

Thematic course: Kinetics and mechanism of acyl transfer reactions. Part 12.

Reactivity of aryl amines in amides formation

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Abstract

Kinetics of aniline, *p*-toluidine and also *m*- and *p*-amino benzoic acids anionic forms reactions with picryl benzoate and *p*-nitrophenyl acetate is studied with indicator spectrophotometrical method in a solvent water–1,4-dioxane at 298 K. The obtained kinetic data are compared with results of kinetic investigation of other acyl transfer reactions: of amino benzoic acids, α -amino acids and aryl amines interactions with esters, benzoyl chloride and sulfonyl chlorides. A number of common regularities are found. Methyl group introduction to aniline molecule *p*-position increases its reactivity in all the pointed out reactions that agrees with representations about electron donative action of this substituent. Rate constants of amino benzoic acids reactions with different acylation agents are lower than aniline and α -amino acids acylation constants. In all considered reactions *p*-amino benzoic acid acylation rate is lower than that of *m*-isomer. Existence of single Brønsted's dependence is established for amino benzoic acids and α -amino acids anions reactions with picryl benzoate. Equations connecting rate constants of aromatic and aliphatic amino acids anionic forms reactions with picryl benzoate and rate constants of the same amino acids reactions with *p*-nitrophenyl acetate and chloro anhydrides of *m*-nitrobenzene sulfonic and benzoic acids in the solvent water–1,4-dioxane are obtained. The kinetic data are compared with results of quantum chemical simulation of the studied nucleophiles electronic structure. It is shown that higher reactivity of picryl benzoate as compared with *p*-nitrophenyl acetate is caused by higher positive charge values of picryl benzoate carbonyl carbon atom and by lower LUMO energy of its molecule, and also by absence of sterical hindrances to nucleophilic attack from substituents in phenoxide radical as it is disposed at the angle 71.1° against the plane of the molecule acyl part. It is established that reactivity of the substituted aryl amines in acylation is determined both by electronic and orbital characteristics of the nucleophilic agents, and regularities of influence of quantum chemical characteristics of amino benzoic acids molecular and anionic forms on their reactivity are different.