

ABSTRACT

THESIS: Anion- π Complexes and Electron-Transfer Reactions of p-Benzoquinones with Halide Anions

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Anion- π bonding, the counter-intuitive attraction of anions to electron-deficient π -systems, has recently become a subject of significant interest. Many works have demonstrated its considerable potential for anion sensing and transport, as well as for catalysis. However, although this interaction has been observed in many solid-state structures recently, characterization of anion- π complexes in solutions are very rare. p-Benzoquinones are known to be very important electron acceptors in chemical and biochemical systems, for example in the electron transport chain, and have potential to participate in anion- π interactions. Even so, investigations of their participation in anion- π bonding are scarce. In this work, interchange between complex formation and electron-transfer reactions between halide anions and a series of p-benzoquinones were established via UV-Vis spectral and x-ray structural measurements. Solution-phase interaction of p-benzoquinone acceptors with chloride (Cl^-), bromide (Br^-), or iodide (I^-) donors led to formation of anion- π complexes showing strong absorption bands in the UV-Vis range. Formation constants and calculated interaction energies of these complexes increased and donor/acceptor interatomic separations decreased with the increase of p-benzoquinone reduction potentials. Mulliken correlation indicated charge-transfer nature of these anion- π associates. Most notably, an increase in π -acceptor strength led to transition between formation of the persistent anion- π complexes to electron-transfer reactions. Thermodynamic analysis accounted for the experimental observations of radical anions and trihalide anions in solutions of p-benzoquinones with strong I^- or (for the strongest acceptor) Br^- donors. Kinetics of these processes indicated that anion- π complexes represent critical intermediates of

redox reactions. In contrast to Cl^- , Br^- , or I^- , interaction of p-benzoquinones with fluoride (F^-) anions led to formation of σ -complexes, and appearance of radical anions in such systems was related to the follow-up reactions of these complexes.