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Thematic course: Kinetics and mechanism of acyl transfer reactions. Part 16.

Quantum chemical simulation of mechanism of *N*-methylaniline sulfonation in aqueous 1,4-dioxane

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Abstract

The RHF/6-31G(d) quantum chemical simulation of the mechanism of the secondary fatty aromatic amine *N*-methylaniline interaction with benzenesulfonyl chloride under conditions of *N*-methylaniline specific solvation by one water molecule and one 1,4-dioxane molecule, and under conditions of *N*-methylaniline specific solvation by two water molecules and one 1,4-dioxane molecule. Three-dimensional potential energy surfaces of the processes pointed out are computed. It is shown that in the both cases a single route of the reactions is realized, starting as an axial nucleophilic attack, which goes further with decreasing of the attack angle as reagent molecules approach each other. It was established that both simulated reactions proceed in accordance with bimolecular concerted mechanism of nucleophilic substitution S_N2, which implies the formation of a single transition state in the reaction path. It was found that geometrical configuration of the reaction center in the transition states of the reactions is medium between the trigonal-bipyramidal and tetragonal-pyramidal, which is associated with the change in the angle of *N*-methylaniline attack as the reactant molecules approach each other. In the benzenesulfonyl chloride reaction with *N*-methylaniline, solvated by one water molecule and one 1,4-dioxane molecule, the transition state is solvated only by 1,4-dioxane molecule, while water molecule moves away from the reaction center, whereas in the benzenesulfonyl chloride reaction with *N*-methylaniline, solvated by two water molecule and one 1,4-dioxane molecule the transition state is solvated by 1,4-dioxane molecule and one water molecule that forms hydrogen bond with chlorine atom and promote the S–Cl-bond loosening. The activation energies of the reactions were calculated; it is shown that specific solvation increases the reactions energetic barrier as compared with the reaction in gaseous phase, that is caused by the partial dehydratation of *N*-methylaniline molecule before the transition state formation. A decrease of the activation energy of the reaction with participation of *N*-methylaniline, solvated by two water molecule and one 1,4-dioxane molecule as compared with the cases of non-specific solvation of the reactants and *N*-methyl-aniline solvation by one water molecule and one 1,4-dioxane molecule is caused by the existence of the second water molecule in the system, forming a bond with amine group and facilitating N–H bond break.

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