VIBRATIONALLY DRIVEN HYDROGEN ABSTRACTION REACTION BY BROMINE RADICAL IN SOLUTION

JAE YOON SHIN, MICHAEL A. SHALOWSKI, and F. FLEMING CRIM, *Department of Chemistry, University of Wisconsin-Madison, WI 53706*.

Previously, we have shown that preparing reactants in specific vibrational states can affect the product state distribution and branching ratios in gas phase reactions. In the solution phase, however, no vibrational mediation study has been reported to date. In this work, we present our first attempt of vibrationally mediated bimolecular reaction in solution. Hydrogen abstraction from a solvent by a bromine radical can be a good candidate to test the effect of vibrational excitation on reaction dynamics because this reaction is highly endothermic and thus we can suppress any thermally initiated reaction in our experiment. Br radical quickly forms CT (charge transfer) complex with solvent molecule once it is generated from photolysis of a bromine source. The CT complex strongly absorbs visible light, which allows us to use electronic transient absorption for tracking Br radical population. For this experiment, we photolyze bromoform solution in dimethyl sulfoxide (DMSO) solvent with 267 nm to generate Br radical and excite the C-H stretch overtone of DMSO with 1700 nm a few hundred femtoseconds after the photolysis. Then, we monitor the population of Br-DMSO complex with 400 nm as a function of delay time between two pump beams and probe beam. As a preliminary result, we observed the enhancement of loss of Br-DMSO complex population due to the vibrational excitation. We think that increased loss of Br-DMSO complex is attributed to more loss of Br radical that abstracts hydrogen from DMSO and it is the vibrational excitation that promotes the reaction. To make a clear conclusion, we will next utilize infrared probing to directly detect HBr product formation.