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Deuterium fractionation in formaldehyde photolysis: The effects of wavelength, temperature and pressure.

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The photolysis of formaldehyde is a key step in the oxidation of virtually all atmospheric hydrocarbons, including methane and isoprene. The reaction proceeds via two channels, the radical channel (1) and the molecular channel (2).[1]

1. HCHO + *hν* ($\lambda < 340$ nm) → H + HCO
2. HCHO + *hν* ($\lambda < 360$ nm) → H_2 + CO

The chain of reactions, $CH_4 \rightarrow CH_3 \rightarrow CH_3O_2 \rightarrow CH_3O \rightarrow HCHO \rightarrow CO+H_2$,[2] links the carbon- and hydrogen cycles in the atmosphere. The budgets and reactivity of these species are important for climate futures and for predicting the impacts of energy carriers such as hydrogen and biofuels. Isotopic analysis provides valuable additional knowledge. We recently reported the relative photolysis rates and product branching ratios for HCHO and HCDO using natural sunlight at the European Photoreactor Facility (EUPHORE) in Valencia, Spain. During the experiment loss of HCHO and HCDO were measured using FTIR and DOAS. The isotopic composition of the hydrogen product was determined using isotope ratio mass spectrometry (IRMS). The channel-specific relative photolysis rates are: $j_{HCHO \rightarrow H_2+CO}/j_{HCDO \rightarrow HD+CO}$ =1.82±0.07, and $j_{HCHO \rightarrow H+HCO}/(j_{HCDO \rightarrow H+DCO} + j_{HCDO \rightarrow D+HCO})$ =1.10±0.06.

We have conducted additional experiments in the laboratory to determine the isotope effects as a function of temperature, pressure and wavelength using the new photochemical reactor at the University of Copenhagen. We present the first results which focus on isotope effects in the molecular channel.

References:

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