

Quantum-chemical study of the elementary reactions acts of 2-phthalimidoethanesulfonylhalides with *N*-trimethylsilylimidazole

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Abstract

Quantum-chemical method DFT with density functional PBE in the basis 3z (similar to basis set cc-pVTZ) in the gas phase and supramolecular approximation was used to study the reactions of 2-phthalimidoethanesulfonylhalides with *N*-trimethylsilylimidazol, where Hal = F, Cl. We discussed in detail the specificity of the reaction systems in the geometric and energy context depending on the nature of the halide and the specific solvation with chloroform.

It is shown that for the studied reaction systems various synchronous one-step reaction mechanisms are not implemented, and a two-step mechanism holds true. The first stage is nucleophilic attack by unsaturated nitrogen center of *N*-trimethylsilylimidazol on sulfur atom of the corresponding sulfonylhalide with simultaneous bond cleavage S-Cl and the formation of middleware intermediate, which is a tight ion pair of galogenaniona and cation-delocalized disubstituted imidazole heterocycle with the preserved N-Si bond and the newly formed covalent bond N-S. The second stage of the reaction is the migration of galogenanion with the position in tight ion pair on the silicon center with simultaneous cleavage of the bond N-Si (that can be classified as ipso-substituted) and the formation of desired products – trimethylsilylhalide and imidazolidine 2-phthalimidoethanesulfonic acid.

The conclusion is made on the need to further clarify the mechanism of the reaction by using a high-precision quantum chemical methods and modeling various promoter effects facilitating the activation barrier of the forward direction of the first reaction step.