

## 4D5) Hydrogen Isotope Fractionation during the Destruction of Formaldehyde in the Atmosphere

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Due to limited fossil energy sources and climate impact of their final products, CO<sub>2</sub>, hydrogen economy has been considered to be alternative. Large scale use of H<sub>2</sub> as an energy carrier may perturb the current global H<sub>2</sub> cycle. Molecular hydrogen in the atmosphere originates from direct emissions from the Earth surfaces and from airborne production by photolysis of formaldehyde. It is destroyed by the reactions with the OH radical in the atmosphere and with microbes in soils. Measurement of stable isotope ratio of H<sub>2</sub> turns out to be useful to investigate atmospheric H<sub>2</sub> cycle. Among the sources, photochemically produced H<sub>2</sub> is uniquely enriched in deuterium compared to the isotopic ratio of atmospheric H<sub>2</sub>. Here we investigated isotopic fractionation of hydrogen species produced from photochemical reactions of CH<sub>2</sub>O. Experiments were conducted to determine the isotopic fractionation of the H<sub>2</sub> produced by photolysis of CH<sub>2</sub>O in flask under atmospheric conditions. The H<sub>2</sub> produced is depleted in deuterium by 500‰ with respect to the initial CH<sub>2</sub>O that does not undergo photolysis. We also found that complete photolysis of CH<sub>2</sub>O under atmospheric conditions produces H<sub>2</sub> that has virtually the same isotopic ratios as that of CH<sub>2</sub>O itself. These findings imply that there must be a strong isotopic fractionation in the radical channel (CH<sub>2</sub>O + hv → CHO + H) compared to the molecular channel (CH<sub>2</sub>O + hv → CO + H<sub>2</sub>) in order to compensate the relatively weak kinetic isotope effect occurring in the reaction of CH<sub>2</sub>O with OH. We applied a simple one-box photochemistry model to calculate the isotopic fractionation factor for the radical channel under the conditions of experiments. The value was estimated to be 0.22, which indicates a 780‰ enrichment of deuterium of remaining CH<sub>2</sub>O with respect to the initial CH<sub>2</sub>O. In the presentation we will discuss the results from the experiments focusing on how photochemical oxidation of CH<sub>4</sub> may produce H<sub>2</sub> enriched in deuterium.