

Thematic course: Quantum-chemical research on organophosphorus compound reactions. Part 6.

## The theoretical description of the elementary acts of cation-chain transformation of the phosphites to phosphonates (Rumpf-Nesterov reaction)

© Alexandre I. Kourdioukov,<sup>1\*</sup> Evgeny N. Ofitserov,<sup>2\*</sup> and Vladimir F. Mironov<sup>3\*</sup>

<sup>1</sup> Center of New Information Technologies. Kazan National Research Technological University. Karl Marx St., 68. Kazan, 420015. Tatarstan. Russia. Phone: +7 (843) 231-42-11. E-mail: [butlerov@mail.ru](mailto:butlerov@mail.ru)

<sup>2</sup> Department of Chemistry and Technology of Biomedical Preparations. D.I. Mendeleev Russian Chemical Engineering University. Miusskaya Sq., 9. Moscow, 125047. Russia. Phone: +7 (495) 978-61-32. E-mail: [ofitser@mail.ru](mailto:ofitser@mail.ru)

<sup>3</sup> Laboratory of Phosphorylated Analogues of Natural Compounds. A.E. Arbuzov Institute of Organic and Physical Chemistry at the Kazan Scientific Center. Arbuzov St., 8. Kazan, 420088. Tatarstan Republic. Russia. Phone: +7 (843) 272-73-84. Fax: +7 (843) 273-22-53. E-mail: [mironov@iopc.ru](mailto:mironov@iopc.ru)

\*Supervising author; <sup>+</sup>Corresponding author

**Keywords:** trimethylphosphite, tetrafluoroborate, trifluoromethylsulfonate, nitrite and chloride of methyltrimetoxyposphonium, interaction, associates, Rumpf-Nesterov reaction, the Michaelis-Arbuzov reaction, cation-chain mechanism, basic acts, quantum-chemical research, PBE method.

### Abstract

Using quantum-chemical calculations with PBE approach (program implementation *Priroda 4.11*) investigated cation-chain mechanism for Rumpf-Nesterov reaction. Energetically and structurally described the reaction of trimethylphosphite with initiating agents: tetrafluoroborate, trifluoromethylsulfonate, nitrite and chloride of methyltrimetoxyposphonium. The products of reaction in these cases are an orientation changed quasiphosphonium and target methyl dimethylphosphonate. It is shown that Rumpf-Nesterov reaction really is cation-chain and autocatalytic process in which the quasiphosphonium unit are a renewable agent.

The reaction were compared with the model transformation into a positively-charged reaction system "trimethyl – methyltrimetoxyposphonium". It is shown if the counterions in the salts of methyltrimetoxyposphonium are anions which actually do not have nucleophilic properties then at the implementation of Rumpf-Nesterov mechanism they fulfill the function of the spatially oriented structural unit resulting in a lack of need for mutual transformation geometry in the reaction process by changing type of associate of the source structure. This entails a decrease in the activation barrier more than 2 times in comparison with the positively-charged reaction system, which has no associate in the initial relative orientation.

Shown phenomenological relationship and differences between the cation-chain Rumpf-Nesterov transformation with the classical mechanism of Michaelis-Arbuzov reaction.