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Molecular electrostatic potential of the reaction center as a descriptor of the reactivity of arylsulfonyl halides

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Abstract

To study the reactivity of arylsulfonyl halides, the molecular electrostatic potential (MEP) was considered for the first time as a descriptor. The reaction of hydrolysis of aromatic sulfonyl halides in the medium of mixed acetone-water solvents (according to the literature data of rate constants) was used as a model. The calculation of the structural parameters of the molecules of substituted arylsulfonyl halides was carried out using the ADF2014 software package at the level of the DFT/M06/6-311+G* (PCM) theory. It was found that the magnitude of the MEP on the sulfonyl sulfur atom is very sensitive to changes in the structure of substrates, which makes it possible to determine the change in the ratio between the rate of nucleophilic attack and anionoid abstraction of the leaving group. In particular, using the example of the hydrolysis reaction of substituted thiophenesulfonyl chlorides, it was shown that the acceleration of the reaction is observed with an increase in the donor properties of the substituents and the associated increase in the negative MEP value on the sulfonyl sulfur atom. The antibate character of the dependence of the hydrolysis constant values on the IEP value indicates that not the nucleophilic attack is the rate determining in the interaction of thiophene sulfonyl chlorides and the hydroxyl anion in this sample, but the abstraction of the chloride anion. This reaction has an unstable mechanism, when the ratio between the degree of S-nucleophile bond formation and S-halogen bond cleavage changes. This makes it possible to use MEP as a descriptor of reactivity in the hydrolysis of aryl sulfonyl halides and to elucidate the details of changes in the structure of transition states during the implementation of mechanisms other than pure SN2 mechanism.

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