult to infer αᵣ from this single value of δD. The authors reported that the photolysis of CH₂O produces isotopically light H₂, the δD value of which is ~−200‰. If the authors meant the value to be the degree of enrichment of the H₂ produced, αᵣ 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, \( J_{CD₂O}/J_{CH₂O} \), was determined as 0.333 (±0.056) (Feilberg et al., 2007a) using an optical technique. This value is smaller than the value for \( J_{CHDO}/J_{CH₂O} \) of 0.40 (±0.03) determined in the present study as expected from the assumption.

As the value of αᵣ 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 αᵣ 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, Φ(H₂), photolysis rates of CH₂O and H₂O₂, kinetic isotope effects for the reaction of CHDO with the radicals, and the uncertainty of δD-H₂ for the final product (Table 2). Among them, αᵣ is the 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 lowers the value of αᵣ to compensate for it (see Eq. 8b). The same effect can be caused by the variation of α₀/αᵣ for CH₂O+OH and by Φ(H₂). Sensitivity runs for the potential error in the δD-H₂ value of the final product shows the largest impact to αᵣ 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 αᵣ originates from the uncertainties in Φ(H₂) and the δD-H₂ of the final products. The quadratic sum of the errors incurred by these parameters amounts to 0.08.
that double-deuterated formaldehyde is more stable than the single-deuterated one due to zero point energy difference.

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(±0.02) and 0.63(±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 $\alpha_v$ between Feilberg et al. (2007b) and the present study: 0.91(±0.05) versus 0.22(±0.08). Unlike the previous work (Feilberg et al., 2005), Feilberg et al. (2007b) took into account the CH$_2$O 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$_2$O between the two studies. Besides the discrepancy in the magnitude of $\alpha_v$, an interesting result of Feilberg et al. (2007b) is that the degree of the isotopic fractionation in CH$_2$O 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 isotopic tracer study using similar amounts of CH$_2$O and CHDO in the EUPHORE reactor in Valencia, Spain, which allowed them to infer $\alpha_{hv}$ directly by a spectroscopic method. $\alpha_m$ was then inferred from the isotope-ratio-mass-spectrometric measurements of HD and modeling of the H$_2$ yield using a given quantum yield for CH$_2$O photolysis. The direct determination of $\alpha_{hv}$ using spectroscopic measurement, however, had to be corrected to account for the losses of CH$_2$O and CHDO by the reaction with OH radical and large leakage of air in the chamber as well as production of CH$_2$O from the wall. In addition, their values of $\alpha_v$ and $\alpha_m$ depend on which value of the quantum yield for CH$_2$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 experimental results that the isotopic compositions of the initial CH$_2$O and of the H$_2$ that are formed from complete photolysis are virtually the same, but it also requires a correction for reaction with radicals. At present we are not able to identify the reason of the large discrepancy in the isotopic fractionation factors of CH$_2$O between the two studies. More experiments can resolve this issue.

4.2 Atmospheric implication

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

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

(19)

where $R_{\text{H}_2}^0$ represents the isotope ratio of H$_2$ produced by photochemical oxidation of CH$_4$ and $R_{\text{CH}_4}$ is that for CH$_4$. 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$_2$ produced from CH$_4$ oxidation is enriched in D by 1.3 times as much as the initial CH$_4$. Gerst and Quay (2001) and Price et al. (2007) also expected D in the H$_2$ from photochemical oxidation of CH$_4$ to be enriched by a factor of 1.2–1.3.

As Gerst and Quay (2001) described in detail, $\alpha_{\text{CH}_4-\text{H}_2}$ is the product of several factors that are associated with photochemical chain reactions from CH$_4$ to H$_2$. These factors include: (1) isotopic fractionation occurring during the reaction of CH$_4$ with OH ($\alpha_{\text{CH}_4}$), the rate-determining step of the photochemical chain reactions of CH$_4$, as well as the subsequent isotopic fractionation processes occurring along the way to CH$_2$O ($\alpha_{\Sigma}$), (2) the branching ratios in the reactions of deuterated species, e.g., CH$_3$D, CH$_2$DOH, and CH$_2$DO, (3) the factor of 2 brought up by the reduction of the number of hydrogen atoms from CH$_4$ to CH$_2$O, and finally (4) isotopic fractionation occurring during the photolytical production of H$_2$ from CH$_2$O. Assuming that CH$_2$O is in a photochemical steady state, as it has a far shorter chemical lifetime than CH$_4$ and H$_2$, point (4) is represented by the ratio of the isotopic fractionation factor of the H$_2$ produced ($\alpha_m$) to that for CH$_2$O ($\alpha_f$), which determines the degree of D enrichment of H$_2$ (Rhee et al., 2006a). Note that $\alpha_f$ differs from $\alpha_{hv}$ by the effect of isotopic fractionation arising from reaction with OH radical ($\alpha_{OH}$) in the troposphere. Combining all these factors yields:

