

Thematic course: Quantum-chemical research on organophosphorus compound reactions. Part 5.

## Elementary acts of the dealkylation stage of Michaelis-Arbuzov reaction including the formation of quasiphosphonium associates

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### Abstract

Transformations of bimolecular quasiphosphonium associates corresponding to the elimination stage of Michaelis-Arbuzov reaction (second stage) have been studied by quantum-chemical DFT method with density functional PBE in 3z basis in pseudogasphase approximation. Specificity of the reaction systems in their geometry and energy contexts has been surveyed in much detail.

The products of the forward reaction in all studied cases are the respective phosphonate, alkyl halide and orientationally modified quasiphosphonium compound.

In general, for the bimolecular quasiphosphonium associates have been shown to be feasible forming the topology with interoriented arrangement of sharing halide-anion and alkoxy group.

It has been established that the nature of substituents at phosphorus and the type of halide-anion in bimolecular quasiphosphonium associates have no essential effect on demethylation energetics of the final stage of Michaelis-Arbuzov reaction (dealkylation stage). Nature of the fragment eliminated has a substantial influence on activation energy increase in forward dealkylation reaction in the case of bimolecular quasiphosphonium associates.

Analysis and comparison of the energetics at the first and the second stages of classical Michaelis-Arbuzov reaction (stages of nucleophilic attack at phosphorous atom and dealkylation) prove nucleophilic attack of phosphorous atom to limit the process.