Photoinitiated H-Atom Reactions in CO₂-HBr Complexes

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Photoinitiated reactions of H atoms with CO₂ in CO₂-HBr complexes have been examined by using ab initio generalized valence bond–configuration interaction calculations. Recent experiments have shown that CO₂-HBr complexes yield OH ~40 times more efficiently than CO₂-HCl complexes for similar values of $h\nu-D_0(HX)$. We find that the calculated equilibrium geometry for the T-shaped CO₂-HBr complex is in excellent agreement with the experimental geometry, which is inertially asymmetric with the Br-C line almost perpendicular to the CO₂ axis and the H-Br bond nearly parallel to the CO₂ molecular axis. We find a linear isomer of CO₂-HBr to also be stable; this species has not been observed experimentally. We find that photoexcitation of the T-shaped HBr moiety leads to two directly dissociative excited states of A′ and A″ symmetries. For both states, the HBr bond expands rapidly following photoexcitation with most H atoms leaving unreactively from the complex. However, for those H atoms that approach CO₂ and form HOCO, the two excited states show dissimilar interactions due to interaction of the Br atom with HOCO. The A′ state has a weak in-plane bonding interaction between the Br p orbital and the C radical orbital of HOCO, whereas the A″ state leads to repulsion. These results are consistent with the experimental observations and underscore the greater variety possible in such relations taking place in complexes vs under single-collision, gas-phase conditions.

I. Introduction

Gas-phase chemical reaction dynamics depend strongly upon the relative orientations, alignments, and velocities of reactants, as well as their electronic configurations and orbital alignments.[1] These entrance-channel parameters determine reaction trajectories on the potential energy surface (PES) and influence overall cross sections, branching ratios, product state distributions, and reaction times. However, in most gaseous environments, there is no control over incident angles, impact parameters, and orbital alignments.

Attempts to control entrance-channel geometric properties have utilized interactions of the molecule with external electric or magnetic fields and have yielded exciting results for specific alignments and orientations.[2-13] In addition, alignment of reactant orbitals in chemical reactions has been achieved via the laboratory anisotropy of electronic excitation using polarized lasers.[14-17] We have employed a third strategy in achieving such orientation by utilizing the intermolecular interactions present in weakly bonded reaction-precursor complexes.[18-37] The anisotropic intermolecular force field responsible for binding the complex aligns precursor–molecular components regioselectively, leading to precursor–geometry-limited (PGL) reactions that offer a novel means of investigating regiospecific effects. In addition, photoinitiation provides control of the reaction energy by varying the photolysis wavelength, as well as "setting the clock" for the reaction by using ultrashort laser pulses.[38-40]

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