

Atomic electrostatic potential on the reaction center and on the leaving group as a descriptor of processes of an aminolysis phenyl- and thiophenylacetates and hydrolysis of acetanilides

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Abstract

Hydrolysis of acetanilides and aminolysis of phenyl- and thiophenylacetates are related reactions since all of them are processes of nucleophilic substitution on the carbon's carbonyl atom. Current views of chemical reactivity based on the DFT theory leaning upon reactivity indices that are descriptors of both the reaction center and the molecule as a whole have not been applied to the given processes before. One of such descriptors is an atomic electrostatic potential characterizing the distribution of electron density on the reaction center. The given parameter was calculated by the DFT theory M06/6-311+G* (MeCN, SMD). There have been calculated with full optimization and without any restrictions as to the type of symmetry the structures of substituted phenylacetates XPhO-C(O)Me, acetanilides XPhNHC(O)Me, thiophenylacetates ZPhSC(=O)Me and benzylamines XPhCH₂NH₂ (X and Z are substitutes). All relationships between the atomic electrostatic potential and the charge on the reaction center in the Hirshfeld scheme are symbasic. In all of the cases the rate is determined by the nucleophilic attack on the reaction center with the activity/selectivity relationship being observed. This suggests that the thiophenolate-anion is a better leaving group compared to the phenolate-anion and as well as that the anionic abstraction of the leaving group does not limit the reaction rate. The fact that the reaction rate is limited by the nucleophilic attack of the reagent is not inconsistent about concerted mechanism of reaction the views, since it is known that such reactions may be quite concerted though not quite synchronous.

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