

Empirical energy - Density relationships for the analysis of substituent effects in chemical reactivity

Pérez, P.

Simón-Manso, Y.

Aizman, A.

Fuentealba, P.

Contreras, R.

Electronic substituent effects may be rationalized in terms of Hammett- like linear relationships between global energy-dependent quantities and local electronic descriptors of reactivity. These linear relationships are framed on a local hard and soft acids and bases (HSAB) principle in accord with previous results reported by Li and Evans [J. Am. Chem. Soc. 1995, 117, 7756]. Chemical substitution is indirectly assessed as local responses at the active center of the substrate, with the Fukui function and local softness as the key quantities within the present approach. This model of chemical substitution has a potential advantage with respect to models based on group properties using the electronegativity equalization principle (EEP), since the transferability of group properties is not required. The formalism is illustrated for the gas-phase basicity of alkylamines, and the gas-phase acidity of alkyl alcohols and alkyl thioalcohols. Our results based on the local HSAB rule agree well