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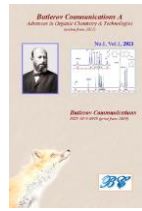

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Kinetics and mechanism of acyl transfer reactions. Part 19. Computer simulation of mechanisms of sulfonation of amides and hydrazides of aromatic benzoic and sulfonic acids

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Abstract

Quantum-chemical simulation of mechanism of 3-nitrobenzenesulfonic acid chloride reaction with 2-sulfobenzoic acid imide in the gas phase is carried out at DFT//B3LYP/6-311G(d,p) level by calculating the three-dimensional potential energy surface of this process. It is shown that in the considered reaction a single route can be realized starting as an axial attack of the nucleophile and containing a single saddle point. At the further reagent molecules approach a decrease in the attack angle of nucleophile molecule proceeds to ≈ 115° in the reaction transition state and to ≈ 100° – in the reaction product. It is established that the studied process proceeds according to the bimolecular concerted mechanism of nucleophilic substitution S_N2, which implies the formation of a single transition state along the reaction pathway. It is found that the geometric configuration of the reaction center in the transition state of the process is close to the tetragonal pyramid, which is explained by the mutual repulsion of the lone pairs of electrons of oxygen atoms of sulfonyl group of 3-nitrobenzenesulfonyl chloride and carbonyl and sulfonyl groups of saccharin which hinders the reagents molecules approach in the axial direction at the short distances. It is found that in the studied reaction a cyclic transition state is formed, in which forming and loosening bonds lie in the same plane, and the H-Cl distance corresponds to the length of the strong hydrogen bond. The activation energy of the reaction is calculated; it was 181 kJ/mol; the value pointed out is compared with values of activation energies of 3-nitrobenzenesulfonyl chloride reactions with benzamide, benzenesulfonamide, benzhydrazide, benzenesulfohydrazide, and also with values of activation enthalpies changes of the pointed out reactions in the solvent water (20 wt.%) – 1,4-dioxane. It is established that the calculated values of the activation energies

of the reactions correlate with experimental values of their activation enthalpies excepting the reaction with benzhydrazide participation. Rate constants of saccharin, benzenesulfonamide, benzhydrazide and benzenesulfohydrazide sulfonylation increase with decrease of the reactions activation enthalpies. Abnormally high value of the rate constant of the reaction with benzamide participation is explained by the relative simplicity of its structure which creates the less steric hindrances in the interaction with the acylation agent in comparison with the other nucleophyles.

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