EXPLORING THE OH + CO REACTION COORDINATE VIA INFRARED SPECTROSCOPY OF THE OH/D–CO REACTANT COMPLEX

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The reaction of carbon monoxide with hydroxyl radicals, OH + CO → H + CO_2, is of fundamental importance in combustion and atmospheric chemistry, since it is the principle source of CO_2 in the oxidation of most hydrocarbon fuels and the primary sink for the OH radical in the lower atmosphere. Kinetic studies of this reaction at low temperatures have suggested that a hydrogen-bonded complex between the OH and CO reactants may serve as a precursor to chemical reaction. Recently, this laboratory has demonstrated that this hydrogen-bonded complex can be stabilized in a supersonic free jet expansion and characterized by infrared spectroscopy. Studies of the deuterated analog of the complex provide additional spectroscopic information on the structure and stability of the complex as well as direct time-domain measurements of its decay dynamics. Infrared excitation of the OH/D–CO complex in the OH/D overtone region supplies sufficient energy to surmount the low activation barrier to chemical reaction or break the weak intermolecular bond leading to inelastic scattering. Deuteration slows the latter process by closing an efficient near-resonant vibrational energy transfer process from OH to CO. The longer lifetime for OD–CO leaves more time for reaction to occur, thereby changing the branching ratio between inelastic scattering and chemical reaction. These studies have also examined the intermolecular bending vibrations (in combination with OH/D stretch) that drive the structural transformation from the hydrogen-bonded complex to the transition state for reaction.[a]

[a]This research was supported by the National Science Foundation with partial equipment support from the Office of Basic Energy Sciences of the Department of Energy. Coworkers include M. D. Marshall, B. V. Pond, D. T. Anderson, M. Tsiouris, and I. B. Pollack.