Tracking methane sinks and sources in the atmosphere using clumped isotopes

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Methane is the second most important long-lived greenhouse gas in Earth's atmosphere. It also reacts with Cl•, OH•, and other reactive molecules to produce the methyl radical (CH_3•). The rates and isotopic signatures of these reactions are of interest for understanding the budgets of methane, water vapor, CO and reactive species in air. In this study we estimate kinetic isotope effects (KIE) for the doubly substituted isotopologues of methane, CH_2D_2 and $^{13}CH_3D$, reacting with OH• and Cl•, using electronic structure modeling and transition state theory. It is known that reactions with OH• and Cl• cause residual atmospheric methane to become enriched in D compared to the source methane. Our models predict distinct signatures of lower $\Delta^{13}CH_3D$ and ΔCH_2D_2 relative to the source composition. The model $\Delta^{13}CH_3D$ results agree with another recent study [1] and the results for ΔCH_2D_2 agree with previous measurements of relative reaction rates [2] [3].

We predict that Δ values are more strongly affected by reaction with Cl•, compared to OH•. In a Rayleigh model at T=293K, assuming initial isotopic equilibrium, $\Delta^{13}CH_3D$ in the reaction with OH• drops from +6.1 at f =1 to +3.2 at f =0.1, whereas in the reaction with Cl• $\Delta^{13}CH_3D$ drops to –11.8 over the same range in f. ΔCH_2D_2 in the reaction with OH• goes from +20.9 to –5.4 whereas in the reaction with Cl• it drops to –76.4. These predictions may be useful to constrain the origin of methane affected by destruction by the hydroxyl and chlorine radicals in the atmosphere. The characteristic relationship between $\Delta^{13}CH_3D$ vs. ΔCH_2D_2 caused by each sink may make it possible to back-project from the composition of methane in air to estimate the contributions from individual sources.

[1] Joelsson L.M.T., et al., (2014), *Chem. Phys. Letters*, **605-606**,152-157 [2] Gierczak T., et al., (1997), *J. Phys. Chem. A*, **101**(**17**), 3125-3134 [3] Feilberg K. L., et al., (2005), *Int. J. Chem. Kinetics*, **37**(**2**), 110-118.