PHOTOCHEMICAL STUDIES OF CH_3OH ISOLATED IN SOLID PARAHYDROGEN

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Our group is studying the 193.3 nm photochemistry of methanol (CH_3OH) isolated in solid pH_2 using high-resolution FTIR spectroscopy to explore the low temperature reactions of H-atoms with CH_3OH. Gas phase studies have shown that the dominant photodissociation channel is $CH_3OH + h\nu \rightarrow CH_3O + H$,[a] and thus the *in situ* photochemistry is expected to produce methoxy and H-atom radicals. After photolysis the methoxy radicals are immobilized at these temperatures, but the H-atoms can still readily move through solid pH_2. For short time 193.3 nm exposures, greater than 90% of the CH_3OH remains intact and therefore repeated FTIR spectra immediately after photolysis can be used to record the kinetics of reactions of H-atoms with CH_3OH. We observe exponential growth in the intensities of a number of peaks that can be assigned to the hydroxymethyl CH_2OH radical. Further, the growth is bi-exponential and we believe there are two processes that lead to the formation of CH_2OH: (1) fast growth by interconversion of CH_3O to CH_2OH and (2) slow growth due to hydrogen abstraction reactions of cold H-atoms with CH_3OH. We have not observed the methoxy radical. Currently we are performing photochemical experiments on fully deuterated methanol (CD_3OD) in solid pH_2 to test these kinetic interpretations, and the most recent results and analysis will be presented.

[a] Y. Wen, J. Segall, M. Dulligan, and C. Wittig, *J. Chem. Phys.* **101**, 5665 (1994).