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Hydrogen isotope effect of the photolysis of formaldehyde to the molecular and radical channels

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A series of experiments was carried out to investigate the hydrogen isotope fractionation during the photolysis of CH_2O. Deuterium content of the H_2 produced by the photolysis of CH_2O was determined by a recently developed technique with continuous-flow isotope ratio mass spectrometry. The deuterium (D) of the H_2 produced is depleted by 500(±20) ‰ with respect to the parent CH_2O. We also observed that complete photolysis of CH_2O under tropospheric conditions produces H_2 that has virtually the same isotope ratio as that of the parent CH_2O. These findings imply that there must be a very strong concomitant isotopic enrichment in the radical channel ($CH_2O + h\nu \rightarrow CHO + H$) as compared to the molecular channel ($CH_2O + h\nu \rightarrow H_2 + CO$) of the photolysis of CH_2O in order to balance the relatively small isotopic fractionation in the competing reaction of CH_2O 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(±90) ‰ enrichment in D of the remaining CH_2O. This isotopic effect is significantly larger than the result obtained from the experiments in the EUPOHORE reaction chamber by *Feilberg et al.* [2007].

References

Feilberg K.L., Johnson M.S., Bacak A., Röckmann T., Nielsen C.J., Relative tropospheric photolysis rates of HCHO and HCDO measured at the European Photoreactor Facility, *J. Phys. Chem. A*, 2007, 111, 9034-9036.