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Experimental studies of deuterium propagation through the atmospheric photochemical series CH_4, CH_3O, CH_2O, H_2

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Anthropogenic changes to the atmospheric cycles of carbon and hydrogen affect air pollution, global warming and stratospheric water vapor. I will present our recent work on photochemical processes involving the key species of the atmospheric C and H cycles: methane, methoxy, formaldehyde and hydrogen.

It is known that atmospheric methane is depleted in deuterium, and that methane is a large source of atmospheric hydrogen:

CH_4 to CH_3 to CH_3O_2 to CH_3O to CH_2O to CO and H_2

However, analysis of the isotope budget shows that 'photochemical hydrogen' produced from methane must be *enriched* in deuterium. (Formaldehyde is also produced from isoprene and other VOCs, and these are also likely to be depleted in D). We conducted an experiment to measure the relative photolysis rate of HCHO and HCDO in natural sunlight, and found that HCDO is photolysed much more slowly than HCHO, and that even when it is photolysed, it produces much less molecular hydrogen product, HD. This result would appear to contradict modeling studies and isotope budgets. However, in another study, we demonstrated that the CD bond is much less reactive than the CH bond. This means that the reaction steps leading from methane through methoxy to formaldehyde cause an enrichment in deuterium of up to ca. 1000‰ that more than compensates for the depletion occurring in the photolysis step.

Formaldehyde photolysis is also interesting from the standpoint of chemical dynamics. A study of the UV spectrum showed that there is essentially no difference in the integrated absorption cross sections of HCHO, HCDO or DCDO, and that they all absorb sunlight at the same rate. However, they have very different photolysis rates and different efficiencies for producing the molecular hydrogen product.

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