Electronic Property and Reactivity of (Hydroperoxo)Metal Compounds

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DFT calculations were done for the (hydroperoxo)metal complexes with η^1-coordination mode, where metal ions are Fe(III), Al(III), Cu(II) and Zn(II). Results shows that 1) the electron density at the two oxygen atoms of the hydroperoxide ion is highly dependent on the angle O-O-H in M-OOH species and the difference in electron density between the two oxygen atoms reaches a maximum at the angle O-O-H = 180°, 2) total electron density at the two oxygen atoms of the peroxide ion increases by approach of methane to the (hydroperoxo)metal species in the cases of Fe(III) and Cu(II); on the other hand, significant decrease of the electron density on peroxide oxygen atoms was observed for the cases of Al(III) and Zn(II) compounds. These findings suggest that the (hydroperoxo)metal species acts as an electrophile in the former cases (M = Fe(III), Cu(II)) and as a nucleophile for the latter two compounds (M = Zn(II), Al(III)). The electrophilicity observed for the Fe(III) and Cu(II) complexes is attributed to the presence of unoccupied- or half-filled d-orbitals interacting with the hydroperoxide ion. 3) Two oxygen atoms of the (hydroperoxo)-compounds of Fe(III) and Cu(II) complexes exhibit quite different reactivity toward the substrate, such as methane. When methane approaches the oxygen atom which is coordinated to a metal ion, a strong decrease of electron density at the methane carbon atom occurs with concomitant increase of electron density at the peroxide oxygen atoms inducing its heterolytic O-O cleavage. When methane approaches the terminal oxygen atom, an oxidative coupling reaction occurs between peroxide ion and methane; at first a nucleophilic attack by the terminal electron-rich oxygen atom occurs at the carbon atom to induce C-O bond formation, and a subsequent oxidative electron transfer proceeds from substrate to the metal-peroxide species yielding CH_3-OOH, CH_3OH, or other oxidized products. These results clearly demonstrate that the (hydroperoxo)-metal compound itself is a rather stable compound, and activation of the peroxide ion is induced by interaction with the substrate, and the products obtained by the oxygenation reaction are dependent on the chemical property of the substrate, redox property of a metal ion, and stability of the compounds formed in the intermediate process.