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Thematic Course: Kinetics and mechanism of acyl transfer reactions. Part 13.

Quantum chemical simulation of mechanisms of the reactions of secondary fatty aromatic amines arensulfonation

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Abstract

The quantum chemical simulation of mechanisms of the reactions of secondary fatty aromatic amines – *N*-methylaniline and *N*-ethylaniline with benzenesulfonyl chloride in the gaseous phase and also of the reaction of *N*-methylaniline with benzenesulfonyl chloride in the conditions of specific and non-specific solvation of the reagents molecules by water is carried out. Three-dimensional potential energy surfaces of the pointed out processes are computed. An impossibility of realization of the nucleophile backside attack on sulfonic reaction center in the gas-phase reaction of *N*-methylaniline with benzenesulfonyl chloride is shown.

Depending on physical chemical properties of the simulated medium in the considered reactions the route with frontside attack of alkylaniline molecule on the sulfonic reaction center or the route with an axial attack of nucleophile proceeding with decrease of the attack angle as the reagents molecules approach each other can realize or the both pointed out routes are equiprobable. It is established that all the considered reactions occur by the bimolecular concerted mechanism of nucleophilic substitution with the only transition state formation on the any of the probable routes. It is found that geometrical configuration of the transition states is determined by the reactions route: when implementing the frontside attack of nucleophile the transition state with the form of tetragonal pyramid is forming; at occurring of the process by the route with an axial attack of nucleophile the transition state forms with configuration intermediate between trigonal-bipyramidal and tetragonal-pyramidal what is connected with the change of the nucleophile attack angle as the reagents molecules approach each other. Activation energies of the studied processes are calculated, in the gaseous phase they significantly exceed the values received experimentally; activation energy of the reaction with participation of *N*-ethylaniline is significantly higher than that of the reaction with *N*-methylaniline participation, that is explained by the sterical hindrances increase with the increase of the size of the substituent in the amine group. It is shown that accounting of *N*-methylaniline molecule solvation by one water molecule influences insignificantly the energy of its reaction with benzenesulfonyl chloride but accounting of non-specific solvation by water increases energetic barrier of the reaction that is probably connected with strengthening of electrostatic repulsion between negatively charged atoms of the functional groups of the reagents molecules in the conditions of non-specific solvation.

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