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

(20)

where $\beta_{\text{CH}_4}$ is the branching ratio for the deuterated product, CH$_2$D, in the reaction of CH$_3$D and OH, and $\beta_p$ is a combined branching ratio for other short-lived intermediates, CH$_2$DOOH, and CH$_2$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 $\alpha_2$ 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 $\alpha_f$ is a combined isotopic fractionation factor due to photolysis and photochemical reactions of CH$_2$O by the fraction of the reaction routes as shown in Eqs. (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 $\alpha_{OH}$ as 0.781($\pm$0.006). The optimal values of $\Phi$(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° (see Fig. 3). In order to determine $\Gamma$, we calculated OH radical concentrations and their uncertainties from the relationship between the photolysis rate of O$_3$ ($J$(O$^1$D)) and OH concentration by Rohrer and Berresheim (2006) (i.e., $[OH]$ = 2.44$J$(O$^1$D)+0.13 and $\sigma$ = 0.07$\times$10$^{-6}$+0.33$\times$[OH]). By inserting these values into Eq. (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 resulting ratio of $\alpha_m/\alpha_f$ ($=0.97(\pm$0.21)) is slightly lower than unity, but because of its large uncertainty, arising from the uncertainty of the OH concentration, it is not possible to predict with certainty whether the CH$_2$O photolysis leads to a depletion or enrichment of D in the H$_2$ produced with respect to the parent CH$_2$O. When using the values of isotopic fractionation factors determined by Feilberg et al. (2007b), the CH$_2$O photolysis leads to the depletion of D in the 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 $\Phi$(H$_2$) and $\Gamma$, assuming that the values of $\alpha_m$, $\alpha_r$, and $\alpha_{OH}$ determined from the present study and Feilberg et al. (2004) are applicable to the entire troposphere. The potential ranges of $\Phi$(H$_2$) for the troposphere were estimated using the TUV radiation model with varying SZA at the altitudes of the US standard atmosphere. In order to estimate $\Gamma$ for the troposphere, it is necessary to know the reaction rate of CH$_2$O+OH at a given time and place. The reaction rate coefficient varies by ~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 $\Gamma$ ~0.45. Thus, the range of $\Gamma$ is likely to be between 0.4 and 1 in the troposphere. As shown in Fig. 6, the ratios of $\alpha_m/\alpha_f$ vary from ~0.8 to ~1.2, which suggests that, depending on the values of $\Phi$ and $\Phi$(H$_2$) in the troposphere, the H$_2$ produced from the CH$_2$O photolysis could 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 H$_2$ in D with respect to the parent CH$_2$O.

Finally, we examine the range of $\alpha_m/\alpha_f$ that can be reconciled with the values of $\alpha_{CH_4-H_2}$ inferred for tropospheric conditions. In the literature it is reported that $\alpha_{CH_4-H_2}$ 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 $\alpha_{CH_4}$ at the tropospheric mean temperature of 272 K is 0.77($\pm$0.08). Inserting these values into Eq. (20), the lower bound for $\alpha_m/\alpha_f$ will be ~0.8 when the branching ratio for deuterated compounds ($\beta_{CH_4}$ and $\beta_p$) and $\alpha_2$ are unity. When the values proposed by Gerst and Quay (2001) are applied (i.e., $\beta_{CH_4} \times \alpha_2 \times \beta_p = 0.96 \times 0.77 \times 0.96$, $\alpha_m/\alpha_f = 1.15$). These two values of $\alpha_m/\alpha_f$ bound the range which was estimated for the typical values of $\Gamma$ and $\Phi$(H$_2$) in the troposphere (Fig. 6). This suggests that even if $\alpha_m/\alpha_f$ 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$_2$DO reacting with 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

