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Thematic course: Kinetics and mechanism of acyl transfer reactions. Part14.

Aminolysis of esters: kinetic experiment and computer simulationof the mechanism

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Abstract

The analysis of literature devoted to the establishment of the mechanisms of the reactions of esters and related compounds with amino compounds of different classes is carried out. It is shown that, despite the existing opinion on the kinetic indistinguis hability of the probable mechanisms of aminolysis – the bimolecular concerted mechanism of nucleophilic substitution and the stepwise mechanism, a number of authors attempt to identify them based on the study of the kinetic regularities of these reactions. As criteria of the implementation of a mechanism, the values of the constants in the modified Hammett equation, the values of the angular coefficients of the Bronsted dependence, the magnitude of the kinetic isotopic effect, and the type of dependences of Hammett, Bronsted, and Yukawa-Tsuno are considered. It is believed that the non-linear character of these dependencies indicates a change in the limiting stage of the process in the stepwise mechanism, whereas linear dependencies indicate a concerted proceeding of aminolysis. It is argued that the mechanism of aminolysis can change when the structure of the reagents and the nature of the used solvent are varied. It is established that little attention is paid in the literature to the direct establishment of aminolysis mechanisms by quantum-chemical simulation; in the available works, the simplest molecular systems are considered as model. The mechanisms of the reactions of esters with ammonia, cyclohexylamine and glycine in the gas phase, as well as taking into account the specific solvation of ammonia and cyclohexylamine, were simulated by constructing their potential energy surfaces. It has been found that these processes proceed in one step in accordance with the mechanism of bimolecular concerted nucleophilic substitution, since at all the obtained potential energy surfaces there is a single saddle point corresponding to a single transition state of the reaction and a single minimum corresponding to the formation of products. The specific solvation of nucleophiles does not change the mechanism of the considered reactions in comparison with the gas phase, but it affects the energy of the processes, significantly reducing their energy barrier. The results of the calculation are consistent with the available experimental data on the kinetics of simulated aminolysis reactions.

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