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Thematic course: Kinetics and mechanism of acyl transfer reactions. Part 17.

Quantum-chemical study of mechanisms of sulfonation of benzoic and benzenesulfonic acids hydrazides in the gas phase

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Abstract

Quantum-chemical simulation of the mechanisms of 3-nitrobenzenesulfonyl chloride interaction with benzhydrazide (RHF/6-31G(d)) and benzenesulfohydrazide (DFT//B3LYP/6-311G(d,p)) in the gas phase was carried out. Three-dimensional potential energy surfaces of these processes are calculated in the coordinates of the angle of attack of the nucleophile and the distance between the reacting molecules. It has been established that in the both cases considered, reactions can proceed in the gas phase along a single route, through a single saddle point corresponding to a single transition state; processes begin as an axial attack of nucleophile, which subsequently proceeds with a decrease in the attack angle as the reagents molecules approach each other. It was shown that the both studied processes proceed in accordance with the bimolecular concerted mechanism of nucleophilic substitution S_N2, which involves the formation of a single transition state in a reaction pathway and the absence of intermediates on it. Scanning the internal coordinate of benzhydrazide reaction with 3-nitrobenzenesulfonyl chloride made it possible to confirm the reaction route and mechanism of the process pointed out and to clarify the structure of its products and reagents. It was found that the geometric structure of the reaction center in the reactions transition states is medium between the trigonal-bipyramidal and tetragonal-pyramidal, which is due to the change in the nucleophilic attack angle when the reagents molecules approach each other. It was found that in reactions involving hydrazides a "synchronous" transition state is formed in which a new S-N bond is formed simultaneously with the loosening of the old S-Cl bond. The activation energies of the reactions are calculated; they amounted to 173 and 113 kJ/mol, respectively. The high values obtained are explained by the fact that the simulation was carried out for processes occurring in a gas hase. It was shown that the decrease in the activation energy of the reaction involving benzenesulfohydrazide as compared to the benzhydrazide reaction is due to a decrease in steric hindrances during nucleophilic attack created by the lone electron pair of the benzenesulfohydrazide secondary amino group as compared to the benzhydrazide molecule. The calculated values of charges on the nitrogen atoms of the –NH– groups in the hydrazides molecules indicate a weakening of the α-effect upon the transition from benzenesufohydrazide to benzhydrazide.

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