CH$_2$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 H$_2$ produced is depleted in D by 500($\pm$20)% relative to the initial CH$_2$O. The radical channel (R1)
appears to have a much stronger isotopic fractionation than the molecular channel (R2), resulting in D enrichment of the remaining CH$_2$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$_2$O photolysis may produce the H$_2$ that is slightly depleted in D. However, the large uncertainty in the combined isotope effects of the photochemical reactions of CH$_2$O, which primarily originates from the uncertainty of OH concentration, makes it impossible to precisely define the role of CH$_2$O in the D enrichment of H$_2$. In the troposphere, CH$_2$O photolysis may produce the H$_2$ either enriched or depleted in D with respect to the parent CH$_2$O depending on the fraction of CH$_2$O that reacts with OH or that is photolyzed to H$_2$. Nonetheless, our estimated range of $\alpha_{\text{H}_2}$ ($\sim$0.8 to $\sim$1.2) in the troposphere can be reconciled with the production of H$_2$ enriched in D with respect to the original CH$_4$ by the factor reported in the literature.

**Table A1.** Photochemical reactions in the model.

<table>
<thead>
<tr>
<th>No.*</th>
<th>Reaction</th>
<th>Rate coefficient**</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1)</td>
<td>CH$_2$O $\rightarrow$ CHO $+ H$</td>
<td>1.109E-5</td>
<td>1</td>
</tr>
<tr>
<td>(R2)</td>
<td>CH$_2$O $\rightarrow$ CO $+ H_2$</td>
<td>2.033E-5</td>
<td>1</td>
</tr>
<tr>
<td>(R3)</td>
<td>CH$_2$O $+ OH$ $\rightarrow$ CHO $+ H_2$</td>
<td>8.6E-12 $\times$ exp(166/RT)</td>
<td>2</td>
</tr>
<tr>
<td>(R3')</td>
<td>CH$_2$O $+ OH$ $\rightarrow$ HCOOH $+ H$</td>
<td>2.01E-13</td>
<td>9</td>
</tr>
<tr>
<td>(R4)</td>
<td>CH$_2$O $+ H$ $\rightarrow$ CHO $+ H_2$</td>
<td>2.14E-12 $\times$ exp($-9063/RT$)$\times$(T/298)$^{1.62}$</td>
<td>8</td>
</tr>
<tr>
<td>(R5)</td>
<td>CH$_2$O $+$ HO$_2$ $\rightarrow$ HCOOH$_2$</td>
<td>6.71E-15 $\times$ exp(4989/RT)</td>
<td>3</td>
</tr>
<tr>
<td>(R6)</td>
<td>H$_2$ $+ OH$ $\rightarrow$ H$_2$O</td>
<td>5.5E-12 $\times$ exp($-16629/RT$)</td>
<td>3</td>
</tr>
<tr>
<td>(R7)</td>
<td>H$_2$O$_2$ $\rightarrow$ 2OH</td>
<td>2.816E-6</td>
<td>1</td>
</tr>
<tr>
<td>(R8)</td>
<td>O$_2$ $+ CH$ $\rightarrow$ CO $+ HO_2$</td>
<td>3.5E-12 $\times$ exp(1164/RT)</td>
<td>3</td>
</tr>
<tr>
<td>(R9)</td>
<td>CHO $+ CH$ $\rightarrow$ CH$_2$O $+ CO$</td>
<td>5.0E-11</td>
<td>4</td>
</tr>
<tr>
<td>(R9')</td>
<td>CHO $+ CHO$ $\rightarrow$ (CHO)$_2$</td>
<td>5.0E-11</td>
<td>5</td>
</tr>
<tr>
<td>(R10)</td>
<td>CHO $+ H$ $\rightarrow$ CO $+ H_2$</td>
<td>1.13E-10</td>
<td>6</td>
</tr>
<tr>
<td>(R11)</td>
<td>CHO $+ OH$ $\rightarrow$ CO $+ H_2$</td>
<td>1.69E-10</td>
<td>4</td>
</tr>
<tr>
<td>(R12)</td>
<td>CHO $+ HO_2$ $\rightarrow$ product</td>
<td>5.0E-11</td>
<td>4</td>
</tr>
<tr>
<td>(R13)</td>
<td>H$_2$O $+ CHO$ $\rightarrow$ CH$_3$O $+ OH$</td>
