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Atmospheric deuterium fractionation: HCHO and HCDO yields in the CH₂DO + O₂ reaction

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Abstract. The formation of formaldehyde via hydrogen atom transfer from the methoxy radical to molecular oxygen is a key step in the atmospheric photochemical oxidation of methane, and in the propagation of deuterium from methane to molecular hydrogen. We report the results of the first investigation of the branching ratio for HCHO and HCDO formation in the CH₂DO + O₂ reaction. Labeled methoxy radicals (CH₂DO) were generated in a photochemical reactor by photolysis of CH₂DONO. HCHO and HCDO concentrations were measured using FTIR spectroscopy. Significant deuterium enrichment was seen in the formaldehyde product, from which we derive a branching ratio of 88.2±1.1% for HCDO and 11.8±1.1% for HCHO. The implications of this fractionation on the propagation of deuterium in the atmosphere are discussed.

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