



Using functional group analysis to derive a condensed photochemical oxidation scheme for the isotope effects in the production of H₂ from deuterated methane and VOC's

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In this work, a photochemical scheme for oxidation of deuterated methane and Volatile Organic Compounds (VOC's) to molecular hydrogen is derived using simplified functional group analysis. This analysis enabled us to derive consistent statistical expressions for the kinetic isotope effects (KIE's) for the different reaction steps and the branching between the deuterated and non-deuterated reaction channels. The resulting reaction scheme was analyzed using a chemical box model and compared with results reported by previously published experimental studies. The results show that enrichments up to 700-800% against Vienna Standard Mean Ocean Water (VSMOW) can occur in the formation of formaldehyde. Because of the significant KIE's involved in the photochemical destruction of formaldehyde, the overall enrichment from deuterated methane to molecular hydrogen is found to be 200-300% against VSMOW. Finally, a detailed sensitivity study was performed to identify the most important reaction steps that influence the final isotopic composition of molecular hydrogen.