

A semiquantitative description of electrostatics and polarization substituent effects: Gas-phase acid-base equilibria as test cases

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A semilocal (regional) model to describe the effects of chemical substitution on gas-phase acid-base reactivity is developed and tested. A simple relationship connecting regional changes in electron density and global changes in electronic chemical potential is used to describe inductive (electrostatic) substituent effects. Electronic (polarization) substituent effects are described in terms of regional changes in local softness at the active site, that are responses to changes in electronic chemical potential induced by chemical substitution. The model correctly explains the variations of the gas-phase acidity of alkyl alcohols and some thio derivatives within a local hard and soft acid and bases (HSAB) rule. Increase in local softness is correlated with a decrease in proton affinity of the conjugated base and therefore with an enhancement of the gas-phase acidity. It is shown that this is basically a HSAB result. The local analysis based on second-order variations in electron density