<td>8.54E-13 $\times$ exp($-108920/RT$)</td>
<td>7</td>
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<tr>
<td>(R14)</td>
<td>H$_2$O$_2$ $+ CHO$ $\rightarrow$ CH$_2$O $+ HO_2$</td>
<td>1.69E-13 $\times$ exp($-29018/RT$)</td>
<td>7</td>
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<tr>
<td>(R15)</td>
<td>O$_2$ $+ H$ $\rightarrow$ HO$_2$</td>
<td>$M \times 5.71E-32 \times (T/298)^{-1.6}$</td>
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<tr>
<td>(R16)</td>
<td>H $+ H$ $\rightarrow$ H$_2$</td>
<td>$M \times 8.58E-33 \times (T/298)^{-0.6}$</td>
<td>4</td>
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<tr>
<td>(R17)</td>
<td>OH $+ H$ $\rightarrow$ H$_2$O</td>
<td>$M \times 4.38E-30 \times (T/298)^{-2.0}$</td>
<td>4</td>
</tr>
<tr>
<td>(R18)</td>
<td>(CHO)$_2$ $+ OH$ $\rightarrow$ product</td>
<td>1.1E-11</td>
<td>2</td>
</tr>
<tr>
<td>(R19)</td>
<td>HCOOH $+ OH$ $\rightarrow$ product</td>
<td>4.0E-13</td>
<td>3</td>
</tr>
<tr>
<td>(R20)</td>
<td>CO $+ OH$ $\rightarrow$ CO$_2$ $+ H$</td>
<td>1.5E-13 $\times$ (1+0.6$\times$P/1013.25)</td>
<td>3</td>
</tr>
<tr>
<td>(R21)</td>
<td>CO $+ HO_2$ $\rightarrow$ CO$_2$ $+ OH$</td>
<td>5.96E-11 $\times$ exp($-95616/RT$)$\times$(T/298)$^{0.5}$</td>
<td>10</td>
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<tr>
<td>(R22)</td>
<td>OH $+ OH$ $\rightarrow$ H$_2$O$_2$</td>
<td>$M \times 6.20E-31 \times (T/298)^{-1}$</td>
<td>3</td>
</tr>
<tr>
<td>(R23)</td>
<td>HO$_2$ $+ H$ $\rightarrow$ product</td>
<td>8.10E-11</td>
<td>3</td>
</tr>
<tr>
<td>(R24)</td>
<td>HO$_2$ $+ OH$ $\rightarrow$ H$_2$O$_2$ $+ O_2$</td>
<td>4.8E-11 $\times$ exp(2079/RT)</td>
<td>3</td>
</tr>
<tr>
<td>(R25)</td>
<td>HO$_2$ $+ HO_2$ $\rightarrow$ H$_2$O$_3$ $+ O_2$</td>
<td>$M \times 1.7E-33 \times$ exp(38314/RT)</td>
<td>3</td>
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<tr>
<td>(R26)</td>
<td>HO$_2$ $+ OH$ $\rightarrow$ HO$_2$ $+ H_2$O</td>
<td>2.91E-12 $\times$ exp($-1330/RT$)</td>
<td>3</td>
</tr>
<tr>
<td>(R27)</td>
<td>HOCH$_2$O$_2$ $\rightarrow$ HO$_2$ $+ CH_2$O</td>
<td>2.4E12 $\times$ exp($-58201/RT$)</td>
<td>2</td>
</tr>
<tr>
<td>(R28)</td>
<td>HOCH$_3$O$_2$ $\rightarrow$ HCOOH $+ H_2$O $+ O_2$</td>
<td>5.6E-15 $\times$ exp(19123/RT)</td>
<td>2</td>
</tr>
<tr>
<td>(R29)</td>
<td>2HOCH$_2$O$_2$ $\rightarrow$ 2HCOOH $+ O_2$</td>
<td>5.6E-12</td>
<td>11</td>
</tr>
<tr>
<td>(R29')</td>
<td>2HOCH$_2$O$_2$ $\rightarrow$ HCOOH $+ CH_2$OH$_2$ $+ O_2$</td>
<td>5.71E-14 $\times$ exp(6236/RT)</td>
<td>11</td>
</tr>
<tr>
<td>(R30)</td>
<td>O$_3$ $+ HCOOH$ $\rightarrow$ HCOOH $+ H_2$O</td>
<td>3.5E-14</td>
<td>12</td>
</tr>
</tbody>
</table>


* 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. The units of the rate coefficients for first-, second-, and third-order reactions are s$^{-1}$, cm$^3$ molecule$^{-1}$ s$^{-1}$, and cm$^6$ molecule$^{-2}$ s$^{-1}$, respectively.
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