

Global and Local Reactivity and Activation Patterns of HOOX (X = H, NO₂, CO₂⁻, SO₃⁻) Peroxides with Solvent Effects

Aparicio, Felipe

Contreras, Renato

Galván, Marcelo

Cedillo, Andrés

A detailed analysis of the global and local reactivity patterns of neutral and charged peroxides, including hydrogen peroxide (HOOH), peroxyntic acid (HOONO₂), the peroxydicarbonic ion (HOOCO₂⁻), and the peroxymonosulfate ion (HOOSO₃⁻) in the presence of a polar solvent (water) is presented. The polar solvent effects are included using an isodensity surface polarized continuum model (IPCM). The (1,2) hydrogen-shift reaction for these peroxides is studied. The transition states involved in the (1,2) hydrogen shift have been located and characterized at the B3LYP/6-311G** level of theory. The global analysis shows that, although the replacement of one hydrogen atom in HOOH by a neutral NO₂ group enhances both the global softness and global electrophilicity, the substitution of one hydrogen atom by charged CO₂⁻ and SO₃⁻ groups results in a significant electrophilic deactivation of HOOCO₂⁻ and a moderate electrophilic activation of HOOSO₃⁻. This result is observed in both the ground