ABSTRACT

THESIS: Characterization of Halogen Bonded Complexes in Systems with Competing Hydrogen Bonding or Electron Transfer

STUDENT: Emmanuel Adeniyi

DEGREE: Master of Science

COLLEGE: Science and Humanities

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Halogen bonding (HaB) is an intermolecular attraction between covalently bonded electron-poor halogen atoms and electron-rich species, similar to hydrogen bonding (HyB). The strengths of HaB and HyB are similar, and if a molecule contains both halogen and hydrogen substituents, these bonds may compete or cooperate. To understand the behavior of such molecules, it is necessary to identify these bonds. In this study, HaB and HyB coexisting in solution were differentiated, and the mode of interaction of these molecules was determined using a combination of UV-Vis and NMR spectroscopy, and computational analysis. These studies showed that HaB complexes of haloforms with aromatic and aliphatic amines exhibit strong absorption bands in their UV-Vis spectra. In comparison, the spectra of the HyB complexes were a superposition of the spectra of their individual reactants. The effects of bonding on NMR spectra depend on the nature of the amine. HyB and HaB with aliphatic amines led to a shift in the proton signals of the NMR spectrum in opposite directions. Studies of HaB and HyB complexes in a solution of (halo)imidazolium and halides have confirmed these distinctions. Overall, this study showed that

combining UV-Vis and NMR measurements allowed us to distinguish between the formation of competing HaB and HyB complexes in the solution. In addition to the formation of the HaB complex, a redox reaction can occur when all electrons are transferred from the electron donor (HaB acceptor) to the electron acceptor (HaB donor). To evaluate the role of the HaB complexes in these processes, we studied the interactions between molecular iodine and various anilines or heterocyclic compounds. This study indicates that HaB complexes represent intermediates of electron transfer reactions and that HaB can significantly reduce the activation barriers for electron transfer.