

Global and local analysis of the gas-phase acidity of haloacetic acids

Ferez, Patricia

Toro-Labbé, Alejandro

Contreras, Renato

The relative gas-phase acidity of halosubstituted acetic acids $\text{CH}_2\text{XCO}_2\text{H}$, $\text{CHX}_2\text{CO}_2\text{H}$ and $\text{CX}_3\text{CO}_2\text{H}$ ($\text{X} = \text{F}, \text{Cl}, \text{and Br}$) is analyzed in terms of global and local descriptors of reactivity. The model is based on the analysis of proton-transfer equilibria with reference to acetic acid $\text{CH}_3\text{CO}_2\text{H}$. The relative acidity pattern displayed by this series is rationalized in terms of the hard and soft acids and bases principle. The relative stability between the neutral species and the corresponding anions is in agreement with the maximum hardness principle. Charge transfer between the conjugated bases present in the proton-transfer equilibria is correctly accounted for by using a classical ion-transport model that introduces the electronic chemical potential of transfer. The local reactivity analysis based on regional Fukui functions and local softness displays a good correlation with the experimental gas-phase acidity within the series. © 2000 American Chemical Society.