

Differences in the electronic structure of sulfenyl chlorides and bromides as possible reasons for their different reactivities toward aromatic compounds

Chmutova G., Ziganshina A., Movchan A.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

The electronic structure of C- and N-sulfenyl chlorides and bromides was studied by semiempirical quantum-chemical methods. The sulfur atom in sulfenyl chlorides always possesses a larger positive charge than the sulfur atom in the corresponding sulfenyl bromides, which is responsible for the higher electrophilicity of sulfenyl chlorides as sulfenylating agents in charge-controlled reactions. Electrophilic properties of sulfenyl bromides stem to a considerable extent from the low-lying lowest unoccupied molecular orbital. The contribution of bromine to the LUMO can exceed that of the sulfur atom, thus favoring formation of the bromination products in orbital-controlled reactions.
